4,4-DIALKYL-1,4-DIHYDROPYRIDINE-3,5-DICARBONITRILES

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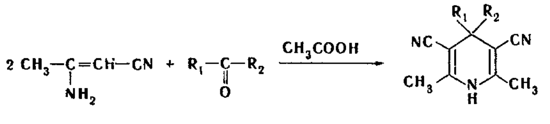
The condensation of β-aminocrotononitrile with dialkyl ketones in glacial acetic acid has given 4,4-dialkyl-2,6-dimethyl-1,4-dihydropyridine-3,5-dicarbonitriles. The mass spectra of these compounds show the molecular ion with low intensity, and the 4-alkyl substituent with the greater molecular weight is split off.

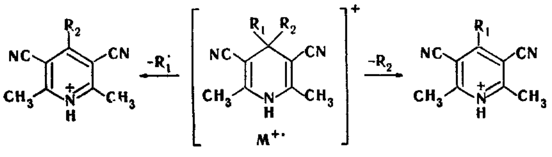
Polynuclear 4,4-disubstituted 1,4-dihydropyridines show peculiar properties; for example, they are cleaved exceptionally easily at the C_4-C bond by atmospheric oxygen in an alkaline medium [1]. The synthesis and properties of the simpler mononuclear 4,4-dialkyl-1,4-dihydropyridines have been studied to a smaller extent, and this only for the case of 2,6-dimethyl-1,4-dihydropyridine-3,5-dicarbonitriles (I) [2-4]. We have modified the method of synthesizing compounds of type (I) and have studied their mass spectra.



I a-f

a $R_1=CH_3$, $R_2=CH_3$; b $R_1=CH_3$, $R_2=C_2H_5$, c $R_1=CH_3$, $R_2=n\text{-}C_3H_7$; d $R_1=CH_3$, $R_2=n\text{-}C_4H_9$; e $R_1=C_2H_5$, $R_2=C_2H_5$; f $R_1-R_2=(CH_2)_5$

All the compounds obtained have the UV spectrum characteristic for 1,4-dihydropyridines [5] with two maxima in the 215-217-nm and 338-344-nm regions. The 4,4-dialkyl-2,6-dimethyl-1,4-dihydropyridine-3,5-dicarbonitriles possess a low resistance to electron impact: the intensities of the peaks of the molecular ions of compounds (Ia-e) are between 0.4 and 4.2% of the total ion current (in the range from M^+ to m/e 40), an increase in the length of the alkyl radical in position 4 leading to a rise in the probability of decomposition. Compound (If) is distinguished by a comparatively high stability to electron impact, the presence of the spirocyclic grouping in it leading to a rise in the intensity of the molecular ion to 8.4%. The main direction of the fragmentation of the molecular ions of compounds (Ia-e) is the elimination of the larger radical R_2 from position 4 with the formation of the stable protonated pyridinium ions (II), which are characteristic for the fragmentation of 1,4-dihydropyridines [6-8]. The formation of the ions (II) from the molecular ions in the fragmentation of compounds (Ib) and (Ic) is confirmed by the corresponding metastable transitions. The detachment from position 4 of the smaller radical R_1 takes place with a considerably lower intensity in parallel with the formation of the ion (II).



III a-e I a-e II a-e

In the fragmentation of compound (If), the most intensive process is the splitting off of a $C_3H_7\cdot$ radical with the formation of the ion (IV).

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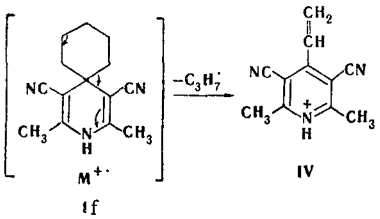
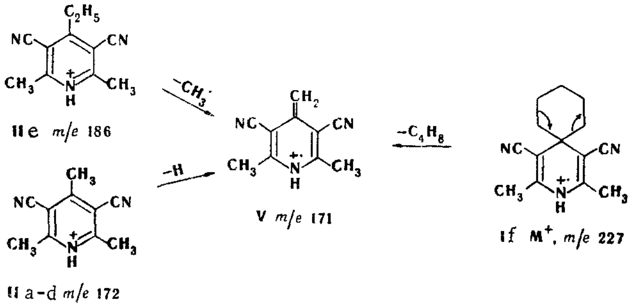


The peaks corresponding to the ions (II) and (III) are the maximum peaks in the spectra and amount to 38-42% of the total ion current for compounds (Ia-d) and to 30% for compounds (Ie, f). In parallel with the splitting out of the whole alkyl radical in compounds (Ib-e), but with a lower probability, the cleavage of the β, γ, and δ bonds of the alkyl group takes place with the formation of the ions $M^+ - 43$, $M^+ - 29$, and $M^+ - 15$, and in the case of compound (If) the appearance of these ions is apparently connected with the cleavage of the ring. In the mass spectrum of compound (If), in addition, low-intensity peaks appear with masses $M^+ - 1$, $M^+ - 2$, $M^+ - 3$, and $M^+ - 4$, which are formed as the result of the successive ejection of four hydrogen atoms from the cyclohexane ring. Characteristic for all the compounds studied is the common ion (V) (m/e 171) which, in the case of compounds (Ia-e) can be formed from the ion (II) by the loss of the radicals H· or CH_3·, while in the case of compound (If) its appearance is connected with the decomposition of the molecular ion:



The ion (V) appears with the greatest intensity in the spectra of compounds (Ie) and (If) (14% and 8.8% of the total ion current, respectively). At mass numbers less than m/e 171, which are common for all the compounds studied, the mass spectra of (Ia-f) are completely identical and their peaks have low intensities.

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EXPERIMENTAL

The UV spectra were taken in ethanol (c 10^{-5} M) on a Specord UV-Vis instrument. The mass spectra were taken on an MKh-1303 instrument at an energy of the ionizing electrons of 70 eV, an accelerating voltage of 2 kV, and an emission current of 1.5 A.

2,6-Dimethyl-4,4-pentamethylene-1,4-dihydropyridine-3,5-dicarbonitrile (If). A mixture of 1.4 g (0.02 mole) of β-aminocrotononitrile, 1 g (0.01 mole) of cyclohexanone, and 5 ml of glacial acetic acid was kept at 70°C for 30 min, and was then left overnight at room temperature. The precipitate of 2,4-dimethyl-6-oxopyridine-3-carbonitrile was filtered off, and the filtrate was diluted with an equal volume of water. After recrystallization from toluene, 1.1 g (50%) of colorless crystals with mp 136°C giving a blue fluorescence in UV light was obtained. The other compounds (Ia-e) were obtained similarly.

TABLE 1. 4,4-Dialkyl-1,4-dihydropyridine-3,5-dicarbonitrile (Ia-f)

Comp.	R_1	R_2	mp, °C	λ_{max}, nm (log ε)	Empirical formula	Found, %			Calc., %			Yield, %
						C	H	N	C	H	N	
Ia	CH_3	CH_3	238 $(238—239)^2$	217; 338 (4,14; 3,60)	$C_{11}H_{13}N_3$	70,3	7,0	22,1	70,5	7,0	22,4	40
Ib	CH_3	C_2H_5	130	217, 343 (4,4; 3,9)	$C_{12}H_{15}N_3$	70,9	8,0	20,3	71,6	7,5	20,9	45
Ic	CH_3	n-C_3H_7	155	216; 344 (4,7; 3,4)	$C_{13}H_{17}N_3$	72,9	8,1	19,5	72,5	7,9	19,5	40
Id	CH_3	n-C_4H_9	145	216; 342 (4,3, 3,8)	$C_{14}H_{19}N_3$	73,7	8,6	18,3	73,3	8,4	18,3	35
Ie	C_2H_5	C_2H_5	164 $(161—163)^2$	215; 341 (4,3; 3,6)	$C_{13}H_{17}N_3$	72,1	7,9	20,2	72,5	7,9	19,5	50
If	$(CH_2)_5$		136	216; 342 (4,3; 3,4)	$C_{14}H_{17}N_3$	74,1	7,6	18,4	73,9	7,5	18,4	50

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