HYDROAMINATION OF 2,2'-METHYLENEBISCYCLOHEXANONE WITH ANILINE AND FORMIC ACID*

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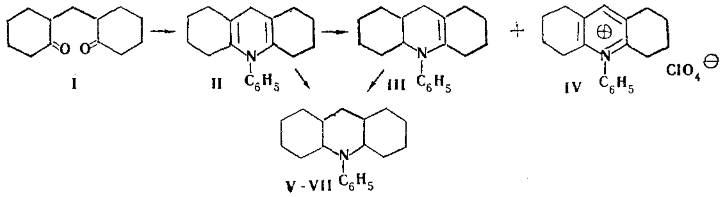
10-Phenyl-sym-octahydroacridinium salts and stereoisomeric 10-phenylperhydroacridines were obtained by the action of aniline and formic acid on 2,2'-methylenebiscyclohexanone.

A mixture of pyridine and piperidine bases is formed by the Leuckart reaction with 1,5-diketones [2, 3], but the problem of the paths for their formation has remained unexplained. It was recently shown that the intermediate $\Delta^{11,12,13,14}$-decahydroacridine system arising during the reaction of 2,2'-methylenebiscyclohexanone (I) with ammonia [4] or aniline [5] in acetic acid disproportionates to sym-octahydroacridine and dodecahydroacridine. All three of these structures may also be intermediates during hydroamination. Starting from this assumption, we examined the reaction of diketone I with aniline and formic acid.



10-Phenyl-sym-octahydroacridinium perchlorate (IV) and three stereoisomeric 10-phenylperhydroacridines with mp 110-110.5° (V), 129-130° (VI), and 96.5-97° (VII) were isolated from the reaction mixture.

The same mixture of compounds IV-VII as obtained from diketone I was also obtained by the action of aniline and formic acid on 10-phenyldecahydroacridine (II). Under these conditions, dodecahydroacridine III is converted to a mixture of perhydroacridines V and VI, and the octahydroacridinium salt IV does not change. On the basis of this it can be assumed that II, which is partially reduced by formic acid to a mixture of perhydroacridines (V-VII) and partially disproportionates to III and IV, of which the first is reduced by formic acid to a mixture of V and VI, is formed during hydroamination of diketone I with aniline.

EXPERIMENTAL

Hydroamination of 2,2'-Methylenebiscyclohexanone (I). A mixture of 0.05 mole of ketone I, 0.4 mole of aniline, and 30 ml of 85% formic acid was refluxed for 4 h, diluted to twice its volume with water, and neutralized with sodium carbonate. The mixture was extracted with ether, and the aqueous layer was treated with a saturated solution of ammonium perchlorate to give 6.17 g (34%) of salt IV with mp 200°. The compound has an IR spectrum which is identical to the spectrum of an authentic sample and does not depress the melting point of this sample. The ether extract was evaporated, and the residue was chromatographed with a column filled with 300 g of activity II Al_2O_3; petroleum ether eluted 3.36 g (25%) of VI, and a mixture of V and VII was eluted with carbon tetrachloride. This mixture was separated by preparative thin-layer chromatography on activity II Al_2O_3 in a CCl_4–petroleum ether system (1 : 1). The spots on the plate were detected by means of iodine vapors. A total of 1.48 g (11%) of V and 0.54 g (4.0%) of VII was obtained.

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10-Phenylperhydroacridines. Compound V had mp 110-110.5° (from acetone). Found %: C 84.8; H 10.4. $C_{19}H_{27}N$. Calculated %: C 84.8; H 10.0. The picrate had mp 242° (from alcohol). Found %: N 11.3. $C_{19}H_{27}N \cdot C_6H_3N_3O_7$. Calculated %: N 11.4. Compound VI had mp 129-130° (from acetone). Found %: C 84.7; H 10.1; N 5.3. $C_{19}H_{27}N$. Calculated %: C 84.8; H 10.0; N 5.2. The picrate had mp 183-184° (from alcohol). Found %: N 11.3. Compound VII had mp 96.5-97° (from alcohol). Found %: C 84.2; H 10.2. The picrate had mp 214-215° (from alcohol). Found %: N 11.6.

Reduction of II-IV. A mixture of 1 g of the compound and 10 ml of 85% formic acid was refluxed for 4 h. The reduction products were isolated as indicated above. Compound II yielded 35% IV, 10% V, 30% VI, and 5% VII; III yielded 15% V and 45% VI; 90% of the starting material was recovered in the case of IV.

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