A New Synthesis of Nitrones from Aromatic Nitro-compounds and Carbanions by Nucleophilic Replacement of Hydrogen

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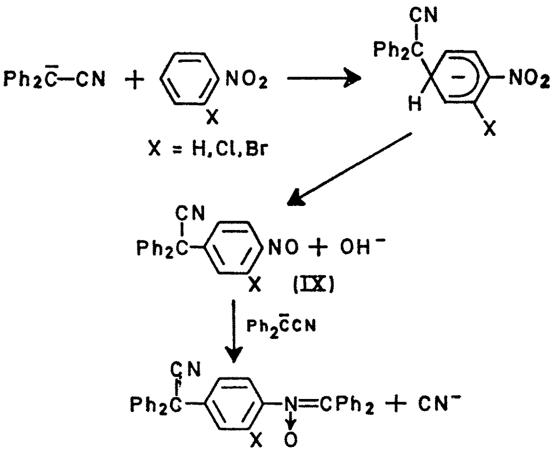
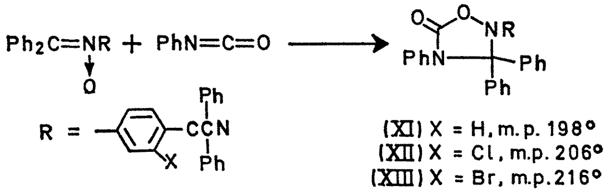
Summary Diphenylacetonitrile and some nitrobenzenes in the presence of saturated KOH or MeONa in methanol react to yield substituted triaryl nitrones.

WE recently reported[1] a new type of nucleophilic substitution process involving nitrobenzene (I) in which the hydrogen in the *para*-position is replaced by carbanions derived from phenylalkylacetonitrile. On the other hand, in the reaction of diphenylacetonitrile (II) with nitrobenzene, only tetraphenylsuccinonitrile (III) was obtained. Further investigation has shown that under appropriate conditions (I) and (II) may also yield products arising from nucleophilic substitution of the hydrogen. The formation of (III) occurs in weakly polar solvents such as benzene, toluene, tetrahydrofuran *etc.* The reaction of (I) with (II) in the saturated methanolic solution of potassium hydroxide (or sodium methoxide) at 30—60° leads to a quantitative yield of αα-diphenyl-*N*-4-(cyanodiphenylmethyl)phenylnitrone (IV), m.p. 212°. *o*-Chloronitrobenzene (V) and *o*-bromonitrobenzene (VI) react with (II) in a similar way to give αα-diphenyl-*N*-4-(cyanodiphenylmethyl)-3-halogenophenylnitrones [(VII; X = Cl) m.p. 201°; (VIII; X = Br) m.p. 205°] in 92 and 85% yields, respectively.



SCHEME 1

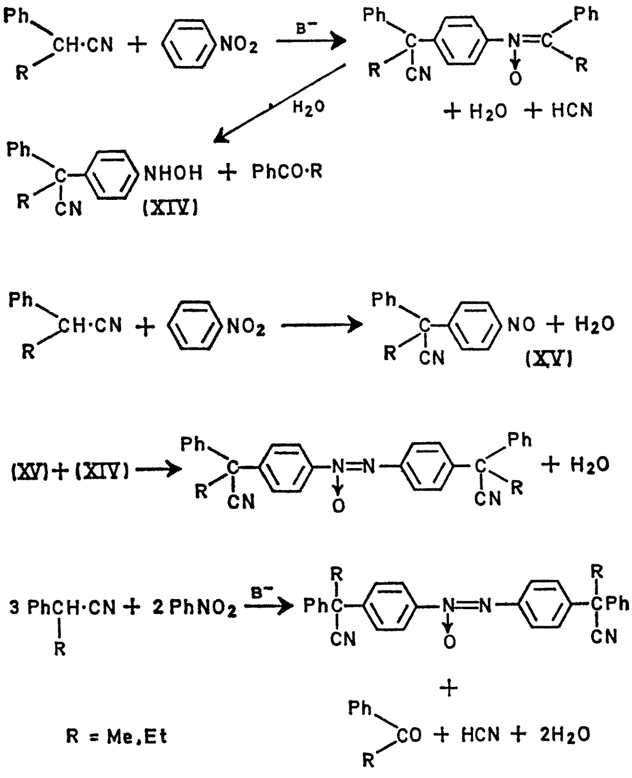


SCHEME 2

The probable reaction sequence is illustrated in Scheme 1.

As a check to see whether the above reaction sequence was taking place, since the nitroso-compounds (IX) are not easily accessible, the reaction of nitrosobenzene with (II) under similar conditions was studied. The well known αα*N*-triphenylnitrone[2] (m.p. 228°) (X) was isolated. In all the experiments, the amount of CN$^-$ ion found in the reaction mixtures was consistent with the calculated value.

The nitrones were identified on the basis of their elemental analysis, and i.r. and u.v. spectra. The i.r. spectra of the nitrones (IV), (VII), (VIII), and (X) show a strong absorption at 1243, 1247, 1250, and 1244 cm^{-1}, respectively. The absorptions in the 1150—1270 cm^{-1} region were assigned[4] to the $N \rightarrow O$ stretching frequencies of nitrones.



SCHEME 3

The u.v. absorption spectrum of (X) in ethanol shows the previously reported[2] maximum at 308 nm (log ε 4·0); (IV), (VII), and (VIII) show similar broad maxima at 310, 304, and 308 nm (log ε 4·1—4·15) respectively. Similarly to (X),[3] (IV), (VII), and (VIII) react with phenyl isocyanate to yield *ca.* 90% of the 1,3-adducts—probably 1,2,4-oxadiazolin-5-one derivatives (XI—XIII).

The results described clarify the mechanism of the formation of the azoxy-compounds reported previously.[1] The nitrones are presumably formed from phenylalkylacetonitriles in a manner analogous to that shown in Scheme 1. Like other nitrones of similar type, they are expected to be hydrolysed to ketones and corresponding substituted hydroxylamines.[4] The reaction of hydroxylamine with a substituted nitrosobenzene (IX) *in situ* yields the appropriate azoxy-compound. The formation of the corresponding ketone, as well as of CN^- ions in the reaction mixture, may also be explained on the basis of the reaction sequences presented in Schemes 1 and 3.

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[3] H. Staudinger and K. Miescher, *Helv. Chim. Acta*, 1919, **2**, 554.

[4] J. Hamer and A. Macaluso, *Chem. Rev.*, 1964, **64**, 473.