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SYNTHESIS AND STRUCTURE OF SOME BIS-ALKYLAMMONIUM SALTS OF 2,4-DINITRO-3-PHENYL-GLUTARIC ACID DINITRILE

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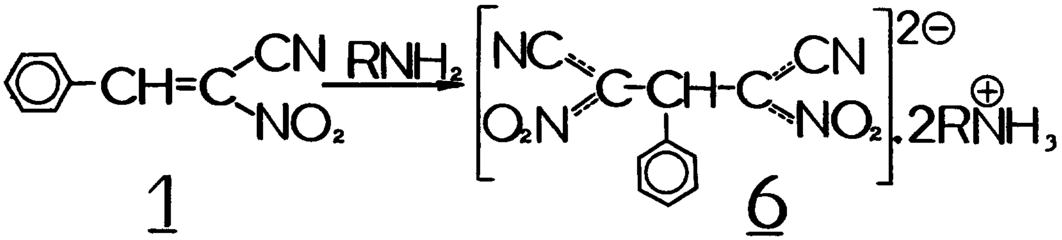
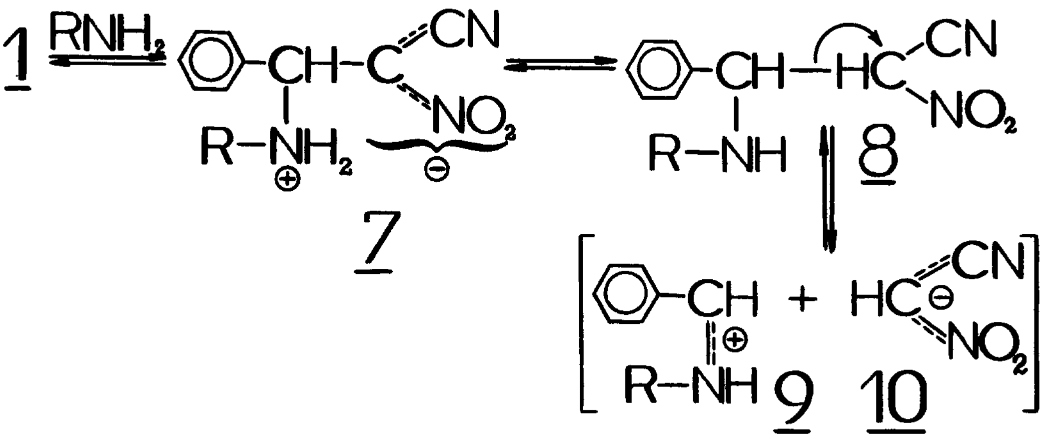
There is only a small number of investigations on the reactions of amines with unsaturated nitro compounds containing two electron withdrawing groups at the alkene system end.[1-3] The nature of the products of the reaction of 1-nitro-1-cyano-2-phenyl-ethylene (1) with lower molecular weight aliphatic, aromatic and hydroaromatic amines is usually determined by the basicity of the corresponding amine.[2] It was of some interest to investigate the reaction of (1) with middle and higher molecular weight amines and to establish the structure of the reaction products.

We carried out the reaction of (1) with heptylamine , octylamine , heptadecylamine and piperidine by mixing equimolar amounts of (1) and the corresponding amine in ethanol,at room temperature. We obtained the following products (m.p.,% yield): bis-heptylammonium (2) (144,80), bis-octylammonium (3) (142,82), bis-heptadecylammonium (4) (137,84) and bis-piperidinium (5) (113, 78) salts of 2,4-dinitro-3-phenyl-glutaric acid dinitrile (general formula 6). All salts obtained are white crystalline solids , soluble in water and polar solvents , insoluble in ether. The elemental analysis data are in agreement with Formula 6.

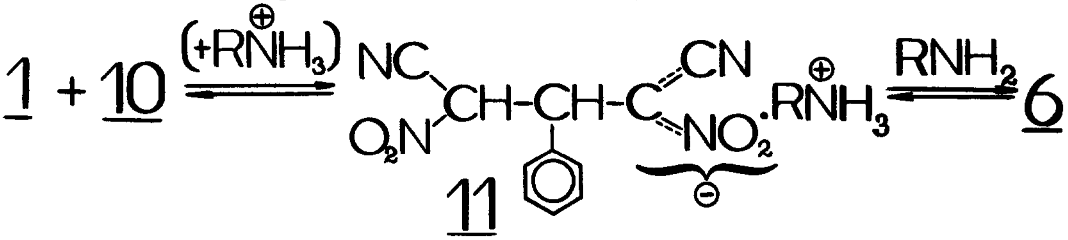


The presence of the alkylammonium counter ions in the salts obtained was proved by acidification of the salts with excess hydrobromic acid; the respective alkylammonium bromides were obtained quantitativelly. We failed, however, to isolate the free C-H acid under these conditions. Instead, we obtained the parent compound (1), i.e. an intermediate elimination of nitroacetonitrile had taken place.

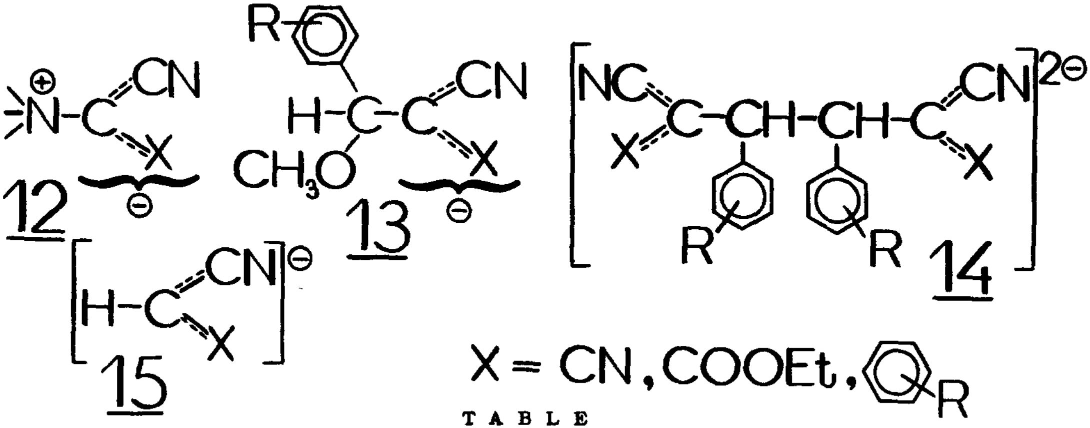
In the reaction studied, the title salts can be formed only after cleavage of the double C = C bond in (1). It has been shown[4] that some similar reactions involve intermediates containing an azomethyne group; in the present case, the formation of Schiff bases is to be excluded, as apparently the reaction course does not change when piperidine instead of primary amines is used. It can be assumed that the reaction involves a stage of addition of the nucleophile to the double bond of (1); isomerization of the adduct (7) leads to the formation of the addition product (8), then the latter undergoes heterolysis[5] (9, 10):



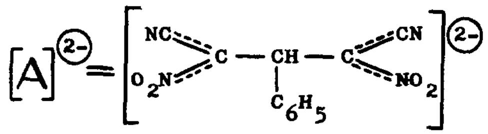
The immonium cation (9) so formed, reacts with the solvent (or with the water, present in the system) yielding the amine as ammonium ion, and benzaldehyde as acetal or free aldehyde.[6] Nucleophillic attack by the nitroacetonitrile anion leads to the formation of the mono-anion (11), which forms with the free amine present the end product (6):

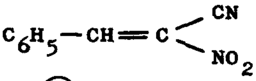
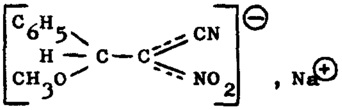
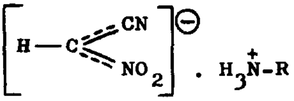


Further evidence for the ionic structure of the products (6) is provided by their I.R. spectra. It was previously found that within each of large series of anions of various types (12 - 15 etc.) differing in the fragment X conjugated with the nitrile group , there is a complete analogy in the I.R. spectra in the ν_{CN} region.[7,8,9]



TABLE



No	COMPOUND	ν_{CN} /cm^{-1}/ in KBr discs	ν_{CN} /cm^{-1}/ in DMSO
1	 $C_6H_5-CH=C(CN)(NO_2)$	2233 w.	2232 w.
2	$[A]^{(2-)}\cdot 2H_3\overset{+}{N}\text{-}C_7H_{15}$	2196 v.s.	2178 v.s.
3	$[A]^{(2-)}\cdot 2H_3\overset{+}{N}\text{-}C_8H_{17}$	2194 v.s.	2176 v.s.
4	$[A]^{(2-)}\cdot 2H_3\overset{+}{N}\text{-}C_{17}H_{35}$	2198 v.s.	2176 v.s.
5	$[A]^{(2-)}\cdot 2H_2\overset{+}{N}(CH_2)_5$	2196 v.s.	2178 v.s.
16		-	2188 v.s.
17		2200-2210 (in nujol)[11]	

Vice versa , in the present case , the data in the Table indicate the identity of the conjugated carbanionic system of the dianions studied and the methoxide adduct of (1) (Compound 16)[10] and also the anion (17)[11]. The differences between the solid state frequencies ν_{CN} of (2 - 5) can be ascribed to the electrostatic interactions dianion-counter ions; the fact that ν_{CN} of the same compounds coincide within experimental error in dimethylsulfoxide indicates that the salts (6) exist as 'free' ions in this solvent, similarly to the cases of other carbanion and anion-radical salts.[8,9] The lower values of ν_{CN} of (6), compared to these of (16) and (17) are probably caused by the mutual influence of the two negative charges in (6).

Comparison with already reported results[8,9] shows that the frequencies of the nitrile group of ions of the type $—C\genfrac{}{}{0pt}{}{\text{CN}}{\text{X}}^{\ominus}$ increase in the following order of X: $CH_3 < H < C_6H_5 < COOR \approx CN^{12} < NO_2$, which corresponds to the order of increasing of σ^- values of these substituents.[13]

The very high intensity of the ν_{CN} bands of compounds (2) - (5) and (16) also evidences their ionic structure, in agreement with the data on various anionic systems containing nitrile groups.[8,9]

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