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Pyrolysis of the Grignard Reaction Products of Benzenesulfonyl Azide[*1]

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Several reports have appeared concerning the reactions of arenesulfonyl azides with carbanionic or organometallic reagents.[1-7] In a previous paper,[8] we ourselves reported the preparation of phenyl azide by the pyrolysis of the triazene salt obtained from benzenesulfonyl azide and phenylmagnesium bromide.[9]

This note will describe the formation of azides, diazo-compounds, and olefins by the reaction of benzenesulfonyl azide and aliphatic Grignard reagents, or by the pyrolysis of the triazene salts resulting from the reactions.

Results and Discussion

When benzylmagnesium chloride in ether was added to the ethereal solution of benzenesulfonyl azide at −20—−10°C, a triazene salt (white pre-

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2) W. von E. Doering and C. H. DePuy, *J. Amer. Chem. Soc.*, **75**, 5955 (1953).

3) M. Regitz, *Ann.*, **676**, 101 (1964); M. Regitz and G. Heck, *Chem. Ber.*, **97**, 1482 (1964); M. Regitz, *ibid.*, **98**, 1210 (1965).

4) F. Klages and K. Bott, *Chem. Ber.*, **97**, 735 (1964).

5) J. M. Tedder and B. Webster, *J. Chem. Soc.*, **1960**, 4417.

6) J. H. Boyer, C. H. Mack, N. Goebel and L. R. Morgan, Jr., *J. Org. Chem.*, **23**, 1051 (1958).

7) E. Robson, J. M. Tedder and B. Webster, *J. Chem. Soc.*, **1963**, 1863.

8) S. Ito, This Bulletin, **39**, 635 (1966).

9) After the previous paper (Ref. 8) had been published, the authors found a report which communicated that phenyl azide resulted by alkaline decomposition of the triazene salt obtained from phenylmagnesium bromide and tosyl azide: The private communication of P. A. Smith and L. Bruner to J. H. Boyer and F. C. Canter; See: J. H. Boyer and F. C. Canter, *Chem. Rev.*, **54**, 17 (1954).

Table 1. The azides, the diazoalkanes, and the olefins obtained by the reaction of Grignard reagents with benzenesulfonyl azide

Grignard reagent	Azide (Yield, %)		Diazoalkane (Yield, %)		Olefin (Yield, %)	
Benzylmagnesium chloride	Benzyl Azide	(7.9)	Phenyldiazomethane	(0.5)	——	
Benzylmagnesium chloride*	Benzyl Azide	(9.1)	Phenyldiazomethane	(14.1)	——	
Allylmagnesium chloride	Allyl Azide	(13.1)	Vinyldiazomethane	(—)**	——	
Methylmagnesium iodide	Methyl Azide	(—)	Diazomethane	(1.5)	——	
n-Hexylmagnesium bromide	*n*-Hexyl Azide	(trace)	Diazo-*n*-hexane	(trace)	1- plus 2-Hexene	(11.2)
Cyclohexylmagnesium chloride	Cyclohexyl Azide	(1.6)	Diazocyclohexane	(0.9)	Cyclohexene	(22.3)
t-Butylmagnesium chloride	*t*-Butyl Azide	(2.7)	——		Isobutylene	(3.1)

* Reaction in THF.

** Red-color development in the reaction of allylmagnesium chloride showed also the formation of vinyldiazomethane, though it could not be confirmed.

cipitates) and phenyldiazomethane (0.5%) were obtained in the ether solution. Benzyl azide (7.9%) was obtained in a cold trap by the vacuum pyrolysis of the triazene salt; the additional formation of a trace of *o*-tolyl azide was confirmed by gas-liquid chromatography.

When tetrahydrofuran (THF) was used as the solvent of sulfonyl azide in the reaction of benzylmagnesium chloride, no precipitates were formed and the yield of phenyldiazomethane was considerably increased (14.1%). In this case, white precipitates could be obtained after the removal of the greater part of the THF, followed by the addition of ether. Benzenesulfinic acid and benzenesulfonamide were isolated from the residue of the pyrolysis of the precipitates.

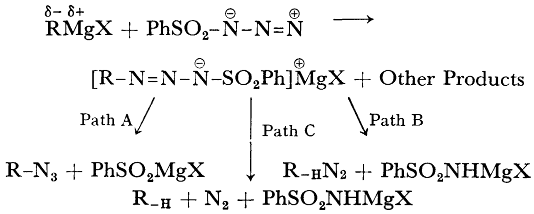
The major product of the pyrolysis of the triazene salt from cyclohexylmagnesium chloride was cyclohexene.

Upon the addition of *t*-butylmagnesium chloride to the ethereal solution of sulfonyl azide, *t*-butyl azide and isobutylene were generated in the solution almost immediately; the azide and the olefin could not be obtained by the pyrolysis of the solid part of the reaction mixture.

The reaction of vinylmagnesium bromide in THF with sulfonyl azide was also attempted, but it did not give any vinyl azide.[10]

The Grignard reagents, the azides, the diazoalkanes, and the olefins obtained are summarized in Table 1. The low yields of these products are probably due to their high volatility or law stability, and also to the complexity of the reaction.

The reaction of aliphatic Grignard reagents with benzenesulfonyl azide can be illustrated as follows:



$$\overset{\delta-}{R}\overset{\delta+}{MgX} + PhSO_2-\overset{\ominus}{N}-N=\overset{\oplus}{N} \longrightarrow$$

$$[R-N=N-\overset{\ominus}{N}-SO_2Ph]\overset{\oplus}{Mg}X + \text{Other Products}$$

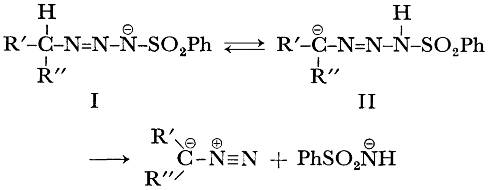
Path A: $R-N_3 + PhSO_2MgX$

Path C: $R_{-H} + N_2 + PhSO_2NHMgX$

Path B: $R_{-H}N_2 + PhSO_2NHMgX$

When the alkyl group of RMgX has no hydrogen atom in the α- and β-positions which can be eliminated, the reaction may proceed through Path A, which involves the α-elimination of the salt of sulfinic acid. On the other hand, when the alkyl group has such a hydrogen atom in the α-position, the reaction can proceed through both Paths A and B, the latter of which involves the elimination of the salt of sulfonamide.

In the reaction of benzylmagnesium chloride under the conditions of pyrolysis, no diazoalkane was obtained from the salt of triazene. However, when the triazene salt was not well dried, pyrolysis gave the benzyl azide, accompanied by a small amount of phenyldiazomethane. Furthermore, as has already been mentioned, the use of THF as the solvent in the Grignard reaction considerably increased the yield of phenyldiazomethane in the solution. Therefore, diazoalkane does not result directly from the triazene salt (I), but may be generated from a carbanion-type intermediate (II), which is itself derived from I in solution through proton transfer:



$$\underset{\text{I}}{R'-\underset{R''}{\overset{H}{C}}-N=N-\overset{\ominus}{N}-SO_2Ph} \rightleftarrows \underset{\text{II}}{R'-\underset{R''}{\overset{\ominus}{C}}-N=N-\overset{H}{N}-SO_2Ph}$$

$$\longrightarrow \underset{R''}{\overset{R'}{\ }}\overset{\ominus}{C}-\overset{\oplus}{N}\equiv N + PhSO_2\overset{\ominus}{N}H$$

If the alkyl group has a structure in which the negative charge of the α-carbon is delocalizable by resonance, or if the R′ and/or R″ are electron-attractive groups, I can probably isomerize to II with ease, in which case the yield of the diazoalkane may increase.

The alkyl groups of cyclohexyl- and *n*-hexylmagnesium halide have eliminatable hydrogen atoms in the α- and β-positions respectively, so, in these cases, the reaction can proceed through Path A, B, or C. From the facts that 2-hexene and isobutylene were obtained, and that olefins are the major products in these types of reactions, the olefins must have been yielded through carbonium-ion

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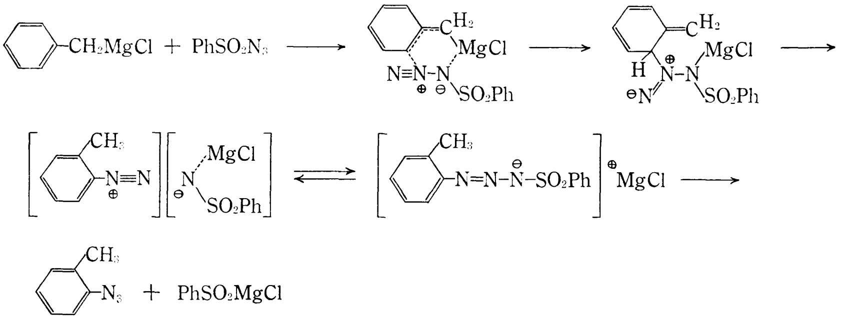
[10] Nitrogen evolved and a certain polymer formed.



intermediates directly derived from the triazene salts.

The formation of *o*-tolyl azide can be explained by a mechanism similar to the cyclic six-membered transition state which was postulated in the reaction of benzylmagnesium chloride with formaldehyde to give 2-methylbenzyl alcohol.[11]

Experimental

Only the reaction of benzylmagnesium chloride will be described. The melting points are uncorrected. The yields of the final products are shown in percentages based on the benzenesulfonyl azide used.

The Reaction of Benzylmagnesium Chloride with Benzenesulfonyl Azide (BSA) in Diethyl Ether. Into a stirred solution of 9.2 g (0.05 mol) of BSA in 80 m*l* of dry ether, was added a solution of benzylmagnesium chloride (prepared from 7.6 g (0.06 mol) of benzyl chloride) in 70 m*l* of ether at −20—−10°C over a period of 45 min; whereupon white precipitates separated simultaneously, and the reaction mixture turned slightly red. The mixture was then separated by filtration into a reddish ether solution and a white solid (A), which was then washed with ether and dried in a vacuum desiccator. The yield of A was 16.5 g.

Upon the addition of a few drops of acetic acid, the red color of the combined filtrate and washings disappeared with an evolution of nitrogen. The ether solution, after being washed with a 5% sodium carbonate solution and then with water, and after being dried over anhydrous sodium sulfate, was concentrated to give 1.4 g of an oily residue.

By means of gas-liquid chromatography (GLC), benzyl acetate (0.5%) was found in the oily residue, which mainly consisted of unaltered BSA and benzyl chloride.

In a 200-m*l* round-bottomed flask, 16.5 g of the powdered solid (A) was placed; the flask was then connected to a series of traps and a vacuum system. The flask was heated to 40°C (oil bath temp.) (0.1 mmHg) to effect sufficient drying, and then to 120—130°C (oil bath temp.) (0.1—3.0 mmHg) in an oil bath for an hour. A colorless liquid (B) (1.57 g) was condensed at −70°C (trap temp.); from this liquid benzyl azide and *o*-tolyl azide were confirmed by means of GLC (7.9% and 0.1% respectively). The reaction of acetylenedicarboxylic acid with the colorless liquid (B) gave white granules with a mp of 183.0—184.0°C (lit,[12] 183°C for 1-benzyl-1,2,3-triazole-4,5-dicarboxylic acid). No depression of the melting point was observed on admixture with an authentic specimen of 1-benzyl-1,2,3-triazole-4,5-dicarboxylic acid.

The residue of the pyrolysis was treated with hydrochloric acid to give 3.5 g of benzenesulfinic acid, from which phenyl benzyl sulfone was then derived; mp 147.0—148.0°C (lit,[13] mp 148°C). No depression of the melting point was observed on admixture with an authentic sample.

The Reaction of Benzylmagnesium Chloride with BSA in THF. The Grignard reagent prepared from 7.6 g of benzyl chloride was allowed to react with 9.2 g of BSA in 80 m*l* of THF in the same manner as the reaction in ether. No precipitates were formed, and a homogeneous red solution was obtained.

After the greater part of the solvent had been removed from the reaction mixture *in vacuo* at 10°C, there were separated white precipitates upon the addition of each 60-m*l* portion of petroleum ether and diethyl ether. After being separated from the reaction mixture, the solid part (17.5 g) was pyrolyzed to give benzyl azide (9.1%) and *o*-tolyl azide (0.1%). From the ethereal-solution part of the reaction mixture, the amount of phenyldiazomethane (14.1%) was determined.

Benzenesulfinic acid (0.82 g, 11.6%) and benzenesulfonamide (3.1 g, 39.2%), mp 150.0—151.0°C (lit,[14] mp 153°C) were obtained from the residue of the pyrolysis of the solid part.

No depression of the melting point of the benzenesulfonamide thus obtained was observed on admixture with an authentic sample.

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