FORMATION OF BENZONITRILE DERIVATIVES IN THE REACTION OF ARYLPOLYNITROMETHANES WITH SODIUM AZIDE

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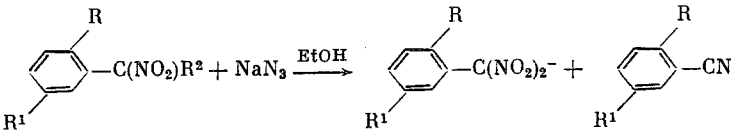
We are the first to establish that sodium azide may act as a reducing agent with phenyltrinitromethane (I) and 2-methoxy-5-nitrophenylchlorodinitromethane (II) in ethanol to give the corresponding anions (III) and (IV) and the unexpected corresponding benzonitriles (V) and (VI).



(I), (II) (III), (IV) (V), (VI)

$R = R^1 = H$, $R^2 = NO_2$ (I), (III), (V); $R = OCH_3$, $R^1 = NO_2$, $R^2 = Cl$ (II), (IV), (VI).

A 10-fold excess of sodium azide was used in the reaction proceeding with the formation of both products. The yield of (V) in this case was 18%, while the yield of (VI) was 37%. The reaction proceeds very slowly at 20°C and was monitored by thin-layer chromatography relative to the disappearance of (I) and (II).

The reaction of phenyltrinitromethane and 2-methoxy-5-nitrophenylchlorodinitromethane with sodium azide has not been described. There has only been a report that the action of sodium azide on fluoronitromethane leads to substitution of the nitro group by the nucleophilic residue [1]. Examples have been reported when azidation proceeds with retention of the trinitromethyl group [2].

The synthesis of starting (I) was carried out according to our previous procedure [3], while a sample of (II) was prepared according to Kolesetskaya et al. [4]. The final products were identified by UV, IR, and PMR spectroscopy and mass spectrometry as well as by the conversion of (III) and (IV) to the corresponding chloro derivatives.

LITERATURE CITED

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