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ACYLPYRIDINE ADDUCTS OF ORGANOTIN AND STANNIC CHLORIDES: SYNTHESIS; p.m.r., i.r. SPECTRAL STUDIES (I)

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(Received October 17, 1983)

Summary

4-Acetylpyridine, 4-benzoylpyridine, 3-acetylpyridine, and 3-benzoylpyridine adducts of the methyltin, phenyltin, and stannic chlorides are made. Elemental analysis, i.r. and n.m.r. spectroscopy show the adducts of Me_3SnCl to be 1:1, and of Me_2SnCl_2, $MeSnCl_3$, $SnCl_4$, $PhSnCl_3$, and Ph_2SnCl_2 to be 1:2. The Lewis bases bind by just the nitrogen donor. N.m.r. spectra of all adducts, and of pyridine adducts of the Lewis acids are run; the chemical shift (δ) values are observed to increase with complexation of the Lewis bases.

Key words: methyltin, phenyltin, stannic chlorides acylpyridine adducts; synthesis; n.m.r., i.r. spectra.

Abbreviations

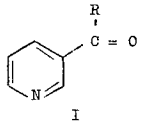
3-Ac. Py = 3-Acetylpyridine, 4-Ac. Py = 4-Acetylpyridine, 3-Be. Py = 3-Benzoylpyridine, 4-Be. Py = 4-Benzoylpyridine.

Introduction

Pyridine has been known to be capable of coordinating, by its nitrogen, on many organotin and stannic halides, giving stable isolable adducts[1]. The ability of many ketones and some carbonyl-bearing ligands to coordinate on organotin and stannic chlorides via the C=O oxygen has also been known[2, 3]. The simultaneous coordination of N and O of a Lewis base on the same lewis acid centre has been reported[4, 5, 6]. Jain et al.[7] have attempted to prepare the 2-acetylpyridine complex of stannic chloride.

No report seems to have been made on the interaction of Lewis acids of medium acceptor strength like organotin chlorides with pyridine Lewis bases having an alternative binding site to nitrogen geometrically far apart enough on the molecule to avoid the donors binding simultaneously on the same site. 3-and 4-acyl-pyridines (I, II) have donor atoms N and O such geometrically placed and therefore free to compete for an accepting site on an organotin Lewis acid.

Of the pyridine adducts of the methyltin, phenyltin and stannic chlorides, the



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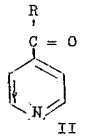

II

where R = CH_3,C_6H_5

p.m.r. spectral properties had been unknown except for $Me_3SnCl \cdot Py$, the only adduct found soluble enough[2].

This research was therefore aimed at studying the effects an electron withdrawing substituent that is also a donor would have on the donor ability of pyridine. I also sought to widen the proton magnetic resonance spectroscopy scope of study of the pyridine adducts of organotin halides, most of whose p.m.r. spectra had hitherto been unknown.

Experimental

All reagents were of high purity. The organotin and stannic chlorides, and Lewis bases were obtained from Aldrich.

The solvents CCl_4 and CH_2Cl_2 were purified by washing with 5% sodium carbonate solution, followed by water, dried over anhydrous calcium chloride, and distilled. 'Dry' acetone was prepared by refluxing the analytical grade of acetone with p-toluenesulphonyl chloride (2g/litre) for $^3/_4$ hr and distilling the acetone into bottles which were then promptly stoppered.

Melting temperatures (°C) are reported uncorrected. I.r. spectra (KBr and CsI discs) were run on the Perkin Elmer SP 700 and 800.

P.m.r. spectra (ref. TMS) of all the products were run on a T-60 spectrometer at an operating temperature of 38°C; the δ-values (ppm) were recorded.

Preparations

Trimethyltin chloride complexes

Equimolar amounts of the trimethyltin chloride and the Lewis base in small (about 0.5 ml/millimole of solute) different portions of carbon tetrachloride were mixed at room temperature. Clear mixtures were obtained. Each mixture was cooled at about 5°C overnight. Crystals separated out in the mixtures containing 4-acetylpyridine and 4-benzoylpyridine. The crystals were removed by filtration, washed with cold solvent, dried in mild vacuum, and recrystallised from the solvent.

Other methyltin, phenyltin, and stannic chlorides

1:2 Lewis acid: Lewis base mole ratios of the dimethyltin, methyltin, stannic, phenyltin, and diphenyltin chlorides, and 3-acetyl, 3-benzoyl-, 4-acetyl-, and 4-benzoyl-pyridines were measured into different portions (4 ml solvent per millimole of solute) of dichloromethane. The hot Lewis base solution was mixed with the hot Lewis acid soluton. The use of a dry box was necessary for preparations involving the monoorganotin and stannic chlorides. All the mixtures were obtained clear, but all yielded crystals on standing overnight at room temperature. Cooling speeded up

crystallization. The products were washed with the cold solvent, and dried **in vacuo.** The adducts of Me_2SnCl_2 were recrystallised from dried acetone.

The pyridine analogues of these complexes were prepared; instant precipitates were obtained.

Analyses

Elemental analyses were carried out for C, H, N and Cl by the Scandianavian Analytical Laboratories, Denmark; and the Sn locally by digesting the organotin in concentrated H_2SO_4, heating to dryness, and burning the residue until a light yellow mass (SnO_2) was obtained; the Sn content of the sample was then worked out[8].

Results and Discussion

Preparations

Dichloromethane has proved to be superior to most other solvents hitherto[1] used in preparing organotin chloride adducts. Even pyridine adducts came out of dichloromethane media as purer powders, as the reactants are extremely soluble in the solvent. All the substituted pyridine adducts crystallised slowly out of the solvent. Recrystallisation from dried acetone has been found possible for the tri- and di-organotin chloride pyridine adducts. Our method of preparation has yielded products of very high purity, as shown by the analyses results (Table I).

Stabilty

The adducts have been found to be stable solids, and could be preserved for long periods of time, unlike the 'unstable' pyridine adducts Me_3SnCl and Ph_2SnCl_2. This stability however could have been produced by the involatile nature of the Lewis bases. Most of the monoorganotin and stannic chloride adducts decomposed on heating; all the di- and mono- organotin, and stannic chloride adducts of the substituted pyridines melted or decomposed below the melting or decomposition temperatures of the analogous pyridine adducts. The trimethyltin chloride adducts melted at higher temperatures than their pyridine analogues.

P.m.r. Spectral Properties

Of the organotin chloride pyridine adducts, only $Me_3SnCl{\cdot}Py$ had been found sufficiently soluble for a meaningful N.m.r. study[2].

The difficulty in making use of N.m.r. spectroscopy in the study of the pyridine adducts of methyltin and even stannic chlorides has been overcome in this work; deutro-DMSO has been found capable of dissolving the adducts well enough to give good N.m.r. spectra. Many of the substituted pyridine adducts dissolve in solvents of lower polarity than DMSO. N.m.r. can therefore now be used along with other spectroscopic methods and elemental analysis, for the qualitative identification of the pyridine adducts of many organotin chlorides.

TABLE I: Table showing the melting points of, and the elemental analysis results for, the 3- & 4-acetyl, and 3- & 4-benzoyl pyridine adducts of the methyltin, phenyltin, and stannic chlorides.

Adduct	M.P. °C	Calculated, %					Found, %				
		C	H	Cl	N	Sn	C	H	Cl	N	Sn
$Me_3SnCl \cdot 4\text{-}Ac \cdot Py$	55-56	37.48	4.99		4.37	37.07	37.69	5.00		4.43	37.25
$Me_3SnCl \cdot 4\text{-}Be \cdot Py$	62-63	47.10	4.71		3.66	31.05	47.34	4.73		3.85	31.50
$Me_2SnCl_2 \cdot bis\text{-}4\text{-}Ac \cdot Py$	117-118	41.60	4.36		6.07	25.70	41.84	4.45		5.76	25.79
$Me_2SnCl_2 \cdot bis\text{-}4\text{-}Be \cdot Py$	157-159	53.27	4.10		4.78	20.26	53.35	4.17		4.75	20.40
$Me_2SnCl_2 \cdot bis\text{-}3\text{-}Ac \cdot Py$	109-110	41.60	4.36		6.07	25.70	41.90	4.41		5.95	25.75
$Me_2SnCl_2 \cdot bis\text{-}3\text{-}Be \cdot Py$	109-111	53.27	4.10		4.78	20.26	53.37	4.14		4.73	20.46
$MeSnCl_3 \cdot bis\text{-}4\text{-}Ac \cdot Py$	138-140	37.33	3.53		5.81	24.61	36.92	3.59		5.65	24.80
$MeSnCl_3 \cdot bis\text{-}4\text{-}Be \cdot Py$	300-303	49.41	3.62		4.61	19.58	49.50	3.65		4.60	19.85
$MeSnCl_3 \cdot bis\text{-}3\text{-}Ac \cdot Py$	185-187	37.33	3.53		5.81	24.61	37.10	3.61		5.70	24.87
$MeSnCl_3 \cdot bis\text{-}3\text{-}Be \cdot Py$	222-225	49.41	3.62		4.61	19.58	49.52	3.66		5.68	19.82
$SnCl_4 \cdot bis\text{-}4\text{-}Ac \cdot Py$	181-183	33.42	2.79	28.25	5.57	23.61	33.12	2.81	28.62	5.45	23.91
$SnCl_4 \cdot bis\text{-}4\text{-}Be \cdot Py$	322-323	45.96	2.87	22.66	4.46	18.94	45.85	2.85	22.81	4.48	19.35
$SnCl_4 \cdot bis\text{-}3\text{-}Ac\text{-}Py$	233-236	33.42	2.79	28.25	5.57	23.61	33.02	2.86	28.57	5.43	23.98
$SnCl_4 \cdot bis\text{-}3\text{-}Be \cdot Py$	250-252	45.96	2.87	22.66	4.46	18.94	45.82	2.83	22.85	4.47	19.28
$PhSnCl_3 \cdot bis\text{-}4\text{-}Ac \cdot Py$	140-143	44.10	3.49		5.15	21.81	44.24	3.64		4.89	22.10
$PhSnCl_3 \cdot bis\text{-}4\text{-}Be \cdot Py$	255-257	53.88	3.44		4.19	17.76	53.95	3.52		4.08	18.10
$PhSnCl_3 \cdot bis\text{-}3\text{-}Ac \cdot Py$	133-135	44.10	3.49		5.15	21.81	44.15	3.55		4.97	22.05
$PhSnCl_3 \cdot bis\text{-}3\text{-}Be \cdot Py$	95-97	53.88	3.44		4.19	17.76	53.96	3.60		4.21	18.05
$Ph_2SnCl_2 \cdot bis\text{-}4\text{-}Ac \cdot Py$	94-96	53.27	4.10		4.78	20.26	53.01	4.05		4.68	20.48
$Ph_2SnCl_2 \cdot bis\text{-}4\text{-}Be \cdot Py$	124-126	60.87	3.95		3.95	16.72	60.56	4.04		3.89	16.94
$Ph_2SnCl_2 \cdot bis\text{-}3\text{-}Ac \cdot Py$	62-64	53.27	3.10		4.78	20.26	52.98	4.14		4.70	20.51
$Ph_2SnCl_2 \cdot bis\text{-}3\text{-}Be \cdot Py$	119-121	60.87	3.95		3.95	16.72	60.64	3.98		3.90	16.85

The Pyridine adducts

It has been found that the chemical shift of the methyl protons increases as the methyltin chloride adds to pyridine (see table III). It is possible that the high polarity of the DMSO solvent enhances ionization or atleast strong polarisation of the organotin chloride moiety and the ionic state is stabilised by the Lewis base which however cannot come too close to the Sn nuclear centre because of internuclear repulsion.

This would lead to a net drift of electrons from the H of the CH_3 to the Sn centre.

It has been found that the chemical shift values for $MeSnCl_3$ and its Py adducts are lower in DMSO than those for Me_2SnCl_2 and its Py adducts. The reason for this is not very clear, but it is possible that the degree of solvation, considering steric freedom, by the solvent molecules on the Sn is higher in $MeSnCl_3$ than Me_2SnCl_2, in both the Lewis acid and the adduct. The empty 5d orbitals of the Sn would accept electrons from the solvent donors, especially since the Sn centre become more positive in $MeSnCl_3$ than in Me_2SnCl_2, the halogen substituents being more in the former than in the latter. The view appears supported by the fact that δ-values for the Sn-CH_3 protons of both organotin chloride and adduct are lower in the more strongly solvating DMSO than in acetone (table III) for $MeSnCl_3$ than Me_2SnCl_2.

The substituted Pyridine adducts

δ-values for the Sn-CH_3 protons in the 3- and 4-acetyl- and benzoyl-pyridine adducts have been found to be slightly higher than those for the parent Lewis acid, but are generally lower than those for the corresponding Py adducts (see Table II), seeming to show the acylpyridines as weaker donors than pyridine.

Not much could be derived from the N.m.r. spectra of the phenyltin chlorides and their adducts, as the spectral bands for the Sn-Phenyl protons interferred with those of the ligand. But the integrals of the few proton signals that do not super impose on the others (Table II) compared with those that are superimposed leave no doubt on the purity and stoichiometry of the adducts.

The Lewis base protons

It has been found in this work that all the pyridine and pyridyl proton signals shift down field as the pyridine complexes (see Table III). The shifts are most pronounced in the $SnCl_4$ adducts, and only slight in Me_3SnCl adducts. This observation seems to be in agreement with the belief that Sn←N coordinate bond is strongest in $SnCl_4$ Py adducts, and weakest in R_3SnCl.

It can be tentatively submitted then, that in addition to other methods known for proving complexation between pyridine and a Lewis acid, n.m.r. could also be used, if only at the qualitative level, as the Py proton signals have been observed to shift slightly downfield with complexation. Yet to be proved however is the exact nature of the species in solution.

TABLE II: The N.M.R. chemical shift values for the pyridine and acylpyridine adducts of the methyltin, phenyltin, and stannic chlorides.

Compound	The Solvent	Sn-CH_3										
Me_3SnCl·4-Ac·Py	$(CD_3)_2$·CO	ppm 0.61s				ppm 9.10d	ppm 7.90d	ppm	ppm	ppm 2.65s	ppm	ppm
Me_3SnCl·4-Be·Py	CCl_4	0.62s				9.10q	7.90q					7.60m
Me_2SnCl_2·2Py	d-DMSO	1.15s				8.74m	7.58m	7.93m				
Me_2SnCl_2·bis-4-Ac·Py	d-DMSO	1.14s				8.98d	7.98d			2.70s		
Me_2SnCl_2·bis-4-Be·Py	d-DMSO	1.15s				9.00q	7.80					7.80
Me_2SnCl_2·bis-3-Ac·Py	$(CD_3)_2CO$	1.20s			8.80 (C6H)d 9.20 (C2H)s		7.50q	8.30d	2.60s			
Me_2SnCl_2·bis-3-Be-Py	$(CD_3)_2CO$	1.30s			9.10 (C6H)q 9.20 (C2H)d		7.80	8.30h			7.80	
$MeSnCl_3$·2-Py	d-DMSO	1.03s				8.74m	7.56m	7.92m				
$MeSnCl_3$·bis-4-Ac·Py	d-DMSO	1.02s				9.00q	8.00q			2.70s		
$MeSnCl_3$·bis-4-Be·Py	d-DMSO	1.02s				9.00s	7.80					7.80
$MeSnCl_3$·bis-3-Ac·Py	d-DMSO	1.05s			9.00 (C6H)q 9.40 (C2H)d		7.70q	8.40h	2.70s			
$MeSnCl_3$·bis-3-Be·Py	d-DMSO	1.00s				8.95q	7.80	8.20h			7.80	
$SnCl_4$·2Py	d-DMSO					8.74m	7.58m	7.93m				

$SnCl_4$·bis-4-Ac·Py	d-DMSO					9.00q	8.00q			2.70s		
$SnCl_4$·bis-4-Be·Py	d-DMSO					9.02q	7.90					
$SnCl_4$·bis-3-Ac·Py	d-DMSO				8.90 9.25	(C6H)m (C2H)d	7.70q	8.50m	2.65s			
$SnCl_4$·bis-3-Be·Py	d-DMSO					8.95q	7.80	8.25h			7.80	
$PhSnCl_3$·2Py	d-DMSO	7.70	7.70	7.70		8.90q	7.70	7.70				
$PhSnCl_3$·bis-4-Ac·Py	d-DMSO	7.90m	7.40m	7.40m		8.95q	7.90m			2.65s		
$PhSnCl_3$·bis-4-Be·Py	d-DMSO	7.70	7.70	7.70		9.00q	7.70					7.70
$PhSnCl_3$·bis-3-Ac·Py	d-DMSO	7.60	7.60	7.60	8.95 9.30	(C6H)q (C2H)d	7.60	8.40h	2.65s			
$PhSnCl_3$·bis-3-Be·Py	d-DMSO	7.75	7.75	7.75		9.00q	7.75	8.20h			7.75	
Ph_2SnCl_2·2Py	d-DMSO	7.60	7.60	7.60		8.85m	7.60	7.60				
Ph_2SnCl_2·bis-4-Ac·Py	$(CD_3)_2CO$	7.80	7.35m	7.35m		8.75q	7.80m		2.60s			
Ph_2SnCl_2·bis-4-Be·Py	$(CD_3)_2CO$	7.70	7.70	7.70		9.05q	7.70					7.70
Ph_2SnCl_2·bis-3-Be·Py	$(CD_3)_2CO$	7.80	7.80	7.80		9.00m	7.80	8.40h			7.80	

s = singlet
d = doublet
q = quardruplet
h = sexlet
m = multiplet
d-DMSO = deuterodimethylsulphoxide

TABLE III: The Sn-CH_3 P.M.R. shift values (δ, ppm) for the methyltin chlorides and their pyridine and some acylpyridine adducts.

Lewis acid, Lewis base, and adduct	Sn—C(H)(H)H shifts (d-DMSO)	Pyridyl H shifts (d-DMSO)			Sn—C(H)(H)H shifts $CD_3 \cdot CO \cdot CD_3$)
		Ortho H	Meta H	Para H	
$MeSnCl_3$	0.98				
Me_2SnCl	1.02				1.23
Me_3SnCl	0.58				
Py		8.70	7.50	7.88	
$SnCl_4 \cdot 2Py$		8.74	7.58	7.93	
$MeSnCl_4 \cdot 2Py$	1.03	8.74	7.56	7.92	
$Me_2SnCl_2 \cdot 2Py$	1.15	8.74	7.58	7.93	1.22
$Me_3SnCl \cdot Py$	0.60	8.72	7.52	7.90	
4-Ac·Py		8.79	7.96		
$SnCl_4 \cdot$bis-4-Ac·Py		9.00	8.00		
$MeSnCl_3 \cdot$bis-4-Ac·Py	1.02	9.00	8.00		
$Me_2SnCl_2 \cdot$bis-4-Ac·Py	1.14	8.98	7.98		1.21
$Me_3SnCl \cdot$4-Ac·Py	0.60	8.98	7.98		0.68
4-Be·Py		8.98			
$SnCl_4 \cdot$bis-4-Be·Py		9.02			
$MeSnCl_3 \cdot$bis-4-Be·Py	1.02	9.00			
$Me_2SnCl_2 \cdot$bis-4-Be·Py	1.15	9.00			1.20
$Me_3SnCl \cdot$4-Be·Py	0.60	9.00			0.68

DMSO as a solvent

DMSO is commonly known to form stable complexes with organotin chlorides. However where N and O compete for coordination, as in the pyridines and DMSO, N, being of lower electronegativity and therefore a stronger donor, would bind in preference, to Sn. It is our assumption that in a solution of DMSO, a pyridine ligand would preferentially bind to an organotn Lewis acid, compared with the DMSO solvent molecules. In any case the pyridine adducts have dissolved well in deuterodimethyl sulphoxide and given NMR spectra good enough for qualitative studies.

Infrared Spectral Properties

The corollary for band assignment has been derived from the reports of Beattie et al.[1], Poller et al.[3], Plyztzanopoulos et al.[4-6] and Popov, et al.[9-11].

Table IV shows the band assignments for some of the i.r. bands of the acylpyridine adducts and the free Lewis bases. It should be mentoned that the band allocations can be confirmed only after appropriate quantum mechanical calculations.

Sn - Cl stretch

This band has been observed for the monoorganotin and stannic chloride adducts. Compared with the band in the free Lewis acid, there is a general shift towards longer wavelengths with complexation. The increased electron density

around the Sn centre in the adduct weakens the Sn-Cl bond, compared with the free Lewis acid.

TABLE IV: Some i.r. spectral bands of the acylpyridine adducts of the methyltin, phenyltin, and stannic chlorides.

Compound	C – H	C = O	C = C arom. (Py)	Sn – Ph	Sn – Me Rock	Sn – Cl
4-Be·Py	3030w	1660vs	1580s			
Me_3SnCl·4-Be·Py	3040vw	1660s	1595s		790m	
Me_2SnCl_2·bis-4Be·Py	3060w	1660s	1600s		790m	
$MeSnCl_3$·bis-4-Be-Py	3040w	1660s	1600s		795w	292s
$SnCl_4$·bis-4-Be·Py	3070w	1665s	1600s			335s
$PhSnCl_3$·bis-4-Be·Py	3030w	1665s	1595s	1065m		300s
Ph_2SnCl_2·bis-4-Be-Py	3030w	1660s	1590s	1065m		270s
4-Ac·Py	3030m	1700s	1580s			
Me_3SnCl·4-Ac·Py	3030vw	1695s	1595s		790m	
Me_2SnCl_2·bis-4-Ac·Py	3030w	1700s	1595s		795m	
$MeSnCl_3$·bis-4-Ac·Py	3040w	1700s	1600s		795w	295s
$SnCl_4$·bis-4-Ac·Py	3060m	1700s	1610s			335s
$PhSnCl_3$·bis-4-Ac·Py	3030w	1700s	1595s	1060		300s
Ph_2SnCl_2·bis-4-Ac-Py	3045w	1700s	1600s	1065m		270s
3-Be·Py	3040m	1660s	1580s			
Me_2SnCl_2·bis-3-Be·Py	3060w	1660s	1600s		795m	
$MeSnCl_3$·bis-3-Be·Py	3050w	1665s	1595s		795w	300s
$SnCl_4$·bis-3-Be·Py	3060w	1660s	1600s			345s
$PhSnCl_3$·bis-3-Be·Py	3030w	1660s	1590s	1060w		325s
Ph_2SnCl_2·bis-3-Be·Py	3040w	1660s	1590s	1075m		275s
3·Ac·Py	3040m	1680s	1580s			
Me_2SnCl_2·bis-3-Ac·Py	3030w	1680s	1595s		795m	
$MeSnCl_3$·bis-3-Ac·Py	3040w	1685s	1595s			305s
$SnCl_4$·bis-3-Ac·Py	3050w	1690s	1595s			350s
$PhSnCl_3$·bis-3-Ac·Py	3030w	1680s	1590s	1060w		325s
Ph_2SnCl_2·bis-3-Ac·Py	3040w	1680s	1600s	1065w		280s

The shift of the Sn-Cl band in the adducts is highest for the pyridine, and lowest for 3-acetylpyridine adducts, seeming to reflect the donor abilities of the Lewis bases.

The C = C arom. band of Pyridine

This band has been observed to shift from 1580cm^{-1} in all the Lewis bases to 1600cm^{-1} in the adducts, suggesting that the pyridine and acylpyridine Lewis bases bind to the Sn of the Lewis acid by their N.

The C = O stretch

Plytzanopoulos et al.[4-6] have observed that the C = O stretch in the 2-ketopyridines shifts to lower frequencies with complexation on transition metals. But the i.r. spectra of the acylpyridine complexes now being reported have not shown

any relative shift in the complex compared with the free Lewis base. It can be inferred then that the Lewis base bind to the Lewis acid by the N only.

It follows then that the 3- & 4-acetyl- and benzoyl-pyridines act as monodentate ligands when they bind on organotin and stannic chloride Lewis acids; they bind with their N rather than O, as evidenced in the pyridine C = C stretching frequency shift in the complexes, while no shift in frequency is exhibited by the C = O stretch in the complex compared with the free Lewis base.

Stoichiometry of Reaction

The elemental analysis results for the adducts suggest that Me_3SnCl forms 1:1 adducts with the 4-acylpyridines, whilst the diorganotin, monoorganotin, and stannic chlorides form 1:2 adducts with both the 3- and 4- acylpyridine series. N.m.r. spectra of the adducts have supported the suggestion. I.r. spectral studies have shown that the N and not O of the Lewis base bind in complex formation.

The failure of the 3-acylpyridines to bind stably with Me_3SnCl could be due to steric factors, produced by possible interference of the acyl substituents with the Lewis acid hydrocarbon substituents.

Structures of the complexes

Various postulations based on corollaries from infrared[1], Mossbauer[3] and other of molecular spectroscopy have been made on possible structures of organotin halide adducts, but only X-ray crystallography would give the best information.

Περίληψη

Ενώσεις προσθήκης ακετυλοπυριδίνης με κασσίτερο

Παρασκευάστηκαν οι ενώσεις προσθήκης των 4-ακετυλο-πυριδίνης, 4-βενζοϋλοπυριδίνης και 3-ακετυλοπυριδίνης με μεθυλο- κα φαινυλο- κασσίτερο και χλωρίδια του κασσιτέρου. Οι στοιχειακές αναλύσεις και τα φάσματα ir και nmr, δείχνουν ότι τα προϊόντα προσθήκης με Me_3SnCl είναι 1:1, ενώ αυτά με Me_2SnCl_2, $MeSnCl_3$, $SnCl_4$, $PhSnCl_3$ κα Ph_2SnCl_2 είναι 1:2. Οι βάσεις κατά Lewis συνδέονται μέσω του ατόμου αζώτου μόνο. Τα φάσματα nmr των προϊόντων προσθήκης των παραγώγων της πυριδίνης με τα οξέα αυτά κατά Lewis, δείχνουν εξ άλλου ότι οι χημικές μετατοπίσεις (δ) αυξάνουν μετά από συμπλοκοποίηση.

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A MASS SPECTRAL STUDY OF O- AND N-AROYLBENZAMIDOXIMES

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Summary

The synthesis of several as yet unknown O- and N-aroylbenzamidoximes is described and their fragmentation pattern in the mass spectra is discussed. O- and N-aroylbenzamidoximes are distinguished on the basis of their mass spectra, since the O-derivatives afford the ion corresponding to the acid $[ArCOOH]^{+\cdot}$, whereas the N-derivatives the amidic fragment $[ArCO\overset{+}{N}H]$. A Beckmann type rearrangement during fragmentation leads finally to ion $[ArN]^{+\cdot}$.

Key words: O-Aroylbenzamidoximes; N-Aroylbenzamidoximes; preparation of; distinction of by means of mass spectra.

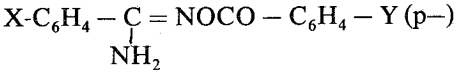
Introduction

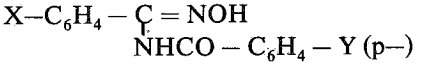
In connection to our previous work on O- and N-aroylbenzamidoximes[1, 2], we have prepared a series of new aroylbenzamidoximes and studied their fragmentation pattern upon electron impact.

While m-chlorobenzamidoximes react with acid chlorides in the usual manner to give[3-6] the expected products Ia, Ib, reaction of methoxybenzamidoximes with acid chlorides leads to mixtures of O- and N-aroylbenzamidoximes.

Pure O-(methoxybenzoyl)benzamidoximes (Ic-If) could be prepared by bringing into reaction the sodium salt of the benzamidoxime[11] with the appropriate acid chloride.

On the other hand, the N-(methoxybenzoyl)benzamidoximes IIa-IId were prepared by treating methoxy-substituted benzohydroximoyl chlorides with the appropriate benzamide in presence of sodium ethoxide, a method in use in the preparation of dibenzamide[7].





Ia X: m—Cl Y : H
Ib X: m—Cl Y: NO_2
Ic X: p—OCH_3 Y: H
Id X: p—OCH_3 Y: NO_2
Ie X: o-OCH_3 Y : H
If X: o-OCH_3 Y : NO_2

IIa X: p-OCH_3 Y : H
IIb X: p-OCH_3 Y : NO_2
IIc X: o-OCH_3 Y : H
IId X: o-OCH_3 Y : NO_2

The reaction of m-chlorobenzamidoxime with benzoylchloride takes place under mild conditions (1h reflux in ether) and with a high yield (about 70%) in Ia. On the contrary, whenever methoxybenzamidoximes react with benzoylchloride the conditions are drastic (2h reflux in benzene) and the yield in O-benzoylbenzamidoxime low (about 30%); a mixture with the N-substituted isomer is obtained.

The difficulty in preparing methoxy-substituted aroylbenzamidoximes compared to chloro-substituted ones could be due to the different electronic behaviour of their caracteristic groups. The chlorine atom acts as an electron acceptor with a positive coefficient ($\sigma_{m\text{-}Cl}$: + 0.373). On the contrary the methoxy group is an electron donor ($\sigma_{p\text{-}OCH_3}$: − 0.270) and possibly inhibits the removal of the hydroxylic hydrogen. Therefore the reaction conditions are more drastic and a mixture with the N-substituted isomer is obtained.

It should be noticed that nitrobenzamidoximes show a behaviour analogous to that of the chloro-substituted ones, while the methyl-substituted compounds act similarly to the methoxy-substituted ones[1].

The two compound classes can be easily distinguished by means of their ir-spectra[1, 6, 8]. The m-chloro-substituted derivatives exhibit a carbonyl absorption at about 1725 cm^{-1}; on the contrary mixtures show two carbonyl absorptions — the O-derivative ν (CO) lies at about 1725 cm^{-1} and the amidic one at 1680 cm^{-1}. In compounds Ic — If the carbonyl band is observed at 1730 cm^{-1}, whereas in N-aroylbenzamidoximes it is to be found at about 1670 cm^{-1} (Table I). Considering the forementioned preparations of O- and N-aroylbenzamdoximes and the spectral data cited, the presence of mixtures in case an acid chloride reacts with methoxy-substituted benzamidoximes is certain.

Deuterium labelling in the N-H group of the mixtures simply confirmed the existence of the isomeric structures[9].

Mass spectral study:

Of great interest are the mass spectra of the two compound classes (Table II)[1,2,9, 10]. All the spectra display the presence of the molecular ion with moderate relative intensity.

TABLE I: Analytical data of the compounds I and II and of their mixtures.

I) Analytical data of the compounds I and II.

Compound	Mol. formula	Mol. weight
Ia	$C_{14}H_{11}ClN_2O_2$	274.7
Ib	$C_{14}H_{10}ClN_3O_4$	319.7
Ic	$C_{15}H_{14}N_2O_3$	270.3
Id	$C_{15}H_{13}N_3O_5$	315.8
Ie	$C_{15}H_{14}N_2O_3$	270.3
If	$C_{15}H_{13}N_3O_5$	315.8
IIa	$C_{15}H_{14}N_2O_3$	270.3
IIb	$C_{15}H_{13}N_3C_5$	315.8
IIc	$C_{15}H_{14}N_2O_3$	270.3
IId	$C_{15}H_{13}N_3O_5$	315.8

Table I continued

Compound	Elem. analysis Calculated (Found)		
	C%	H%	N%
Ia	61.31 (61.38)	4.01 (3.99)	10.22 (10.29)
Ib	52.66 (52.87)	3.13 (3.17)	13.17 (13.27)
Ic	66.65 (66.88)	5.22 (5.29)	10.37 (10.73)
Id	57.14 (57.37)	4.16 (4.23)	13.33 (13.58)
Ie	66.65 (66.48)	5.22 (5.16)	10.37 (10.21)
If	57.14 (56.78)	4.16 (4.26)	13.33 (12.99)
IIa	66.65 (66.37)	5.22 (5.49)	10.37 (10.29)
IIb	57.14 (57.92)	4.16 (4.02)	13.33 (13.07)
IIc	66.65 (66.81)	5.22 (5.37)	10.37 (10.59)
IId	57.14 (57.31)	4.16 (4.29)	13.33 (13.41)

Compound	Melting point, °C	Yield %	ir-spectrum (Nujol) ν CO (cm^{-1})
Ia	138[a]	69	1730
Ib	190[a]	83	1725
Ic	136[a]	34	1725
Id	177[a]	47	1720
Ie	152[a]	29	1720
If	176[a]	38	1725
IIa	124[b]	19	1670
IIb	169[b]	22	1665
IIc	147[b]	8	1680
IId	163[b]	14	1670

II) Analytical data of the mixtures of compounds I and II.

Mixture	Melting point, °C	Yield	ir-spectrum (Nujol) ν CO (cm^{-1})
Ic-IIa	110[a]	62[c]	1720/1665
Id-IIb	166[a]	75[c]	1725/1680
Ie-IIc	133[a]	47[c]	1720/1670
If-IId	154[a]	66[c]	1730/1685

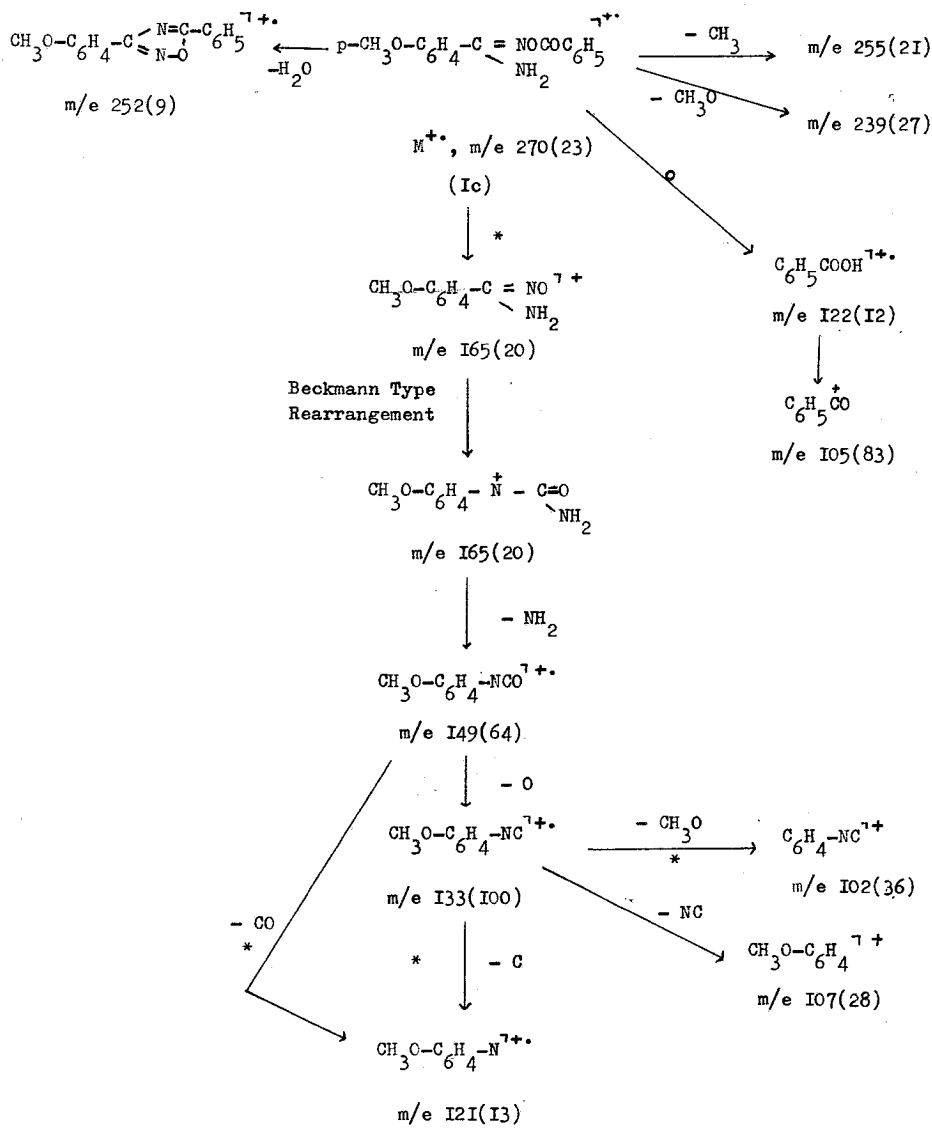
a) Recrystallisation solvent hot ethanol.
b) Recrystallisation solvent ethanol-water 1:1.
c) Overall yields as mixture.

TABLE II: Principal fragment ions in the mass spectra of the compounds I and II and their mixtures.

Compound	m/e (% relative intensity)
Ia	276/274 (25, $M^{+\cdot}$), 258/256 (5), 239 (22), 171/169 (9), 155/153 (61), 139/137 (41), 127/125 (23), 122 (22), 113/111 (6), 105 (100), 102 (17), 77 (54), 51 (22).
Ib	321/319 (52, $M^{+\cdot}$), 303/301 (47), 284 (37), 275/273 (8), 171/169 (11), 167 (67), 155/153 (100), 150 (93), 139/137 (16), 127/125 (29), 122 (37), 113/111 (9), 104 (47), 102 (39), 77 (19), 51 (37).
Ic	270 (23, $M^{+\cdot}$), 255 (21), 252 (9), 239 (27), 165 (20), 149 (64), 133 (100), 122 (12), 121 (13), 107 (28), 105 (83), 102 (36), 77 (37), 51 (30).
Id	315 (10, $M^{+\cdot}$), 300 (60), 297 (8), 284 (5), 269 (7), 167 (18), 165 (31), 150 (70), 149 (46), 133 (100), 122 (19), 121 (16), 107 (10), 104 (7), 102 (9), 77 (15), 51 (10).
Ie	270 (34, $M^{+\cdot}$), 255 (50), 252 (7), 239 (12), 165 (18), 149 (40), 133 (100), 122 (15), 121 (13), 107 (26), 105 (79), 102 (28), 77 (81), 51 (40).
If	315 (11, $M^{+\cdot}$), 300 (41), 297 (16), 284 (7), 269 (3), 167 (63), 165 (17), 150 (100), 149 (6), 133 (71), 122 (12), 121 (17), 107 (10), 104 (14), 102 (19), 77 (35), 51 (32).
IIa	270 (20, $M^{+\cdot}$), 255 (5), 252 (13), 239 (19), 165 (64), 150 (19), 149 (90), 133 (100), 122 (4), 121 (3), 120 (56), 107 (49), 105 (17), 102 (21), 77 (52), 51 (69).
IIb	315 (16, $M^{+\cdot}$), 300 (28), 297 (12), 284 (6), 269 (15), 167 (4), 165 (79), 150 (100), 149 (17), 133 (86), 122 (3), 121 (3), 119 (68), 107 (20), 104 (4), 102 (24), 77 (31), 51 (42).
IIc	270 (20, $M^{+\cdot}$), 255 (6), 252 (17), 239 (13), 165 (60), 150 (19), 149 (76), 133 (100), 122 (3), 121 (3), 120 (46), 107 (53), 105 (22), 102 (36), 77 (58), 51 (29).
IId	315 (11, $M^{+\cdot}$), 300 (17), 297 (12), 284 (6), 269 (18), 167 (4), 165 (68), 150 (100), 149 (21), 133 (89), 122 (5), 121 (2), 119 (72), 107 (18), 104 (6), 102 (33), 77 (26), 51 (37).
Mixtures:	
Ic-IIa	270 (19, $M^{+\cdot}$), 255 (62), 252 (4), 239 (12), 165 (9), 150 (17), 149 (38), 133 (100), 122 (27), 121 (18), 120 (31), 107 (18), 105 (89), 102 (15), 77 (19), 51 (24).
Id-IIb	315 (11, $M^{+\cdot}$), 300 (18), 297 (22), 284 (9), 269 (6), 167 (56), 165 (60), 150 (100), 149 (28), 133 (87), 122 (49), 121 (36), 119 (76), 107 (10), 104 (12), 102 (16), 77 (37), 51 (41).
Ie-IIc	270 (34, $M^{+\cdot}$), 255 (71), 252 (10), 239 (17), 165 (16), 150 (20), 149 (35), 133 (100), 122 (33), 121 (15), 120 (42), 107 (17), 105 (29), 102 (11), 77 (49), 51 (73).
If-IId	315 (20, $M^{+\cdot}$), 300 (7), 297 (20), 284 (16), 269 (4), 167 (50), 165 (53), 150 (100), 149 (22), 133 (76), 122 (38), 121 (60), 119 (85), 107 (11), 104 (16), 102 (17), 77 (49), 51 (52).

By fragmentation of compound Ic (Scheme I, Fig. 1) ion m/e 165 is obtained. A Beckmann type rearrangement in this ion is followed by further fragmentation to ions m/e 149, m/e 133 and finally m/e 121. It should be noticed that the proposed structure of fragment m/e 121 is supported by metastable ion peaks and exact molecular weight measurements[1, 12]. The transition from the molecular ion to ion m/e 165 leads also to a benzoic acid fragment m/e 122, which further on gives fragment m/e 105[1]. The fragmentation of Ia, Ie follows analogous pattern.

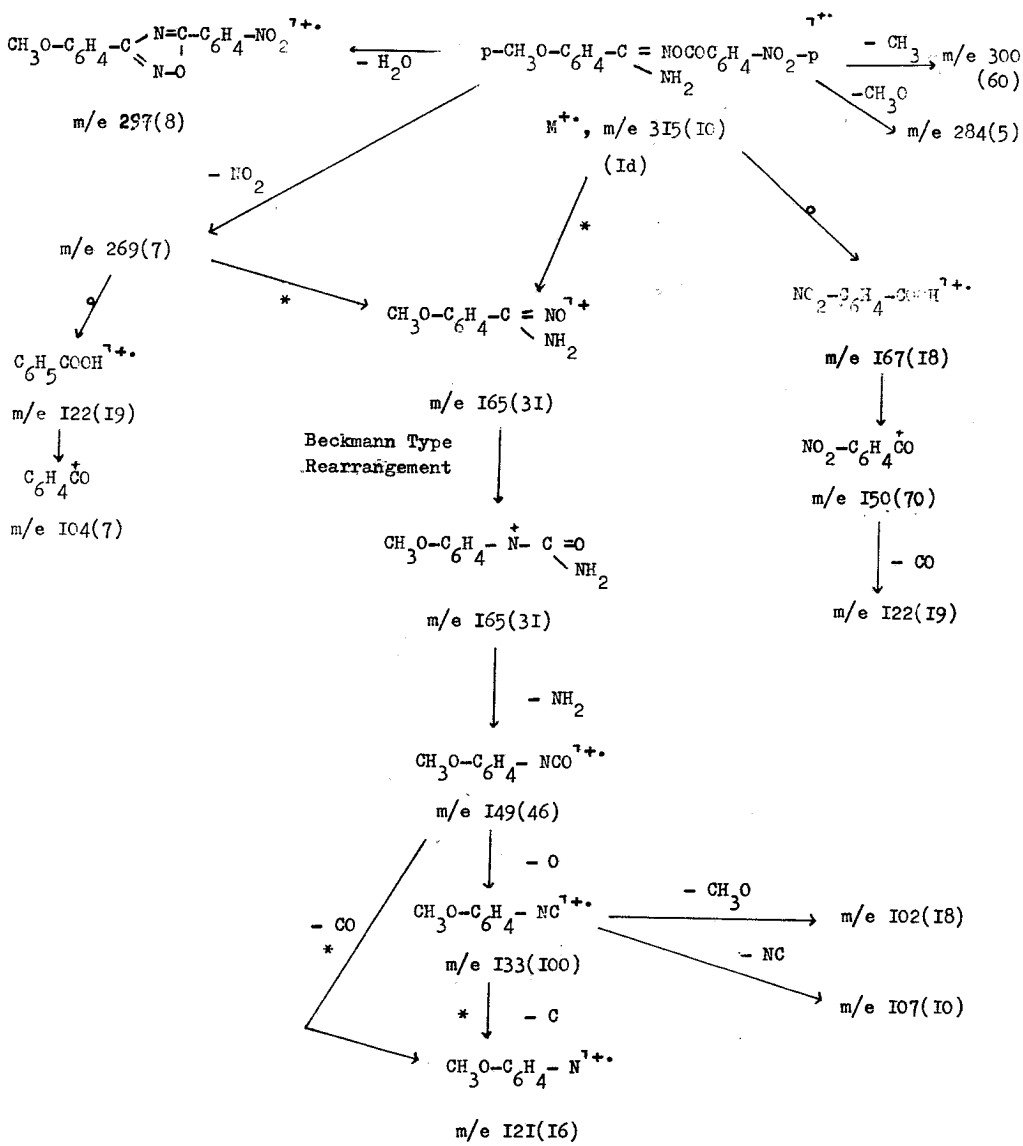
The p-nitro-substituted derivatives Ib, Id, If (Scheme II, Fig. 2) display also the acid on m/e 167[1], leading to ion m/e 150. A Beckmann type rearrangement in frag-



SCHEME I: *Fragmentation pattern of O-benzoyl-4-methylbenzamidoxime (Ic).*

ment m/e 165 explains the presence of ions m/e 149, m/e 133, m/e 121.

In the case of the N-benzoylbenzamidoximes IIa, IIc the Beckmann type rearrangement is only possible in the secondary fragment m/e 165 leading finally to ion m/e 121. At the same time the acid ion m/e 122 and ion m/e 105 are obtained, all with moderate to low relative intensities. On the contrary the main fragmentation reveals the ion $[CH_3O\text{-}C_6H_4 - \dot{C} = NOH]$ (m/e 150) and thus also the amidic fragment m/e 120. In that way they are unambiguously distinguished from their isomers Ic, Ie displaying instead the acid ion m/e 122.



SCHEME II: *Fragmentaton pattern of O-(4'-nitrobenzoyl)-4-methoxybenzamidoxime (Id).*

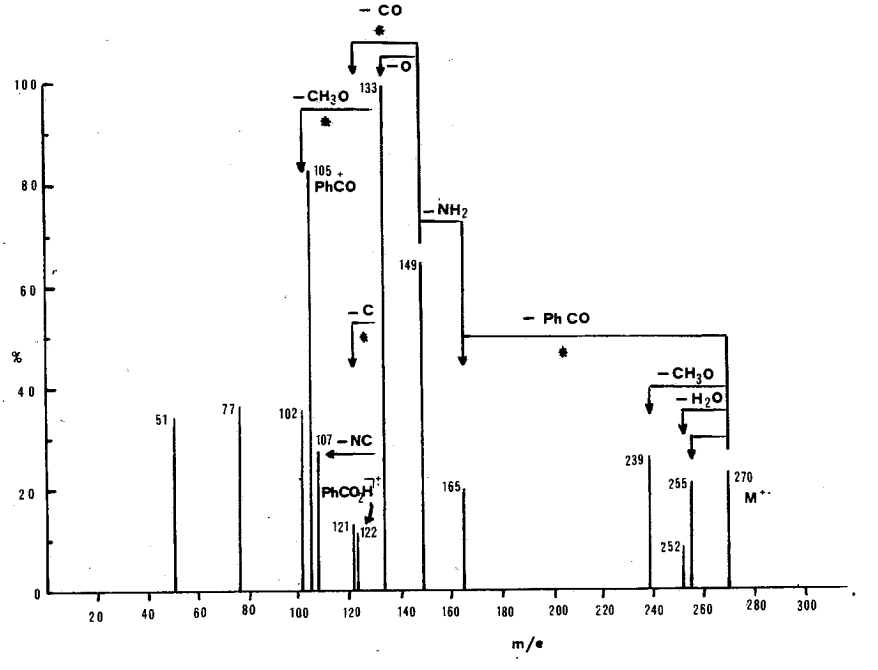


FIG. 1: *Mass spectrum of O-benzoyl-4-methoxybenzamidoxime (Ic).*

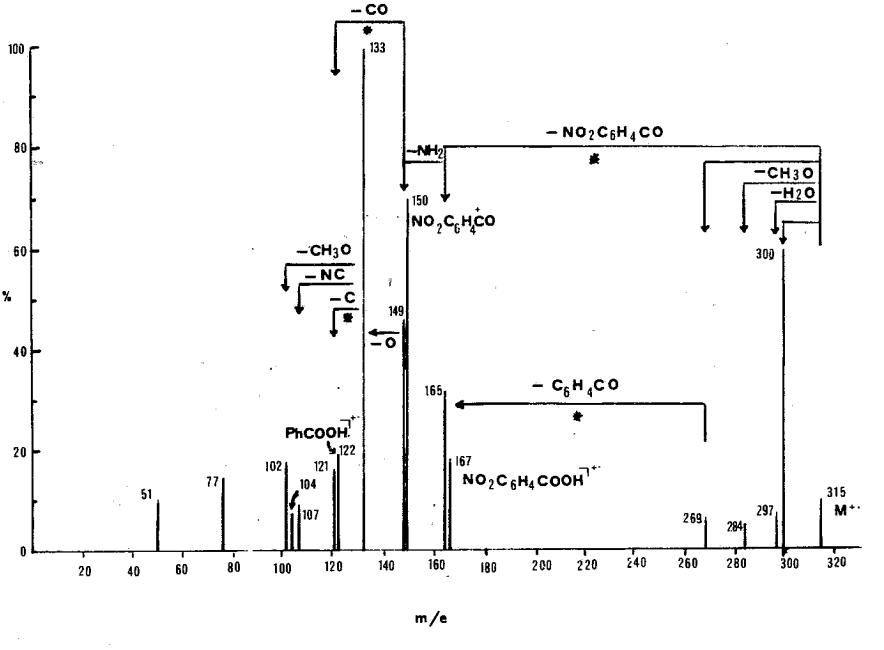
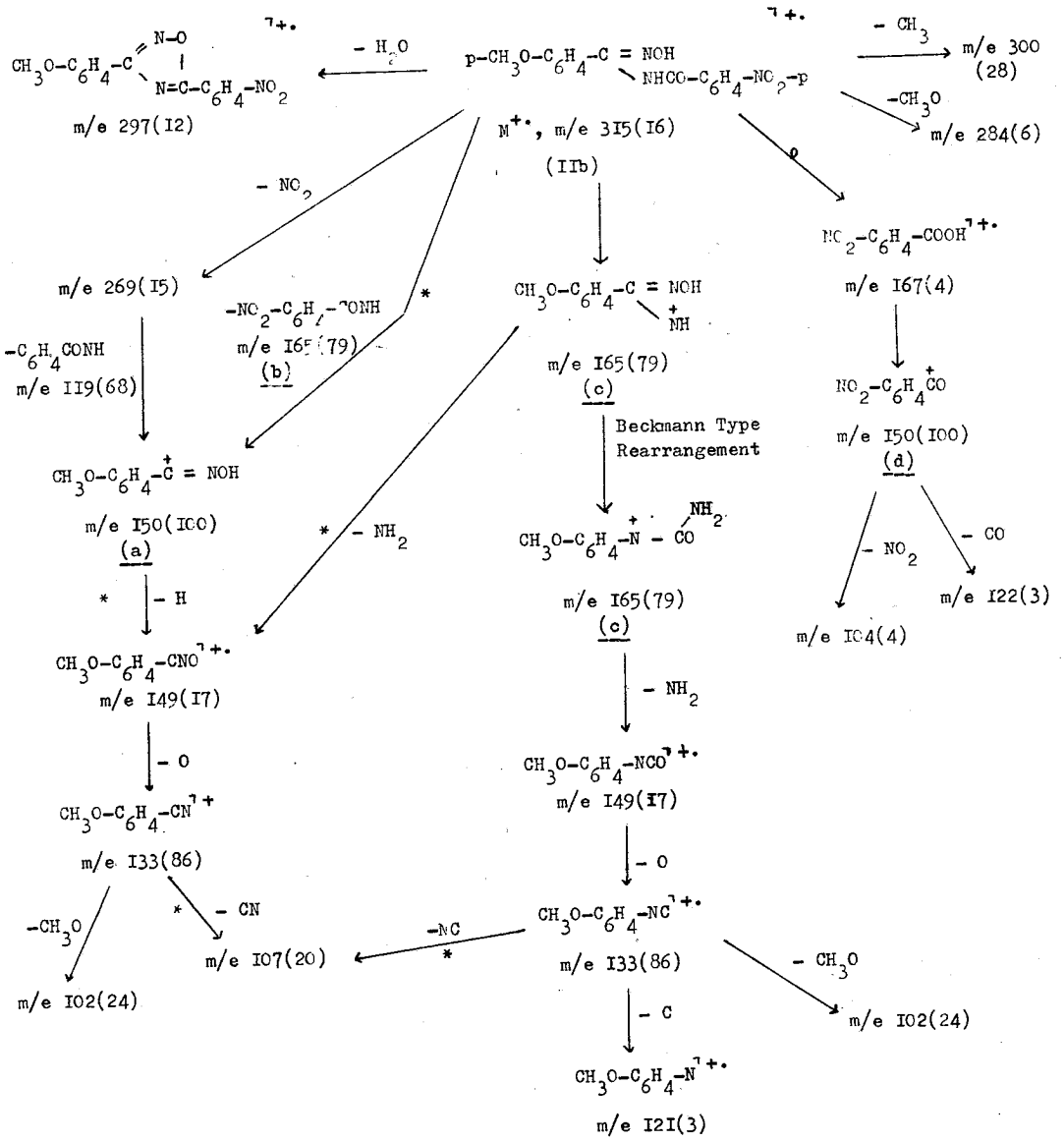


FIG. 2: *Mass spectrum of O-(4'-nitrobenzoyl)-4-methoxybenzamidoxime (Id).*

The p-nitro-derivatives IIb, IId (Scheme III, Fig. 3) exhibit also the oxime ion m/e 150 (a), as well as the amidic fragments m/e 165 (b) and m/e 119, all with high relative intensities. From the secondary fragmentation to ion m/e 165 (c) there are obtained fragment m/e 121 and the aroylium ion m/e 150 (d), as well as the acid ion m/e 167 and further on m/e 122, all with low relative intensities. This secondary fragmentation follows closely the pattern of Id (Scheme II).



SCHEME III: *Fragmentation pattern of N-(4'-nitrobenzoyl)-4-methoxybenzamidoxime (IIb).*

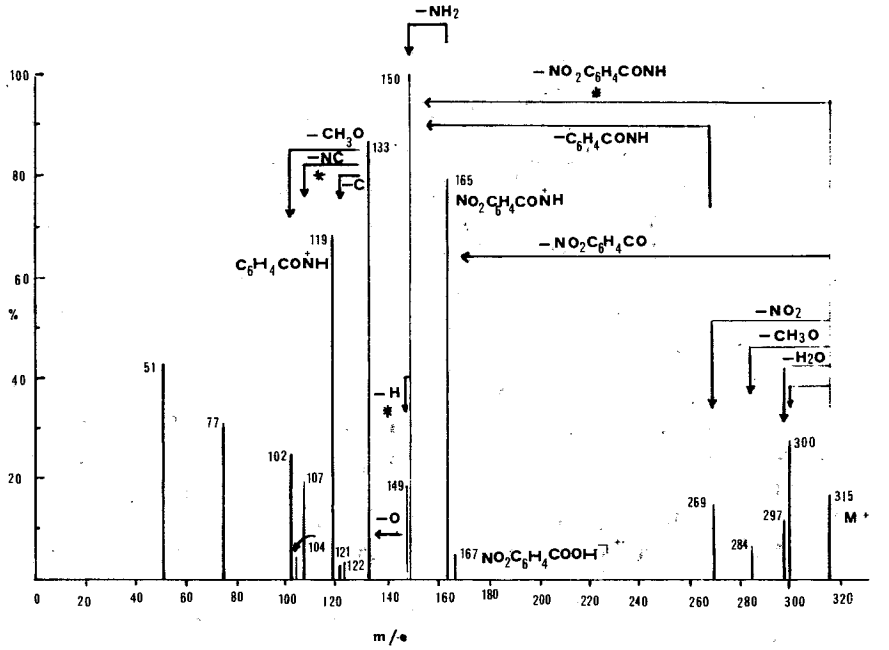


FIG. 3: *Mass spectrum of N-(4'-nitrobenzoyl)-4-methoxybenzamidoxime (IIb).*

The two isomeric compound classes can therefore be easily distinguished on the basis of their mass spectra, since the O-aroylbenzamidoximes display the acid ion $[ArCOOH]^{+\cdot}$, whereas the N-derivatives afford the amidic fragment [ArCONH]. A Beckmann type rearrangement in fragment m/e 165 finally leads to ion $[ArN]^{+\cdot}$.

Experimental

All melting points are uncorrected and were obtained with a Kofler hot stage apparatus. The mass spectra were run at 70 eV on a RMU-6L Hitachi - Perkin - Elmer single focusing mass spectrometer using the direct insertion probe of the samples. The analyses were performed with a Perkin-Elmer analyser, model 240. The ir-spectra were measured in Nujol with a Perkin-Elmer 297 infrared spectrophotometer.

Synthesis of O-aroylbenzamidoximes I:

An ether solution containing equivalent amounts of m-chlorobenzamidoxime and the appropriate aroyl chloride[1] in presence of pyridine was stirred for 2h under reflux. Addition of water yielded the crude O-aroylbenzamidoximes Ia, Ib, which were recrystallised from hot ethanol.

The previous method failed whenever methoxy-substituted benzamidoximes reacted with aroyl chlorides. In these cases mixtures of O- and N-aroylbenzamidoximes were obtained. To prepare pure O-aroyl-methoxybenzamidoximes, the sodium salt of the benzamidoxime[11] was brought to reaction with an equivalent amount of the appropriate acid chloride in ether. The solution was stirred for 1h under reflux in

presence of pyridine. By adding water the crude O-aroylbenzamidoximes Ic - If were obtained, which were recrystallised from hot ethanol.

Synthesis of N-aroylbenzamidoximes II:

Compounds II were obtained by refluxing for 3h in pyridine one equivalent of methoxy-substituted benzohydroximoyl chloride with two equivalents[6, 7] of the appropriate benzamide in presence of sodium ethoxide. By adding water the crude N-aroylbenzamidoxime II was obtained, which was recrystallised from water-ethanol.

For the analytical data of the compounds I and II see Table I.

Περίληψη

Μελέτη φασμάτων μαζών των O- και N-αροϋλοβενζαμιδοξιμών

Περιγράφεται η σύνθεση ορισμένων νέων O- και N-αροϋλοβενζαμιδοξιμών και μελετώνται τα φάσματα μαζών τους. Οι δύο κατηγορίες ενώσεων διαφοροποιούνται σαφώς στα φάσματα μαζών, διότι στα O-παράγωγα εμφανίζεται το ιόν που αντιστοιχεί στο οξύ $[ArCOOH]^{+\cdot}$, ενώ στα N-παράγωγα το αμιδικό θραύσμα $[ArC\overset{+}{O}NH]$. Μετάθεση τύπου Beckmann κατά τη διάσπαση οδηγεί τελικά στο ιόν $[ArN]^{+\cdot}$.

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TRANSANNULAR OXIDATION REACTIONS OF NITROGEN DERIVATIVES OF CYCLODECANE-1,6-DIONE

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Summary

The bis-arylhydrazones of cyclodecane-1,6-dione (1) are oxidised by lead tetraacetate into 9,10-bis-arylazo-decalines (2) and 1,6-bis-acetoxy-1,6-bis-arylazo-cyclodecanes (3). Oxidation of the same bis-arylhydrazones with silver oxide leads also to the formation of transannular products (2). No transannular products are obtained from the oxidation of the dioxime of cyclodecane-1,6-dione (8) with lead tetraacetate.

Key words: Transannular oxidation, lead tetraacetate oxidation, cyclodecane-1,6-dione bis-arylhydrazones.

Introduction

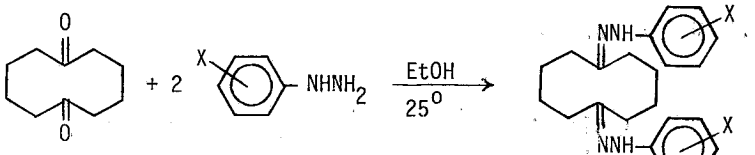
It is well established that medium-sized ring compounds exhibit unusual physical and chemical properties[1] due to their steric nature. One feature of medium-ring geometry is the existence of certain comformations in which opposite sides of the ring come into close proximity to each other. Thus, reactions which involve the formation of a bond between atoms on opposite sides of the ring or reactions which occur on an atom activated only by the proximity in space of a functional group located across the ring are called transannular reactions[2], and characterize the medium-ring compounds.

Oxidation reactions of the bis-hydrazones of medium-ring diketones are not referred in the literature. In order to investigate if these oxidation reactions take place through a transannular way, we have undertaken the synthesis of some bis-arylhydrazones of cyclodecane-1,6-dione and their oxidation with lead tetraacetate (LTA) and silver oxide[3]. In this paper also, the behaviour of the dioxime of the same diketone upon oxidation with LTA is studied[4].

Results and discussion

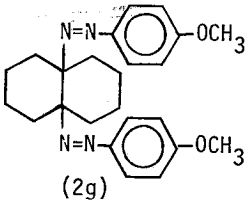
The bis-arylhydrazones (1) are prepared by treatment of cyclodecane-1,6-dione with two equivalents of the arylhydrazine in ethanol solution.

Treatment of cyclodecane-1,6-dione with p-methoxy-phenylhydrazine under the same conditions leads directly to the formation of the oxidized product, 9,10-bis-(p-methoxy-phenylazo)-decaline (2g), in 35% yield.



a: X=H
b: X=CH_3 – p
c: X=Cl – p
d: X=NO_2 – p
e: X=CH_3 – o
f: X=NO_2 – o

(1)



(2g)

The bis-arylhydrazones (1) are proved to be sufficiently sensitive to heat and oxidation. They are changed to the transannular oxidation products (2) upon heating or by leaving for a long time at oxygen atmosphere even at 0 °C, with an exception for derivatives (1d) and (1f) which appear to be stable enough. The analytical data for bis-arylhydrazones (1) are presented in Table I.

In the IR spectra they show peaks in the region 3320-3370 cm^{-1} for ν(NH) and in the NMR spectra they show a multiplet at δ 1.07-3.21 for the methylene protons. In the mass spectra low intensity peaks for molecular ions are observed.

Oxidation of bis-hydrazones (1) with LTA in methylene chloride at room temperature was complete in about 2 hrs. The products were 9,10-bis-arylazo-decalines (2) and 1,6-bis-acetoxy-1,6-bis-arylazo-cyclodecanes (3).

Both products (2) and (3) are coloured and exhibit in the visible region absorption peaks at 418-445 (ε=250-550) and 400-413 nm (ε=500-700) respectively. Products (3) show IR peaks in the region 1720-1740 cm^{-1} for ν(CO) and their NMR spectra run in $CDCl_3$ show a singlet for the methyl acetate protons at δ 2.10-2.15 and two multiplets for the methylene protons at δ 1.50-2.83. In the mass spectra compounds (3) show the presence of the ion $[M-58]^+$ instead of the molecular ion, while compounds (2) show a low intensity peak for the molecular ion. In the NMR spectra compounds (2) show a broad multiplet for the methylene protons at δ 1.00-2.66. The analytical data for compounds (2) and (3) are reported in more details in Tables II and III respectively and their yields are presented in Table IV.

Concerning the reaction mechanism[5] it is considered that two parallel reactions take place (Scheme). For the formation of 9,10-bis-arylazo-decaline (2) it is accepted that the first step of the reaction is the formation of a bond between the nitrogen of one NH group of bis-hydrazone and lead (4). Heterolysis of the N-Pb bond and simultaneous transannular elimination of acetic acid leads to product (2). Product (3) is considered to originate from an intermediate like (5) in which N-Pb bonds are formed from both NH groups of the bis-hydrazone[5]. Heterolysis of these bonds and attack of the carbon atoms by the acetoxy-groups yields product (3).

From the results recorded in Table IV it is obvious an influence of the electronic effect of substituent X on the relative yields of the two oxidation products. In more

TABLE I: Analytical Data for the Bis-arylhydrazones of Cyclodecane-1,6-dione (1).

Compound	M.p. °C[a]	Yield %	Formula	Molecular Weight (MS, $M^{+\cdot}$, %)	Analysis % Calcd. C	H	N	Found C	H	N
(1a)	155-170	80	$C_{22}H_{28}N_4$	348.48 348(11)	75.82	8.10	16.08	75.76	8.16	15.99
(1b)	138-151	50	$C_{24}H_{32}N_4$	376.53 376(4)	76.55	8.57	14.88	76.71	8.65	14.86
(1c)	144-160	75	$C_{22}H_{26}Cl_2N_4$	417.37 416/418/420(7)	63.31	6.28	13.42	63.26	6.27	13.39
(1d)	257-266	70	$C_{22}H_{26}N_6O_4$	438.48 438(2)	60.26	5.98	19.15	60.39	6.02	18.99
(1e)	160-173	75	$C_{24}H_{32}N_4$	376.53 376(1)	76.55	8.57	14.88	76.20	8.52	14.67
(1f)	178-182	60	$C_{22}H_{26}N_6O_4$	438.48 438(12)	60.26	5.98	19.15	60.47	6.06	19.12

[a] The broad m.p.s. are probably due to the existence of certain stereoisomers (E, Z) or due to the partial oxidation of the sample.

TABLE II: Analytical Data for the 9,10-Bis-arylazo-decalines (2).

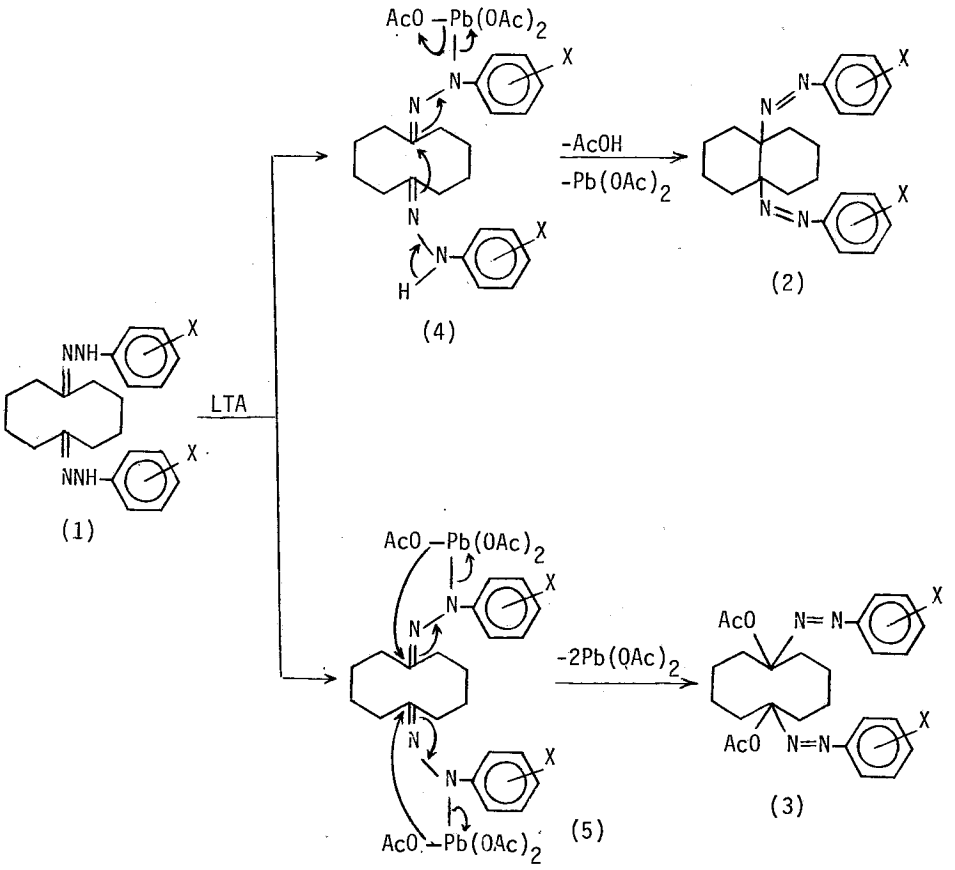
Compound	M.p. °C[a]	Formula	Molecular Weight (MS, $M^{+\cdot}$, %)	Analysis % Calcd. C	H	N	Found C	H	N
(2a)	91-93	$C_{22}H_{26}N_4$	346.46 346(5)	76.26	7.56	16.17	75.92	7.58	16.23
(2b)	124-126	$C_{24}H_{30}N_4$	374.51 374(12)	76.96	8.07	14.96	77.03	8.08	14.95
$(2c)_1$	227-229	$C_{22}H_{24}Cl_2N_4$	415.35 414/416/418 (<0.5)	63.61	5.82	13.49	63.52	5.79	13.49
$(2c)_2$	121-123	$C_{22}H_{24}Cl_2N_4$	415.35 414/416/418(2)	63.61	5.82	13.49	63.28	5.82	13.56
(2d)	163-165	$C_{22}H_{24}N_6O_4$	436.46 436 (<0.5)	60.54	5.54	19.26	60.71	5.59	19.38
$(2e)_1$	176-178	$C_{24}H_{30}N_4$	374.51 374 (<0.5)	76.96	8.07	14.96	77.09	8.11	14.56
$(2e)_2$	103-105	$C_{24}H_{30}N_4$	374.51 374(3)	76.96	8.07	14.96	77.04	8.04	15.03
(2f)	191-193	$C_{22}H_{24}N_6O_4$	436.46 436 (<0.5)	60.54	5.54	19.26	60.38	5.65	19.37
(2g)	119-121	$C_{24}H_{30}N_4O_2$	406.51 406(20)	70.91	7.44	13.78	70.68	7.44	14.00

[a] Recrystallization from ethanol.

TABLE III: Analytical Data for the 1,6-Bis-acetoxy-1,6-bis-arylazo-cyclodecanes (3).

Compound	M.p. °C[a]	Formula	Molecular Weight [MS, $(M-58)^{+\cdot}$, %]	Analysis % Calcd. C	H	N	Found C	H	N
$(3c)_1$	175-177	$C_{26}H_{30}Cl_2N_4O_4$	533.45 474/476/478 (<0.5)	58.54	5.67	10.50	58.59	5.71	10.47
$(3c)_2$	132-135	$C_{26}H_{30}Cl_2N_4O_4$	533.45 474/476/478 (<0.5)	58.54	5.67	10.50	58.53	5.72	10.40
(3d)	201-205	$C_{26}H_{30}N_6O_8$	554.54 496 (<0.5)	56.31	5.45	15.16	56.36	5.47	14.99
(3e)	162-167	$C_{28}H_{36}N_4O_4$	492.60 434 (<0.5)	68.27	7.37	11.37	68.19	7.32	11.12
$(3f)_1$	236-238	$C_{26}H_{30}N_6O_8$	554.54 496 (<0.5)	56.31	5.45	15.16	56.07	5.50	15.07
$(3f)_2$	150-153	$C_{26}H_{30}N_6O_8$	554.54 496 (<0.5)	56.31	5.45	15.16	56.22	5.45	15.20

[a] Recrystallization from ethanol except for compound $(3f)_1$ which was recrystallized from chloroform.

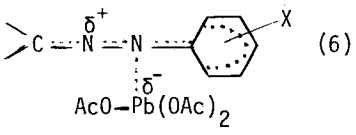


Scheme

detail, it is indicated that electron-releasing substituents X favour transannular products (2), while electron-withdrawing substituents X favour the formation of monocyclic products (3). An approach to the explanation of this effect can be obtained assuming an intermediate moiety like (6), during the oxidation reaction.

TABLE IV: Products Obtained by the Oxidation of Bis-aryl-hydrazones (1) with LTA.

Bis-arylhydrazone	9,10-Bis-arylazo-decaline	Yield %	1,6-Bis-acetoxy-1,6-bis-arylazo-cyclodecane	Yield %
(1a)	(2a)	63	—	—
(1b)	(2b)	60	—	—
(1c)	$(2c)_1$	2	$(3c)_1$	15
	$(2c)_2$	44	$(3c)_2$	23
(1d)	(2d)	25	(3d)	53
(1e)	$(2e)_1$	3	(3e)	5
	$(2e)_2$	35	—	—
(1f)	(2f)	14	$(3f)_1$	23
			$(3f)_2$	51



(6)

Assuming the $-NO_2$ group as X, the positive charge belongs rather to the carbon atom, which becomes sensitive to the attack of the acetoxy-group, thus resulting product (3). If X is CH_3- or CH_3O- group, the positive charge is mainly distributed to the aromatic ring, thus giving rise to the formation of the transannular product (2). On the other hand the above mentioned influence of the substituent X to the species of the oxidation products supports the proposed view for a polar oxidation mechanism.

From the oxidation of bis-hydrazones (1c) and (1e) two stereoisomers $(2c)_1$, $(2c)_2$ and $(2e)_1$, $(2e)_2$ were separated after repeated thin layer chromatographic analyses, having different melting points and different relative yields. The products with higher melting points $(2c)_1$, $(2e)_1$ (trans-) were isolated in smaller yields than the other isomers $(2c)_2$, $(2e)_2$, the relative ratio yield being equal to ~ 1:10. On the other hand, X-ray crystallographic analysis made by Rentzeperis[5] and his coworkers[6] demonstrated the cis- decaline structure (Figure) for the compound $(2c)_2$.

Two isomeric 1,6-bis-acetoxy-1,6-bis-arylazo-cyclodecanes $(3c)_1$, $(3c)_2$ and $(3f)_1$, $(3f)_2$ were also isolated from the oxidation of hydrazones (1c) and (1f) respectively, which are supposed to be cis-trans isomers.

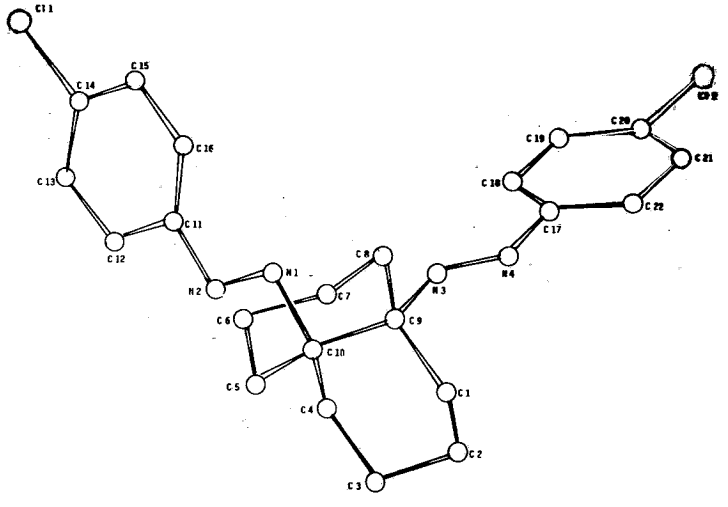
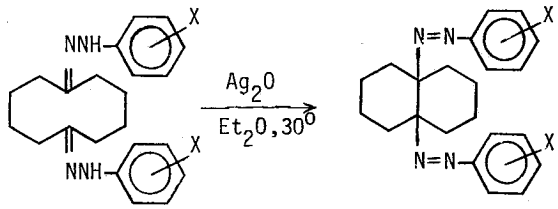


FIGURE: *Clinographic projection of (E,E) 9,10-bis-(p-chloro-phenylazo)-cis-decaline* $(2c)_2$.

The oxidation of bis-hydrazones (1) with silver oxide in refluxing ether, for 30 hrs, leads exclusively to the formation of the transannular products (2) in remarkable high yields (~90%).

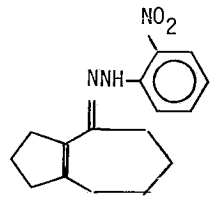
It is mentioned that the bis-hydrazones (1d) and (1f) were oxidised in very low yields (~20%), probably because of their particularly low solubility in ether.



(1) (2)

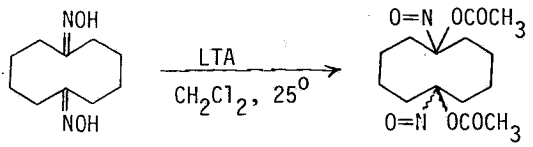
However, when tetrahydrofuran was used as solvent, the yields of products (2d) and (2f) were also increased up to 80%.

From the oxidation of hydrazone (1f), we have also isolated an 1,5-transannular reaction product, the o-nitro-phenyl-hydrazone of bicyclo[5.3.0]dec-1 (7)-en-2-one (7).



(7)

The behaviour of the dioxime of cyclodecane-1,6-dione (8) upon oxidation was completely different, in comparison with bis-arylhydrazones (1). Thus, no transannular reaction products were isolated from the oxidation of dioxime (8) with LTA. From the oxidation products two isomeric blue coloured 1,6-bis-acetoxy-1,6-bis-nitroso-cyclodecanes (9) were only identified.



(8) (9)

There are indications from the EPR spectrum of the reaction mixture, that this oxidation proceeds via a free radical reaction pathway, in agreement with previous results received by Lown[7], but this subject is under further consideration.

Experimental

NMR (60 MHz, tetramethylsilane internal standard) and mass spectra (70 eV) were recorded on a Varian A-60A and Hitachi-Perkin-Elmer RMU-6L spectrometers, respectively. IR spectra were recorded on a Perkin-Elmer 297 spectrometer and analyses were performed with a Perkin-Elmer Model 240 CHN Analyser. Melting points have been obtained on a Kofler hot stage apparatus and they are uncorrected.

General procedure for the Preparation of Bis-arylhydrazones of Cyclodecane-1,6-dione (1). The bis-arylhydrazones (1) were prepared by stirring cyclodecane-1,6-dione (0.01 mol) and the appropriate arylhydrazine (0.022 mol) in ethanol solution at room temperature for about 20 hrs. An exception was observed for nitro- substituted hydrazones (1d) and (1f), which require reaction periods of about 100 hrs. The precipitated hydrazones (1) are further purified by washing with ethanol and ether many times. Further purification by recrystallization was not attempted because these compounds are unstable on heating, as it has been mentioned above. The bis-hydrazones (1d) and (1f) however were recrystallized from dimethylsulfoxide and benzene, respectively.

The hydrazone (1d) was also prepared by refluxing a solution of cyclodecane-1,6-dione and p-nitro-phenylhydrazine in n-propanol for 4 hrs. When these conditions were applied for the preparation of hydrazones (1a-c) and (1e) the corresponding oxidation products (2a-c) and (2e) were formed.

General Procedure for the Oxidation of Bis-arylhydrazones (1) with Lead Tetraacetate. A general procedure is described[8]. To a suspension of 0.01 mol of hydrazone (1) in 40 ml methylene chloride, a solution of 0.02 mol of LTA in 40 ml methylene chloride was added and the mixture was stirred at room temperature for 2 hrs. The methylene chloride solution was treated with water, filtered and the organic layer was washed with sodium carbonate solution, water and then dried. The reaction products were in some cases solids or they were crystallized by addition of ethanol. They were further purified by recrystallization from ethanol. However, in the cases where more than one products were formed, the reaction mixture was subjected to column chromatography on silica gel (petroleum ether 40-60°-ethyl acetate 10:1 or $CHCl_3$ as eluant). Particularly, in that cases where mixtures of isomers were isolated further separation and purification of products were effected with preparative TLC and recrystallization, usually from ethanol.

General Procedure for the Oxidation of Bis-arylhydrazones (1) with Silver Oxide[9]. A mixture of bis-arylhydrazone (1) (0.001 mol) and silver oxide (0.006 mol) in dry ether was stirred under reflux for 30 hrs. The remaining solids were filtered off and washed many times with ether and chloroform. The combined mother liquor and the washings contained usually one product (2), which was collected by evaporation of the solvent. The oxidation of hydrazone (1f) with silver oxide, besides product (2f) afforded the o-nitro-phenyl-hydrazone of bicyclo [5.3.0] dec-1 (7)-en-2-one (7) in 6% yield. M.p. 151-154 °C; ν_{max} (Nujol) 3325 cm^{-1} (NH); δ_H ($CDCl_3$) 1.50-2.10 (6H, m), 2.20-3.10 (8H, m), 6.63-7.01 (1H, m), 7.35-8.32 (3H, m); m/e 285 (2) $M^{+\cdot}$, 148 (25), 138 (61), 105 (67), 91 (100). (Found: C, 67.23; H, 7.00; N, 14.94. $C_{16}H_{19}N_3O_2$ requires C, 67.34; H, 6.71; N, 14.73).

Oxidation of Dioxime of Cyclodecane-1,6--dione (8) with Lead Tetraacetate. The dioxime (8) is a known compound which was oxidised with LTA according the general procedure[8] described above with bis-hydrazones (1). The reaction mixture was then separated by column chromatography on silica gel, using a mixture of petroleum ether 40-60° and ethyl acetate 5:1 as eluant. There were isolated two blue coloured isomeric 1,6-bis-acetoxy-1,6-bis-nitroso-cyclodecanes (9). On the basis of the difference in melting points we could possibly propose the "cis" structure for the compound with low melting point and the "trans" structure for that of the high melting point. The analytical data for compounds (9) are the following:

i) "trans"-1,6-bis-acetoxy-1,6-bis-nitroso-cyclodecane. Yield 6%, M.p. 143-150° C (dec) (from EtOH); λ_{max} (EtOH) 665 nm (ε=43); ν_{max} (Nujol) 1740 and 1765 cm^{-1} (CO); δ_H ($CDCl_3$) 1.30-2.60 (16H, m), 2.21 (6H, s); m/e 314 (–) $M^{+\cdot}$, 284 (<0.5), 254 (<0.5), 241 (<0.5), 211 (1), 198 (2), 182 (2), 152 (28), 134 (34), 60 (15), 43 (100). (Found: C, 52.93; H, 6.98; N, 9.08. $C_{14}H_{22}N_2O_6$ requires C, 53.49; H, 7.05; N, 8.91).

ii) "cis"-1,6-bis-acetoxy-1,6-bis-nitroso-cyclodecane. Yield 18%. M.p. 87-101°C (dec) (EtOH); λ_{max} 675 nm (ε=30); ν_{max} (Nujol) 1750 cm^{-1} (CO); δ_H ($CDCl_3$) 1.10-2.70 (16H, m), 2.16 (6H, s); m/e 314 (–) $M^{+\cdot}$, 284 (2), 254 (<0.5), 241 (<0.5), 211 (2), 198 (<0.5), 182 (5), 152 (39), 134 (48), 60 (21), 43 (100). Found: C, 53.02; H, 7.16; N, 9.01. $C_{14}H_{22}N_2O_6$ requires C, 53.49; H, 7.05; N, 8.91).

Περίληψη

Υπερκυκλικές οξειδώσεις αζωτούχων παραγώγων της κυκλοδεκανοδιόνης-1,6

Οι διαρυλο-υδραζόνες της κυκλοδεκανοδιόνης-1,6 οξειδώνονται με οξείδιο του αργύρου και με τετραοξικό μόλυβδο προς 9,10-διαρυλαζω-δεκαλίνια, ο σχηματισμός των οποίων επιβεβαιώνει τη λειτουργία του υπερκυκλικού φαινομένου στην τάξη αυτή των ενώσεων. Εκτός από τα 9,10-διαρυλαζω-δεκαλίνια, σχηματίσθηκαν και 1,6-διακετοξυ-1,6-διαρυλαζω-κυκλοδεκάνια, από την οξείδωση των ίδιων δι-υδραζονών με τετραοξικό μόλυβδο. Ωστόσο, η οξείδωση της διοξίμης της κυκλοδεκανοδιόνης-1,6 δεν έδωσε υπερκυκλικά προϊόντα, αλλά δύο ισομερή 1,6-διακετοξυ-1,6-δινιτρωδο-κυκλοδεκάνια.

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THE SOLVENT EFFECT ON THE STEREOSPECIFICITY OF THE METHOXIDE INITIATED D,L-VALINE NCA POLYMERIZATIONS

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Summary

The base initiated D,L-NCA polymerizations are thought to proceed through either the strong base or the carbamate ion mechanism. In any case, the ionic nature of the polymerization mechanism suggests that the polymerization is subjected to significant solvent effects. The ratio of homopropagation and syndiopropagation constants (k_{DD}/k_{DL}), which is designated as **a**, can be measured from NMR experiments and has been found to depend strongly on the polymerization solvent. In this article, a correlation is attempted between **a** and the empirical parameter $E_T(30)$ of the solvent.

Key Words: D,L-Valine NCA, polymerization, stereospecificity, methoxide, methanol, NMR spectra, empirical parameter $E_T(30)$

Abbreviations and Terminology

$E_T(30)$	: Empirical parameter characterizing the solvent polarity and measured at 30°C.
a	: The stereospecificity coefficient $k_{LL}/k_{LD} = k_{DD}/k_{DL}$ measured from the splitting pattern of the 300 MHz NMR spectra of poly-(D,L-Valines).
<**a**>	: The extrapolated **a** values to 0% methanol of the **a** vs. % methanol lines, of the polyvalines obtained with different methoxide initiators in a variety of solvents.
q	: The formal charge of the cation of the methoxide.
r_c	: The crystal radius of the cation of the methoxide.
NMR	: Nuclear magnetic resonance.
NCA	: N-carboxy-anhydride (Leuch's anhydride).
$G^{\neq}_{DD} = G^{\neq}_{LL}$	: Free energy of activation of the homopropagation reaction.
$G^{\neq}_{DL} = G^{\neq}_{LD}$	: Free energy of activation of the syndiopropagation reaction.

Introduction

D,L-Val-NCA can be readily polymerized by using methoxides as initiators, in a variety of solvents. Recent studies[1] suggest that the polymerization may proceed through the carbamate ion mechanism, thus leading to the incorporation of the

methoxide into the polypeptide chain. 300 MHz high resolution NMR spectroscopy revealed[2,3] that the methoxy resonance, normally expected to be a singlet at 3.8 ppm, exhibits a characteristic splitting pattern, dependent on the stereosequence distribution of the D- and L- units at the C- terminal chain end. These NMR measurements offer a convenient method of calculating the ratio of the homopropagation to syndiopropagation constant for the following reactions:

$$CH_3O\text{-}Val_{(D)} + \text{D-Val-NCA} \xrightarrow{k_{DD}} CH_3O\text{-}Val_{(D)}\text{-}Val_{(D)} \quad (1)$$

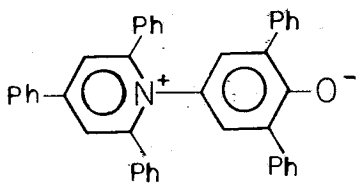
$$CH_3O\text{-}Val_{(D)} + \text{L-Val-NCA} \xrightarrow{k_{DL}} CH_3O\text{-}Val_{(D)}\text{-}Val_{(L)} \quad (2)$$

By symmetry considerations $k_{LL} = k_{DD}$ and $k_{LD} = k_{DL}$. It is evident that this ratio of rate constants (kinetic parameters) carries information about the steroselectivity of the polymerization, at least in the initial stages of the chain growth.

Previous studies showed[4] that the k_{DD}/k_{DL} ratio depends on the polymerization solvent and on the cation of the methoxide initiator CH_3OM (M: Li, Na, K, $\overset{+}{N}Bz(CH_3)_3$, Al), suggesting the importance of the electrostatic interactions in the transition state of the polymerization process.

In this article, the empirical parameter $E_T(30)$ of the polymerization solvent will be correlated with the k_{DD}/k_{DL} ratio. Such a correlation will contribute to a better understanding of the solvent participarion in the stereoregulation of the polymerization process.

The $E_T(30)$[5] is based on the solvatochromatism of a pyridinium phenoxide dye:



The positive charge of the dye is highly screened and consequently the solvation of the anionic part predominates. Therefore, the $E_T(30)$ value reflects the electrophilicity and the H-bond donor activity of the solvent.

The carbamate anion $CH_3OCOCHRNHCOO^-$, which is believed to propagate the NCA polymerizations[1], is expected to interact with the solvent in an analogous fashion like the pyridinium phenoxide dye. Therefore, the $E_T(30)$ values which were calculated for the pyridinium phenoxide dye-solvent interactions are expected to be a good measure of the carbamate-solvent interactions.

Experimental

A. Initiators

Lithium, Sodium and Potassium Methoxides were prepared from the corresponding metal and anhydrous methanol in an inert solvent (petr. ether). Benzyltrimethylammonium Methoxide was purchased as a methanolic solution from

HEXCEL, under the trade name Sumquat 2300. The material was further purified by successive evaporation and addition of absolute methanol, until a coloured compound precipitated. The residue was treated with ethyl acetate and enough petroleum ether was added until a colourless compound precipitated, which was filtered and dried **in vacuo.** Aluminium Methoxide was prepared by refluxing overnight a suspension of Al powder with $HgCl_2$ in catalytic amounts, in excess of absolute methanol. After the removal of the excess methanol by distillation, the grey-white powder of Aluminum Methoxide was collected. The initiators were employed as 0.1 M solutions in absolute methanol, except for Aluminum Methoxide which was added as solid to the polymerization medium.

B. Solvents

p-Dioxane (Baker analyzed reagent) was first refluxed over Na metal and $LiAlH_4$ and distilled prior to use (b.p.: 101-102° C).

Benzene (Baker analyzed reagent) was refluxed overnight over Na turnings and distilled prior to use (b.p.: 80-81° C).

1,2-Dichloroethane (Matheson Coleman and Bell) was refluxed over BaO overnight and distilled prior to use (b.p.: 82-83° C).

In all other cases, spectroquality solvents were used without further purification.

C. Monomer

D,L-Val-NCA was synthesized according to the procedure described by Farthing[6] and was recrystallized from ethyl acetate hexane mixtures at least 3 times before use (m.p.: 79-81° C).

D. Polymerization Procedure

The polymerization bottles were meticulously cleaned and dried. In all experiments, a 2% solution of D,L-Val-NCA was employed (1 gr. of NCA in 50 ml of the solvent).

After the NCA had dissolved, 1.0 ml of the initiator solution was injected directly into the rapidly stirred solution along with any additional amts of methanol, necessary to bring the system to the desired methanol content. The polymerization bottle was then sealed with a rubber septum, which was fitted with a small gauge hypodermic needle, connected to a drying tube. At the end of the polymerization, the solvent was removed with the rotary evaporator. The residue was treated with 200 ml of water, filtered and dried **in vacuo.**

E. NMR Measurements

The spectra of the prepared polyvalines were recorded at room temperature, in tubes with 5 mm o.d., using a High Resolution 300 MHz NMR spectrometer (Varian Associates). The instrument operated at a modulation frequency of 40 KHz and the receiver gain was set at 40 decibel. The ratio-frequency level didn't exceed 30 decibel in order to avoid saturation. The samples were dissolved in a $CDCl_3$-CF_3COOH (2:1 v/v) mixture and their concentration was approximately 10%. Initially the polyvaline spectrum was recorded in a sweep range of 2,500 Hz. Then the region at 3.8 ppm, where the methoxy resonance appears, was expanded and recor-

ded in a sweep range of 100 Hz. A typical expanded methoxy proton resonance pattern, looks like the one shown in Fig. 1. The area of the peaks A, B, C, D offers information concerning the stereospecificity of the D,L-Val-NCA polymerizations. The area of these peaks was measured with a planimeter.

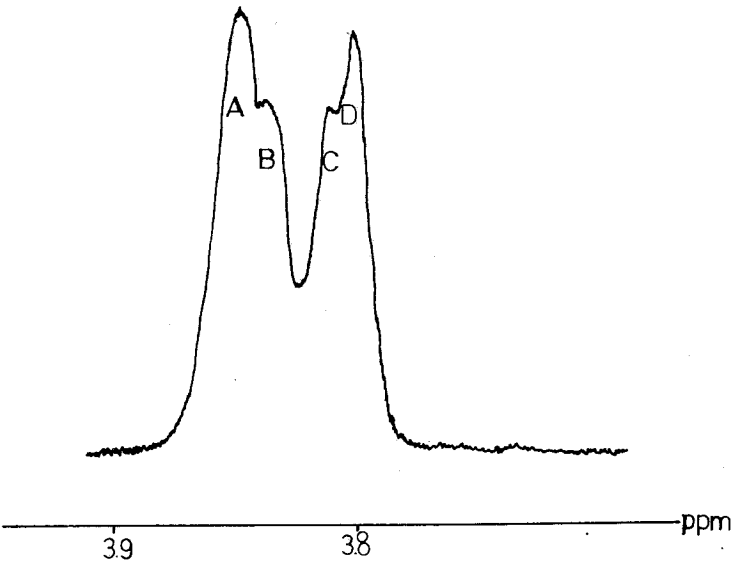


FIG. 1: *Expansion of the Methoxy Proton Resonance of the 300 MHz NMR Spectrum of Poly(D,L-Valine) Prepared from Methoxide Initiated D,L-Valine NCA Polymerization. The Polymer is Dissolved in a 2:1 (v/v) $CDCl_3/CF_3COOH$ Mixture (Ref. 4).*

Results and Discussion

Sawan and Harwood[2,3] proved that during the methoxide initiated polymerizations of NCAs, the initiator fragment (CH_3O-) is incorporated into the resulting polypeptide chain. It also exhibited a splitting pattern, which was found to depend on the distribution of the D- and L- aminoacid units at the vicinity of the methoxy protons. Consequently, this methoxy resonance pattern provides a measure of the stereoselectivity of the methoxide initiated D,L-NCA polymerizations.

The stereoselectivity coefficient **a**, defined as

$$\mathbf{a} = \frac{k_{LL}}{k_{LD}} = \frac{k_{DD}}{k_{DL}}$$

can be experimentally calculated by measuring the areas A, B, C, D (Fig. 1).

$$\mathbf{a} = \frac{\text{area of (A+B) signal}}{\text{area of (C+D) signal}}$$

The stereoselectivity coefficient was found[4] to vary linearly with the methanol content of the polymerization media, for methanol contents from 2% v/v to 10% v/v. Table 1 shows the slopes of the **a** vs. % methanol concentration plots obtained with different initiators and polymerization solvents. The extrapolated **a** values to 0%

TABLE I: Slopes of a Values versus % Methanol Concentration Plots Solvent

Initiator	⌀H	1,2-DCE	DMF	DIOXANE	Et_2O	$EtNO_2$	CH_3CN	THF	THF-CH_3CN 1:1 (v/v)
CH_3OLi	0.27	0.23	0.10	0.02	0.09	0.16	0.08	0.05	0.11
CH_3ONa	0.16	0.17	0.12	0.03	0.05	0.17	0.08	0.03	0.08
CH_3OK	0.00	0.02	0.10	0.00	0.03	0.14	0.12	0.02	0.05
$CH_3O\bar{B}_2\overset{+}{N}(CH_3)_3$	0.32	0.18	0.12	0.02	0.03	0.12	0.11	0.03	0.05
$(CH_3O)_3$ Al	0.62	–	–	–	–	–	0.11	–	–

methanol concentration, designated as <**a**>, were found[4] to vary systematically with the size of the cation of the methoxide initiator and a linear relation was found to hold between <**a**> and q/r_c^2, where q is the formal charge of the cation of the methoxide initiator and r_c its crystal radius (see Table II).

TABLE II: <**a**> Values Obtained from Extrapolation of **a** Values vs MeOH % plots to Zero MeOH Concentrations for Different Initiators and Polymerization Solvents

Initiator	⌀H	1,2-DCE	Et_2O	THF	DIOXANE	CH_3CN	$EtNO_2$	DMF	THF-CH_3CN 1:1 (v/v)
CH_3OLi	0.80	0.43	0.65	0.36	0.39	0.42	0.45	0.35	0.37
CH_3ONa	0.30	0.39	0.51	0.29	0.29	0.30	0.15	0.25	0.33
CH_3OK	0.38	0.34	0.44	0.28	0.24	0.19	0.21	0.41	0.30
$CH_3O\bar{B}z\overset{+}{N}(CH_3)_3$	0.06	0.16	0.33	0.25	0.20	0.12	0.15	0.21	0.14
$(CH_3O)_3$ Al	3.25	–	–	–	–	0.56	–	–	–

It was attempted[4] to correlate the slopes of the **a** vs. q/r_c^2 lines with a parameter characterizing the solvent polarity. Initially, the dielectric constant of the solvent was used, because the low dielectric constant solvents (Benzene, Diethyl Ether) had higher slopes than the slopes of the more polar solvents (DMF, CH_3CN). This correlation though, exhibited anomalies that remained poorly understood.

The dielectric constant indeed describes the ability of a solvent to separate electrical charges and orient its dipolar molecules. However, the sum of the interactions between the solute and solvent molecules is much more extensive and complicated. Besides the nonspecific coulombic, inductive and dispersion interactions, there are also specific H-bond, electron pair donor-acceptor and solvophobic interactions. it was then reaseonable to assume, that dielectric constant is insufficient to describe the dependence of the stereoselectivity coefficient **a** on the solvent polarity. In fact an empirical parameter is needed that will reflect with greater accuracy the complex solvent - solute interaction.

The Dimroth-Reichardt parameter $E_T(30)$[5] was chosen as an empirical measure of the solvent polarity. This parameter is measured from the bathochromic shift of the solvent dependent absorption band of pyridinium phenolate dye and mainly reflects the electophilicity and the H-bond donor activity of the solvent.

It is well known[7], that the rate constant of a reaction is determined by the free energy difference (ΔG) between reactants and transition state. Consequently it can be written:

$$a = \frac{k_{LL}}{k_{LD}} = \frac{k_{DD}}{k_{DL}} = \exp(G^{\neq}_{DD} - C^{\neq}_{DL}/RT) = \exp(G^{\neq}_{LL} - G^{\neq}_{LD}/RT) \qquad (3)$$

Equation (3) means that the stereoselectivity coefficient **a** reflects the free energy difference of the diastereomeric transition states of the homopropagation and the syndiopropagation reactions (1) and (2).

By plotting the $\ln \frac{\langle a \rangle}{\frac{q}{r_c^2}}$ vs. $E_T(30)$ data of table III,

it is observed that the solvents fall into two categories (Fig. 2). The etheric solvents stay separately in their own linear correlation, while the other solvents fall in another linear correlation. From these observations, the following equation can be proposed, which holds for both groups of solvents (only the constant A is different):

$$\mathbf{a} = k_{DD}/k_{DL} = k_{LL}/k_{LD} = A \exp (E_T(30)\ q/r_c^2) \qquad (4)$$

TABLE III: Slopes of the $\langle \mathbf{a} \rangle$ vs $1/r_c^2$ Plots for Each Solvent The $E_T(30)$ Values of the Solvents are also Shown

Solvent	$d\langle \mathbf{a} \rangle / d\ r_c^{-2}$	$E_T(30)$
Benzene	0.27	34.5
Diethyl Ether	0.20	34.6
1,2-Dichloroethane	0.14	41.9
Dioxane	0.11	36.0
Tetrahydrofuran	0.06	37.4
THF-CH_3CN 1:1 (v/v)	0.11	41.7*
Acetonitrile	0.04	46.0
Nitroethane	0.18	43.6
Dimethylformamide	0.05	43.8

* Calculated as the arithmetic mean of the THF and CH_3CN $E_T(30)$ values.

If the linear dependence of the **a** values on the methanol % content is taken into consideration[4], the following equation is derived:

$$\mathbf{a} = A \exp(E_T(30)\ q/r_c^2) + B \cdot (CH_3OH\ \%\ v/v) \qquad (5)$$

A and B are constants.

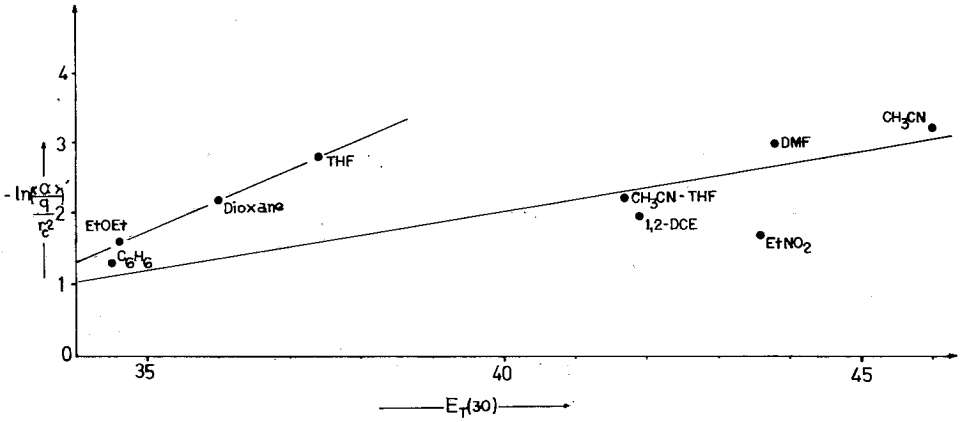


FIG. 2: *Plot of the Natural Logarithm of the Slopes of the <a> vs. q/r_c^2 Lines Observed for D,L-Valine NCA Polymerizations Conducted in Various Solvents, Versus the Empirical Parameter $E_T(30)$ of These Solvents.*

The behaviour of the etheric solvents can be attributed to their known inability of solvating anions[8], despite the fact that cations can be extensively solvated by these solvents. The etheric solvents were also found to exhibit similar deviations elsewhere[5-9]. In fact, by plotting the molecular ellipticity of solutions containing 2-Benzoylbenzoic acid–(–)–R-Amphetamine salt (1:1), versus the $E_T(30)$ value of the solvent, it is observed that the etheric solvents stand away from the correlation line. This deviation was ascribed to a competetive H-bond formation between the acid and the etheric solvent.

The significant deviation of nitroethane from the correlation line of the rest of the media in Fig. 2, probably has to do with the poor cation solvation capability of nitroethane, despite its high electrophilicity[10].

Nitroethane with its poor cation solvation ability and etheric solvents with their good cation solvation ability, appear to influence the stereospecificity of the D,L-Val-NCA in opposing way. This indicates the significance of the solvent-cation interactions on the stereospecificity of the D,L-Val-NCA polymerization.

The successful correlations shown in Fig. 2 indicate, that the empirical parameter $E_T(30)$ can adequately describe the complex solvent-solute interactions, in the methoxide initiated D,L-Val-NCA polymerization.

The data presented so far support the view that both, the non-specific Coulombic and the specific (H-bond) interactions, are important in determining the stereospecificity of the methoxide initiated D,L-Val-NCA polymerizations. These polymerizations tend to be stereoalternating due to the steric interactions of the bulky isopropyl groups of Valine. This trend can be overcome though, with the active participation of solvent in the transition state along with the contribution of the cation of the methoxide[11].

As a conclusion, it seems desirable to speculate on the significance of the equation (5) in Biology. This equation implies that, if a racemic NCA mixture is polymerized in a medium having high methanol content (methanol is a protic solvent

like water) with a high charge density initiator (such as Al^{3+}), a highly stereoselective polymerization will take place. The obtained polypeptide chains will contain mainly either of the two enantiomeric forms of the aminoacid.

Something analogous may have happened in the abiotic oceans of the earth, billion years ago. A racemic mixture of aminoacids was dissolved in the warm oceans (water is a highly protic solvent), which also contained high concentrations of metal salts (high q/r_c^2). These aminoacids condensed to form the first polypeptides. These polypeptides should have been enantiomerically highly homogeneous, as precursors of the exclusively L- aminoacid containing proteins of living organisms. It appears that stereoselection may have operated as a microscopic Maxwellian demon[12] which decreased the entropy of the resulted polypeptide mixture, by not permitting the random D- and L- aminoacid copolymerization (state of high entropy). Thus, the stereospecific polypeptide formation can be considered as a decisive step on the way that finaly led to biogenesis.

Περίληψη

Επίδραση του διαλύτου στη στερεοχημεία του πολυμερισμού της D,L-Βαλίνης NCA

Οι ανυδρίτες του Leuch (NCAs) πολυμερίζονται παρουσία βάσεων και δίνουν πολυπεπτίδια. Ο μηχανισμός του πολυμερισμού είναι ανιονικός και πιθανότατα πραγματοποιείται με τον ενδιάμεσο σχηματισμό ενός καρβαμικού ιόντος. Η ιονική φύση του πολυμερισμού αυτού έχει σαν αποτέλεσμα την σημαντική επίδραση του διαλύτου στην στερεοχημεία του πολυμερισμού. Με φασματοσκοπία πυρηνικού μαγνητικού συντονισμού (NMR) μετρήθηκε η παράμετρος <**a**>, που εκφράζει τον λόγον της σταθερά ομοπολυμερισμού (k_{DD}) προς την σταθεράν συνδυοπολυμερισμού (k_{DL}). Αυτή η παράμετρος συσχετίσθηκε ικανοποιητικά με την εμπειρικήν παράμετρον $E_T(30)$ που υπολογίσθηκε με τη βοήθεια φασματοσκοπίας υπερύθρου, δίνοντας έτσι πληροφορίες για το είδος των αλληλεπιδράσεων που είναι υπεύθυνες για την παρατηρούμενη στερεοχημεία του πολυμερισμού.

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ERRORS APPEARING ON TESTING ISOTHERMS USING ϑ vs c DATA

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Summary

The test of an isotherm using ϑ vs c data may lead to erroneous values of the isotherm parameters or even to erroneous conclusions about the applicability of the isotherm. These errors appear when (a) there is a scatter in the experimental values of ϑ and (b) the curvature of the experimental surface pressure curves corresponds to a value of the interaction parameter of the theoretical isotherm greater than its critical value. These errors are easily detected by using the surface pressure method which can be used in order to overcome errors of the first category.

Key words: Adsorption isotherm

Introduction

A common procedure for testing a simple isotherm is to convert it to a linear form and plot experimental data accordingly.[1,2] More generally, but absolutely equivalently, this test can be performed as follows:

An isotherm can be written in the following form:

$$\beta c = f(\vartheta) \cdot g(B_0, B_1, ..., B_n, \vartheta) \quad (1)$$

where β is the equilibrium constant, ϑ is the surface coverage, c the concentration of the adsorbate and B_i, $i = 0,1, ..., n$ are constants due to particle-particle interactions in the adsorption layer. $f(\vartheta)$ is the configurational term of the isotherm due to the entropy of mixing of the adsorbed particles, while the term $g(B_0, ..., B_n, \vartheta)$ provides the contribution of the particle-particle interactions to the adsorption free energy. In order to test the isotherm (1) using ϑ vs c data, we write it in the form

$$\ln \left[f(\vartheta)/c \right] = \ln \left[\beta / g(B_0, ..., B_n, \vartheta) \right] \quad (2)$$

and we determine its parameters β, B_0, ..., B_n by the least squares procedure which minimizes the sum

$$S = \Sigma (\Delta G^{exp} - \Delta G^{calc})^2 \quad (3)$$

where

$$\Delta G^{exp} = RT\ln\left[f(\vartheta)/c\right] \tag{4}$$

and

$$\Delta G^{calc} = RT\ln\left[\beta/g\,(B_0, \ldots, B_n, \vartheta)\right] \tag{5}$$

The mean square deviation between calculated and experimental values of ΔG:

$$\sigma = \sqrt{S/N}$$

where N is the number of data points, may be used as a measure of the applicability of the isotherm.

We will show that this test which is widely used for testing isotherms may lead to erroneous conclusions especially in the case of the Bennes and the generalized Flory-Huggins isotherms used for studies of adsorption from solution.

An indicative example

The defects of this test can be illustrated by the following example. We will analyze the experimental data of dodecyldiphenylphosphine oxide (DDPO) adsorption on a polarized Hg electrode from methanolic solutions of LiCl by means of the isotherms:

a. Frumkin[3,4]

$$\beta c = \frac{\vartheta}{1-\vartheta} \exp(-2\alpha\vartheta) \tag{7}$$

b. Bennes[5,6]

$$\beta c = \frac{x}{(1-x)^r} \exp\{Bo\,[\,(1-x)^2 - rx^2]\} \tag{8}$$

c. Generalized Flory-Huggins[6,7]

$$\beta c = \frac{\vartheta}{e^{r-1}(1-\vartheta)^r} \cdot \frac{f_A}{f_S^r} \tag{9}$$

where $\beta = (1/c_S)\exp(-\Delta G^{\circ}/RT)$ (10)

$$x = \vartheta/\left[r - (r-1)\vartheta\right] \tag{11}$$

and

$$\ln \frac{f_A}{f_S^r} = \sum_{i=0}^{n} B_i \, (2x-1)^{i-1} \times$$

$$\times \{ [(1-x)^2 - rx^2] (2x-1) + 2ix\,(1-x)\,(1-x+rx) \} \qquad (12)$$

In these isotherms, ΔG^0 is the standard free energy of adsorption, c_S is the solvent concentration in the bulk of the solution, r is the size ratio of the adsorbate and solvent, f_A and f_s are the activity coefficients of the adsorbate and the solvent, respectively, at the interface and finally α and B_i, $i = 0,....,n$ are constants depending on the particle-particle interactions at the interface.

The experimental data for the system under investigation are given in ref. (8). For their proper elaboration the surface pressure data, Φ vs lnc, at the potentials −0.6, −0.8 and −1.0V (SCE) were drawn on a large scale and the surface concentration of DDPO was determined graphically from the slopes.

These values were used for the determination of ΔG^{exp} from Eq. (4) as a function of ϑ at each potential. The curves of ΔG^{exp} vs ϑ at −0.8 and −1.0 V (SCE) were shifted parallel to the Yaxis till they were superimposed on the corresponding curve at −0.6V (SCE). The change of ΔG^{exp} caused by this shift, was kept at each potential equal to the corresponding change of ΔG^{exp} obtained from the surface pressure method. In this way, a composite ΔG^{exp} vs ϑ curve was obtained (fig. 1)

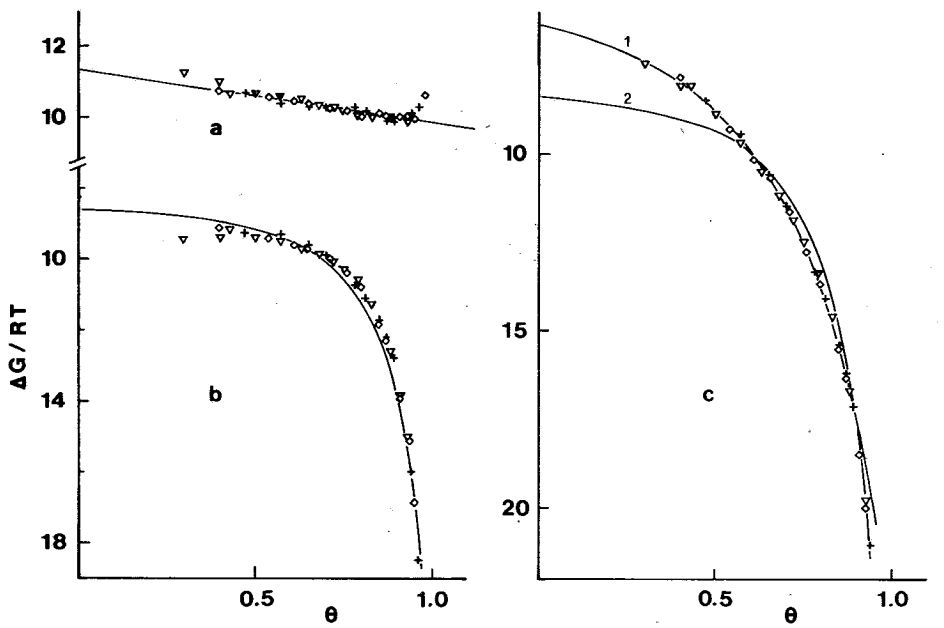

FIG.1: *Tests of Frumkin (a), Bennes (b), Flory-Huggins, n=2 (1c), Flory-Huggins, n=0 (2c) isotherms for the adsorption of DDPO on Hg from 0.1N LiCl methanolic solutions at potentials. (+) −0.6, (◇) −0.8, (△) −1.0 V(SCE). Points are experimental data plotted according to Eq (4), solid lines are calculated from Eq (5) with parameters as indicated in Table I.*

TABLE I: Isotherm parameters for DDPO adsorption at the mercury-methanolic solution interface

Isotherm	Isotherm parameters obtained by using ϑ vs c data					using the surface pressure method		
	$\ln\beta$	$B_0(\alpha)$	B_1	B_2	σ	$\ln\beta$	$B_0(\alpha)$	σ
Frumkin	11.37	−0.75			0.17	11.35	−0.75	0.13
Bennes	10.33	1.72			0.43	10.40	1.47	0.15
Equ. (9), n = 0	11.46	3.10			0.60	—	—	—
Equ. (9), n = 2	10.84	3.28	0.37	−0.80	0.09	—	—	—

and by applying a least squares procedure the isotherm parameters provided in Table I were calculated. It is seen that the Frumkin and the generalized Flory-Huggins, with n = 2, isotherms have the highest applicability, while the Bennes and the generalized Flory-Huggins with n = 0 isotherms seem to provide a less good, although still satisfactory, description of the experimental data.

In order to check these results we used two tests: We compared (a) the experimental isotherms, ϑ vs c, with the corresponding theoretical ones and (b) the experimental with the corresponding theoretical curves of the surface pressure Φ vs lnc. The equation of states used in these calculations were determined by means of the Gibbs adsorption theorem and they are the following:

a. Frumkin

$$\Phi = -RT\Gamma_S\{\ln(1-\vartheta) + \alpha\vartheta^2\} \tag{13}$$

b. Bennes

$$\Phi = -rRT\Gamma_S\{\ln(1-x) + B_0x^2\} \tag{14}$$

c. Generalized Flory-Huggins:

$$\Phi = -rRT\Gamma_S\{(r-1)\vartheta/r + \ln(1-\vartheta) - \sum_{i=0}^{n} B_iF_i(x)\} \tag{15}$$

$$F_i(x) = \frac{2i+1}{4(i+2)}(2x-1)^{i-1} \times$$

$$\times \{i\,1 - (2x-1)(8x^2 - 2ix - i) - \frac{8i(i-1)}{2i+1}x^3\} \tag{16}$$

where Γ_S is the value of the relative surface excess Γ at saturation. In order to obtain Eqs (14) and (15) we assumed that the relative surface excess calculated from

$$RT\Gamma = (\partial\gamma/\partial\ln c)_E \tag{17}$$

is equal to the real surface concentration of the adsorbate.
This approximation is valid in the case of DDPO adsorption since dilute solutions were used.

The experimental isotherms, ϑ vs, c, with the corresponding theoretical ones are compared in figure 2. It is seen that from the isotherms under investigation the

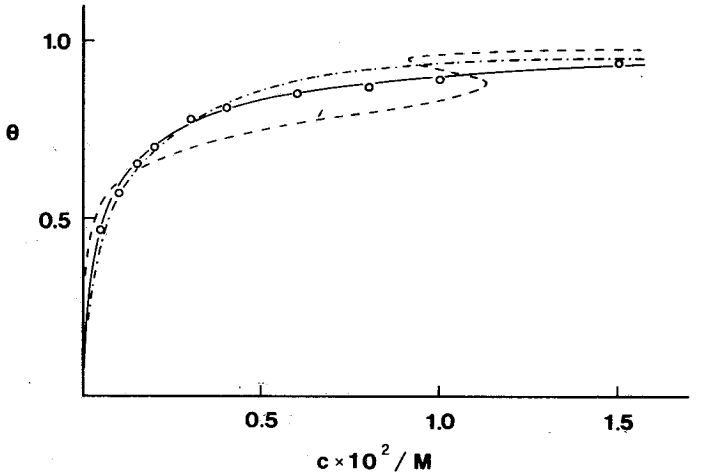

FIG. 2: *Experimental adsorption isotherm of DDPO on Hg from 0.1 N LiCl methanolic solutions at −0.6 V (SCE) Solid line corresponds to Frumkin, broken line to Flory-Huggins with n=0 and broken dotted line to Bennes isotherm with parameters as indicated in Table I.*

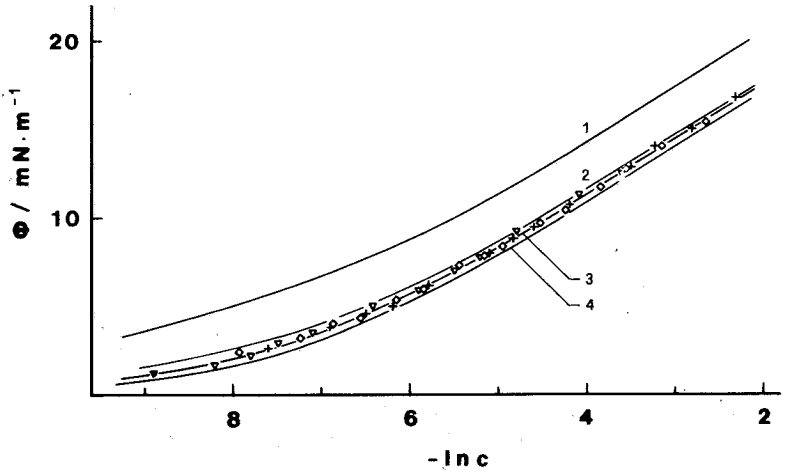

FIG. 3: *Composite surface pressure curve for adsorption of DDPO on Hg from 0.1N LiCl methanolic solutions. Solid line are calculated by the ϑ—c data analysis method from: (1) Flory-Huggins, n=0, (2) Flory-Huggins, n=2, (3) Frumkin, (4) Bennes isotherm with parameters as indicated in Table I. Symbols as in Fig. 1.*

generalized Flory-Huggins isotherm with n = 0 deviates from the experimental data since a part of this isotherm corresponds to unstable states of the adsorption layer. On the contrary the other isotherms seem to provide a satisfactory description of the expetimental data.

The results of the surface pressure method are provided in figure 3. Contrary to the above results, with the single exception of the Frumkin isotherm, all the isotherms calculated from the minimization of the sum (3) on the basis of ϑ vs c data show remarkable deviations from the experimental points.

Therefore, the test of an isotherm should not be based only on the comparison between ΔG^{exp} and ΔG^{calc} values in various surface coverages (fig. 1) or even on the comparison between experimental and theoretical isotherms, ϑ vs c, (fig. 2). In order to be sure about applicability of an isotherm we should test the isotherm by using the surface pressure method.

For isotherms with a single interaction parameter the surface pressure method can also be used for the accurate calculation of the isotherm parameters by comparing the experimental with the theoretical Φ vs lnc curves. The results obtained by this method using a least squares fit are also provided in Table I. It is seen that there are differences in the values of the isotherm parameters obtained from the two methods. Obviously, the values of the surface pressure method should be considered as the most reliable ones, since they result from initial experimental data. It was not possible for the technique used to get results for the isotherm (9) with n = 0.

The curvature of the experimental Φ vs lnc curve corresponds to a value of B_0 greater than its critical value, a fact which shows that this isotherm is invalid for the system under investigation. The other isotherms, i.e. Frumkin and Bennes, describe absolutely satisfactorily the experimental data of DDPO adsorption on Hg. These isotherms with parameters calculated by the surface pressure method give in the diagram Φ vs lnc curves which coincide with that of the Frumkin isotherm calculated on the basis of ϑ vs c data.

Discussion and Conclusions

The above results show that the test of an isotherm using ϑ vs c data may lead to erroneous values of the isotherm parameters or even to erroneous conclusions about the applicability of the isotherm. A careful study of the test shows that erroneous results may be obtained in the following cases:

a) When there is a scatter of ϑ values at the limits of the experimental isotherms. This scatter affects strongly the values of ΔG^{exp} and consequently the values of the isotherm parameters.

b) When the curvature of the experimental Φ vs lnc points corresponds to a value of the interaction parameter of the theoretical isotherm greater than its critical value. In this case, the calculated isotherm parameters by minimizing the sum (3) correspond to an isotherm with Φ vs lnc curve almost parallel to the experimental one. Because the value of σ is possible to be low in this case, indicating a high applicability of the isotherm, the existence of parts of the isotherm corresponding to unstable states has to be checked by recording the theoretical ϑ vs c curve. In the case of Bennes and generalized Flory-Huggins with n=0 isotherms, we can simply com-

pare the interaction parameter B_o with its critical value B_{oc}. If B_o is greater than B_{oc} then the isotherm is invalid for the adsorption system studied. The critical value of the interaction parameter may be determined from the relationships:

$$(\partial\Phi/\partial x) = 0 \tag{18}$$

$$(\partial^2\Phi/\partial x^2) = 0 \tag{19}$$

Eqs (18), (19) are easily solved to obtain the results of table II for the case of isotherm (9) with $n = 0$ and the value $B_{oc} = 2$ for the Bennes isotherm.

TABLE II: Critical constants B_{oc}, θ_c for the generalized Flory-Huggins isotherm with $n = 0$

r	1	2	3	4	5	6	7	8	9	10
B_{oc}	2.0	2.220	2.474	2.652	2.775	2.864	2.930	2.981	3.022	3.055
ϑ_c	0.5	0.682	0.787	0.846	0.881	0.903	0.918	0.930	0.938	0.495

From the above sources of errors the case (b) is extremely rare, while the opposite holds for the case (a). For this reason we should always check the calculated isotherms from ϑ vs c data by means of the surface pressure method or better, to use this method directly for the determination of the isotherm parameters.

Περίληψη

Σφάλματα που εμφανίζονται κατά τον έλεγχο ισοθέρμων με ϑ— c δεδομένα. Στην εργασία αυτή μελετάται ο έλεγχος ισοθέρμων προσρόφησης με τη χρησιμοποίηση ϑ-c δεδομένων. Διαπιστώνεται ότι ο έλεγχος αυτός μπορεί να οδηγήσει σε εσφαλμένες τιμές των παραμέτρων της ισόθερμης ή ακόμη σε εσφαλμένα συμπεράσματα σχετικά με την εφαρμοσιμότητα της ισόθερμης. Μια προσεκτική ανάλυση των δεδομένων δείχνει ότι σφάλματα εμφανίζονται όταν: α) υπάρχει μια διασπορά των πειραματικών τιμών του ϑ κυρίως στα άκρα της ισόθερμης και β) η κλίση της πειραματικής καμπύλης επιφανειακής πίεσης αντιστοιχεί σέ τιμές της παραμέτρου αλληλεπίδρασης της θεωρητικής ισόθερμης μεγαλύτερες από τήν κρίσιμη τιμή της. Τα σφάλματα αυτά προσδιορίζονται εύκολα με την μέθοδο της επιφανειακής πίεσης, η οποία μπορεί να χρησιμοποιηθεί για να ξεπεραστούν σφάλματα της πρώτης κατηγορίας.

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SHORT PAPER

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SYNTHESIS OF 3,4,4,5,5,6-HEXAMETHYL-1,4,5,6-TETRAHYDROPYRIDAZINES FROM THE REACTION OF 3,3,4,4-TETRAMETHYL-2,5-HEXANEDIONE WITH AROYLHYDRAZINES

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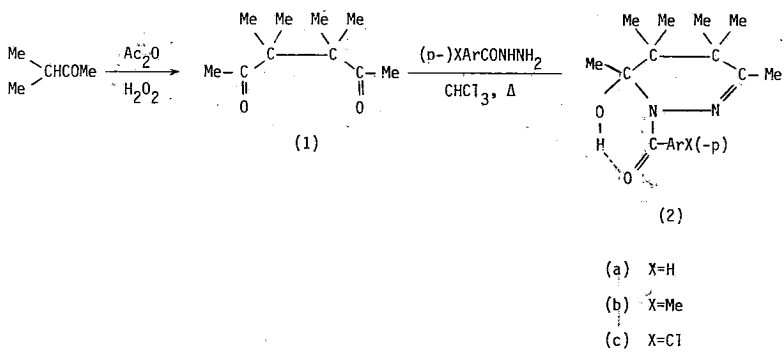
Because of our interest in the synthesis of heterocyclic compounds[1, 2] and the expanding interest in the chemistry of pyridazines[3] the synthesis of some hexamethyltetrahydropyridazine derivatives was undertaken.

Dimerizaton of 3-methyl-2-butanone upon treatment with acetic anhydride and hydrogen peroxide[4] gave the 3,3,4,4-tetramethyl-2,5-hexanedione (1). By refluxing this diketone (1) with aroylhydrazines in chloroform the tetrahydropyridazines (2) were obtained in good yields (Scheme 1). The analytical data of the tetrahydropyridazines (2) are given in Table.



SCHEME 1

Ir spectral evidence supports[5] a structural assignment of the tetrahydropyridazines (2) with an intramolecular hydrogen bond between the hydroxyl and the aroylcarbonyl groups (Scheme 1). The tetrahydropyridazines (2) exhibit a broad absorption between 3100 and 3170 cm^{-1} which may be due to an intramolecularly hydrogen bonded OH group and a strong absorption between 1585 and 1595 cm^{-1} characteristic of intramoleculary hydrogen bonded carbonyls. However, after refluxing the tetrahydropyridazines (2) in $CHCl_3$-D_2O for 4 hours the characteristic amide carbonyl absorption at 1635 cm^{-1} could be observed. The -OD absorption could also be observed at 2400 cm^{-1}.

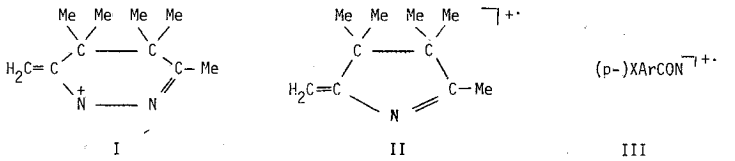
TABLE: Analytical Data for the 1-Aroyl- 3,4,4,5,5,6-hexamethyl-6-hydroxy-1,4,5,6-tetrahydropyridazines (2)[a].

Pyridazine	I.r. (Nujol) cm^{-1}		^{1}H-N.m.r. ($CDCl_3$)[b] δ (ppm)						Formula	Molecular Weight	MS m/e (Relative Intensity %)
	νOH	νCO	4,4-C(Me)$_2$	5,5-C(Me)$_2$	6-Me	3-Me	p-Me	aromatic protons			
2a	3170	1590	0.99	1.27	1.47	2.20	—	7.13-7.43 [3]m 7.83-8.16 [2]m	$C_{17}H_{24}N_2O_2$	288.4	$M^{+\cdot}$ 288(1.5), 270(49), 255(10), 165(22), 151(22), 119(33), 105(100)
2b	3100	1585	1.02	1.28	1.47	2.22	2.35	ν_A 7.11 [4] AB ν_B 7.89 system J_{AB} 8Hz	$C_{18}H_{26}N_2O_2$	302.4	$M^{+\cdot}$ 302(<0.5), 284(51), 269(9), 165(12), 151(51), 133(79), 119(100)
2c	3110	1585	1.01	1.28	1.47	2.21	—	ν_A 7.26 [4] AB ν_B 7.94 system J_{AB} 8 Hz	$C_{17}H_{23}N_2O_2Cl$	322.8	$M^{+\cdot}$ 324/322 (<0.5), 306/304(68), 291/289(18), 165(48), 151(98), 155/157(100), 141/139(100)

[a] All compounds gave satisfactory elemental analysis (C ± 0.26%, H ± 0.31%, N ± 0.24%).
[b] The OH proton appears only in dimethylsulphoxide-d_6 as a broad singlet at 10.57, 10.48 and 10.66 δ for compounds 2a, 2b and 2c respectively.

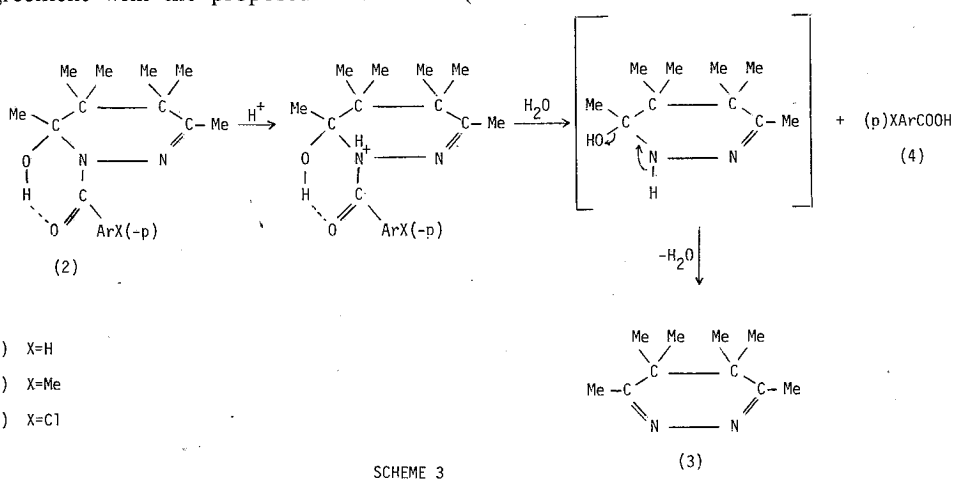
In the ^1H nmr spectrum four singlets are observed at approximately 1.00, 1.28, 1.47 and 2.20 δ for the six methyl groups of the 4-, 5-, 6- and 3-position of the heterocyclic ring, respectively. The OH proton appears only in dimethylsulphoxide-d_6 as a broad singlet at ~10.60δ (Table).

In the mass spectra they show a low intensity peak for the molecular ion followed by the high intensity peak $[M\text{-}H_2O]^{+\cdot}$. Other prominent peaks are those corresponding to the ions I to III (Scheme 2) whereas the ion (p-) $XArC\overset{+}{O}$ appears as the base peak in the spectra.



SCHEME 2

The structure of the tetrahydropyridazines (2) has also been proved by acid hydrolysis with concetrated hydrochloric acid[6]. The 2,3,3,4,4,5-hexamethyl-4,5-dihydropyridazine (3) and the corresponding aromatic acids (4) were isolated in agreement with the proposed mechanism (Scheme 3).



SCHEME 3

The dihydropyridazine (3) shows in the ^1H-nmr spectrum a twelve-proton singlet at 0.92 δ and a six-proton singlet at 1.98 δ. In the mass spectrum the high intesity peak for the molecular ion is followed by the less intensive peak $[M\text{-}CH_3]^+$. Other prominent peaks are those corresponding to the ions $[Me_2C=CMe_2]^{+\cdot}$ and $Me_2C = \overset{+}{C}Me$.

Experimental

Nmr (60 MHz, Me_4Si internal standard) and mass spectra (70 eV) were recorded on Varian A-60A and Hitachi-Perkin-Elmer RMU-6L spectrometers, respectively. Ir spectra were recorded on a Perkin - Elmer 257 spectrophotometer. Melting points

have been obtained on a Kofler hot stage apparatus and they are uncorrected.

General procedure for the preparation of 1-aroyl-3,4,4,5,5,6-hexamethyl-6-hydroxy-1,4,5,6-tetrahydropyridazines (2). A solution of 0.01 mole of 3,3,4,4-tetramethyl-2,5-hexanedione (1) and 0.012 mole aroylhydrazine in 15 ml chloroform was refluxed for 8 hours. The solution was evaporated to dryness and the residue chromatographed on a silica gel column, using as eluent petroleum ether-ethylacetate to give the 1-aroyl-3,4,4,5,5,6-hexamethyl-6-hydroxy-1,4,5,6-tetrahydropyridazine (2) in 47-65% yield (3a 55%, m.p. 193-195 °C; 2b 65%, m.p. 184-186 °C; 2c 47%, m.p. 200-201 °C).

Hydrolysis of 1-aroyl-3,4,4,5,5,6-hexamethyl-6-hydroxy-1,4,5,6-tetrahydropyridazines (2) to 3,4,4,5,5,6-hexamethyl-4,5-dihydropyridazine (3). A mixture of 0.01 mole of the tetrahydropyridazine (2) and 20 ml of concentrated hydrochloric acid was refluxed for 4 hours. The reaction mixture was neutralised with sodium hydroxide solution and extracted with chloroform. Evaporation of the solvent afforded the 3,4,4,5,5,6-hexamethyl-4,5-dihydropyridazine (3) as an unstable oil in 80-85% yield. Picrate m.p. 152-154 °C (yellow needles from ethanol). The corresponding p-substituted benzoic acids (4) were obtained in 70-75% yield by acidification of the water layer with hydrochloric acid and extraction with chloroform.

Summary

A number of 1-aroyl-3,4,4,5,5,6-hexamethyl-6-hydroxy-1,4,5,6-tetrahydropyridazines have been synthesized from the reaction of 3,3,4,4-tetramethyl-2,5-hexanedione with aroylhydrazines. The spectral data of the new compounds and their hydrolysis to 3,4,4,5,5,6-hexamethyl-4,5-dihydropyridazine are discussed.

Key words: Dihydropyridazine, hydrolysis, diketone, tetrahydropyridazine.

Περίληψη

Σύνθεση 3,4,4,5,5,6εξαμεθυλο-1,4,5,6-τετραϋδροπυριδαζινών από την αντίδραση της 3,3,4,4-τετραμεθυλο-εξανο-2,5-διόνης με αροϋλοϋδραζίνες

Αναφέρεται η σύνθεση ορισμένων 1-αροϋλο- 3,4,4,5,5,6-εξαμεθυλο-6-υδροξυ-1,4,5,6-τετραϋδροπυριδαζινών από την αντίδραση της 3,3,4,4-τετραμεθυλο-εξανο-2,5-διόνης με αροϋλοϋδραζίνες.

Μελετώνται τα φασματοσκοπικά δεδομένα των νέων ενώσεων και η υδρόλυσή τους προς την 3,4,4,5,5,6-εξαμεθυλο-4,5-διϋδροπυριδαζίνη.

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