

The Separation of Racemates by Gas Chromatography

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Gas chromatography was employed in order to eliminate the effect of solvent which, appears to oppose selective adsorption of the optical antipodes. Optically active solids [starch; saccharose; (+)-camphor-10-sulfonic acid, (+)-tris(ethylenediamine)cobalt(III) chloride] or liquids [(+)-ethyl tartrate; (+)-isoamyl phthalate; hexamethyl-lactose; hexamethyl-saccharose] were used to cover the optically inactive support (Sterchamol, silica gel etc.).

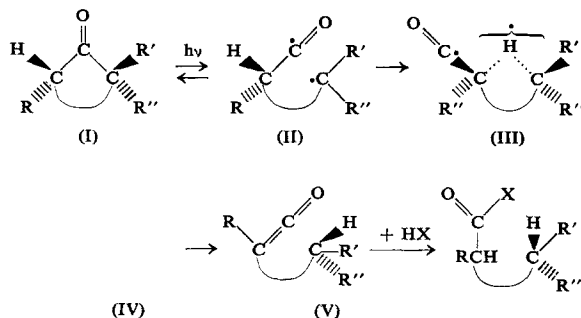
In eight cases [(±)-2-methoxybutane; (±)-1,2-dichlorohexafluorocyclobutane; (±)-methyl bromopropionate; (±)-2-methylbutan-1-ol, (±)-1-acetyl-1-hydroxyethane; (±)-s-butanol; (±)-2-bromopentane; (±)-ethyl α-bromobutyrate] a clearly discernible splitting of the peaks was observed in the presence of an optically active stationary phase. The time differences between the maxima lie in the range 1–3 minutes so that preparative scale applications of the technique should be possible. A specially prepared rotameter must be employed as a detector, since it appears likely that the use of currently available detectors (heat conductance cells etc.) might induce racemisation. At any given gas-flow velocity through a rotameter, the position of the "swimmer" depends upon density and viscosity of the gas. On passage of organic vapours, the change in height can be used as a signal for the fraction cutter.

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Photochemical Investigations on Non-Conjugated Ketones in Solution

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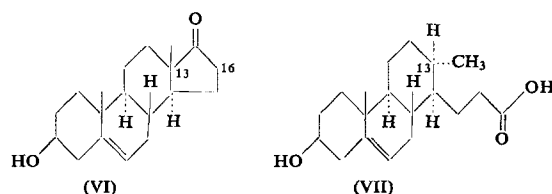
The alkyl/acyl radical-pair (II), formed from the ketone (I) in the primary process of photolysis, undergoes an intramolecular homolytic hydrogen migration from the α-position of the acyl radical towards the alkyl radical (III). By this process both radicals disappear and the ketene (IV) is formed as the actual photochemical reaction product. The hydrogen migration takes place alongside a recombination process which does not result in structural changes. (If the carbonyl chromophore lies in close proximity to an asymmetric centre, photoepimerisation with change of configuration can occur). The band characteristic for the ketene group (2150 cm⁻¹) appears in the infrared spectrum after brief irradiation; in the presence of substances which add to ketenes, this band vanishes. Irradiation in aqueous organic solvents leads to the acids (V; X = OH). Amides (V; X = -NR₂) are formed in the presence of primary or secondary amines.



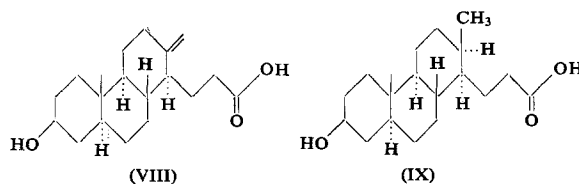
No ketene formation takes place if neither of the carbon atoms adjacent to the carbonyl group carries a hydrogen atom.

That the homolytic hydrogen migration proceeds via (III) follows from the experimentally detectable ring strain. In the presence of cyclohexylamine, irradiation of camphor yields the corresponding amide in less than 1 % yield; under the same conditions, the amide resulting from homocamphor is isolable in yields higher than 15 %.

The irradiation of Δ⁵-androsten-3β-ol-17-one (VI), and its C-13-epimer, in aqueous organic solvents yields only (VII). The reaction is stereospecific and the hydrogen atom migrates from C-16 towards C-13 on the β-side. Proof for the α-configuration of the 13-CH₃ group in (VII) is adduced from the reduction of the exocyclic, isolated, double bond in the C-ring of compound (VIII) with lithium and ethylenediamine. This reduction leads to the thermodynamically more stable product. The catalytic hydrogenation of (VIII) results in the formation of the other epimer (IX).



If the acyl radical of the alkyl/acyl radical-pair can stabilize itself by elimination of CO and the formation of a benzyl or allyl radical, then this radical decomposition is preferred and practically no acid is formed.



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SELECTED ABSTRACTS

Gaseous SNCl is formed by heating N₃S₃Cl₃ in high vacuum to 110 °C. It has a green-yellow color and possesses a band at 1330 cm⁻¹ in the NaCl region of the infrared spectrum which is very similar to that of SNF. Upon hydrolysis with NaOH it yields Cl⁻ and NH₃ ions. SNCl polymerizes rapidly to N₃S₃Cl₃ at room temperature. It is also formed during the preparation of N₃S₃Cl₃ when Cl₂ is introduced into a solution of S₄N₄ in CCl₄. / *Naturwissenschaften* 48, 620 (1961). — Ma. [Rd 973/7 IE]

For separate determination of pyridine and nitrile nitrogen in acrylonitrile-methylvinylpyridine copolymers, a sample is dissolved in a mixture of nitromethane and formic acid, and the pyridine-nitrogen titrated potentiometrically against a glass electrode in dioxane-HClO₄ solution. In order to determine the nitrile nitrogen, the sample is dissolved in conc. alcoholic KOH and heated. Ammonia liberated by saponification is taken up in HCl and back-titrated. *J. A. Emelin et al. Zavod. Lab. (Moscow)* 27, 283 (1961) / —Gä. [Rd 53/31 IE]