AMINOPEROXIDATION OF 2,2'-METHYLENEDICYCLOHEXANONE

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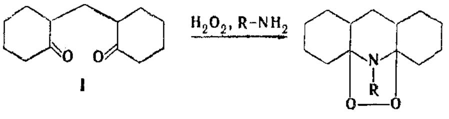
It was recently established that a number of monoketones react with ammonia and hydrogen peroxide to give cyclic aminoperoxides [1,2]. When ammonia is replaced by primary amines, the reaction stops with the formation of the aminohydroperoxide [3]. In the case of a 1,4-diketone – acetonylacetone – 5-hydroperoxy-2,2-dimethyl-Δ^1-pyrroline was obtained even when ammonia was used [3].

We have found that an alicyclic 1,5-diketone – 2,2'-methylenedicyclohexanone (I) – reacts with hydrogen peroxide (II) and ammonia or certain primary amines (aniline, benzylamine) (III) to give tetracyclic aminoperoxides (IV-VI).



I

IV-VI

IV R=H; Va,b R=C_6H_5; VI R=CH_2—C_6H_5

The reaction proceeds at room temperature in 10-12 h in aqueous alcohol. The highest yields of aminoperoxides are obtained when the ratio of I, II, and III is 1 : 10 : 1. The reaction proceeds stereospecifically with ammonia and aniline: one isomer (IV or Va) is formed when the threo form of I is used; two isomers (according to thin-layer chromatography) are obtained when the mixture of threo and meso forms formed in the synthesis of I is used, and we were able to isolate the second isomer (Vb) in the case of aniline. The reaction does not proceed stereospecifically with free benzylamine (owing to its considerable basicity, benzylamine probably induces enolization of I and partial conversion of the threo form to the meso form), but the reaction proceeds almost completely stereospecifically when an equimolar mixture of benzylamine hydrochloride and dimethylaniline is used.

Compounds IV-VI give qualitative reactions for peroxides. There is no absorption at 3400-3600 cm^{-1} (OH) and at 1600-1800 cm^{-1} (C =O or C =C) in their IR spectra. In the PMR spectra of IV and Va,b, all of the nonaromatic protons give signals (on the δ scale) below 1.9 ppm; in the spectrum of VI there is also a two-proton singlet at 4.0 ppm (benzyl CH_2). The structures of IV-VI were also confirmed by their conversion to the previously described [4] N-R-11,14-dicyanoperhydroacridines by the action of potassium cyanide in acetic acid. The reduction of IV with KBH_4 in ethanol gives the known β-perhydroacridine [5].

TABLE 1. N-R-11,14-Peroxyperhydroacridines

Comp.	R	Mp, °C	Empirical formula	Found, %			Calc., %			Yield, %
				C	H	N	C	H	N	
IV	H	97—98	$C_{13}H_{21}NO_2$	69,9	9,4	6,0	70,0	9,4	6,3	58
Va	C_6H_5	95—96	$C_{19}H_{25}NO_2$	76,1	8,5	4,9	76,1	8,4	4,7	78
Vb	C_6H_5	133—134	$C_{19}H_{25}NO_2$	76,3	8,7	5,4	76,1	8,4	4,7	—
VI	$CH_2C_6H_5$	125—126	$C_{20}H_{27}NO_2$	76,2	8,7	4,4	76,7	8,6	4,5	58

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Compounds Va,b and VI are completely stable on storage and normally can be recrystallized from alcohol. Compound IV undergoes partial decomposition on storage for 2 months, and it is possible to purify it only by freezing out from petroleum ether. The physical constants and yields of the compounds obtained are given in Table 1.

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