Reaction of Nitrostyrenes and 1-Nitrohexane with Sodium Polysulfides and Sodium Hydroxide[1)]

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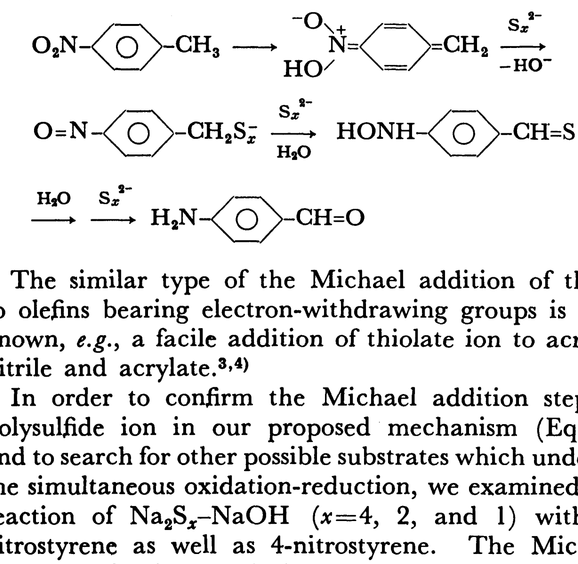
Synopsis. The reaction of β-nitrostyrene with NaOH in refluxing EtOH–H_2O (1 : 2) gives benzaldehyde, benzyl alcohol, benzoic acid, phenylacetic acid, β-phenylethyl alcohol, and polymeric materials. On the other hand, the reaction of β-nitrostyrene with Na_2S_4–NaOH in the same solvent gave acetophenone besides the same products obtained with NaOH. Acetophenone was likewise detected in the Na_2S–NaOH and Na_2S_2–NaOH reactions. 4-Nitrostyrene was also allowed to react with Na_2S_4–NaOH in EtOH–H_2O (4 : 1) to give a small amount of 4-aminoacetophenone. The formation of acetophenones suggests the occurrence of the Michael addition of polysulfide ion and supports our mechanism proposed previously for the reaction of *p*-nitrotoluene with Na_2S_4. The reaction of 1-nitrohexane with Na_2S_4–NaOH, in which the Michael addition is not conceivable, gives the same products as the reaction with NaOH.

In our previous report[2)] on the mechanism for the reaction of *p*-nitrotoluene with sodium polysulfides, we assumed the addition of polysulfide ion to a quinonoid isomer of *p*-nitrotoluene as the steps to *p*-(hydroxyamino)thiobenzaldehyde and then to *p*-aminobenzaldehyde (Eq. 1).


(1)

The similar type of the Michael addition of thiols to olefins bearing electron-withdrawing groups is well known, *e.g.*, a facile addition of thiolate ion to acrylonitrile and acrylate.[3,4)]

In order to confirm the Michael addition step of polysulfide ion in our proposed mechanism (Eq. 1) and to search for other possible substrates which undergo the simultaneous oxidation-reduction, we examined the reaction of Na_2S_x–NaOH (x=4, 2, and 1) with β-nitrostyrene as well as 4-nitrostyrene. The Michael addition of thiols to β-nitrostyrene is known.[5)] For comparison, 1-nitrohexane, the analogous saturated substrate, was examined on the reaction with Na_2S_4–NaOH.

Results and Discussion

β-Nitrostyrene was refluxed with Na_2S_x–NaOH in EtOH–H_2O (1 : 2) for 3 h. The products were acetophenone, benzaldehyde, benzyl alcohol, benzoic acid, phenylacetic acid, β-phenylethyl alcohol, and polymeric materials. The yields of identified products were listed in Table 1. On the other hand, the reaction of β-nitrostyrene with NaOH in the same solvent gave similar products besides acetophenone (Table 1).

TABLE 1. PRODUCTS FROM THE REACTION OF β-NITROSTYRENE (β-NS) WITH Na_2S_x–NaOH OR NaOH IN EtOH–H_2O (2 : 1) BY REFLUXING FOR 3 h

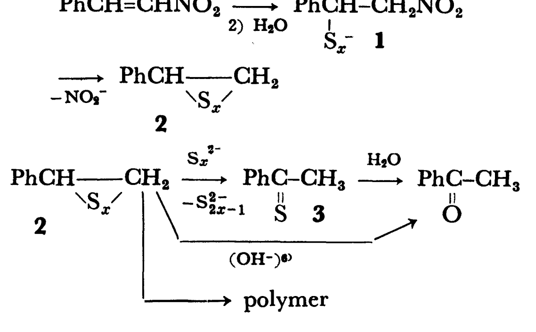
Product	Yield/%				
	NaOH[a)]	Na_2S[b)]	$Na_2S_{2.1}$[c)]	$Na_2S_{4.3}$[d)]	$Na_2S_{4.8}$[e)]
$PhCOCH_3$	0	1.7	4.5	5.4	8.3
PhCHO	6.4	3.4	4.8	4.4	3.0
$PhCH_2OH$	4.4	0.4	0.6	0.7	0.8
$PhCO_2H$	6.4	0.2	0.2	8.9	15
$PhCH_2CO_2H$	1.3	0.6	0.1	2.0	1.5
$PhCH_2CH_2OH$	0.3	0.2	0.3	0.6	0.6

a) $[\beta\text{-NS}]_0=0.22$ M,† $[NaOH]_0=0.40$. b) $[\beta\text{-NS}]_0=0.35$ M, $[Na_2S\cdot 9H_2O]_0=0.35$ M, $[NaOH]_0=0.70$ M. c) $[\beta\text{-NS}]_0=0.35$ M, $[Na_2S\cdot 9H_2O]_0=0.35$ M, $[S_0]=0.40$ M, $[NaOH]_0=0.70$ M. d) $[\beta\text{-NS}]_0=0.22$ M, $[Na_2S\cdot 9H_2O]_0=0.09$ M, $[S]_0=0.30$ M, $[NaOH]_0=0.42$ M. e) $[\beta\text{-NS}]_0=0.22$ M, $[Na_2S\cdot 9H_2O]_0=0.22$ M, $[S]_0=0.84$ M, $[NaOH]_0=1.2$ M.

$$PhCH{=}CHNO_2 \xrightarrow{Na_2S_x\text{-}NaOH} PhCOCH_3,\ PhCHO,\ PhCH_2OH,\ PhCO_2H,\ PhCH_2CO_2H,\ PhCH_2CH_2OH \quad (2)$$

Hence, a characteristic product in the presence of sulfide and polysulfide ions is only acetophenone. The reactions of β-nitrostyrene with Na_2S–NaOH and Na_2S_2–NaOH gave a rather low yield of acetophenone with the similar products as shown in Table 1. Hence, for the formation of acetophenone the participation of sulfide or polysulfide ion is conceivable.

The mechanism for the formation of acetophenone may be as follows. The α-carbon of β-nitrostyrene is attacked by polysulfide ion to give a Michael adduct (**1**), and then the polysulfide ion in the adduct (**1**) may attack internally the β-carbon with simultaneous elimination of nitrite ion. The resulting cyclic polysulfide **2** will decompose to thioacetophenone which is hydrolyzed to acetophenone (Eq. 3).


(3a)

$$PhCH{=}CHNO_2 \xrightarrow[2)\ H_2O]{1)\ S_x^{2-}} \underset{S_x^-}{PhCH}\text{-}CH_2NO_2\ \mathbf{1} \xrightarrow[-NO_2^-]{} \mathbf{2}$$

(3b)

The step giving **3** from **2** must be the spontaneous intramolecular hydride shift in the case of Na_2S, causing

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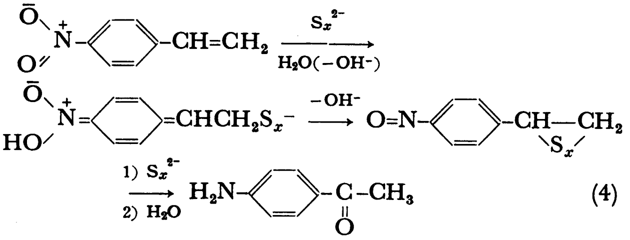
† 1 M=1 mol dm^{-3}.

the lower yield of acetophenone.

Benzaldehyde may be formed *via* the reverse reaction of the synthesis of β-nitrostyrene,7) and it can give benzyl alcohol and benzoic acid *via* the Cannizzaro reaction. Benzoic acid may be formed by autoxidation of benzaldehyde. Phenylacetaldehyde which is produced *via* analogous reaction of nitroalkanes with NaOH8) is autoxidized to give phenylacetic acid.

A decrease of the NaOH concentration resulted in the low yield of acetophenone; *e.g.*, the yield of acetophenone was only 0.4% with 0.15 M NaOH in contrast to 5.4% with 0.42 M NaOH.

The reaction of 4-nitrostyrene with Na_2S_4–NaOH gave a considerable amount of polymeric and monomeric 4-aminostyrenes and a small amount of 4-aminoacetophenone which was detected by NMR in comparison with the authentic specimen. The formation of 4-aminoacetophenone suggests the Michael addition of polysulfide ion to the β-position, and the following path *via* a cyclic sulfide.



(4)

The formation of acetophenones supports the hypothetical Michael addition of polysulfide ion to the quinonoid form of *p*-nitrotoluene, which has been proposed as a step to the formation of *p*-aminobenzaldehyde from *p*-nitrotoluene (Eq. 1).2)

On the other hand, the reaction of 1-nitrohexane (a saturated counterpart of nitrostyrenes) with Na_2S_4–NaOH gave hexanal, hexanal oxime, hexanoic acid, *etc.* All the products detected by the GLC peaks were the same as those of the reaction of 1-nitrohexane with NaOH, in which the yields and reaction rates were lower than those with Na_2S_4–NaOH. This fact shows that no oxidation of internal carbon atoms occurs unless a nitro group is conjugated with a C=C bond.

Experimental

Melting points were measured by a Yanagimoto micro melting point apparatus and were not corrected. NMR spectra were recorded on a Hitachi R-24B spectrometer using Me_4Si as an internal standard. The GLC analysis was performed with a Yanagimoto G 180 gas chromatograph with a flame ionization detector. GC-MS analysis was performed with a JEOL JMS-D300 mass spectrometer.

Materials. β-Nitrostyrene was prepared according to the literature;7) mp 56—58 °C (lit,7) 57—58 °C); NMR (CCl_4): δ 7.3—8.0 (dd, 2H, -CH=CH-), 7.4 (s, 5H, ArH). 4-Nitrostyrene was prepared by the method of Strassburg *et al.*;9) NMR (CCl_4): δ 7.8 (d, 2H, ArH), 7.2 (d, 2H, ArH), 6.5 (m, 1H, α-CH), 5.2 (t, 2H, β-CH_2). 1-Nitrohexane was prepared by the method of Kornblum *et al.*;10) bp 96—98 °C/22 Torr† (lit,10) 76 °C/10 Torr); NMR (CCl_4); δ 4.3 (t, 2H, 1-CH_2), 1.8 (m, 2H, 2-CH_2), 1.2 (m, 6H, 3,4,5-CH_2), 0.8 (t, 3H, CH_3).

Reaction of β-Nitrostyrene with Na_2S_x–NaOH. A hot aqueous solution (20 ml) of $Na_2S \cdot 9H_2O$ and NaOH (and S) was poured into a 100 ml round-bottomed flask containing a hot ethanolic solution (10 ml) of β-nitrostyrene (1.00 g, 6.7 mmol) (Table 1). The mixture was heated under reflux for 3 h and then cooled in an ice bath. The resulting solution containing the precipitate of polymeric materials and elemental sulfur was filtered off, and the filtrate was steam-distilled. The distillate was extracted with ether, and the extract was dried (Na_2SO_4), and analyzed by GLC using two sorts of columns (2.5 mm × 1 m, packed with PEG 20M and KG-02) at 100—240 °C. Biphenyl was used as an internal standard. The residual solution after distillation was acidified with HCl and, after removal of elemental sulfur precipitated, it was extracted with ether. The extract was esterified by diazomethane and analyzed by GLC (PEG 20M) using benzophenone as an internal standard. Similar work-up was employed for the reaction with NaOH.

Reaction of 4-Nitrostyrene with Na_2S_4–NaOH. The reaction analogous to that of β-nitrostyrene was carried out with a mixture of 4-nitrostyrene (1.00 g, 6.7 mmol), $Na_2S \cdot 9H_2O$ (0.53 g, 2.2 mmol), S (0.28 g, 8.7×10^{-3} g atom), and NaOH (0.53 g, 13 mmol) in EtOH–H_2O (16 ml–4 ml). After refluxing for 3 h the solution was cooled, and the precipitate was removed by filtration. The filtrate was extracted with ether, and the extract was dried over anhydrous sodium sulfate. Then the extract was analyzed by NMR after distilling ether off. 4-Aminoacetophenone was identified by NMR in comparison with its authentic specimen; NMR ($CDCl_3$): δ 7.8 (d, 2H, ArH), 6.6 (d, 2H, ArH), 4.2 (s, 2H, NH_2), 2.5 (s, 3H, CH_3).

Reaction of 1-Nitrohexane with Na_2S_4–NaOH. According to the procedure analogous to that for β-nitrostyrene, 1-nitrohexane (0.21 g, 1.6 mmol), $Na_2S \cdot 9H_2O$ (0.15 g, 0.62 mmol), S (0.06 g, 2×10^{-3} g atom), and NaOH (0.18 g, 4.5 mmol) were refluxed for 9 h in EtOH–H_2O (5 ml–2 ml). The products were extracted with ether from the alkaline solution and also from the acidified solution. Both extracts were analyzed by GLC (PEG 20M) and GC-MS (2.5 mm × 2 m, packed with Silicone OV-1). The similar work-up was applied to the reaction of 1-nitrohexane (0.24 g, 1.8 mmol) with NaOH (0.20 g, 5.0 mmol).

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1) Contribution No. 290.

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† 1 Torr≈133.322 Pa.