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"VICARIOUS" NUCLEOPHILIC SUBSTITUTION OF HYDROGEN IN AROMATIC NITRO COMPOUNDS[x]

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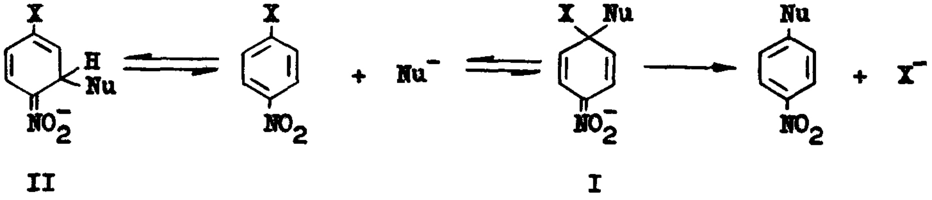
The nucleophilic substitution of halogen, alkoxy group etc. in aromatic nitro compounds is a process of great importance. This reaction proceeds via addition of a nucleophile to the aromatic ring which results in the formation of an intermediate σ-complex I, which subsequently loses the leaving group in the form of anion yielding the substitution product[1,2]. Similar complexes II are formed even faster by addition of a nucleophile to a nitroaromatic ring in a position bearing hydrogen[3].



Scheme I

The hydride anion is however a poor leaving group, therefore such complexes dissociate back (no reaction takes place) or redox processes occur. One could expect however that if the attacking nucleophile contains a substituent able to leave as an anion, the complex II could then react further in such a way

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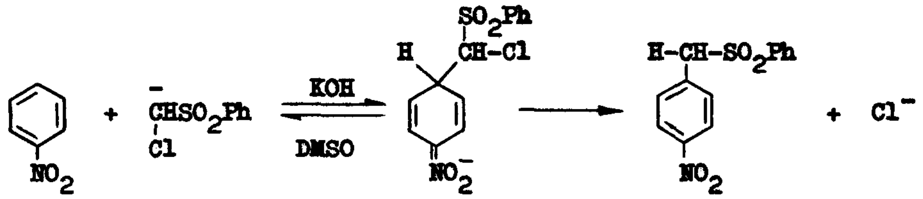
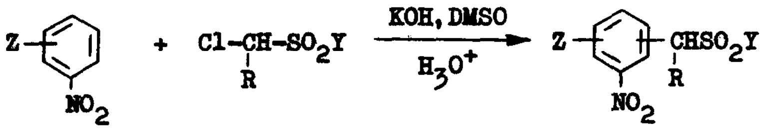
[x] Reactions of Organic Anions, Part LXXXVII; Part LXXXVI: M.Fedoryński, K.Wojciechowski, Z.Matacz and M.Mąkosza, J.Org.Chem., submitted for publication.

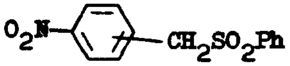
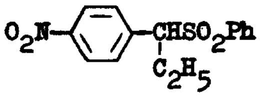
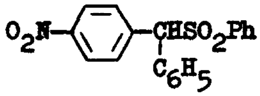
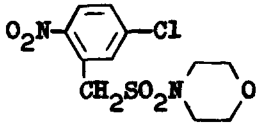
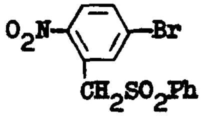
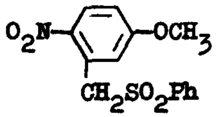
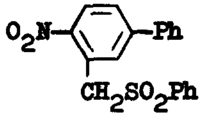
that the mentioned substituent leaves in the form of an anion simultaneously with the migration of the hydride anion from the aromatic carbon to the central carbon atom of the nucleophile. Hence the entire process could be considered as a nucleophilic substitution of a hydride anion in the aromatic ring whereas actually the leaving group is present in the nucleophilic agent. The term "vicarious substitution" seems therefore adequate for the phenomena[4]. In order to observe the process defined as above, one should have a C-H acid containing a leaving group and at the some time inactive as an alkylating agent in S_N2 type processes. These requirements are well met by α-halosulfones and N,N-dialkyl-1-haloalkanesulfonamides. On the basis of these considerations we have undertaken studies of reactions of α-halosulfones and sulfonamides with aromatic nitro compounds in the presence of strong bases. The results obtained fully confirm the anticipated scheme of the "vicarious substitution".



Scheme II

For example when equimolar amounts of nitrobenzene and chloromethylphenylsulfone in DMSO were treated with an excess of sodium hydroxide (powdered) an exothermic reaction proceeded with development of deep blue colouration of the mixture. Dilution with water and acidification yielded nitrobenzylphenylsulfone (mixture ortho and para isomers) in total yield 72 %. The tendency for substitution of hydrogen is so strong that the reaction of p-chloronitrobenzene with for example chloromethane sulfomorpholide results in the formation of 2-(2-nitro-5-chloro)-toluenesulfomorpholide without notable substitution of the chloride anion in the aromatic ring. Other examples of this type of substitution are given in the table.



N^o	Z	Y	R	Product	Yield (%)	mp (°C)
1	H	Ph	H		72	207[x]
2	H	Ph	C_2H_5		56	104–105.5
3	H	Ph	Ph		90	116–117.5
4	p-Cl		H		67	172–173
5	p-Br	Ph	H		61	145–147
6	p-OCH_3	Ph	H		48	167–168.5
7	p-C_6H_5	Ph	H		57	157–158

[x] The mixture of ortho and para isomers (1:1). The para isomer was isolated by multiple recrystallization, mp.207°, Lit.[5] 209.5°. New compounds (entry 2-7) gave correct elemental analyses. Their structure was supported by IR and PMR spectra and in some case by oxidation to known substituted nitrobenzoic acids.

Further study have shown that this novel kind of substitution can be extended onto some other systems. The results will be published elsewhere.

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4) There are a few reports in which similar transformations were described. For example, nitrobenzene is methylated by dimethylsulfoxonium methylide, H.Metzger, H.König and K.Sedert, Tetrahedron Lett., 867 (1964), V.J.Traynelis and Sr.J.V.McSweeney, J.Org.Chem., 31, 243 (1966); methylation and further oxidation to o- and p-nitrobenzoic acids occured when nitrobenzene was treated with dimsylsodium and oxygen, G.A.Russell and S.A.Weiner, ibid., 31, 248 (1966). Similar scheme seems also resonable for dichloromethylation of p-halonitrobenzenes. E.T.McBee, E.P.Weesseler and T.Hodgins, ibid., 36, 2907 (1971).

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