CYCLOHYDROXYLAMINOCYANATION OF 2'2'-METHYLENEDICYCLOHEXANONE

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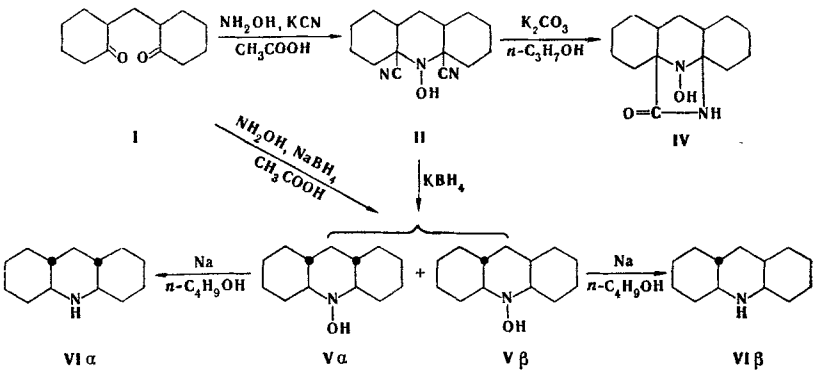
The hydroxylaminocyanation reaction has been applied only to monocarbonyl compounds [1]. Using 2,2'-methylenedicyclohexanone (I) as an example, we have established that 1,5-diketones are capable of taking part in a cyclohydroxylaminocyanation reaction, which is analogous to the cycloaminocyanation reaction [2]. The reaction takes place readily when the diketone (I) is mixed with hydroxylamine and potassium cyanide in dilute acetic acid; this gives an 85% yield of 11,14-dicyanoperhydroacridine N-oxide (II), $C_{15}H_{21}N_3O$,* mp 208°C (from propanol); IR spectrum (paraffin oil): 2245 cm^{-1} (C ≡ N), 3370 cm^{-1} (OH).



On reacting with acetic anhydride in pyridine, (II) gave the O-acetyl derivative (III), $C_{17}H_{23}N_3O_2$, mp 187-188°C (from ethanol); IR spectrum (KBr): 1790 cm^{-1} (C = O); 2235 cm^{-1} (C ≡ N). On alkaline saponification, (II) formed the lactam (IV), $C_{14}H_{22}N_2O_2$, deco.np. p. 208-210°C (from dioxane), analogous to that described previously [2,3]; IR spectrum (paraffin oil): 1690 cm^{-1} (C = O), 3200-3400 cm^{-1} (NH). The reduction of (II) with potassium tetrahydroborate in ethanol led to a mixture of isomeric N-hydroxyperhydroacridines (Vα and Vβ) (yield 81%), which were separated by chromatography on Al_2O_3. The ratio Vα:Vβ = 2:2.7 [Vα: $C_{13}H_{23}NO$, mp 158-160°C (from ethanol). Vβ: $C_{13}H_{23}NO$, mp 154-156°C (from ethanol). IR spectrum ($CHCl_3$): 3600 cm^{-1} (OH)]. The reduction of the individual compounds (Vα) and (Vβ) with sodium in butanol gave the known [4] perhydroacridines (VIα) and (VIβ), respectively. The isomeric (Vα) and (Vβ) were also obtained by independent synthesis from (I), hydroxylamine, and sodium tetrahydroborate in acetic acid by a modified method for the hydroamination of 1,5-diketones.

LITERATURE CITED

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*All the compounds obtained for the first time had satisfactory elementary analyses.

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