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The Formation of 3,4,5-Tris(substituted phenyl)-4,5-dihydro-1,2-oxazole *N*-Oxides in the Oxidations of (Substituted phenyl)nitromethanide Anions with Silver Nitrate or Peroxodisulfate

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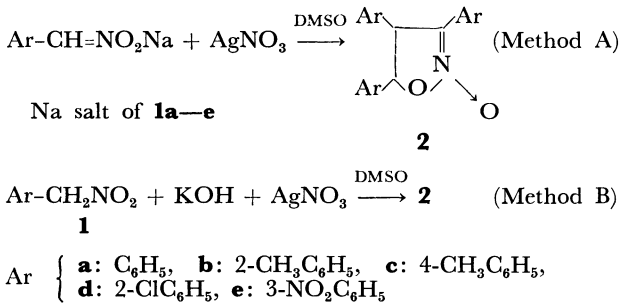
Synopsis. The reaction of an alkali metal salt of (substituted phenyl)nitromethane (**1**) with silver nitrate or peroxodisulfates in dimethyl sulfoxide (DMSO) gives 3,4,5-tris(substituted phenyl)-4,5-dihydro-1,2-oxazole *N*-oxides (**2**) in a good yield.

The oxidations of an alkali metal salt of primary nitroalkane with peroxodisulfates[1-3] or silver ions[1,3,4] have been known to be a general method for the formation of vicinal dinitro compounds. Particularly, the oxidation of the alkali metal salt of α-arylnitroalkane with silver nitrate in aqueous dimethyl sulfoxide (DMSO) or acetonitrile has been recognized as one of the most convenient methods for the formation of vicinal dinitro compounds.[4] Little information is, however, available about the formation of 4,5-dihydro-1,2-oxazole *N*-oxides in the oxidation of an alkali metal salt of nitroalkane under similar reaction conditions to those described above. Shechter and Kaplan[1] have reported that the reaction of nitroethane with peroxodisulfate in alkaline medium gives 3,4,5-trimethyl-1,2-oxazole in a 25% yield. Nenitzescu[5] has reported that anodic oxidation of an aqueous solution of sodium salt of phenylnitromethane (**1a**) gives 3,4,5-triphenyl-1,2-oxazole (**4a**). The mechanism of these reactions has not been discussed but it should involve the intermediate 4,5-dihydro-1,2-oxazole *N*-oxide ring formation. Recent studies by Pagano and Shechter have shown that the sodium salt of **1a** reacts with ammonium peroxodisulfate in aqueous sodium hydroxide to give 3,4,5-triphenyl-4,5-dihydro-1,2-oxazole *N*-oxide (**2a**) in a 1.3% isolated yield together with other products.[3] We describe here the reactions of alkali metal salts of (substituted phenyl)nitromethanes (**1a**—**e**) with peroxodisulfates or silver nitrate[6] in DMSO to give 3,4,5-tris(substituted phenyl)-4,5-dihydro-1,2-oxazole *N*-oxides (**2a**—**e**) without concomitant formation of the corresponding vicinal dinitro compounds (**3a**—**e**).

Alkali metal salts of **1a**—**e** were allowed to react with an equimolar amount of silver nitrate in DMSO according to methods A and B, and the corresponding **2a**—**e** were obtained in good yields, as shown in Scheme 1. The structures of **2a**—**e** were confirmed by the analytical and spectral data reported in Ref. 6.



Scheme 1.

The reaction of the sodium salt of **1a** with silver nitrate in *N*,*N*-dimethylformamide (DMF) or acetonitrile, however, gave yellow (*E*)-α-nitrostilbene (**5a**) as the main product. When a mixture of the sodium salt of **1a** and peroxodisulfate was stirred in DMSO at room temperature for 1 h, only **2a** was obtained. The reaction also took place in other solvents such as DMF and acetonitrile, but it was slower and the yield of **2a** was lower than that in DMSO. Typical results are summarized in Tables 1 and 2. The reason for the ineffectiveness of silver nitrate or peroxodisulfate

TABLE 1. REACTION OF (SUBSTITUTED PHENYL)NITROMETHANIDE ANION WITH SILVER NITRATE[a]

Run	Substrate (mmol)	$AgNO_3$ (mmol)	Solvent (ml)	Reaction time (h)	Products and yields[b] (%)
1	**1a** (50)	60	DMSO (150)	2	**2a** (57.1[c], 49.5[d])
2	**1b** (44)	45	DMSO (120)	4	**2b** (41.9[c], 44.0[d])
3	**1c** (44)	45	DMSO (120)	4	**2c** (46.3[c], 41.9[d])
4	**1d** (44)	45	DMSO (120)	4	**2d** (47.2[c], 43.8[d])
5	**1e** (25)	28	DMSO (120)	4	**2e** (40.4[d])
6[c]	**1a** (25)	26	DMF (30)	2	**2a** (3,8), **5a** (16.5), benzaldehyde[e] (8.2), **1a**[f] (trace)
7[c]	**1a** (25)	26	CH_3CN (50)	2	**2a** (7.6), **5a** (17.8), benzaldehyde[e] (8.9), **1a**[f] (trace)
8	**1a** (20)	23	DMSO (90) + H_2O (25)	2	**2a** (50.5[c])

a) All the reactions were conducted at room temperature. b) Yields were based upon **1**, and referred to isolated ones. c) By Method A. d) By Method B. e) Benzaldehyde was identified and analyzed as its 2,4-dinitrophenylhydrazone. f) A trace amount of **1a** was determined by means of gas chromatography using Tenax GC column at 240 °C.

Table 2. Reactions of sodium salt of phenylnitromethane (**1a**) with peroxodisulfates[a]

Run	Peroxodisulfate (mmol)	Solvent (ml)	Reaction time (h)	Product and yield[b] (%)
1	$K_2S_2O_8$ (15)	DMSO (30)	12	**2a** (62.4)
2	$K_2S_2O_8$ (15)	DMF (30)	12	**2a** (22.8)
3	$K_2S_2O_8$ (15)	CH_3CN (50)	12	**2a** (19.0)
4	$(NH_4)_2S_2O_8$ (15)	DMSO (25)	12	**2a** (63.5)
5	$K_2S_2O_8$ (25)	DMSO (25)	1	**2a** (64.7)

a) All the reactions were carried out using 3.98 g (25 mmol) of sodium salt of **1a** and 1.05 g (12.5 mmol) of sodium hydrogencarbonate at room temperature. The amounts of peroxodisulfates and solvents are given in parentheses. b) Yields were based upon **1a**, and referred to isolated ones.

in DMF or acetonitrile seems to be the low solubility of the sodium salt of **1a** in these cases. Two possible mechanisms for this reaction may be considered. The first mechanism is an ionic pathway postulated originally by Pagano and Shechter[3] for the reaction of the sodium salt of **1a** with ammonium peroxodisulfate. The second possible mechanism involves both $S_{RN}1$ and $E_{RC}1$ reactions, as shown in Scheme 2. This Scheme is based on the observation that the reaction of α-bromophenylnitromethane with the sodium salt of **1a** in DMSO gives also **2a**.[6,8] The exclusive formation of **2** can be well explained by S_{RN} and E_{RC} processes, but there is no experimental evidence for excluding an ionic pathway.

$$\mathrm{Ar\text{-}CH{=}NO_2^-} \xrightarrow{+AgNO_3} \mathrm{Ar\text{-}\dot{C}HNO_2} + NO_3^- + Ag \quad (Ia)$$

$$\mathrm{Ar\text{-}CH{=}NO_2^-} \xrightarrow{+1/2S_2O_8^{2-}} \mathrm{Ar\text{-}\dot{C}HNO_2} + 1/2HSO_4^- + 1/2SO_4^{2-} \quad (Ib)$$

$$\mathrm{Ar\text{-}\dot{C}HNO_2} + \mathrm{Ar\text{-}CH{=}NO_2^-} \longrightarrow \mathrm{[Ar\text{-}CH(NO_2)\text{-}CH(NO_2)\text{-}Ar]^{\cdot -}} \quad (II)$$

3

$$\mathbf{[3]}^{\cdot -} \longrightarrow \mathrm{Ar\text{-}\dot{C}H\text{-}CH(NO_2)\text{-}Ar} + NO_2^- \quad (III)$$

$$\mathrm{Ar\text{-}\dot{C}H\text{-}CH(NO_2)\text{-}Ar} + \mathrm{Ar\text{-}\dot{C}HNO_2} \longrightarrow \mathrm{Ar\text{-}CH(NO_2)\text{-}CH(Ar)\text{-}CH(Ar)\text{-}NO_2} \quad (IV)$$

6

$$\mathbf{6} \longrightarrow \mathbf{2} + NO_2^- \quad (V)$$

Ar = phenyl and substituted phenyl group

Scheme 2.

The only alternative route to **2a** is the reaction of **5a** with **1a**,[7] but the present reaction seems to provide a more convenient one-step method for preparation of **2**, because readily available **1** is the only starting material.

Experimental

Materials. Silver nitrate, potassium peroxodisulfate, ammonium peroxodisulfate, and sodium hydrogencarbonate were commercial reagent-grade. Commercial DMSO, DMF, and acetonitrile were distilled prior to use. (Substituted phenyl)nitromethanes (**1a—d**) were prepared from the corresponding arylacetonitriles[9] according to the method of Black and Bakers.[10] 3-Nitrophenylnitromethane (**1e**) was prepared by nitration of **1a** with fuming nitric acid.[11] The sodium salts of **1a—e** were prepared by addition of methanol solution of **1a—e** to an equivalent amount of sodium methoxide in methanol.

*General Procedure for Reaction of **1** with Silver Nitrate. General Procedure by Method A.* A sodium salt of **1** (0.05 mol) was added in portions to a stirred solution of silver nitrate (0.06 mol) in DMSO (150 ml) at room temperature. The mixture was stirred at the same temperature for 2 h, and then the silver deposited was removed by filtration, and washed with small amounts of DMSO. The filtrate and washings were poured into cold water to give a pale yellow precipitate, which was collected by filtration, washed with water, and dried. Crystallization from acetic acid or ethanol gave **2** as colorless needles.

General Procedure by Method B. A mixture of **1** (0.05 mol), water (20 ml), and potassium hydroxide (0.05 mol) was added rapidly to a solution of silver nitrate (0.06 mol) in DMSO (150 ml) with stirring. The mixture was stirred at room temperature for 2 h and work-up was carried out as described under Method A.

*General Procedure for Reaction of the Sodium Salt of **1a** with Peroxodisulfates.* To a stirred mixture of potassium peroxodisulfate (0.015 mol) and sodium hydrogencarbonate (0.0125 mol) in DMSO (30 ml), the sodium salt of **1a** (0.025 mol) was added in portions and the mixture was stirred at room temperature for 12 h. The solution was then poured into cold water to give slightly yellow precipitates, which were collected, washed with water, and dried. Crystallization from acetic acid gave **2a**.

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