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REACTIONS OF ORGANIC ANIONS XVI^x. CATALYTIC NITROARYLATION OF PHENYLACETONITRILE DERIVATIVES IN AQUEOUS MEDIUM.

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The previous papers in this series described the catalytic alkylation of phenylacetonitrile and its derivatives with mono- and dihaloalkanes which, in some cases, contained other functional groups (1). The alkylation was carried out in the presence of aqueous NaOH and triethylbenzyl ammonium chloride (TEBA chloride) rather than the commonly used alkali metal amides or hydrides in anhydrous solvents (2).

It was shown in this work that the catalytic method may be employed for the preparation of nitroaryl derivatives of phenylacetonitriles.

Halogen-substituted aromatic hydrocarbons are not prone to undergo nucleophilic substitution; the action of strong bases results usually in the formation of unstable intermediates of benzyne type structure. The strong electrophilic effect of the nitro group in the para or ortho position makes the nucleophilic substitution easier so that halonitroaromatic compounds react with many nucleophiles including anions of cyanoacetic (3), malonic, and acetoacetic (4) esters to give the corresponding nitroaryl derivatives. The synthesis of phenyl-p-nitrophenylacetonitrile from phenylacetonitrile and p-chloronitrobenzene (in the presence of KOH in pyridine), reported by Davis (5) is the only example of such nucleophilic substitution by a mononitrile anion.

Attempts at carrying out this reaction by the catalytic method (aqueous NaOH, TEBA chloride) failed, probably because of a higher acidity, as compared

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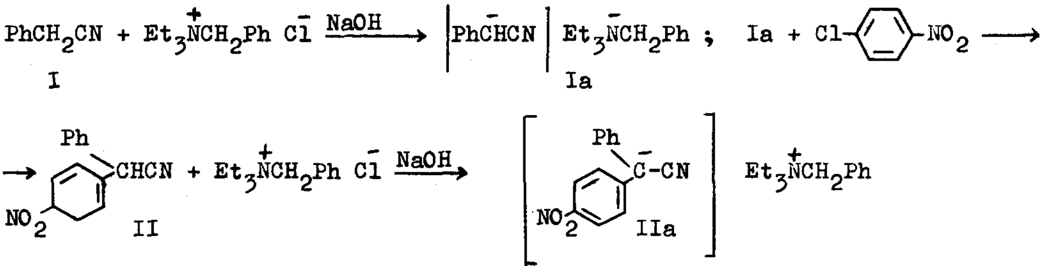
[x] Part XV. M.Mąkosza Bull.Acad.Polon.Sci., Ser.sci.chim., 15, 165 (1967).

with the substrate (I), of the nitroarylation product (II), which may neutralize the catalyst, i.e., the active base. This case seems to be very similar to the reaction of phenylacetonitrile with chloroacetonitrile (6). The anion formed from the cyanomethylated product reacted, however, with chloroacetonitrile to give phenyltricarballylic nitrile (7), while the nitrophenylphenylacetonitrile anion (IIa) did not react with chloronitrobenzene and the reaction was arrested.



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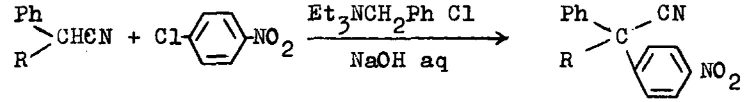
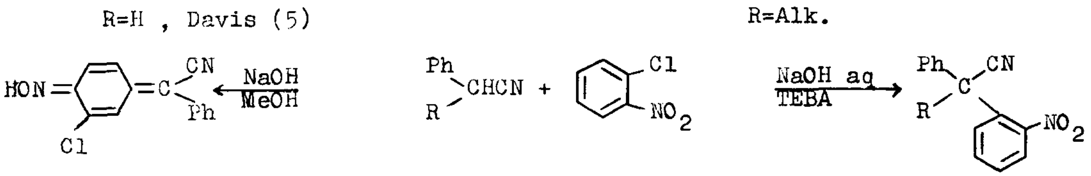


If this assumption were true, the catalytic nitroarylation would be operative with phenylalkylacetonitriles yielding in this reaction products with no acidic hydrogen atoms. Actually, the mixture of 14.3 g (0.11 mole) of 2-phenylpropionitrile, 15.8 g (0.1 mole) of p-chloronitrobenzene and 15 ml of a 50% NaOH solution without TEBA chloride did not react at all, while the addition of 0.25 g of TEBA chloride resulted in an exothermic reaction yielding 82% of 2-(p-nitrophenyl)-2-phenylpropionitrile. Similar reactions were observed with other nitriles of this type; some benzene was added in the case of solid nitriles.

According to Davis (5), the phenylacetonitrile anion reacts with o-chloronitrobenzene at the para position to the nitro group, giving a phenylcyanomethylenequinonoxime. However, under the conditions described in this work, ordinary substitution of the chlorine atom took place.

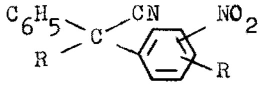


Investigation of the nitroarylation of 2-phenylpropionitrile was extended to cover certain cases with a third substituent in the benzene ring (e.g., Cl, CH_3, COOR, etc.) in addition to the nitro group and the chlorine atom in the position para to each other. In all cases the chlorine atom in the position para to the nitro group was replaced and nitroarylated nitriles were obtained in good yields.

Physical properties of some of the products obtained in this work are given in Table 1.

Table 1

Nitroaryl derivatives of phenylacetonitrile



No.	R-	Subst. position.	Yield %	B.p. °C/mmHg	m.p. °C
1.	CH_3	p-NO_2	82	175/0,6	77[a]
2.	C_3H_7	p-NO_2	63	185/0,8	76[a]
3.	C_6H_5	p-NO_2	71		96[a]
4.	$C_6H_5CH_2$	p-NO_2	87		95[a]
5.	CH_3	o-NO_2	53	180/0,8	74[a]
6.	CH_3	p-NO_2, o-Cl	92		92[a]
7.	CH_3	p-NO_2, o-$COOtC_4H_9$	83		166[b]
8.	CH_3	p-NO_2, o-CH_3	88	155/0,15	1,5908[c]

[a] from methanol, [b] from propanol, [c] n_D^{20}. Melting points are uncorrected.

The infrared spectra exhibit absorption bands characteristic for -CN (2240 cm^{-1}) and $-NO_2$ groups (1540 and 1360 cm^{-1}); compound 7 shows additional bands at 1320 and 1730 cm^{-1} (-COOR group).

The compounds (Table 1) may be transformed, on ordinary chemical routes, into aminonitriles, nitroacids, etc. For example, the reduction of compound 1 with Fe/HCl or Sn/HCl yields 2-phenyl-2-(p-aminophenyl)propionitrile (b.p. 169°/0,3 mmHg, m.p. 64°, yield 96%); the hydrolysis of compound 1 in CH_3COOH - H_2SO_4 mixture gives 2-phenyl-2-(p-nitrophenyl)propionic acid (m.p. 176°, yield 88%) etc.

Satisfactory analyses have been obtained for all compounds.

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