

OXIDATIVE SUBSTITUTION IN SALTS OF NITROALKANES***

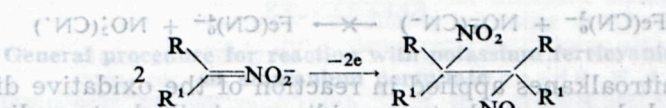
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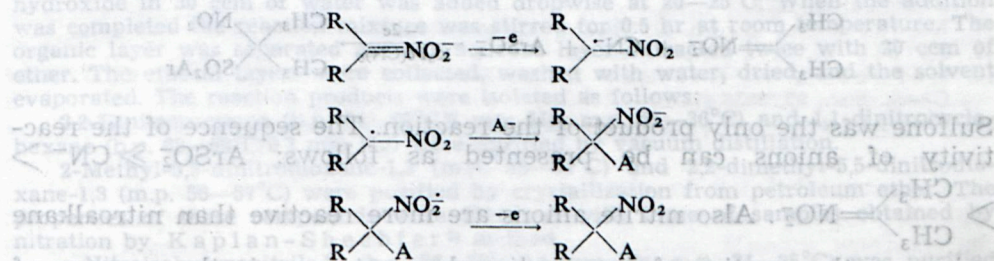
Aniony nitroalkanów poddano reakcji z anionami: cyjankowym, arylo-sulfonowym lub azotynowym w obecności cyjanożelazinu potasu jako środka utleniającego. Reakcja przebiega według mechanizmu jono-rodnikowego. Otrzymano α -pochodne nitroalkanów.

Nitroalkane anions were bonded with cyanide, arylsulfonic or nitrile anions in the presence of potassium ferricyanide as oxidizing agent according to the anion-radical mechanism. α -Derivatives of nitroalkanes were formed.

Oxidative dimerization of anions of nitroalkanes has already been known¹⁻³⁾.



Persulfates, hydrogen peroxide, ferric, cupric and silver salts have been used as oxidizing agents. Edg e⁴⁾ has shown that the reaction occurs with an intermediate formation of anion-radicals and radicals, according to the diagrams:



In the instance of oxidative dimerization A⁻ is an anion of a nitroalkane. The Kaplan-Shechter⁵⁾ reaction yielding gem-dinitroalkanes while A⁻ is the nitrite ion belongs to the same group of reactions. Kaplan and Shechter used silver and mercuric salts as oxidizers.

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*** Dedicated to Professor Osman Achmatowicz on the occasion of his 80th birthday.

Also Zeilstra and Engberts⁶⁾ described the method of preparing α -nitrosulfones by acting with iodine and salts of arylsulfinic acids on sodium salt of a nitroalkane in DMF. They accepted the anion-radical mechanism of the reaction.

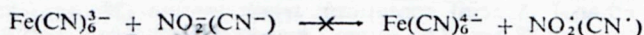
It seemed interesting to find out whether or not oxidizing agents other than silver and mercuric salts can be applied in oxidative "nitration" of Kaplan and Shechter. Also it appeared interesting to find out if other anions can be used for the oxidative substitution.

Indeed we were able to develop a novel, convenient method of formation of α -nitronitriles, α -nitrosulfones, α -nitrosulfides, salts of α -nitrosulfonic acids and *gem*-dinitro compounds. We used potassium ferricyanide or sodium persulfate in an aqueous medium or mercuric chloride in DMSO as oxidizing agents. Nitrite, cyanide, arylsulfinic, arylsulfide and sulfite anions were used as the agent A⁻. The experimental results are tabulated below.

Particularly favorable results were obtained while using potassium ferricyanide in the oxidative "nitration" and in the reactions of introducing cyanide and arylsulfonic group. The yields were 60–80%.

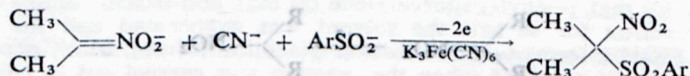
The reaction does not occur with such anions as halogenides. Also we did not succeed in obtaining definite products when using anions of primary nitroalkanes, contrary to the reaction of Kaplan-Shechter which is successful with primary nitroalkanes.

It seems that our reaction occurs according to the mechanism given above, as by comparing normal redox potentials^{7,8)}, the mechanism by means of oxidation of nitrite and cyanide ions should be excluded:



Salts of nitroalkanes applied in reaction of the oxidative dimerization can be regarded as monoelectron oxidizers, similarly to radicals HO[•] or SO₄^{•-}⁹⁾ which can be obtained from a mixture of peroxides and titanium salts.

By carrying competitive reactions we were able to compare the reactivity of anions with nitroalkyl radicals:



Sulfone was the only product of the reaction. The sequence of the reactivity of anions can be presented as follows: $\text{ArSO}_2^- \gg \text{CN}^- >$

$> \begin{array}{c} \text{CH}_3 \\ \diagdown \\ \text{CH}_3 \end{array} = \text{NO}_2^-$. Also nitrite anions are more reactive than nitroalkane anions, as the reaction of dimerization does not occur in the presence of nitrite anion.

EXPERIMENTAL

All melting points and boiling points are uncorrected. 2-Methyl- and 2,2-dimethyl-5-nitrodioxane-1,3 were prepared by methods described by Kędzierski¹⁰⁾.

Table
Oxidative substitution reactions

$$\text{C}=\text{NO}_2^{(-)} + \text{A}^{(-)} \xrightarrow{-2e} \text{C} \begin{matrix} \text{NO}_2 \\ \text{A} \end{matrix}$$

No	Sodium salt of	Anion A ⁽⁻⁾	Oxidant	Yield %
1	2-Nitropropane	NO ₂ ⁽⁻⁾	K ₃ Fe(CN) ₆	60
2	2-Nitropropane	NO ₂ ⁽⁻⁾	(NH ₄) ₂ S ₂ O ₈	— ^a
3	Nitrocyclohexane	NO ₂ ⁽⁻⁾	K ₃ Fe(CN) ₆	74
4	2-Methyl-5-nitrodioxane-1,3	NO ₂ ⁽⁻⁾	K ₃ Fe(CN) ₆	80
5	2,2-Dimethyl-5-nitrodioxane-1,3	NO ₂ ⁽⁻⁾	K ₃ Fe(CN) ₆	70
6	2-Nitropropane	CN ⁽⁻⁾	K ₃ Fe(CN) ₆	52
7	2-Nitropropane	CN ⁽⁻⁾	(NH ₄) ₂ S ₂ O ₈	10
8	Nitrocyclohexane	CN ⁽⁻⁾	K ₃ Fe(CN) ₆	63
9	2,2-Dimethyl-5-nitrodioxane-1,3	CN ⁽⁻⁾	K ₃ Fe(CN) ₆	57
10	2-Nitropropane	C ₆ H ₅ SO ₂ ⁽⁻⁾	K ₃ Fe(CN) ₆	62
11	2-Nitropropane	C ₆ H ₅ SO ₂ ⁽⁻⁾	HgCl ₂ ^b	25
12	2-Nitropropane	<i>p</i> -ClC ₆ H ₄ S ⁽⁻⁾	K ₃ Fe(CN) ₆	36 ^c
13	2-Nitropropane	SO ₃ Na ⁽⁻⁾	(NH ₄) ₂ S ₂ O ₈	12

^a Only 2,3-dimethyl-2,3-dinitrobutane was formed.

^b The reaction was carried out in DMSO.

^c 25% of (*p*-ClC₆H₄S)₂ was isolated.

General procedure for reaction with potassium ferricyanide or ammonium persulfate

A sample of 0.05 mole of the corresponding nitro compound was dissolved in a solution of 0.06–0.08 mole of sodium hydroxide in 30 ccm of water. Then 0.1 mole of sodium nitrite or sodium cyanide or 0.05 mole of sodium benzenesulfinate or *p*-chlorothiophenolate or 0.1 mole of sodium sulfite and 30 ccm of ether were added. To the stirred solution a saturated aqueous solution of 0.1 mole of potassium ferricyanide or a solution of 0.05 mole of ammonium persulfate and 0.1 mole of sodium hydroxide in 30 ccm of water was added dropwise at 20–25°C. When the addition was completed the reaction mixture was stirred for 0.5 hr at room temperature. The organic layer was separated and the aqueous layer extracted twice with 20 ccm of ether. The ethereal layers were collected, washed with water, dried, and the solvent evaporated. The reaction products were isolated as follows:

2,2-Dinitropropane (b.p. 64–65°C/8 mm Hg, m.p. 35–36°C) and 1,1-dinitrocyclohexane (b.p. 68–69°C/0.3 mm Hg) were purified by vacuum distillation.

2-Methyl-5,5-dinitrodioxane-1,3 (m.p. 33–34°C) and 2,2-dimethyl-5,5-dinitrodioxane-1,3 (m.p. 56–57°C) were purified by crystallization from petroleum ether. The properties of these compounds were identical with those of samples obtained by nitration by Kaplan-Shechter⁵⁾ method.

α -Nitroisobutyronitrile¹¹⁾ (b.p. 76–78°C/13 mm Hg, m.p. 34–35°C) was purified by distillation. Its properties were identical with those of the sample prepared according to the literature.

1-Cyano-1-nitrocyclohexane (b.p. 76–78°C/0.6 mm Hg) was purified by distillation.

Analysis:

For C₇H₁₀O₂N₂ — Calcd.: 54.5% C, 6.5% H, 18.2% N;
found: 54.6% C, 6.5% H, 18.3% N.

2,2-Dimethyl-5-cyano-5-nitrodioxane-1,3 (m.p. 61–62°C) was purified by crystallization from isopropanol.

Analysis:

For $C_7H_{10}O_4N_2$ — Calcd.: 45.2% C, 5.4% H, 15.0% N;
found: 45.1% C, 5.5% H, 15.2% N.

α -Nitroisopropyl phenyl sulfone¹²⁾ (m.p. 117–119°C) was purified by crystallization from ethanol.

α -Nitroisopropyl *p*-chlorophenyl sulfide¹³⁾ (m.p. 86–88°C) was separated by fractional crystallization from hexane. The properties of both compounds are identical with those described by Kornblum^{12,13)}.

Sodium salt of 2-nitropropane-2-sulfonic acid was isolated as follows: after extraction with ether the aqueous layer was evaporated to dryness under reduced pressure, 10 ccm of methanol added, and the inorganic salts filtered off. The methanol solution was evaporated to dryness, and this operation was repeated several times yielding the product of m.p. 240–245°C (decomp.).

Analysis:

For $C_3H_6O_5NSNa$ — Calcd.: 18.9% C, 3.1% H, 7.3% N;
found: 19.0% C, 3.1% H, 7.1% N.

Oxidation with mercuric chloride in DMSO. 5.55 g (0.05 mole) of sodium salt of 2-nitropropane were dissolved in DMSO (30 ccm), 8.2 g (0.05 mole) of sodium benzenesulfinate was added, and to this mixture there was added dropwise a solution of 27.15 g (0.1 mole) of mercuric chloride dissolved in 20 ccm of DMSO at 20–25°C. The reaction was exothermic. After addition of mercuric chloride the reaction mixture was stirred for 0.5 hr, poured into 200 ccm of water, and extracted with ethyl acetate. The organic layer was washed with dilute sodium hydroxide solution and water, dried, and the solvent evaporated. The reaction product was purified by crystallization from ethanol. The yield of α -nitroisopropyl phenyl sulfone was 2.86 g (25%), m.p. 116–118°C.

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