The Reaction of Benzenesulfonyl Azide with Phenylmagnesium Bromide

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Diazocyclopentadiene has been prepared by the reaction of cyclopentadienyllithium with *p*-toluenesulfonyl azide,[1] and some active methylene compounds have been diazotized by *p*-toluenesulfonyl azide in the presence of a base.[2]

This communication will report that benzenesulfonyl azide reacts with phenylmagnesium bromide to yield the salt of 3-benzenesulfonyl-1-phenyltriazene, which then decomposes to give phenyl azide and the salt of benzenesulfinic acid.

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

$$\longrightarrow C_6H_5N_3 + C_6H_5SO_2MgBr$$

Benzenesulfonyl azide was prepared by a modification of the procedure of Curtius,[3] by means of the action of sodium nitrite on benzenesulfonhydrazide in dilute hydrochloric acid. The almost colorless oily sulfonyl azide (n_D^{25}: 1.5488) was stored over anhydrous sodium carbonate in a dark place.

Into a stirred solution of 9.2 g. (0.05 mol.) of benzenesulfonyl azide in 60 ml. of dry ether, there was added over a period of 30 min., a solution of phenylmagnesium bromide (prepared from 1.5 g. (0.064 mol.) of magnesium and 9.4 g. (0.06 mol.) of bromobenzene in the usual way) in 60 ml. of ether at −18——15°C; hereupon white precipitates separated simultaneously and the reaction mixture turned slightly yellow. The mixture was then separated by filtration into a yellow ether solution and a slight yellow solid, which was then washed with ether and dried in a vacuum desiccator. The yield was 21.4 g.

From the filtrate, 0.9 g. of unreacted sulfonyl azide was recovered.

In a 300 ml. round-bottomed flask 21.0 g. of the powdered solid was placed; the flask was then connected to a series of traps and a vacuum system. The flask was heated to 50°C (0.1 mmHg) to effect a final drying and then to 120—130°C (0.1—3.0 mmHg) in an oil bath for an hour.

Yellow crude phenyl azide was condensed at −70°C (4.9 g.; 82% of the theoretical amount); distillation in vacuo (4 mmHg) gave purified pale yellow azide (n_D^{25}: 1.5593), the infrared spectrum of which was spectroscopically identical with that of an authentic sample.

The reduction of the product with sodium and ethanol gave aniline, which was then acetylated with ketene to yield acetanilide, m. p. 114.0—114.5°C.

The residual powder obtained after the pyrolysis was dissolved in alkaline water and filtered; the filtrate was then acidified with hydrochloric acid. The resulting precipitate was filtered and dried to give 4.0 g. of benzenesulfinic acid, the infrared spectrum of which was spectroscopically 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, m. p. 147.0—148.0°C, its infrared spectrum was spectroscopically identical with that of an authentic sample.

1) W. von E. Doering and C. H. DePuy, *J. Am. Chem. Soc.*, **75**, 5955 (1953).
2) M. Regitz, *Ann.*, **676**, 101 (1964); M. Regitz and G. Heck, *Chem. Ber.*, **97**, 1482 (1964); M. Regitz, ibid., **98**, 1210 (1965).
3) T. Curtius, *J. prakt. Chem.* [2], **58**, 174 (1898); "Beilsteins Handbuch der Organischen Chemie," Bd. XI (1928), p. 53.