Reaction of 1-Deuterio-2-phenylcyclopropylamine Hydrochloride with Sodium Nitrite in HCl. 1-Deuterio-2-phenylcyclopropylamine hydrochloride (485 mg, 2.84 mmol) was suspended in 6 N HCl (1.46 mL) and stirred in an ice bath while a solution of sodium nitrite (201 mg, 2.91 mmol) in 1.2 mL of H_2O was added dropwise. After 5 min, a few granules of urea were added, and the mixture was heated on a steam bath for 5 min, cooled, and extracted with 3 × 10 mL of ether. The combined ether extracts were washed with saturated $NaHCO_3$, H_2O, and brine, dried ($MgSO_4$), and rotary evaporated to an orange-yellow liquid (119 mg). TLC (ether) revealed five spots (R_f 0.65, 0.56, 0.40, 0.29, 0.0); the spots at R_f 0.65 and 0.40 comigrated with cinnamyl chloride and cinnamyl alcohol, respectively.[14] Silica gel column chromatography (2.8 × 28 cm; ether) was used to isolate the compounds having R_f values of 0.65 (61.7 mg) and 0.40 (4.4 mg). NMR ($CDCl_3$) of the cinnamyl chloride: δ 4.20 (s with deuterium coupling, 2 H), 6.60 (s with deuterium coupling, 1 H), 7.2–7.5 (m, 5 H). NMR ($CDCl_3$) of the cinnamyl alcohol: δ 4.30 (s, 2 H), 6.60 (s with deuterium coupling, 1 H), 7.2–7.5 (m, 5 H).

(14) In a reaction starting with nonlabeled 2-phenylcyclopropylamine, these compounds were identified by comparison of their NMR and IR spectra with those of authentic samples of cinnamyl chloride and cinnamyl alcohol.

Reaction of 2-Phenylcyclopropylamine Hydrochloride with Sodium Nitrite in DCl. The same procedure as above was followed starting with 500 mg of 2-phenylcyclopropylamine hydrochloride in 1.5 mL of 6 N DCl. The sodium nitrite was dissolved in 1.2 mL of D_2O before addition. The crude reaction product (182 mg) was chromatographed as above, and the cinnamyl chloride (112.7 mg) and cinnamyl alcohol (11.1 mg) were isolated. The NMR spectra were identical with those of cinnamyl chloride and cinnamyl alcohol, respectively; no deuteration was evident.

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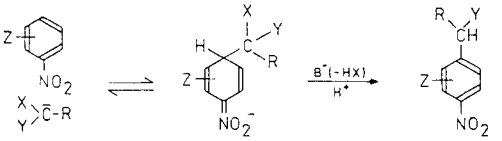
Registry No. 2-PCPA, 95-62-5; 1-deuterio-2-phenylcyclopropanecarboxylic acid, 92456-24-1; 1-deuterio-2-phenylcyclopropylamine hydrochloride, 92456-25-2.

Communications

Vicarious Nucleophilic Substitution of Hydrogen in Nitrophenols and Polynitroarenes. Examples of Nucleophilic Addition to Nitrocyclohexadienonenitronate Anions[1]

Summary: The vicarious nucleophilic substitution of hydrogen in dinitrophenols with chloromethyl phenyl sulfone carbanion 1 follows an orientation pattern due to quinoid resonance structures of the dinitrophenolate anions which behave as dinitrocyclohexadiene derivatives; di- and even trisubstitution is observed in the reaction with polynitroarenes leading to a sixfold-substituted benzene ring.

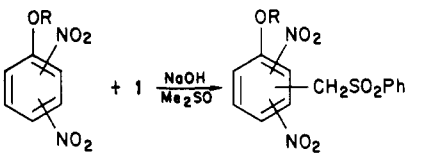
Sir: Vicarious nucleophilic substitution of hydrogen in nitroaromatic compounds proceeds via the addition of carbanions RCYX (X = leaving group, Y = carbanion stabilizing group) to the ortho and para positions of the nitroarene ring, with the formation of anionic σ complexes which undergo β-elimination of HX, giving rise to the anions of the substituted products.[2,3]



The reaction of nitroarenes with the carbanion of chloromethyl phenyl sulfone, 1, practically has no limitations as far as the substituents in the nitroarene ring are concerned. Electron donating (NMe_2, OR, CH_3) as well as electron accepting substituents (CN, SO_2Ph, CF_3) and even negatively charged (COO^-) groups located in the ortho, meta, and para positions to the nitro group usually do not impede this reaction.[4] However ortho, meta, and para nitrophenols do not enter this reaction. This is obviously due to the fact that the negative charge of the nitrophenolate anion is mostly located on the nitro group, or on the ring as in *m*-nitrophenol, hence the nucleophilic addition of the carbanion is hindered. Here we would like to report that this effect can be circumvented by the introduction of a second nitro group into the nitroarene ring. One can roughly consider that in a dinitrophenolate anion one of the nitro groups is engaged in the delocalization of the negative charge, whereas the second can sufficiently activate the ring toward nucleophilic attack.

Indeed dinitrophenols, which in the presence of strong alkali exist in the form of corresponding phenolate anions, react with 1 according to the vicarious nucleophilic sub-

Table I.[a] Reactions of Dinitrophenols and Dinitroanisoles with 1



substrate	product	yield, %	mp, °C
24	**243**[b]	89	226–228
24a	**245a**	61	180–183
25	**256**[c]	64	197–199
25a	**256a**	42	177–180
26	**263**	69	214–217
34	**342**[c]	23	216–218
34a	**342a**	26	170–172.5
35	**352**[c]	20	255 dec
35a	**352a**	78	173–175

[a] Notations: see ref 5. [b] **243a** obtained via methylation of **243**; mp 200–203 °C. [c] Methylation of these phenols gives anisoles identical with **256a**, **342a**, and **352a**, respectively.

(1) Part 120 in the series Reactions of Organic Anions. Part 119: Mąkosza, M.; Wojciechowski, K. *Bull. Acad. Polon. Sci., Ser. Sci. Chim.*, in press.

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(3) Mąkosza, M.; Glinka, T. *J. Org. Chem.* **1983**, *48*, 3860.

(4) Mąkosza, M.; Goliński, J.; Baran, J. *J. Org. Chem.* **1984**, *49*, 1488.

0022-3263/84/1949-4562$01.50/0

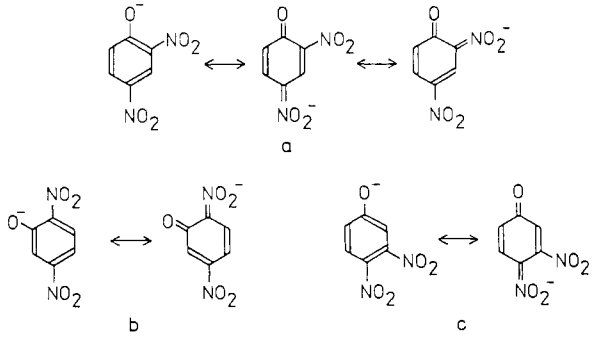


Figure 1.

stitution scheme to yield products in which a hydrogen atom in the nitrophenolate ring has been replaced by the (phenylsulfonyl)methyl substituent.

Amongst six possible isomeric dinitrophenols, five react with **1** to give the substitution products in good to moderate yields (Table I).[5]

Although the reaction of **1** with **24** can proceed at positions 3 and 5, actually only **243** is formed. No traces of another isomer (**245**) have been detected. At first glance this result contradicts our previous observations[4] that the reaction of 1,3-dinitrobenzene with an equimolar amount of **1** occurs only at position 4; the replacement of hydrogen at position 2 (between the nitro groups) does not occur.

The exclusive formation of **243** from **24** can be rationalized by taking into account that the anion of **24** is a resonance hybrid of the phenolate anion and the nitrocyclohexadienonenitronate anions (Figure 1a) and, furthermore, that the contribution of the latter structures is much greater. Thus it can be roughly considered as a Michael acceptor, able to add nucleophiles mainly at position 3.

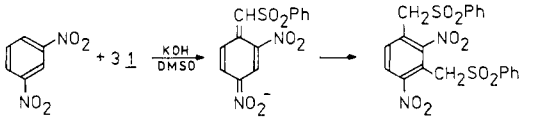
This explanation is strongly supported by the result of the reaction of **1** with **24a**—namely, the formation of **245a**. Contrary to the case of $\mathbf{24}^-$, the aromaticity of the ring in **24a** is conserved. In consequence of that the steric effects hindering the addition of the carbanion to the position between the two nitro groups operate similarly as in the case of *m*-dinitrobenzene, hence 5-H is replaced exclusively.

The orientation in the reactions of **25** and **34** with $\mathbf{1}^-$ can be explained similarly as in the case of **24**.

In the anions of **25** and **34** one can assume that the nitro groups in positions 2 and 4 are mostly in the form of nitronate anions and those in positions 5 and 3, respectively, activate the ring toward the nucleophilic attack (Figure 1, b and c), being responsible for the observed orientation.

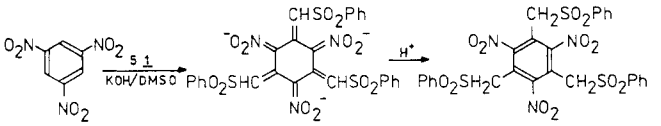
The orientation of vicarious nucleophilic substitution in **25a** and **34a** is the same as in the corresponding phenols. It seems that in these cases the nitro groups in positions 2 and 4 are deactivated by conjugation with the methoxy substituent and that the reaction is governed by the nitro groups located in positions 5 and 3, respectively, giving **256a** and **342a**.

The reaction of **1** with *m*-dinitrobenzene results in the formation of 2,4-dinitrobenzyl phenyl sulfone.[4] Its anion, to a great extent, resembles that of $\mathbf{24}^-$. Consequently the reaction of *m*-dinitrobenzene with an excess of **1** should result in the formation of the disubstituted product in which the second CH_2SO_2Ph substituent should be located in position 3 of the 2,4-dinitrobenzyl ring. This indeed was the case; the expected product, 1,3-bis[(phenylsulfonyl)-methyl]-2,4-dinitrobenzene, mp 218–220 °C, was produced in a 82% yield. Another isomer has not been detected.



The vicarious nucleophilic substitution of hydrogen with **1** can be extended to picric acid in which mono- and disubstitution can be performed stepwise yielding 2,4,6-trinitro-3-[(phenylsulfonyl)methyl]phenol, mp 263–264 °C, and 2,4,6-trinitro-3,5-bis[(phenylsulfonyl)methyl]phenol, mp 225 °C dec.

Most interesting is the fact that in 1,3,5-trinitrobenzene, all three hydrogen atoms can be replaced with (phenylsulfonyl)methyl substituents according to eq 1.



+ disubstituted product 32%, mp 234 °C dec 30%, mp 280 °C dec

(1)

The identity of all products was confirmed by NMR spectra and elemental analyses and also via chemical conversion of the phenolic substitution products into the corresponding anisoles which have been compared with the products of the reaction of **1** with the nitroanisoles.

Typical experimental procedure: to an intensively stirred mixture of **25** (5.0 mmol) and NaOH (1 g, 25 mmol) in Me_2SO was added a solution of chloromethyl phenyl sulfone (0.95 g, 5 mmol) in Me_2SO while the temperature was kept at 20 °C. The reaction mixture was stirred for 1 h and diluted with acidified water, and the product was isolated by column chromatography.

Vicarious nucleophilic substitution in nitrophenols opens up new possibilities for organic synthesis. These reactions are also interesting examples of nucleophilic addition to nitrophenolate anions which exist in the form of quinoid structures—nitrocyclohexadienonenitronate anions. Electrophilic addition to cyclohexadienonate structures of phenolate anions is well documented—here we present first examples of the nucleophilic addition to nitroarenes directed by the existence of the latter in the form nitrocyclohexadienonenitronate anions.

Further studies in this field concerning vicarious nucleophilic substitution in dinitroanilines, thiophenols, and toluenes are presently under way and will be reported in the future.

Registry No. **1**, 7205-98-3; **24**, 51-28-5; **24a**, 119-27-7; **25**, 329-71-5; **25a**, 3962-77-4; **26**, 573-56-8; **34**, 577-71-9; **34a**, 4280-28-8; **35**, 586-11-8; **35a**, 5327-44-6; **243**, 92241-27-5; **245a**, 92241-28-6; **256**, 92241-29-7; **256a**, 92241-30-0; **263**, 92241-31-1; **342**, 92241-32-2; **342a**, 92241-33-3; **352**, 92241-34-4; **352a**, 92241-35-5; *m*-$(NO_2)_2C_6H_4$, 99-65-0; 1,3-bis[(phenylsulfonyl)methyl]-2,4-dinitrobenzene, 92241-36-6; picric acid, 88-89-1; 2,4,6-trinitro-3-[(phenylsulfonyl)methyl]phenol, 92241-37-7; 2,4,6-trinitro-3,5-bis[(phenylsulfonyl)methyl]phenol, 92241-38-8; 1,3,5-trinitrobenzene, 99-35-4; 1,3,5-trinitro-2,4,6-tris[(phenylsulfonyl)methyl]benzene, 92241-39-9.

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(5) Following notations are used throughout the paper: **23**, **24**, **25**, **26**, **34**, **35** denote 2,3, 2,4, etc., dinitrophenols and **23a**, **24a**, etc., 2,3, 2,4, etc., dinitroanisoles correspondingly. The three digit numbers denote the products in which the third digit shows the position of CH_2SO_2Ph substituent, for example **243** denotes 2,4-dinitro-3-[(phenylsulfonyl)-methyl]phenol and **256a** 2,5-dinitro-6-[(phenylsulfonyl)methyl]anisole.

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