PHOTOCHEMICAL OXIDATION OF 1,2,2,6,6-PENTAMETHYL-4-PIPERIDOL BY KETONES

L. M. Kostochka, A. M. Belostotskii, and A. P. Skoldinov

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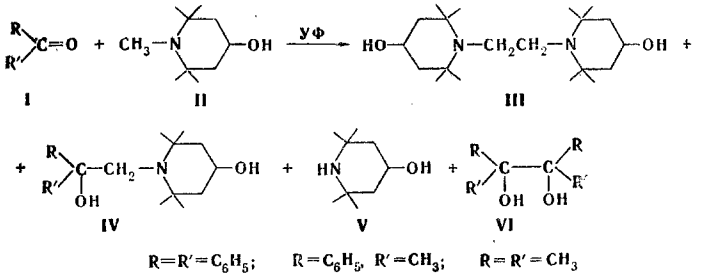
In the photoreduction of ketones with alkylamines the principal pathway of the transformations of the latter is dealkylation [1, 2].

We have established that the photoreaction of ketones RCOR' (Ia-c) with a cyclic amino alcohol, viz., 1,2,2,6,6-pentamethyl-4-piperidol (II), in benzene (with mixing of equal amounts of 0.2 mole/liter solutions of the reagents and irradiation for 5-6 h with the total light of a PRK-2M mercury-quartz lamp as argon is bubbled through the mixture) leads primarily to addition products, viz., dimer III and cross products IVa-c; with respect to their structure the latter are of interest as potential biologically active substances.



Dimer III was obtained in 34, 41, and 52% yields, respectively, while IVa-c were obtained in 31, 10, and 9% yields [according to the results of gas–liquid chromatography (GLC), IVb, c were obtained in ∿30% yields]. Amino alcohol II undergoes demethylation to only a slight extent and gives 2,2,6,6-tetramethyl-4-piperidol (V) in 6, 4, and 1.4% yields, respectively. Pinacol was not isolated from acetone, benzopinacol (VIa) was obtained in 46% yield, and acetopinacol (VIb) was obtained in 26% yield; according to the PMR data (for solutions in CCl_4), the latter was a mixture of d, l and meso forms in approximately equal amounts. The structures of the amino diols obtained were confirmed by data from the PMR and mass spectra.

4,4'-Dihydroxy-2,2,2',2',6,6,6',6'-octamethyl-1,1'-ethylenebispiperidine (III), $C_{20}H_{40}N_2O_2$, had mp 265-266°C. 1-(2-Hydroxy-2,2-diphenylethyl)-2,2,6,6-tetramethyl-4-piperidol (IVa), $C_{23}H_{31}NO_2$, had mp 228-229°C. 1-(2-Hydroxy-2-phenylpropyl)-2,2,6,6-tetramethyl-4-piperidol (IVb), $C_{18}H_{29}NO_2$, had mp 185-186°C. 1-(2-Hydroxy-2-methylpropyl)-2,2,6,6-tetramethyl-4-piperidol hydrochloride (IVc), $C_{13}H_{27}NO_2 \cdot HCl$, had mp 212-214°C.

LITERATURE CITED

1. S. G. Cohen, A. Parola, and G. H. Parsons, Chem. Rev., 73, 141 (1973).
2. S. G. Cohen and N. M. Stein, J. Am. Chem. Soc., 93, 6542 (1971).

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