The Reaction of Nitrosobenzene with Benzenesulfonylhydrazide in the Presence of a Base

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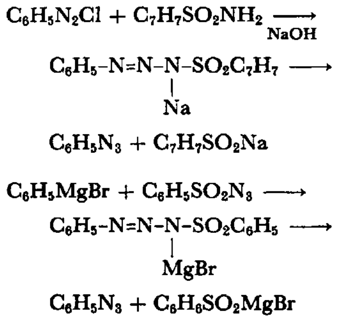
The action of benzenediazonium salt upon *p*-toluenesulfonamide in the presence of an excess of sodium hydroxide,[1] and the reaction of benzenesulfonyl azide with phenylmagnesium bromide, followed by the hydrolysis[2] or pyrolysis[3] of the product, lead to the formation of phenyl azide.

These reactions involve the formation of the salt of 1-*p*-toluenesulfonyl- or 1-benzenesulfonyl-3-phenyltriazene and the elimination of the salt of arenesulfinic acid from the triazene salt.



$$C_6H_5N_2Cl + C_7H_7SO_2NH_2 \xrightarrow[NaOH]{} C_6H_5\text{-}N{=}N\text{-}\underset{\underset{\displaystyle Na}{|}}{N}\text{-}SO_2C_7H_7 \longrightarrow C_6H_5N_3 + C_7H_7SO_2Na$$

$$C_6H_5MgBr + C_6H_5SO_2N_3 \longrightarrow C_6H_5\text{-}N{=}N\text{-}\underset{\underset{\displaystyle MgBr}{|}}{N}\text{-}SO_2C_6H_5 \longrightarrow C_6H_5N_3 + C_6H_6SO_2MgBr$$

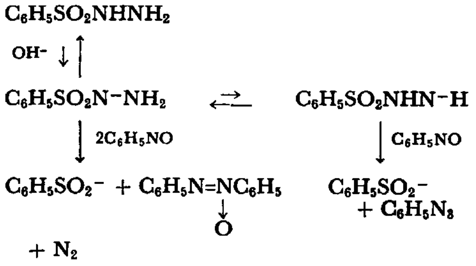
Accordingly, one can expect to obtain phenyl azide from the disubstituted triazene or its salt, prepared in a different reaction sequence. Since the triazene may be regarded as the condensation product of nitrosobenzene with arenesulfonylhydrazide, it is conceivable that the triazene can be prepared by the condensation of these compounds. However, the nitroso compounds do not give triazenes by reaction with hydrazines,[4,5] although the condensation reactions of aromatic nitroso compounds with such compounds as aniline,[6] hydroxylamine,[7] *N*-phenylhydroxylamine,[8] and benzyl cyanide[9] are similar to those of carbonyl compounds. In the present study, the reaction of nitrosobenzene with benzenesulfonylhydrazide was attempted for the purpose of obtaining phenyl azide.

Results and Discussion

When a mixture of nitrosobenzene and benzenesulfonylhydrazide was refluxed in absolute ethanol for thirty minutes, and then for one more hour with sodium ethoxide, azoxybenzene was obtained; the additional formation of a trace amount (0.5%) of phenyl azide was confirmed by infrared spectroscopy. The addition of a small amount of sulfuric acid in the first run of the reaction did not promote the yield of phenyl azide.

When powdered nitrosobenzene was added to an aqueous solution of equimolar amounts of benzenesulfonylhydrazide and potassium or sodium hydroxide at 45—50°C with vigorous stirring, there separated a yellowish-brown oil, and nitrogen evolved. The yield of phenyl azide increased as much as 1.4%. Along with unaltered benzenesulfonylhydrazide (24%), azoxybenzene (45%) and benzenesulfinic acid (47%) were also obtained.

The results can be outlined by the following scheme:



$$\begin{tikzcd}
C_6H_5SO_2NHNH_2 \arrow[d, shift right, "OH^-"'] & \\
C_6H_5SO_2N\text{-}NH_2 \arrow[u, shift right] \arrow[d, "2C_6H_5NO"] & C_6H_5SO_2NHN\text{-}H \arrow[l, shift left] \arrow[d, "C_6H_5NO"] \\
C_6H_5SO_2^- + C_6H_5N{=}\underset{\underset{\displaystyle O}{\downarrow}}{N}C_6H_5 + N_2 & C_6H_5SO_2^- + C_6H_5N_3
\end{tikzcd}$$

When benzenesulfonylhydrazide was treated in an aqueous alkaline solution at 60°C for an hour, no remarkable reaction occurred and no benzenesulfinic acid was obtained.[10] Furthermore, the amount of benzenesulfinic acid obtained in the reaction of benzenesulfonylhydrazide with nitrosobenzene was, as has been shown above, almost equimolar to that of azoxybenzene. Phenyl azide did not react with nitrosobenzene at 70°C, even

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[1] P. K. Dutt, H. R. Whitehead and A. Wormall, *J. Chem. Soc.*, **119**, 2088 (1921); *Chem. Abstr.*, **16**, 915 (1922).

[2] The private communication of P. A. Smith and L. Bruner to J. H. Boyer; See: J. H. Boyer and F. C. Canter, *Chem. Revs.*, **54**, 17 (1954).

[3] S. Ito, This Bulletin, **39**, 635 (1966).

[4] See: Beilsteins "Handbuch der Organischen Chemie," Hw. Bd. V, p. 231—232 (1922).

[5] H. Minato and T. Fujisawa, This Bulletin, **39**, 1054 (1966).

[6] E. Bamberger, *Ber.*, **26**, 483 (1893); Beilsteins "Handbuch der Organischen Chemie," Hw. Bd. V, p. 231 (1922).

[7] E. Bamberger, *ibid.*, **28**, 1218 (1895); *ibid.*,

[8] E. Bamberger, *ibid.*, **30**, 2278 (1897); *ibid.*

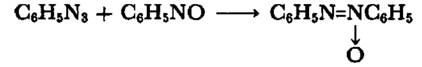
[9] F. Sachs, *ibid.*, **34**, 494 (1901); *ibid.*, Hw. IX, p. 442 (1926).

[10] It has been reported that benzenesulfonylhydrazide decomposes by heating with water, alcohol or alkali for a long time.[11]

in the presence of alkali. Therefore, it can be concluded that the following reactions did not occur to any significant extent:

$$C_6H_5SO_2NHNH_2 \xrightarrow[OH^-]{} C_6H_5SO_2^- + H\text{-}N{=}N\text{-}H$$

$$C_6H_5NO + H\text{-}N{=}N\text{-}H \longrightarrow C_6H_5NHOH + N_2$$



$$C_6H_5N_3 + C_6H_5NO \longrightarrow C_6H_5N{=}\underset{\substack{\downarrow \\ O}}{N}C_6H_5$$

The reaction in the presence of sodium ethoxide was also carried out in ethanol or *N,N*-dimethylformamide, but phenyl azide was thus obtained in lower yields than in water.

In conclusion, by benzenesulfonylhydrazide, nitrosobenzene is mainly subjected to reduction to *N*-phenylhydroxylamine, which then easily condenses with nitrosobenzene to give azoxybenzene.

Experimental

The reaction in an aqueous alkaline medium was described alone. The melting points are uncorrected.

Materials. Benzenesulfonylhydrazide was prepared by the action of benzenesulfonyl chloride (1 mol) upon an aqueous solution of hydrazine hydrate (1 mol) and sodium hydroxide (1 mol); yield: 76%, and recrystallized from ethanol, mp 104.5—105.5°C (lit.[11] mp 104—106°C).

The Reaction of Nitrosobenzene with Benzenesulfonylhydrazide in aqueous Potassium Hydroxide Solution. Into a vigorously-stirred solution of 17.2 g (0.1 mol) of benzenesulfonylhydrazide and 6.5 g (*ca.* 0.1 mol) of potassium hydroxide in 150 m*l* of water, there were added, over a period of 30 min, 10.7 g (0.1 mol) of powdered nitrosobenzene at 45—50°C. The reaction mixture was kept at this temperature for an additional 30 min with stirring. During the reaction, a yellowish-brown oil separated, the aqueous solution turned light brown, and nitrogen evolved.

The reaction mixture was then cooled, extracted with ether, and separated to an ether layer (A) and an aqueous layer (B). By removing the solvent from the ether solution (A), which was then washed with water and dried over anhydrous sodium sulfate, a brown liquid (A′) (9.4 g) was obtained. This liquid became solid on cooling. The infrared spectrum of the brown residue showed the absorption of azoxybenzene, accompanied with a small amount of phenyl azide. By using the absorption of the azido group at 2170 cm^{-1}, the yield of phenyl azide was determined to be 1.4%, calculated from nitrosobenzene.

The ether extract (A′) (9.3 g) was then chromatographed on 30 g of silica gel and eluted with *n*-hexane and *n*-hexane - ether; phenyl azide was concentrated in the first 20-m*l* fraction of the elution. After the solvent had been removed from the fraction, the yellow residue was fractionally distilled *in vacuo* (5 mmHg). Pure pale yellow phenyl azide was collected in a trap at −70°C (131 mg, n_D^{23}: 1.5587); its infrared spectrum was identical with that of an authentic sample. Found: N, 34.90%. Calcd for $C_6H_5N_3$: N, 35.27%.

By the reaction of dimethyl acetylenedicarboxylate with the phenyl azide, the 1-phenyl-1,2,3-triazole-4,5-dicarboxylic acid dimethyl ester, mp 127.5—128.5°C (lit.[12] mp 127—128°C), was obtained. (Found: C, 55.10; H, 4.63; N, 16.02%.)

The chromatographic treatment of the ether extract (A′) also gave 9.0 g (45%, calculated from nitrosobenzene) of yellow crystals of azoxybenzene, which melted at 35.5—36.5°C (lit.[13] mp 35.5—36.5°C) after recrystallization from methanol. (Found: C, 72.60; H, 5.43; N, 14.42%). Its infrared spectrum was identical with that of an authentic sample.

The water layer (B), when combined with washings of the ether extract of the reaction mixture, was acidified with concentrated hydrochloric acid and fully extracted with ether. From the acidic aqueous layer, by neutralization, 4.1 g (24%) of unaltered benzenesulfonylhydrazide were recovered. The ether layer was extracted with a solution of sodium hydroxide and water; the alkaline solution was then acidified with hydrochloric acid and saturated with sodium chloride. The resulting precipitate was filtered and dried to give 6.7 g (47%, calculated from benzenesulfonylhydrazide) of benzenesulfinic acid, the infrared spectrum of which was identical with that of an authentic sample.

By the treatment of the sodium salt of the sulfinic acid with benzyl chloride in ethanol, phenyl benzyl sulfone was obtained; it melted at 147.0—148.0°C (lit.[14] mp 148°C) after recrystallization from ethanol. (Found: C, 67.09; H, 5.29%.) No depression of the melting point was observed on admixture with an authentic sample.

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11) T. Curtius, *J. Prakt. Chem.*, [2], **58**, 166 (1898); Beilsteins "Handbuch der Organischen Chemie," Hw. Bd. XI, p. 52 (1938).

12) A. Michael, *J. Prakt. Chem.*, [2], **48**, 94 (1893); Beilsteins "Handbuch der Organischen Chemie," Hw. Bd. XXVI, p. 298 (1937).

13) H. E. Bigelow and A. Palmer, "Organic Syntheses," Coll. Vol. II, p. 57 (1943).

14) E. Knoevenagel, *Ber.*, **21**, 1349 (1888); Beilsteins "Handbuch der Organischen Chemie," Hw. Bd. VI, p. 455 (1923).