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Reaction of N-Haloamide. XVIII.[1] Oxidation of Ether to Ester with N-Haloamide

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The oxidation of tetrahydrofuran, tetrahydropyran or *n*-butyl ether with N,N-dibromobenzenesulfonamide (DBBS) in the presence of water gave γ-butyrolactone, δ-valerolactone or *n*-butylbutyrate, respectively (Table I).

The mechanism of reaction was discussed in connection with the reaction of tetrahydrofuran with DBBS in nonaqueous solvent.

In the preceding paper of this series, reactions of various ethers with N,N-dibromobenzenesulfonamide (DBBS) in a nonaqueous solvent were examined; aliphatic ethers[3] gave corresponding aldehyde and alkyl bromides, and tetrahydrofuran[4] gave *trans*-2-(4′-bromobutoxy)-3-bromotetrahydrofuran (I).

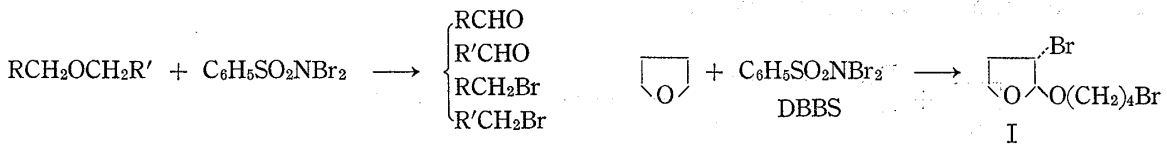

Chart 1

We have experienced that the crude product (I) of the reaction of tetrahydrofuran with DBBS was often contaminated with a by-product showing a distinct absorption band at 1770 cm^{-1}. This by-product was assumed to be γ-butyrolactone produced by a reaction participated with a slight amount of water in the solvent.

This observation prompted us to examine the reaction of ethers with N-haloamides in the presence of an excess water expecting the direct conversion of α-methylene of ethers to carbonyl groups. The examinations were successful and a general procedure of oxidation of ethers having α-methylene to ester or lactone with N-haloamide was established. Juenge, *et al.*[5] has reported an example of oxidation of ether with trichloroisocyanuric acid.

In general, the equimolar amount of DBBS was added into a suspension of ether in water on cooling under stirring, the mixture turned once to deep red with the liberation of free

1) Part XVII: H. Niizato, Y. Ueno, and S. Takemura, *Chem. Pharm. Bull.* (Tokyo), **20**, 2707 (1972).
2) Location: *321 Kowakae, Higashiosaka-shi, Osaka.*
3) S. Takemura, Y. Ando, H. Terauchi, and Y. Ueno, *Chem. Pharm. Bull.* (Tokyo), **15**, 1331 (1967).
4) Y. Kamiya (née Ando), S. Takemura, and Y. Ueno, *Chem. Pharm. Bull.* (Tokyo), **17**, 520 (1969).
5) E.C. Juenge, P.L. Spangler, and W.P. Duncan, *J. Org. Chem.* 31, 3836 (1966); E.C. Juenge and D.A. Beal, *Tetrahedron Letters*, **1968**, 5819.

bromine and the reaction was subsequently completed with rapid consumption of bromine by heating on a water bath. After completion of the reaction the separated crystals of benzene sulfonamide were filtered off and the product was extracted with organic solvent from the mixture.

The reaction of tetrahydrofuran, tetrahydropyran, and *n*-butyl ether with DBBS gave *γ*-butyrolactone, *δ*-valerolactone, and *n*-butylbutyrate, respectively. The presence of alkali enhanced the rates of these reactions and increased the yields as shown in Table I. The oxidation with N-bromosuccinimide (NBS), chloramine T, and free bromine was also studied in the similar condition. These results are summarized in Table I.

Table I. Yield of Oxidation Products (%)

Starting material			$(C_4H_9)_2O$
Product / Reagent			$C_3H_7COOC_4H_9$
$C_6H_5SO_2NBr_2$ (DBBS)	31	—	17
$C_6H_5SO_2NBr_2$,Na_2CO_3	58	22	30
NBS	27	—	8.3
Chloramine T, HCl	35	—	—
Br_2	a small amount		

The oxidation of ether with DBBS seems to be not simple one such as a oxidation with intermedially liberated bromine because, contrary to this case, in the reaction of ether with simple bromine (Table I), the rate was not only significantly slow but the yield of the product was very low.

Furthermore, the overall rate of the reaction with DBBS is accelerated by irradiation with a fluorescent light as observed in the reaction in nonaqueous solvent, so this reaction may also involve some active intermediates.

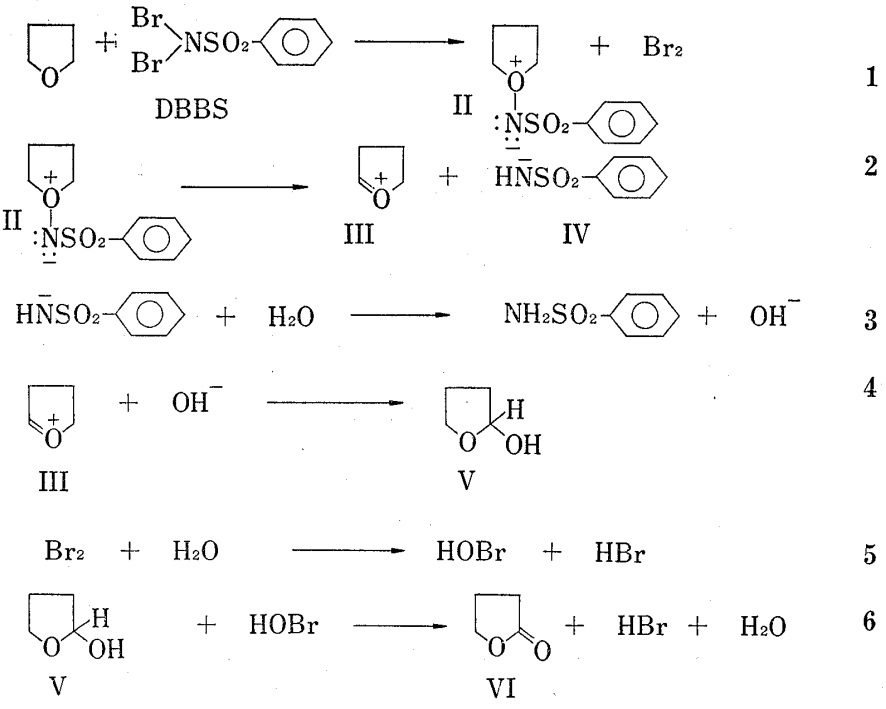

Chart 2

On the previous kinetic studies[6] of the reaction of tetrahydrofuran with DBBS in nonaqueous solvent, two intermediates were presumed. Therefore, in connection with kinetic studies, the mechanism of reaction of tetrahydrofuran with DBBS in the presence of water may also be considered as shown with Eq. 1—6.

The stage of bromine-liberation may be considered to be same as that in the nonaqueous solvent, that is, simultaneously a ylid-like complex (II) may be formed.[6b] Subsequently, elimination of α-hydrogen and the benzenesulfonimino group from II may result in formation of an ion pair of the oxonium ion (III) and benzenesulfonium anion (IV). This oxonium ion (III) may be a common intermediate of both reactions in aqueous and non-aqueous solvents. Hydroxide anion may attack on III to give hemiacetal, V (Eq. 4), which may be oxidized by HOBr to form final product as shown in Eq. 6. Acceleration of the reaction and increase of yields by alkali support above ionic process shown in Eq. 4—6.

Experimental

General Procedure——Ether was allowed to react with reagent in the presence of excess water. When the reagent was added in small portions into a suspension of ether in excess water on cooling under stirring, the reagent dissolved with exothermic reaction. The reaction mixture was colored with free halogen. After the reaction subsided, the reaction mixture was maintained a gentle reflux for 30 min. The solution turned to nearly colorless and crystals of the corresponding haloamide appeared. Crystals were filtered off, and the oxidation product was extracted with ethyl ether or dichloromethane from the filtrate by salting-out with sodium chloride and dried over sodium sulfate. After evaporation of solvent, the product was distilled.

γ-Butyrolactone——i) Reaction with DBBS in Water: Tetrahydrofuran (THF, 10 ml) suspended in water (10 ml) was allowed to react with DBBS (9.5 g, 0.03 mole) by the forementioned procedure. γ-Butyrolactone, bp 50—55° (bath temperature) (3 mmHg), was obtained in 31% yield. It was identified with an authentic sample. IR (liquid) cm^{-1}: 1770 (C=O).

ii) Reaction with DBBS in Aqueous Na_2CO_3: The reaction of THF (3.6 g, 0.05 mole) with DBBS (15.7 g, 0.05 mole) in aqueous Na_2CO_3 (Na_2CO_3 2.6 g, H_2O 20 ml) was carried out by the procedure as described above. Yield: 2.4 g, 56%.

iii) Reaction with NBS in Water: THF (7.2 g, 0.1 mole) in water (50 ml) allowed to react with NBS (17.8 g, 0.1 mole). Yield: 2.1 g, 27%.

iv) Reaction with Chloramine T in 10% HCl: THF (2.1 g, 0.03 mole) in 10% HCl (15 ml) was allowed to react with chloramine T (8.4 g, 0.03 mole) by the similar procedure. Yield: 0.9 g, 35%.

v) Reaction with Free Bromine: THF (0.7 g, 0.01 mole) in water (20 ml) was allowed to react with free bromine (1.6 g, 0.01 mole). A small amount of γ-butyrolactone was detected.

δ-Valerolactone——Tetrahydropyran (4.3 g, 0.05 mole) in suspended aqueous Na_2CO_3 (Na_2CO_3 2.6 g, H_2O 20 ml) was allowed to react with DBBS (15.8 g, 0.05 mole). δ-Valerolactone, bp 91—94° (9 mmHg), was obtained in 22% yield and identified with an authentic sample. IR (liquid) cm^{-1}: 1735 (C=O).

***n*-Butyl Butyrate**——i) Reaction with DBBS in Water: *n*-butyl ether (20 ml) suspended in water (18 ml) was allowed to react with DBBS (15.8 g, 0.05 mole). *n*-Butyl butyrate (1.2 g, 17.2%), bp 157—160°, was obtained by repeated fractional distillations. It was identified with an authentic sample come from oxidation of *n*-butanol with $Na_2Cr_2O_7$. IR (liquid) cm^{-1}: 1730.

ii) Reaction with DBBS in aqueous Na_2CO_3: The reaction of *n*-butyl ether (13 g, 0.1 mole) with DBBS (31.5 g, 0.1 mole) in aqueous Na_2CO_3 (Na_2CO_3 5.3 g, H_2O 50 ml) was carried out by the procedure as described above. Yield: 4.3 g, 30%.

iii) Reaction with NBS in Water: *n*-Butyl ether (13 g, 0.1 mole) in water (50 ml) allowed to react with NBS (17.8 g, 0.1 mole) by the method as described above. Yield: 1.2 g, 8.3%.

6) *a*) Y. Kamiya and S. Takemura, *Chem. Pharm. Bull.* (Tokyo), **18**, 848 (1970); *b*) Y. Kamiya and S. Takemura, *Chem. Pharm. Bull.* (Tokyo), **20**, 2471 (1972). This paper deals with the kinetic studies on the reaction of tetrahydrofuran with DBBS in nonaqueous solvent. It has been discussed that the formation of semistable complex, a ylid-like complex (II), and oxonium ion (III) was presumed.