Chem. Pharm. Bull.
15(9)1331～1333(1967)

UDC 547.541'171.04

168. Shoji Takemura, Yoshiko Ando, Hiromi Terauchi, and Yoshio Ueno: Reaction of N-Halosulfonamide. Ⅳ.[*1] A Cleavage Reaction of Ether with N,N-Dihalobenzenesulfonamide. (1).

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It was found that N,N-dibromobenzenesulfonamide (I) reacted with various ethers in mild conditions. Aliphatic ethers were thereby cleaved in aldehyde and alkyl bromide. Reaction of ethyl, butyl, butyl benzyl, and benzyl ethers with I were also investigated and benzaldehyde and benzyl bromide formed were chemicaly identified and other products were directly detected by gas chromatography.

(Received October 10, 1966)

In the previous works of this series,[*1],[1] some unique addition reaction of N,N-dihalobenzenesulfonamide with cycloalkenes have been shown.

During the course of investigation of the chemical behavior of N,N-dihalobenzenesulfonamide, it was found that this reagent reacts with various ethers. The present paper deals with the reaction of this reagent with aliphatic ethers.

Concerning the cleavage reaction of ethers, Imoto, *et al.*[2] reported on the reaction rates of N-bromosuccimide (NBS) with benzyl, butyl benzyl, ethyl benzyl, 1,3,5-tribromophenyl benzyl, and benzyl phenyl ethers, etc. Their experiments were, however, limited to the reaction being carried out in dioxane-water under the irradiation of ultraviolet ray or in the presence of benzoyl peroxide as a catalyst. Thus the formation of benzaldehyde from benzyl ethers was confirmed.

N,N-Dibromobenzenesulfonamide (I) readily reacts with various aliphatic ethers in nonpolar solvent without any catalyst or irradiation of light. In the case of simple ether, an aldehyde and an alkyl bromide were formed due to the cleavage of carbon-oxygen bonding while mixed ether gave each two kinds of the corresponding aldehydes and bromides.

After few minutes of mixing the reagent (I) with ether in carbon tetrachloride, an exothermic reaction generally occurred and the mixture turned to a deep red color. The reaction was subsided with rapid decolorization of the solution by keeping it to stand at room temperature or by heating it gently. On the reaction of benzyl ether with I, benzaldehyde formed was identified as its 2,4-dinitrophenylhydrazone, m.p. 233～238°, and the formation of benzyl bromide was confirmed by converting it to benzylthiuronium picrate, m.p. 179～184°. The reaction of butyl benzyl ether with I also afforded benzaldehyde and benzyl bromide which were identified as their derivatives as given above.

Formation of the aldehydes and alkyl bromides in the cases of reacting ethyl, butyl, butyl benzyl, and benzyl ethers with I was also confirmed by gas chromatography (Fig. 1). The expected peaks of the corresponding aldehydes (or their oxidized acids) and bromides were observed in cases.

Although it is hard, at present, to discuss whether these reactions proceed in radical or in ionic mechanism, no significant electron spin resonance absorption was observed during the periods of overall reactions.

[*1] Part Ⅲ: This Bulletin, **15**, 1328 (1967).

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1) Y. Ueno, S. Takemura, Y. Ando, H. Terauchi: This Bulletin, **15**, 1193 (1967); *Ibid.*, **15**, 1198 (1967).

2) M. Okawara, H. Sato, E. Imoto: J. Chem. Soc. Japan, **58**, 924 (1955).

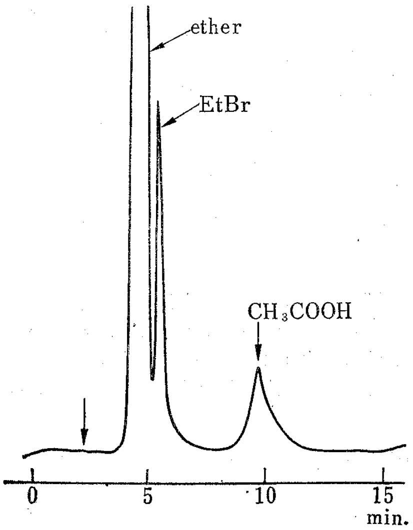

Fig. 1a. Reaction Products from Ethyl Ether with I in Ethyl Ether

Sample, 10 μl.
Column, tricresyl phosphate, 0.75 m., 3 mm. ϕ, 40~60 mesh, 40°.
Carrier gas, He.
Detector, hydrogen flame ionization detector.

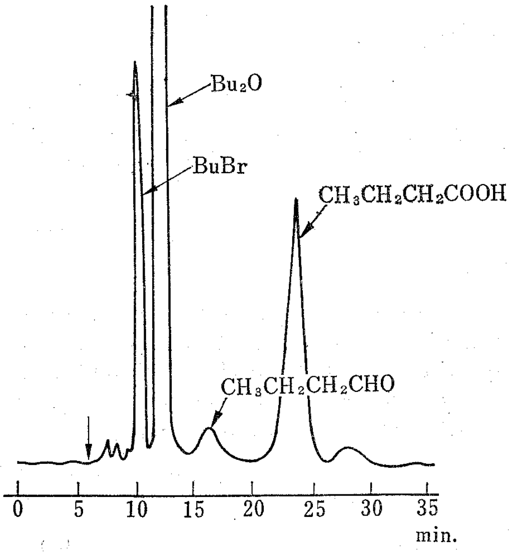

Fig. 1b. Reaction Products from Butyl Ether with I in Butyl Ether

Sample, 3 μl.
Column, tricresyl phosphate, 0.75 ml., 3 mm. ϕ, 40~60 mesh, 80°.
Carrier gas, He.
Detector, hydrogen flame ionization detector.

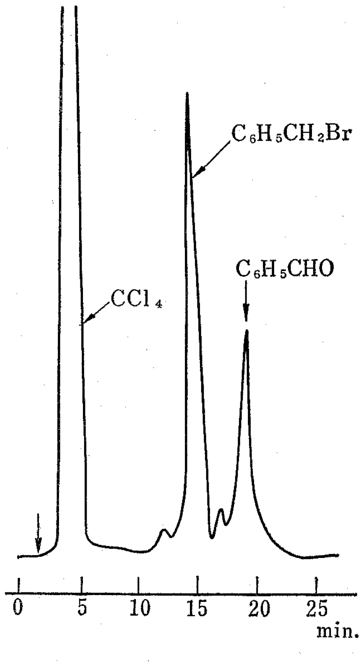

Fig. 1c. Reaction Products from Benzyl Ether with I in Carbon Tetrachloride

Sample, 7 μl.
Column, polyethylene glycol 6000 (30%), 1.5 m., 3 mm. ϕ, 120°.
Carrier gas, He.
Detector, thermal conductivity detector.

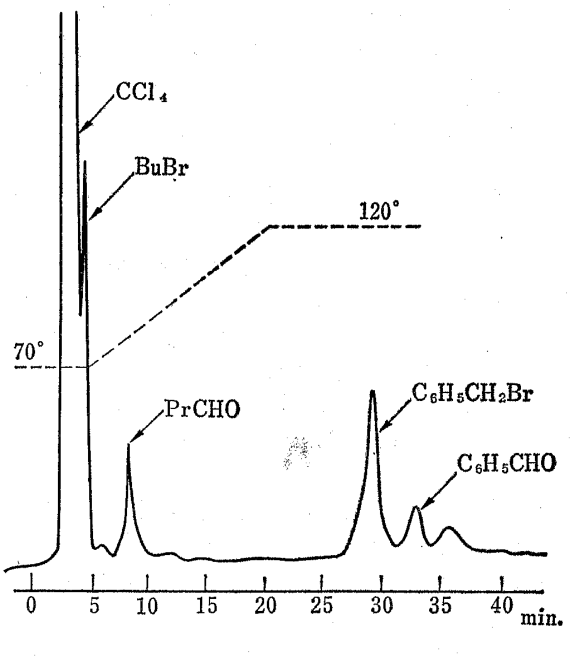

Fig. 1d. Reaction Products from Butyl Benzyl Ether with I in Carbon Tetrachloride

Sample, 4 μl.
Column, polyethylene glycol 6000 (30%), 1.5 m., 3 mm. ϕ, 70~120°
Carrier gas, He.
Detector, thermal conductivity detector.

Some crystalline unstable complex seemed to be formed in the initial step of the reaction. The formation of a complex between I and ether is possibly supported by the isolation of relatively stable complex in the reaction of amines with I, which will be reported later.

N,N-Dihalobenzenesulfonamide also reacts with alicyclic ethers such as tetrahydrofuran giving no simple ω-haloaldehyde but products of the ether type, the details of which will be described in the following papers.

Experimental

Reaction of N,N-Dibromobenzenesulfonamide (I) with Ether——Ethyl, *n*-butyl, *n*-butyl benzyl, and benzyl ethers were allowed to react with I. When I was directly added to ethers, violent reaction was soon induced. Suitable procedure is allowing them to react in carbon tetrachloride or in a large excess of ether.

When one molar I was added in small portions into a solution of two molar ether in seven to ten the volume of CCl_4 or excessive ether, the reagent (I) dissolved although I itself is insoluble in CCl_4, and after keeping to stand the mixture at room temperature for several minutes, exothermic reaction was initiated. The initial yellow color changed into orange to deep red during the course of the reaction. When the evolution of heat was subsided, a large amount of crystals separated out from the deeply colored solution.

The crystals seemed likely some unstable intermediates since their appearance easily changed at the final stage of the reaction. When the deeply colored mixture was allowed to stand at room temperature or to warm at 50° for 20 min., the solution rapidly tured to nearly colorless. The separated crystals were filtered off, and they were identified as benzenesulfonamide by mixed melting point determination and IR spectra with the authentic sample. The contents of the mother liquor freed from benzenesulfonamide were examined by the following manner.

Products from the Reaction of I with Benzyl Ether——1) Benzaldehyde: The mixture obtained by the reaction of I (3.15 g., 0.01 mole) and benzyl ether (4 g., 0.02 mole) was freed from benzenesulfonamide (1.8 g.) by the above-mentioned manner. The mother liquor was then stirred with 40% aq. $NaHSO_3$ solution (20 ml.) for 1 hr. to separate a bisulfite addition compound. After addition of H_2O to dissolve the addition compound, the aqueous solution was acidified with conc. HCl, then it was distilled, and the distillate was received into 95% EtOH (20 ml.). The ethanolic solution was treated with 2,4-dinitrophenylhydrazine to give yellow-orange crystals, m.p. 233~238° (3.2 g.), which were identified with the authentic 2,4-dinitrophenylhydrazone of benzaldehyde by a mixed melting point determination.

2) Benzyl bromide: The CCl_4 layer separated from the above aq. $NaHSO_3$ solution was evaporated on a water bath, the residue was added to a solution of thiourea (1.5 g.) in EtOH (20 ml.), and the whole was refluxed for 2 hr. Addition of a saturated solution of picric acid (4.6 g.) in EtOH and subsequent chilling gave crystals, which were washed with benzene and recrystallized from 95% EtOH to green-yellow needles, m.p. 179~184° (3.7 g.). These were identical with the authentic S-benzylthiuronium picrate by IR spectral comparison and by a mixed fusion.

3) Gas chromatography (Fig. 1): The above reaction mixture freed of benzenesulfonamide was subjected to gas chromatography under the following condition: Sample, 7 μl.; Column, polyethylene glycol 6000, 30%, 1.5 m., 3 ϕ, 120°; Carrier gas, He; Detector, thermal conducting detector.

Products from the Reaction of I with Butyl Benzyl Ether——1) Benzaldehyde and benzyl bromide: The separated benzenesulfonamide (1.55 g.) from the reaction mixture of I (3.15 g., 0.01 mole) with butyl benzyl ether (3.3 g., 0.02 mole) was filtered out. The mother liquor was then treated in the same manner as described in the case of benzyl ether to give 2,4-dinitrophenylhydrazone of benzaldehyde (2.1 g.) and S-benzylthiuronium picrate (1.4 g.).

2) Gas chromatography (Fig. 1): The mother liquor, freed from benzenesulfonamide and kept standing overnight, was analyzed by gas chromatography and the peaks of benzaldehyde, benzyl bromide, butylaldehyde and butyl bromide were detected. The analysis was carried out under the following condition: Sample, 4 μl.; Column, polyethylene glycol 6000, 30% 1.5 m. 3 ϕ, 70~120°; Carrier gas, He; Detector, thermal conductivity detector.

Products from the Reaction of I with Butyl Ether——Direct chemical identification of the products from the reaction mixture of I (3.15 g., 0.01 mole) with excess butyl ether was failed. Thus, the mother liquor freed from benzenesulfonamide was subjected to gas chromatography (Fig. 1). The peaks of butylaldehyde, its oxidated product, butylic acid, and butyl bromide were detected on the chromatogram. The condition of the analysis carried out was as follows: Sample 3 μl.; Column, tricresyl phosphate, 40~60 mesh, 0.75 m., 3 ϕ, 80°; Carrier gas He; Detector, hydrogen flame ionization detector.

Products from the Reaction of I with Ethyl Ether——Since the chemical identification of the products in a mixture from the reaction of I (3.15 g., 0.01 mole) with excess of ethyl ether, was unsuccesfull, the analysis by gas chromatography (Fig. 1) was carried out by the same manner as in the preceding case. The observed peaks were identified as ethyl bromide and acetic acid. The latter was probably formed from acetaldehyde. The condition of the analysis was as follows: Sample, 10 μl.; Column, tricresyl phosphate, 40~60 mesh, 0.75 m., 3 ϕ, 40°; Carrier gas, He; Detector, hydrogen flame ionization detector.