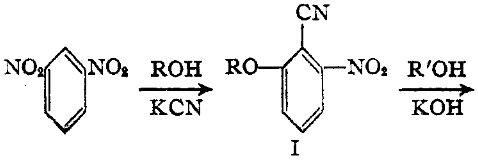
[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT, UNIVERSITY OF NORTH CAROLINA]

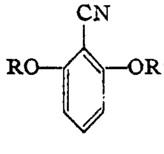
Vicinal Substituted Resorcinols. III. Extension of the Reaction between *m*-Dinitrobenzene, Potassium Cyanide and Methanol to Other Alcohols. The Mechanism of the Reaction

BY ALFRED RUSSELL AND L. M. ADDISON

The reaction shown below (R = R′ = CH_3) is a convenient way of introducing a carbon side chain into the vicinal position in the resorcinol nucleus.[1] The only other practical method for reaching this rather inaccessible position is through the use of 4-methyl-7-hydroxycoumarin (III) obtained by condensation of resorcinol with acetoacetic ester.[2]



I



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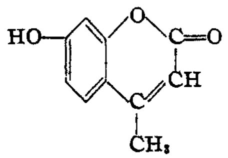


III

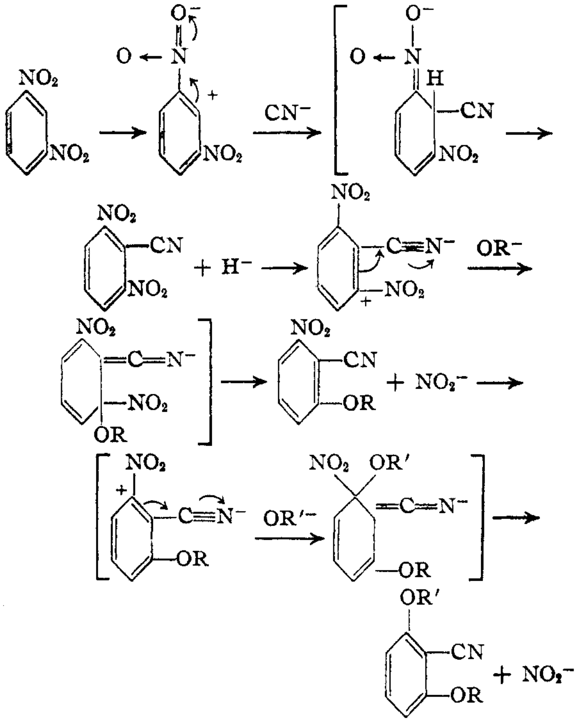
The reaction between *m*-dinitrobenzene, methanol and potassium cyanide has now been extended to include several alcohols, other than methanol. The reaction between the nitroalkoxybenzonitriles and various alcohols has also been examined. In both cases, judging by the yields obtained, the limits of the reaction have been reached.

Any attempt to explain the replacement of the nitro group by alkoxyl, accompanied simultaneously by the introduction of a vicinal nitrile group, by a process of 1,4-addition of potassium cyanide to the α,β-unsaturated nitro system is unsatisfactory.

Indeed it seems certain that an explanation of the reaction involving a non-ionic mechanism cannot be given and this would appear to be verified by the fact that cyanide ions are essential.[3] The reaction will not take place if anhydrous alcohols are used. Incidentally this finding has been verified in the course of the present work.

The reaction between *m*-dinitrobenzene and alcohols in the presence of cyanide ions becomes more difficult as the alcohol series is ascended. This is reflected in the yields of alkoxybenzonitrile which decrease in the same order. The same effect is observed in the step involving the replacement of the remaining nitro group by alkoxyl.

The mechanism below is suggested for the complete conversion of *m*-dinitrobenzene to a 2,6-dialkoxybenzonitrile.



Experimental

Table I gives a list of the known nitroalkoxybenzonitriles,[4] and dialkoxybenzonitriles.[4]

TABLE I

Benzonitrile	M. p., °C.	N Anal., % Calcd.	N Anal., % Found	Yield, %
2-Nitro-6-methoxy-	172			11
2-Nitro-6-ethoxy-	136			9
2-Nitro-6-*n*-propoxy-	109			3.5
2-Nitro-6-isopropoxy-	102	13.59	13.62	7.5
2-Nitro-6-*n*-butoxy-	101	12.73	12.70	5.5
2-Nitro-6-*s*-butoxy-	109	12.73	12.85	4.5
2-Nitro-6-*n*-pentoxy-	103	11.97	11.93	4.0
2-Nitro-6-*n*-hexoxy-	88	11.29	11.11	1.5
2,6-Dimethoxy-	118			85
2,6-Diethoxy-	122			50
2-Methoxy-6-ethoxy-	66			..
2,6-Dipropoxy-	45	6.39	5.58	6

Summary

The route to vicinal substituted resorcinols, through the reaction between *m*-dinitrobenzene and alcohols in the presence of cyanide ions and

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(1) Russell and Tebbens, "Org. Syn.," **22**, 35 (1942).

(2) Russell and Frye, "Org. Syn.," **21**, 22 (1941).

(3) Lobry de Bruyn and van Geuns, *Rec. trav. chim.*, **23**, 34 (1904).

(4) Only products for which analyses are given are new. The others are included to make the list complete.

the subsequent reaction of the alkoxy benzonitriles with alcohols, has been extended to its, apparent, limit.

Possible mechanisms for the somewhat obscure reactions involved are suggested.

CHAPEL HILL, N. C. RECEIVED AUGUST 16, 1943

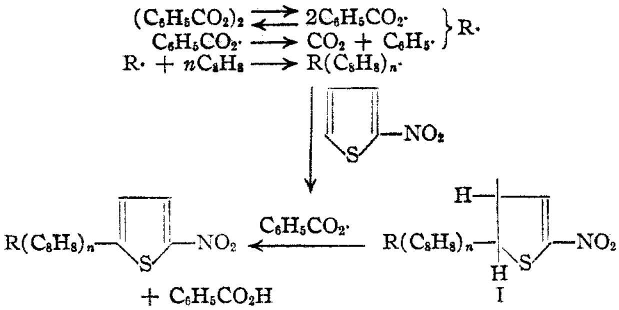
[CONTRIBUTION FROM NOYES CHEMICAL LABORATORY, UNIVERSITY OF ILLINOIS]

The Polymerization of Styrene in the Presence of Nitrothiophene and Chloranil

BY CHARLES C. PRICE

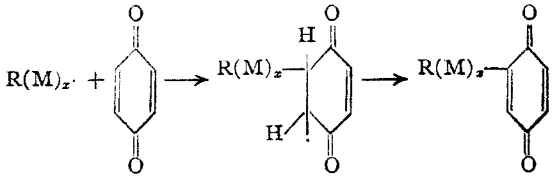
Since thiophene analogs of aromatic compounds are frequently of similar character but considerably more reactive, it was of some interest to compare the effect on free-radical addition polymerization of nitro derivatives of the two classes. Actually, the retardation of the polymerization of styrene in the presence of nitrothiophene was indeed much more pronounced than in the presence of nitrobenzene.[1]

Furthermore, polystyrene formed in the presence of nitrothiophene was found to contain the elements of the retarder in the proper amount for one nitrothienyl residue per polymer chain. Since the retardation is due to coupling of the growing free-radical polymer chain with the nitro compound, these results would indicate that the thiophene ring is more reactive toward free radical attack than the benzene ring. The radical is believed to attack the open α-position since this is the reactive position in thiophene and also reaction in this manner will enable the nitro group to lend resonance stability to the adduct.

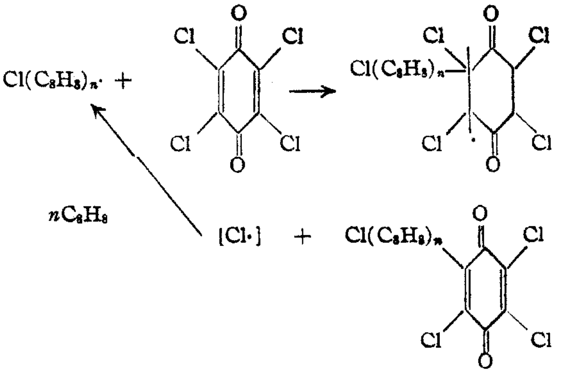


It is this stabilizing influence of the nitro group in the adduct I which evidently prevents it from reacting further with monomer molecules. Reaction of the growing chains with nitrothiophene thus serves to deactivate them thereby retarding the progress of the polymerization. The free radical adduct I, although stabilized toward reaction with monomer, will, of course, undergo disproportionation with another radical, such as, *e. g.*, the benzoxy radical.

The ease with which free radicals attack quinones to yield substitution products[2] has suggested that, in this case also, retardation or inhibition may be due to coupling of free radical chains with the quinone. (The symbol *M* is used to represent monomer units.)



Since chloranil is a quinone with no hydrogen to displace in this manner an investigation of its effect on free-radical addition polymerization was undertaken. Polystyrene prepared in the presence of chloranil was found to contain the elements of the added reagent in the proper proportion for one chloranil residue per polymer molecule. However, this compound did not appear to act as a retarding agent since the yield of polymer was not markedly decreased as is the case for a retarder or inhibitor. The action is more nearly analogous to that of carbon tetrachloride,[3] which appears to involve *transfer* of the activity of the growing chain through chlorine atoms rather than destruction of the activity.



To confirm the chemical nature of the union of chloranil with polystyrene prepared in its presence, a sample of polystyrene of about the same molecular weight as that formed in the presence of chloranil was mixed with chloranil. The procedure used for isolating polystyrene led to a practically quantitative separation of the two

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[1] Price and Durham, THIS JOURNAL, **65**, 757 (1943).

[2] Fieser and Chang, *ibid.*, **64**, 2043 (1942); Fieser and Oxford, *ibid.*, 2060.

[3] Breitenbach and Maschin, *Z. physik. Chem.*, **A187**, 175 (1940).