

In a number of instances,³ ready halogenation of chlorins has been observed, but it has been assumed that the reactions involve substitution at the 7 or 8 positions. Although these cases deserve reinvestigation in detail, there can now be little doubt that the views previously advanced are erroneous, and that the products of these reactions are γ or δ halogenated derivatives.

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(3) (a) H. Fischer and K. Herrle, *Ann.*, **530**, 236 (1937); (b) H. Fischer and E. A. Dietl, *ibid.*, **547**, 234 (1941); (c) H. Fischer, H. Kellermann and F. Baláz, *Ber.*, **75**, 1778 (1942); (d) H. Fischer and F. Baláz, *Ann.*, **555**, 81 (1943); (e) H. Fischer and F. Gerner, *ibid.*, **559**, 77 (1948).

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INTRAMOLECULAR CYCLIZATION OF UNSATURATED DIAZOKETONES

Sir:

The intermolecular reaction of diazoketones with olefins has been described by Sorm and his collaborators.¹

So far as we are aware the *intramolecular* counterpart of this reaction has not yet been reported. We were interested in exploring the feasibility of such a reaction for the synthesis of [0,1,4]bicycloheptane derivatives and have succeeded in synthesizing [0,1,4]bicycloheptanone-2 (III), one of the simplest substances that might be prepared by the " Δ^5 diazoketone" route.

Pure 5-hexenoic acid (I) was prepared from 4-penten-1-ol² via the corresponding bromide and nitrile.³ The unsaturated acid was transformed into its acid chloride by reaction with oxalyl chloride in benzene at room temperature, and the acid chloride was converted, without distillation, into its diazoketone (II).

The diazoketone (5 g.) was refluxed for eleven hours in 250 ml. of cyclohexane in the presence of 0.5 g. of copper bronze. Shorter time led to incomplete reaction as evidenced by the presence of diazoketone in the mixture (infrared). Distillation gave 2.5 g. of a fraction boiling at 74–76° (8 mm.). This consisted mainly (see below) of the desired [0,1,4]bicycloheptanone-2 but was not completely homogeneous, as shown by the presence of two absorption bands in the carbonyl region of the infrared and by gas chromatography. The latter (5 ft. silicone column, 150°) showed the product to be contaminated with about 20% of a substance with absorption at 5.85 μ in the infrared. The pure III from the chromatogram had its carbonyl absorption at 5.96 μ , $\lambda_{\text{max}}^{\text{EtOH}}$ 220 m μ and 275 m μ (ϵ 34),⁴ and gave its 2,4-dinitrophenylhydrazone, m.p. 158° (calcd. for $\text{C}_{13}\text{H}_{14}\text{N}_4\text{O}_4$: C, 53.79; H, 4.86; N, 19.30. Found: C, 53.96; H, 4.90; N, 19.47). The same 2,4-dinitrophenylhydrazone was obtained before

(1) F. Sorm and J. Novak, *Collection Czechoslov. Chem. Commun.*, **22**, 1836 (1957); F. Sorm and J. Ratusky, *ibid.*, **23**, 467 (1958); F. Sorm and J. Novak, *ibid.*, **23**, 1126 (1958).

(2) R. Paul and H. Normant, *Bull. soc. chim.*, 484 (1943).

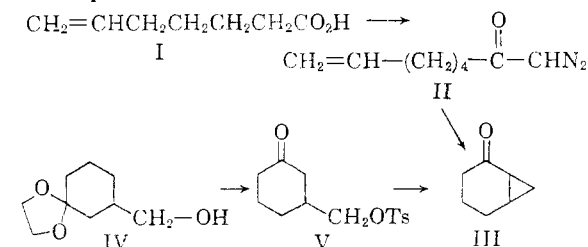
(3) F. B. LaForge, N. Green and W. Gersdorff, *J. Am. Chem. Soc.*, **70**, 3709 (1948).

(4) Cf. A. Sandoval, G. Rosenkrantz and C. Djerassi, *ibid.*, **73**, 2383 (1951).

gas chromatography in 75% yield. The ultraviolet absorption spectrum of this derivative had $\lambda_{\text{max}}^{\text{CHCl}_3}$ 370 m μ as anticipated (cf. 2,4-dinitrophenylhydrazone of acetylcyclopropane: $\lambda_{\text{max}}^{\text{CHCl}_3}$ 371 m μ ⁵). The n.m.r. spectrum of III showed absorption due to two non-equivalent hydrogens of the cyclopropane methylene at τ ca. 8.9 (lowered by conjugation with the carbonyl).

Unambiguous confirmation of the structure of our [0,1,4]bicycloheptanone-2 was obtained by an independent synthesis. Catalytic hydrogenation (rhodium-charcoal) of *m*-hydroxybenzoic acid, then esterification and oxidation with chromic acid-acetone-sulfuric acid, gave the known⁶ ethyl-3-oxocyclohexanecarboxylate. Ketalization with ethylene glycol and reduction with lithium aluminum hydride gave the ketal of 3-oxo-cyclohexanemethanol (IV) b.p. 116–124° (0.2 mm.) (found: C, 62.32; H, 9.43). Reaction of IV with *p*-toluenesulfonyl chloride in pyridine and deketalization with aqueous methanolic hydrochloric acid produced the tosylate of 3-oxocyclohexanemethanol (V); 2,4-dinitrophenylhydrazone, m.p. 118° (found: C, 52.21; H, 4.99).

Cyclization of the keto tosylate V with sodium hydride⁷ in tetrahydrofuran gave, in low yield, the bicyclic ketone III; 2,4-dinitrophenylhydrazone, m.p. 162–163°, undepressed by the sample from the diazoketone decomposition. The infrared spectra of the ketones made by the two routes were essentially identical, and so were the characteristic n.m.r. spectra.



(5) D. H. R. Barton, T. Bruun and A. S. Lindsey, *J. Chem. Soc.*, 2210 (1952).

(6) G. K. Komppa, T. Hirn, W. Rohrmann and S. Beckmann, *Ann.*, **521**, 242 (1936).

(7) Cf. N. A. Nelson and G. A. Mortimer, *J. Org. Chem.*, **22**, 1146 (1957).

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THE STRUCTURE OF INDOLMYCIN

Sir:

We wish to propose structure 1 for indolmycin, previously designated PA-155A.^{1,2} This antibiotic is the first example of a new structural type.

Indolmycin was isolated from a culture of *Streptomyces albus*¹ and some of its properties have been described.^{2,3} The compound has the molecular formula $\text{C}_{14}\text{H}_{16}\text{N}_3\text{O}_2$ and an ultraviolet absorption spectrum closely resembling that of tryptophan.

(1) W. S. Marsh, A. L. Garretson and E. M. Wesel, *Antibiotics and Chemotherapy*, **10**, 316 (1960).

(2) K. V. Rao, *ibid.*, **10**, 312 (1960).

(3) A. R. English, T. J. McBride, *ibid.*, in press.