Halogen Substitution in Liquid Sulfur Dioxide. I. Formation of Alkyl Halides from Alcohols and Halogens

By Niichiro TOKURA, Ritsuro TADA and Ryoichi IGARASHI

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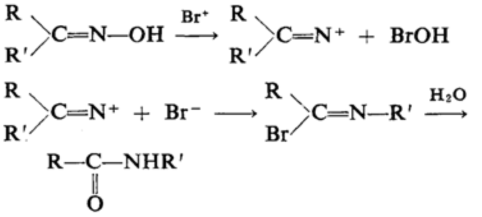
The writers clarified the point previously[1] that ketoximes undergo rearrangement by the action of a halogen in liquid sulfur dioxide at room temperature. Scheme 1 was tentatively assigned to the mechanism of the rearrangement. The solvation by the solvent (liq. SO_2) may favor the ionization of the bromine molecule.

Sheme 1

$$Br_2 \overset{\text{liq. } SO_2}{\rightleftharpoons} Br^+ + Br^- \qquad (1)$$



$$\begin{matrix}R\\R'\end{matrix}\!>\!C{=}N{-}OH \xrightarrow{Br^+} \begin{matrix}R\\R'\end{matrix}\!>\!C{=}N^+ + BrOH \qquad (2)$$

$$\begin{matrix}R\\R'\end{matrix}\!>\!C{=}N^+ + Br^- \longrightarrow \begin{matrix}R\\Br\end{matrix}\!>\!C{=}N{-}R' \xrightarrow{H_2O} R{-}\underset{\underset{O}{\|}}{C}{-}NHR' \qquad (3)$$

$$BrOH + SO_2 \longrightarrow HBr + SO_3 \qquad (3)$$

From the structural similarity between alcohols R–C–OH and oximes R–C=H–OH, it is expected that all alcohols have a similar behavior towards bromine in liquid sulfur dioxide and, consequently, the reaction will proceed to form the corresponding alkyl halides. (Scheme 2).

Scheme 2

$$ROH + Br^+ \longrightarrow R^+ + BrOH \qquad (5)$$

$$R^+ + Br^- \longrightarrow RBr \qquad (6)$$

$$BrOH + SO_2 \longrightarrow HBr + SO_3 \qquad (7)$$

The borderline nature[2] of liquid sulfur dioxide as a solvent was first recognized by Ingold[2] and, if the reaction follows the S_N1 mechanism, Eq. 5 being a slow step, the ease of the reaction of alcohols will be in the order of just tertiary, then, secondary, and finally, primary.[3]

A direct substitution of an alcoholic hydroxyl by a bromine atom has been reported to be the case, though only in tertiary alcohols, but this method[4] is not used because of its low yield. Substitution of the hydroxyl in liquid sulfur dioxide by a halogen has already been carried out[5], but with such halogenating reagents as thionyl halides, phosphorus trihalides and pentahalides, liquid sulfur dioxide being used as a solvent because of its excellence.

In expectation of obtaining alkyl halides by direct application of a halogen in liquid sulfur dioxide at room temperature, the lower members of aliphatic and alicyclic alcohols were submitted to the reaction with bromine with the results summarized in Table I.

The total amount of the products increased in the order of primary, secondary and tertiary alcohols. Only small amounts of alkyl halides were obtained from primary alcohols. Higher boiling halides were produced by further

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[1] N. Tokura, R. Asami and R. Tada, *J. Am. Chem. Soc.*, **76**, 3135 (1957).

[2] C. K. Ingold, *Proc. Chem. Soc.*, 279 (1957).

[3] C. K. Ingold, "Structure and Mechanism in Org. Chem.", Cornell Univ. Press, Ithaca, N.Y. (1955), p. 317.

[4] C. Hell and F. Urech, *Ber.*, **15**, 1249 (1882).

[5] For example, R. B. Woodward et al., *J. Am. Chem. Soc.*, **76**, 5256 (1954), used thionyl chloride in liq. SO_2 for the substitution of hydroxyl with chlorine in their synthetic course to lysergic acid, one of the ergot alkaloids.

TABLE I. REACTION OF BROMINE AND ALCHLOLS IN LIQ. SO_2
Alcohol: 0.4 mol., Bromine: 0.4 mol. (64 g.)
Liq. SO_2: 100 mol., Time: 5 hr. at room temperature

Alcohol ROH	R	Ethyl	*n*-Propyl	Iso-propyl	*n*-Butyl	Iso-butyl	*sec*-Butyl	*tert*-Butyl	Iso-amyl.
	g.	18.4	24.0	24.0	30.0	30.0	30.0	30.0	35.0
Product: Total	g.	3.0	3.0	30.0	8.0	17.0	60.0	69.0	4.0
	Yield weight %	3.6	3.4	34.1	8.5	18.1	63.9	73.3	4.0
Product: Alkyl bromide RBr	b.p., °C	37∼38	68∼70	59∼60	99∼101	88∼91	90∼92	71∼73	120∼121
	g.	2.0	2.5	19.0	5.0	1.5	18.0	13.0	3.0
	Yield, %	5.3	5.1	38.6	7.2	2.7	32.5	23.4	6.7
	n_D^{26}	1.425	1.435	1.423	1.440	1.438	1.438	1.430	1.443
	Br % found.	71.5	63.0	62.5	57.9	58.1	56.1	57.3	53.0
	Br % calcd.	73.0	64.9	64.9	58.3	58.3	58.3	58.3	52.9
	$RCONHC_6H_5$ m.p., °C	104	91∼92	101∼10	62∼63	108∼109	107∼108	127∼128	107∼108
Product: Higher boiling fractions				b.p. 42∼43 (20 mmHg) 7.0 g.		b.p. 41∼44 (10 mmHg) 9.0 g. b.p. 90∼99 (10 mmHg) 5.0 g.	b.p. 41∼44 (12 mmHg) 30.0 g. b.p.90∼100 (10 mmHg) 2.0 g.	b.p. 46∼51 (20 mmHg) 31.0 g. b.p.80∼110 (20 mmHg) 4.0 g.	

elimination, dimerization and bromination. In all experimants sulfuric acid separated out on the bottom of the reaction vessel. The highest yield was 38.6% of isopropyl bromide, but it was accompanied by a hexyl bromide with a carbon number twice as large as the original alkyl, and most of the butyl bromides were contaminated with butylene dibromides. (Scheme 3)

Scheme 3

$$R_1R_2\cdot(R_3CH_2)\cdot C{-}OH \xrightarrow{Br^+} A^+ + BrOH \quad (8)$$

$$A^+;\ R_1R_2\cdot(R_3CH_2)\cdot C^+$$

$$A^+ + Br^- \longrightarrow R_1R_2(R_3CH_2)\cdot C\cdot Br \quad (9)$$

$$A^+ \longrightarrow R_1R_2(R_3CH_2)\cdot C{=}CH\cdot R_3\ (B) + H^+ \quad (10)$$

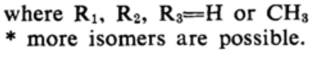
$$BrOH + SO_2 \longrightarrow HBr + SO_3 \quad (11)$$

$$R_1R_2(R_3CH_2)\cdot C{-}OH + SO_3 \longrightarrow A^+ + HSO_4^- \quad (12)$$

$$H^+ + HSO_4^- \longrightarrow H_2SO_4 \quad (13)$$

$$B + A^+ \longrightarrow R_1R_2\cdot C{-}R_3CH{-}C\cdot R_1R_2\cdot(CH_2R_3)$$

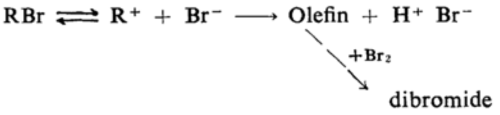
$$\xrightarrow{Br^-} R_1R_2{-}C{-}R_3CH{-}CR_1R_2(CH_2R_3)^* \quad (14)$$



$$B + Br_2 \longrightarrow R_1R_2\underset{Br}{C}{-}\underset{Br}{C}H\cdot R_3 \quad (15)$$

where R_1, R_2, R_3=H or CH_3
* more isomers are possible.

Thus, as might be expected, elimination reaction prevails to a considerable extent in liquid sulfur dioxide. The rather complicated feature of the reaction will be understood if the sulfur trioxide produced by the secondary step is assumed to play an important role in the elimination reaction and the dimerization.



$$RBr \rightleftharpoons R^+ + Br^- \longrightarrow Olefin + H^+\ Br^-$$
$$Olefin \xrightarrow{+Br_2} dibromide$$

The equilibrium tends to the formation of the dibromide. It is further supported by the fact that phenethyl chloride and bromine in liquid sulfur dioxide afford styrene, polystyrene and styrene dibromide[6].

As the reaction proceeds, sulfur trioxide, formed according to Eq. 7, will favor the formation of the alkyl cation followed by elimination to olefin and sulfuric acid thus produced separates out owing to its slight solubility in liquid sulfur dioxide. Since this is an irreversible reaction, the reaction reaches a final state when the whole acid is precipitated.

In the case of the Beckmann rearrangement, the formation of a nitrogen cation or its ion-pair is the main reaction and no elimination occurs, the secondarily formed sulfur trioxide bearing a lesser meaning.

In the bromination of alcohols by bromine in liquid sulfur dioxide, the decisive factor is the SN1 tendency of both alcohols and the solvent. The larger amounts of reaction products from secondary and tertiary alcohols are well consistent with the above consideration.

The writers have no evidence to rule out the participation of hydrogen bromide afforded by Eq. 7 in the bromine substitution reaction. An exact elucidation of the reaction needs further examination.

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[6] E. D. Hughes, C. K. Ingold and A. D. Scott, *J. Chem. Soc.*, 1937, 1271.

TABLE II. EFFECT OF THE AMOUNT OF BROMINE ON THE YIELD AND ACTION OF HYDROGEN BROMIDE ON ISOPROPYL ALCOHOL

Isopropyl alcohol: 24 g. (0.4 mol.).
Liq. SO_2: 100 ml., Time 5 hr., at room temperature.

Bromine g.	Mol. ratio Alcohol : Bromine	Isopropyl bromide g.	Isopropyl bromide yield, %	Higher boiling fraction 42~43°C (20 mmHg)
32	1 : 0.5	8.0	16.2	5.1
48	1 : 0.75	18.5	38.0	7.0
64	1 : 1.0	19.0	38.6	7.4
77	1 : 1.2	18.8	38.1	8.3
32 (with H_2O 7.2 g.)	1 : 0.5 : (H_2O) 1,	0.5	2.0	trace

TABLE III. ACTION OF CHLORINE AND OF CHLORINE WITH A CATALYTIC AMOUNT OF BROMINE

Alcohol: 0.4 mol., Chlorine: 0.4 mol.
Liq. SO_2: 100 ml., Time: 5 hr. at room temperature.

Alcohol	Reagent	Mole ratio of alcohol to halogen	Alkyl chloride b.p., °C	Alkyl chloride Yield, %
n-Butyl	Cl_2	1 : 1	77~79	11.6
	Cl_2+Br_2	1 : 1 : 0.02	77~79	11.6
Isobuyl	Cl_2	1 : 1	60~65	trace
	Cl_2+Br_2	1 : 1 : 0.02	60~65	2.4
sec-Butyl	Cl_2	1 : 1	67~69	6.2
	Cl_2+Br_2	1 : 1 : 0.02	67~69	3.5
tert-Butyl	Cl_2	1 : 1	49~53	18.6
	Cl_2+Br_2	1 : 1 : 0.02	49~53	17.2
Cyclohexyl	Cl_2	1 : 1	98~102	6.5
	Cl_2+Br_2	1 : 1 : 0.02	98~102	9.4

A considerable isomerization is also expected in the alkyl cation, but the writers are not yet in a position to discuss the structures of the carbon skeletons of the dimeric alkyl bromides produced.

In the bromine substitution of isopropyl alcohol, besides 38.6% of isopropyl bromide, a hexyl bromide, (probably 2-bromo-4-methylpentane) b. p. 42~43°C (20 mmHg) was formed in a yield of 21.2% of the theoretical. This substance afforded a hexyl acetate of b. p. 135~140°C with potassium acetate in glacial acetic acid. Its hydrolysis gave a hexene, C_6H_{12}, b. p. 70~73°C, possessing a comphor-like aroma, and a small amount of a hexyl alcohol, b. p. 125~130°C.

Similar phenomena were observed in the reactions of secondary or tertiary butyl alcohols with bromine, large amounts of octyl bromides being formed besides butyl bromides. Further, formation of dibromobutanes were also observed, which are assumed to have been formed by the addition of bromine to butenes produced from butyl cations.

In the alicyclic alcohols, it was observed that the formation of the cycloalkylene dibromides predominated over the cyclohexyl bromides. Thus, cyclohexyl alcohol afforded dibromocyclohexane in a yield of 64.2% and *d*-borneol afforded 71.2% of 2,10-dibromocamphane, indicating that a path through the Wagner-Meerwein rearrangement was followed.

The relation between the yield of the alkyl bromide vs. the amount of bromine was examined with isopropyl alcohol, the results being listed in Table II.

Only a small yield of the products was obtained with hydrogen bromide formed in the liquid sulfur dioxide[7] according to the formula:

$$Br_2 + 2H_2O + SO_2 \longrightarrow 2HBr + H_2SO_4 \qquad (16)$$

In the next place, the action of chlorine on aliphatic alcohols was examined. The results shown in Table III indicate that chlorine is not so reactive as bromine, the yields being depressed. Subsequently, a small amount of bromine was added to chlorine (0.02 mol. of bromine to one mol. of chlorine) in expectation of a better result as in the case of the Beckmann rearrangement by chlorine[1] in liquid sulfur dioxide, but it proved ineffective.

Experimental

Materials.—*1. Liquid Sulfur Dioxide.*—Liquid sulfur dioxide, dehydrated and purified in the plant and filled in an iron cylinder, was used. The water content measured in accordance with the principle of the Karl Fischer method

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[7] J. Ross, T. H. Percy, R. L. Brandt, A. I. Gebhart, J. E. Mitchell and S. Yolles, *Ind. Eng. Chem.*, **34**, 924 (1942).

was 0.05~0.2%. This was further dehydrated with concentrated sulfuric acid and then with phosphorus pentoxide to bring the water content below 0.01%. However, practically no difference was found between these two kinds of liquid sulfur dioxide with respect to the reaction,

2. *Alcohols.* — All the alcohols were commercial products of the purest grade, which were dehydrated by the known method and redistilled.

3. *Bromine.* — Commercial bromine was washed with water and with concentrated sulfuric acid, dehydrated, and distilled once.

4. *Chlorine.*—Commercial chlorine was dehydrated with concentrated sulfuric acid and distilled.

5. *Reaction Vessel.*—A glass pressure bottle of 200 ml. capacity was used.

Experimental Method.—The amount of alcohols was 0.4 mol. each and that of bromine 0.4 mol. The solution of bromine in 50 ml. of liquid sulfur dioxide was added gradually to 50 ml. of liquid sulfur dioxide containing the alcohol at room temperature (20°C). The mixture was allowed to stand for a definite time. The reaction of secondary and tertiary alcohols occurred at once, the bromine color disappeared immediately, and the liquid sulfur dioxide solution became turbid. Sulfuric acid separated out as a colorless, translucent liquid on the bottom of the pressure bottle. After a definite time (usually 5 hr.), liquid sulfur dioxide was distilled off and the residual liquid was poured into ice water. The unchanged alcohols, especially butyl alcohols and lower aliphatic alcohols, dissolved out in water. The oily layer, after repeatedly being washed with water and with 1 N sodium carbonate solution and again with water, was dried over calcium chloride, and distilled to examine the amount of the lakyl halide formed.

Results.—*(A) Reaction of Alcohols with Bromine.*—1. Ethyl alcohol: From the reaction of 18.4 g. (0.4 mol.) of ethyl alcohol and 64 g. (0.4 mol.) of bromine in 100 ml. of liquid sulfur dioxide for 5 hours, 3.0 g. of a bromide was obtained. B. p. 37~38°C. Yield, 2.0 g. (5.3%). $n_D^{26}=1.425$. The bromide was identified with ethyl bromide by deriving propioanilide from it. Namely, the bromide was changed into a Grignard reagent and the latter was treated with phenyl isocyanate, and propionanilide (m. p. 104°C)[8] was obtained, which showed no depression of the melting point on admixture with an authentic specimen.

2. *n*-Propyl alcohol: A mixture of 24.0 g. (0.4 mol.) of *n*-propyl alcohol, 64 g. of bromine, and 100 ml. of liquid sulfur dioxide was kept at 20°C for 5 hr. and 3.0 g. of a crude halide was obtained. Redistillation afforded 2.5 g. (5.1%) of colorless, translucent liquid, b. p. 68~70°C, $n_D^{26}=1.435$. The bromide was identified with *n*-propyl bromide by deriving butyranilide, m. p. and mixed m. p. 91~92°C.[8]

3. Isopropyl alcohol: A mixture of 24 g. (0.4 mol.) of isopropyl alcohol, 64 g. (0.4 mol.) of bromine, and 100 ml. of liquid sulfur dioxide was kept at 20°C for 5 hr. The bromine color disappeared immediately after the starting of the reaction, the whole liquid became orange-colored and turbid, and ca. 10 ml. of a colorless, translucent liquid was deposited on the bottom. After 5 hr. this liquid was collected and titration gave a value corresponding to 13.2 g. of sulfuric acid. Liquid sulfur dioxide was then evaporated, the residual liquid was poured into ice water, and the oily layer was repeatedly washed with water and with 1 N sodium carbonate as described above. The crude halide thus obtained (30.0 g.) was fractionally distilled into the following fractions:

1) b. p. 59~60°C (760 mmHg), $n_D^{26}=1.425$, 19.0 g. (38.6%).

2) b. p. 42~43°C (20 mmHg), $n_D^{26}=1.525$, 7.0 g. (21.2%).

3) Residue, 0.3 g.

Fraction 1 was isopropyl bromide, forming isobutyranilide,[8] m. p. and mixed m. p. 101~102°C. Fraction 2 was a hexyl bromide (Found: Br, 47.9. Calcd for $C_6H_{13}Br$: Br, 48.41). Five grams of Fraction 2 was refluxed with 30 ml. of glacial acetic acid and 5 g. of potassium acetate, and 3.8 g. of a hexyl acetate, b. p. 135~140°C. (Found: CH_3CO, 30.11. Calcd. for $CH_3COOC_6H_{13}$; CH_3CO, 29.82), was obtained. Hydrolysis of this hexyl acetate by warming with ethanolic potassium hydroxide for 1 hr. afforded an olefin with camphor-like aroma, a hexene, C_6H_{12}, b. p. 70~73°C (Found: C, 85.98, H, 14.02, bromine number, 188.0. Calcd. for C_6H_{12}: C, 85.63, H, 14.37%, bromine number, 190.5).

Further, 0.3 g. of an oil, b. p. 125~130°C, assumed to be a hexyl alcohol, was obtained. This hexyl bromide may be assumed to be 2-bromo-4-methylpentane.

4. *n*-Butyl alcohol: A mixture of 30.0 g. (0.4 mol.) of *n*-butyl alcohol, 64 g. (0.4 mol.) of bromine, and 100 ml. of liquid sulfur dioxide was similarly treated and 8.0 g. of the product was fractionated, affording 5 g. (7.2%) of *n*-butyl bromide, b. p. 99~101°C, $n_D^{26}=1.440$ (Found: Br, 57.9. Calcd. for C_4H_9Br: Br, 58.33%). Valeranilide[8], m. p. and mixed m. p. 62~63°C. Further distillation of the residual

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[8] R. L. Shriner and R. C. Fuson, "Sstematic Identification of Organic Compounds", John Wiley & Sons, Inc., New York (1948), p. 255.

liquid afforded about 2.5 g. of an oil which boiled over a wide range of 40～90°C at 10 mmHg.

5. Isobutyl alcohol: Thirty grams of isobutyl alcohol was treated with bromine as above and 17.0 g. of the reaction product was obtained. This liquid was fractionated into three components.

1) b. p. 88～91°C, 1.5 g. (2.7%).
2) b. p. 32～38°C (10 mmHg), 9.0 g. (8.6%).
3) b. p. 90～99°C (10 mmHg), 5.0 g. (5.7%).

Fraction 1, $n_{\rm D}^{26}=1.438$, was isobutyl bromide, affording isovaleranilide[8], m. p. and mixed m. p. 108～109°C. Fraction 2 was an octyl bromide, (Found: Br, 40.25, Calcd. for $C_8H_{17}Br$: Br, 41.38%). Fraction 3 corresponded to dibromo-isobutane (Found: Br, 72.56. Calcd. for $C_4H_8Br_2$: Br, 73.61%).

6. *sec*-Butyl alcohol: Thirty grams (0.4 mol.) of *sec*-butyl alcohol was similarly treated and 60.0 g. of the reaction product was obtained and fractionated.

1) b. p. 90～92°C, 18.0 g. (32.5%).
2) b. p. 41～44°C (12 mmHg), 25.0 g. (51.8%).
3) b. p. 90～110°C (10 mmHg), 2.0 g. (2.3%).
4) Residue, 3.1 g.

Fraction 1, $n_{\rm D}^{26}=1.438$, was *sec*-butyl bromide (Found: Br, 57.60. Calcd. for C_4H_9Br, 58.3%), forming α-methylbutyranilide[8], m. p. and mixed m. p. 107～108°C. Fraction 2 was an octyl bromide (Found: Br, 40.59. Calcd. for $C_8H_{17}Br$; Br, 41.38%), and Fraction 3 was assumed to be a dibromobutane with some impurity (Found: Br, 70.56. Calcd. for $C_4H_8Br_2$: Br, 73.61%).

7. *tert*-Butyl alcohol: Thirty grams (0.4 mol.) of *tert*-butyl alcohol was similarly treated and 69.0 g. of the oil formed was fractions.

1) b. p. 71～73°C, 13.0 g. (23.4%).
2) b. p. 46～51°C (20 mmHg), 31.5 g. (65.1%).
3) b. p. 80～110°C (20 mmHg), 4.0 g. (4.5%).
4) Residue, 7.0 g.

Fraction 1 was *tert*-butyl bromide, $n_{\rm D}^{26}=1.655$, (Found: Br, 41.96. Calcd. for C_4H_9Br: Br, 41.38%). Trimethylacetanilide, m. p. and mixed m. p. 127～128°C. Fraction 2 was an octylbromide, $n_{\rm D}^{26}=1.655$ (Found: Br, 41.96. Calcd. for $C_8H_{17}Br$: Br, 41.38%). Ten grams of Fraction 2 was refluxed with 10 g. of potassium acetate and 30 g. of glacial acetic acid for 1 hr. and 60 g. of an octyl acetate, with characteristic sweet aroma, was obtained, b. p. 120～126°C, $n_{\rm D}^{26}=1.644$ (Found: CH_3CO, 20.5. Calcd. for $C_{10}H_6O_2$: CH_3CO, 21.04%). Hydrolysis of this substance with ethanolic potassium hydroxide afforded 3 g. of a colorless, translucent oil, b. p. 118～121°C, with camphor-like odor (Found: bromine number, 139.0. Calcd. for C_8H_{16} (F_1); bromine number, 142.3). Fraction 3 was assumed to be a dibromobutane with some impurity (Found: Br, 71.74. Calcd. for $C_4H_8Br_2$: Br, 73.61%).

The amount of sulfuric acid formed during this reaction was 13.0 g. (titrated as H_2SO_4).

8. Isoamyl alcohol: A similar treatment of 35.0 g. (0.4 mol.) of isoamyl alcohol afforded 4.0 g. of a product which was distilled to give 3.0 g. (6.6%) of isoamyl bromide, b. p. 120～121°C, $n_{\rm D}^{26}=1.443$. Isohexananilide[8], m. p. and mixed m. p. 107～108°C.

9. Cyclohexyl alcohol: Forty grams (0.4 mol.) of cyclohexyl alcohol was treated with 0.4 mol. of bromine in 100 ml. of liquid sulfur dioxide at room temperature for 5 hr. to give 72.2 g. of an oily product, which was fractionated into two fractions:

1) cyclohexyl bromide, b. p. 55～61°C (20 mmHg), 9.2 g. (14.1%), $n_{\rm D}^{23}=1.496$ (Found: Br, 50.4. Calcd. for $C_6H_{11}Br$; Br, 49.0%).
2) dibromocyclohexane, b. p. 97～108°C (20 mmHg), 62.2 g. (64.2%).

The dibromocyclohexane was redistilled, b. p. 98～101°C (17 mmHg), $n_{\rm D}^{24}=1.549$ (literature[9]: b. p. 100°C (13 mmHg), $n_{\rm D}^{25}=1.5506$) (Found: Br, 65.0. Calcd. for $C_6H_{10}Br_2$: Br, 66.0%).

10. *d*-Borneol: *d*-Borneol, m. p. 201～204°C, $[\alpha]_{\rm D}^{21.5}=+31.88°$, was prepared, according to the procedure of Amagasa et al., by reduction of *d*-camphor with sodium in liquid ammonia followed by rectification and recrystallization. A similar treatment of 15.5 g. (0.1 mol.) of *d*-borneol and 17.6 g. (0.11 mol.) of bromine in 140 ml. of liquid sulfur dioxide at room temperature for 18 hours afforded 26.0 g. of products, from which 11.6 g. of dark crystals were separated and recrystallized from ethyl alcohol in white crystals of m. p. 90～91°C. From the filtrate, 9.7 g. of an oil was distilled at 120～134°C (4.5 mmHg) which after recrystallization showed m.p. 90～91°C, alone and in admixture with the above specimen. Total yield, 71.2%. $[\alpha]_{\rm D}^{16}=-15.0°$. This was identified with 2, 10-dibromocamphane[11] by a mixed melting point. The small amount of the forerun of the filtrate, b. p. 70～75°C (3 mmHg), 1.8 g. and b. p. 110～122°C (4 mmHg), is yet unidentified. (The optical rotations were measured in 95% ethyl alcohol in a tube of 2 cm. length.)

(B) The Mole Ratios of Bromine to Alcohols and Yields of Alkyl Bromides.—Similar treatments were carried out with various mole ratios of bromine to isopropyl and to *tert*-butyl alcohols.

(C) The Preparation of Alkyl Bromides with 1 mol. of Bromine and 2 mol. of Water in Liquid Sulfur Dioxide.—The procedures were

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[9] S. Winstein, *J. Am. Chem. Soc.*, **64**, 2792 (1942).

[10] M. Amagasa and K. Yamaguchi, presented at the 6th Annual Meeting of the Chemical Society of Japan, April, (1953), Tokyo.

[11] P. Lipp and F. Lausberg, *Ann.*, **436**, 274 (1924).

similar to those described above but two mol. of water was added to liquid sulfur dioxide to produce hydrogen bromide(7).

(D) Action of Chlorine with a Small Amount of Bromine on Alcohols in Liquid Sulfur Dioxide. —In these experiments, chlorine or chlorine with 0.1 mol. of bromine to improve the yield of the chlorides was applied to aliphatic alcohols, the procedures being essentially similar as in the case of bromine.

Summary

The reaction between aliphatic alcohols and bromine in liquid sulfur dioxide at room temperature was investigated in order to obtain further information concerning the behavior of bromine in liquid sulfur dioxide. The reactivity of the alcohols increased in the order of primary <secondary<tertiary.

In addition to alkyl bromides, higher boiling bromides were also produced. The latter resulted from further elimination, dimerization and bromine addition. The rather complicated feature of the bromination is attributable to the presence of sulfur trioxide secondarily formed in the reaction mixture.

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Chemical Research Institute
of Non-aqueous Solutions
Tohoku University
Katahiracho, Sendai