Equilibration of Cryptone and Its β,γ-Unsaturated Isomer

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One of the two recently reported[1] synthetic routes to *dl*-cryptone proceeds through the collidine dehydrobromination of 2-bromo-4-isopropylcyclohexanone, which gives a roughly equal mixture, separable by fractionation, of the α,β- and the β,γ-unsaturated ketones.

The formation of the β,γ-derivative under these conditions is of special interest since the method is in general use for the preparation of α,β-unsaturated ketones, and the apparent equilibration is an interesting example of favorable competition between conjugation and hyperconjugation effects.[2] That the ketones themselves form the same equilibrium mixture under the conditions of the dehydrohalogenation has now been demonstrated by treating the conjugated isomer with collidine and collidine hydrobromide. The distilled product appeared (λ_{max} 227 mμ, ε 7,620) to be a mixture comparable with that obtained from the collidine dehydrobromination (λ_{max} 227 mμ, ε 6,670) and this was confirmed by separating the pure isomers[1] (Δ^2 isomer, λ_{max} 227 mμ, ε 12,370; Δ^3isomer, no maximum at 210–360 mμ) which were converted in good yield to their characteristic dinitrophenylhydrazones.

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EXPERIMENTAL[3]

DL-*Cryptone* was regenerated[4] from a highly purified sample (9.50 g.) of the synthetic semicarbazone[1] (m.p. 194°).[5] Air was excluded with nitrogen, and an efficient steam distillation apparatus was used to effect a rapid continuous separation of the free ketone as it was formed in the acidic hydrolysis mixture. The colorless fragrant product was extracted with ether, dried over sodium sulfate, and distilled; 5.23 g. (78%), b.p. 76–80° (5 mm.), n_D^{20} 1.4815, λ_{max} 227 mμ, ε 11,100.

Equilibrium of DL-*cryptone.* Repeating as closely as possible the dehydrobromination conditions,[1] a mixture of 5.00 g. of cryptone, 7.3 g. of washed and dried collidine hydrobromide (from collidine in ether), and 18.9 g. of collidine, was refluxed under nitrogen for 20 min. The neutral fraction was extracted with ether, washed well in the cold with dilute hydrochloric acid, sodium bicarbonate solution, and water, dried over sodium sulfate, and distilled; 3.22 g. b.p. 60–68° (2 mm.), n_D^{20} 1.4776, λ_{max} 227 mμ, ε 7,620. Fractionation at 0.5 mm. through a sixty-plate Podbielniak Miniature Hypercal column[1] gave three fractions as follows: (I) 0.66 g. of *4-isopropyl-3-cyclohexenone*, b.p. 46–50°, n_D^{20} 1.4738, no maximum at 210–360 mμ (reported n_D^{20} 1.4710[1]). (II) 0.97 g. of an intermediate fraction, b.p. 51–55°, n_D^{20} 1.4824, λ_{max} 227 mμ, ε 9,540; and (III) 0.94 g. of *4-isopropyl-2-cyclohexenone*, b.p. 55–60°, n_D^{20} 1.4828, λ_{max} 227 mμ, ε 12,370 (reported for natural *l*-cryptone n_D^{20} 1.4810,[6] λ_{max} 226.3 mμ, ε 12,600[4]).

Treatment in the manner described previously[1] gave from fraction I the orange-yellow 4-isopropyl-3-cyclohexenone 2,4-dinitrophenylhydrazone, m.p. 105–106°.[1,7]

Similarly, from fraction III there was obtained[1] a 90% yield of the orange-red isopropyl-2-cyclohexenone 2,4-dinitrophenylhydrazone, m.p. 126–129°, which after recrystallization from ethanol had m.p. and mixed m.p. 134–135°.[1]

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[1] M. D. Soffer and M. A. Jevnik, *J. Am. Chem. Soc.*, **77**, 1003 (1955).

[2] *Cf.* W. C. Wildman, R. B. Wildman, W. T. Norton, and J. B. Fine, *J. Am. Chem. Soc.*, **75**, 1912 (1953).

[3] Melting points are corrected and boiling points uncorrected. Ultraviolet absorption spectra were determined in 95% ethanol.

[4] R. G. Cooke and A. K. Macbeth, *J. Chem. Soc.*, 1408 (1938).

[5] The reported melting points of the racemic product vary from 183° to 192° (*cf.* ref. 1), probably due to traces of the Δ^3 isomer.

[6] D. T. C. Gillespie and A. K. Macbeth, *J. Chem. Soc.*, 1531 (1939).

[7] This derivative tends to isomerize to the Δ^2 derivative and to decompose, if heated slowly, and it also shows a "double" melting point; the melt resolidifies and melts again at a temperature intermediate between the melting points of the derivatives of the two isomeric ketones. The temperature recorded represents the initial fusion.

Isolation of a Thiosulfonate from Reaction of Lithium Aluminum Hydride and a Sulfonyl Chloride

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Field and Grunwald[2] postulate that reduction of sulfonyl chlorides to mercaptans by lithium aluminum hydride may occur *via* two routes, one of which involves the reaction of a sulfinate salt with a sulfonyl chloride giving a disulfone, or with a metal mercaptide to give a thiosulfonate. Either of these intermediates then goes to the mercaptan *via* the disulfide. Apparently no one has isolated a thiosulfonate, although disulfides have been obtained.[2,3] The authors would like to report the isolation in 23% yield of *p-tert*-butylphenyl *p-tert*-butylbenzenethiosulfonate from the action of lithium aluminum hydride on *p-tert*-butylbenzenesulfonyl chloride. Structure of the thiosulfonate was indicated by its independent preparation from reduction of *p-tert*-butylbenzenesulfonyl chloride with zinc and hydrochloric acid by a procedure known to give the thiosulfonate.[4]

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[2] L. Field and F. A. Grunwald, *J. Org. Chem.*, **16**, 949 (1951).

[3] J. Strating and H. J. Backer, *Rec. trav. chim.*, **69**, 638 (1950).

[4] E. Vinkler and F. Klivenyi, *Acta Chim. Acad. Sci. Hung.*, **1**, 319 (1951); *Chem. Abstr.*, **49**, 2346 (1955).