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Bromination of Alkenes and Related Compounds by Use of Benzyltrimethylammonium Tribromide in Aprotic and Protic Solvents[1)]

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Dedicated to Professor Otohiko Tsuge on the occasion of his retirement

The reaction of alkenes and related compounds (**1**) with benzyltrimethylammonium tribromide (BTMA Br_3) in aprotic solvents such as dichloromethane and chloroform gave 1,2-dibromo adducts in fairly good yields. The reaction of **1** with BTMA Br_3 in protic solvents such as methanol and acetic acid gave the corresponding dibromo adducts along with substantial amounts of solvent-incorporated products in a regioselective manner.

Quaternary ammonium tribromide such as pyridinium hydrobromide perbromide,[2)] tetramethylammonium tribromide,[3)] and phenyltrimethylammonium tribromide[4)] have already been used as brominating agents in order to avoid the disadvantage of toxic and corrosive property of bromine. Recently, Berthelot et al.[5)] have reported the addition reactions of bromine on double bonds of serveral alkenes by use of tetrabutylammonium tribromide (TBA Br_3). In this paper, we wish to report on the bromination of much more alkenes and related compounds (**1**) with benzyltrimethlammonium tribromide (BTMA Br_3), more effective brominating agent that TBA Br_3, in aprotic and protic solvents.

Results and Discussion

The reaction of **1** with BTMA Br_3 in aprotic solvents (dichloromethane at room temperature, or chloroform under reflux) gave 1,2-dibromo adducts (**2**) in fairly good yields. The results are summarized in Table 1.

As shown in Table 1, BTMA Br_3 reacted with **1** in a manner of stereospecific anti-dibromo addition. Thus, E-stilbene (**1e**) and cinnamic acid (**1g**) gave the meso-dibromide (**2e**) and erythro-dibromide (**2g**), respectively. The reactions of cyclohexene (**1a**) and cyclooctene (**1b**)

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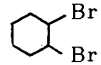
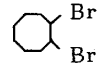
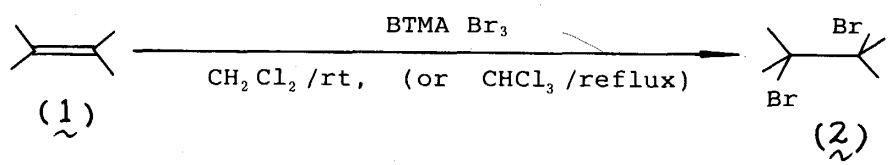
Table 1. Bromination of **1** with BTMA Br_3 in Aprotic Solvent

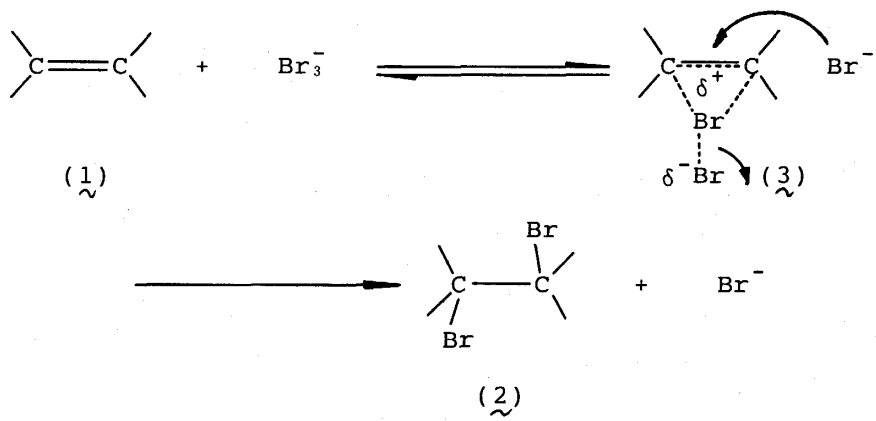
Substrate (1)	Reaction conditions: temp (℃)	Reaction conditions: time (h)	Solvent	Product (2)	Yield[a] %	Mp(℃) or Bp(℃)/mmHg: Found	Mp(℃) or Bp(℃)/mmHg: Reported
 (**1a**)	25	2	CH_2Cl_2	 (**2a**) (dl—)	84	oil	110—112/23[6]
 (**1b**)	25	2	CH_2Cl_2	 (**2b**) (dl—)	91	oil	70/0.15[7]
Ph—CH=CH_2 (**1c**)	25	2	CH_2Cl_2	Ph—CHBr—CH_2—Br (**2c**) (dl—)	98	73—75	72[8]
Ph—(CH_3)C=CH_2 (**1d**)	25	2	CH_2Cl_2	Ph—(CH_3)CBr—CH_2—Br (**2d**) (dl—)	95	oil	95—97/0.07[9]
Ph—CH=CH—Ph (**1e**) (E—)	25	2	CH_2Cl_2	Ph—CHBr—CHBr—Ph (**2e**) (meso—)	83	238—240	237[10]
Ph—CH=CH—CHO (**1f**) (E—)	25	10	CH_2Cl_2	Ph—CHBr—CHBr—CHO (**2f**) (erythro—)	58	oil	45—48[11]
Ph—CH=CH—COOH (**1g**) (E—)	25	10	CH_2Cl_2	Ph—CHBr—CHBr—COOH(**2g**) (erythro—)	74	198—201	197[12]
Ph—CH=CH—$COOCH_3$ (**1h**) (E—)	reflux	24	$CHCl_3$	Ph—CHBr—CHBr—$COOCH_3$ (**2h**) (erythro—)	87	117—119	117[12]
CH_3OCO—CH=CH—$COOCH_3$ (**1i**) (E—)	reflux	24	$CHCl_3$	CH_3OCO—CHBr—CHBr—$COOCH_3$ (**2i**) (meso—)	53	64—65	61.5—62[13]
CH_3OCO—CH=CH—$COOCH_3$ (**1j**) (Z—)	reflux	24	$CHCl_3$	**1i**	40	100—102	102[13]
				2i	47	64—65	61.5—62[13]

a) Yield of isolated product.



Scheme 1

with BTMA Br_3 gave dl-1, 2-dibromocyclohexane (**2a**) and dl-1, 2-dibromocyclooctane (**2b**), respectively. The complete anti-selective dibromo addition of **1** with BTMA Br_3 can be explained by attack of a bromide ion to a three-center bound π complex-type intermediate (**3**),[14] as shown in Scheme 2.



Scheme 2

Although the reaction of dimethyl fumarate (**1i**) with BTMA Br_3 in refluxing chloroform gave meso-dimethyl-2,3-dibromosuccinate (**2i**), dimethyl maleate (**1j**) gave a mixture of **1i** and **2i** under the same reaction conditions. That is, it can be found that **1j** isomerizes to **1i** under the reaction conditions.

The bromination of **1** with BTMA Br_3 in such protic solvents as methanol and acetic acid gave the corresponding dibromo adducts along with considerable amounts of solvent-incorporated products, 2-bromo-1-methoxy- (**4**) and 1-acetoxy-2-bromo adducts (**5**), in regioselective manner, respectively. The results are summarized in Table 2 and 3. The formation of the solventincorporated products **4** and **5** cannot be attributed to the subsequent secondary reaction of the dibromo compounds **2** with the protic solvents, since prolonged reaction did not cause any change in the ratio of the products.

The regiochemistry of the reactions of **1** (**1c-1h**) with BTMA Br_3 in protic solvents is in particularly interesting. Recently, Negoro et al.[22] reported that the bromochlorination of styrene derivatives with tetrabutylammonium dichlorobromate (TBA $BrCl_2$) in protic solvents (acetic acid and methanol) gave the corresponding bromo chloro adducts along with solventincorporated products in regioselective manner, and discussed the regiochemistry of these products obtained. Our experimental results showed similarly that the reactions involved an

Table 2. Bromination of **1** with BTMA Br_3 in Dichloromethane-Methanol

Substrate (1)		Reaction conditions: temp (℃)	time (h)	Product (2)	Yield[a] %	Mp (℃) or Bp (℃)/mmHg: Found	Reported
	(**1a**)	25	2	 (dl—) (**2a**)	26	oil	110—112/23[6]
				 (threo—) (**4a**)	46	oil	50/20[15]
Ph—CH=CH^2	(**1c**)	25	2	Ph—CHBr—CH_2Br (**2c**)	17	73—75	72[8]
				Ph—CH(OCH_3)—CH_2Br (**4c**)	80	108—109/20	65—66/2[16]
Ph—(CH_3)C=CH_2	(**1d**)	25	2	Ph—C(CH_3)Br—CH_2Br (**2d**)	5	oil	95—97/0.07[9]
				Ph—C(CH_3)OCH_3—CH_2Br (**4d**)	94	oil	—
Ph—CH=CH—Ph (E—)	(**1e**)	25	2	Ph—CHBr—CHBr—Ph (**2e**) (meso—)	6	238—240	237[10]
				Ph—CH(OCH_3)—CHBr—Ph (**4e**) (erythro—)	91	117—120	120—121[17]
Ph—CH=CH—COOH (E—)	(**1g**)	25	24	Ph—CHBr—CHBr—COOH (**2g**) (erythro—)	48[b]	—	197[12]
				Ph—CH(OCH_3)—CHBr—COOH (**4g**) (erythro—)	48[b]	—	183—184[18]
Ph—CH=CH—$COOCH_3$ (E—)	(**1h**)	25	24	Ph—CHBr—CHBr—$COOCH_3$ (**2h**) (erythro—)	31	117—119	117[12]
				Ph—CH(OCH_3)—CHBr—$COOCH_3$ (**4h**) (erythro—)	58	78—79	65—67[19]

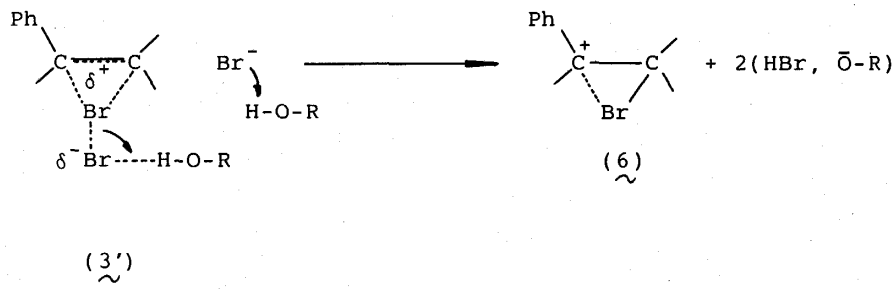
a) Yield of isolated product. b) Yield was based on ^{1}H NMR.

Table 3. Bromination of **1** with BTMA Br_3 in Dichloromethane-Acetic acid

Substrate (1)	Reaction conditions temp (℃)	time (h)	Product (2)	Yield[a] %	Mp(℃) or Bp(℃)/mmHg Found	Repor ed
 (**1a**)	25	2	 (dl—) (**2a**)	75	oil	110—112/23[6]
			 (threo—) (**5a**)	10	oil	109—110/12[20]
Ph—CH=CH_2 (**1c**)	25	2	Ph—CHBr—CH_2Br (**2c**)	79	73—75	72[8]
			Ph—CH($OCOCH_3$)—CH_2Br (**5c**)	13	oil	oil[21]
Ph—CH=CH—Ph (**1e**) (E—)	25	2	Ph—CHBr—CHBr—Ph (**2e**) (meso—)	69	238—240	237[10]
			Ph—CH($OCOCH_3$)—CHBr—Ph (**5e**) (erythro—)	19	102—104	100—100.7[17]
Ph—CH=CH—COOH (**1g**) (E—)	25	24	Ph—CHBr—CHBr—COOH (**2g**) (erythro—)	81	198—201	197[12]
			Ph—CH($OCOCH_3$)—CHBr—COOH (**5g**) (erythro—)	—		
Ph—CH=CH—$COOCH_3$ (**1h**) (E—)	25	24	Ph—CHBr—CHBr—$COOCH_3$ (**2h**) (erythro—)	83	117—119	117[12]
			Ph—CH($OCOCH_3$)—CHBr—$COOCH_3$ (**5h**) (erythro—)	—		

a) Yield of isolated product.

Rep. Inst. Advanced Material Study, Vol.2, No.1 (1988)



Scheme 3

attack of bromide ion or solvent molecule to a bridged benzylic carbonium ion intermediate (**6**), which should be introduced from a bromonium ion intermediate (**3′**) as shown in scheme 3. That is, the solvent molecules such as methanol and acetic acid attacked exclusively on the phenyl-substituted carbon atom of the double bond.

Experimental

1,2-Dibromo-1-phenylethane (2c). Typical procedure in dichloromethane at room temperature: To a solution of styrene (**1c**) (0.25g, 2.40mmol) in dichloromethane (20ml) was added BTMA Br_3 (0.94g, 2.40mmol). The mixture was stirred at room temperature for 2h. The orange color of the solution gradually changed to light yellow during the period. Sodium sulfite solution (5%, 20ml) was added to the solution and the mixture was washed with water (20ml). Dichloromethane layer was separated and dried on magnesium sulfate, filtered and evaporated in vacuo to give **2c** as colorless crystals; yield 0.62g (98%); Mp 73–75°C (methanol-water (1:1)) (Lit.,[8] 72°C).

Methyl 2,3-dibromo-3-phenylpropionate (2h). Typical procedure in chloroform under reflux: To a solution of methyl cinnamate (**1h**) (0.25g, 1.54mmol) in chloroform (20ml) was added BTMA Br_3 (0.60g, 1.54mmol). After the mixture was refluxed for 24h, aqueous sodium sulfite (5%, 20ml) was added to the solution; the mixture was washed with water (20ml). The chloroform layer was separated and dried on magnesium sulfate, filtered and then evaporated in vacuo to give residue which was purified by column chromatography on silica gel using benzene as solvent and eluant. Compound **2h** was obtained from the first eluate as colorless crystals; yield 0.42g (87%); Mp 117–119°C (hexane-benzene(1:1)) (Lit.,[12] Mp 117°C).

Reaction of 1c with BTMA Br_3 in dichloromethane-methanol. Typical procedure using methanol: To a solution of **1c** (0.25g, 2.40mmol) in methanol (50ml) was added dropwise a solution of BTMA Br_3 (0.94g, 2.40mmol) in dichloromethane (20ml) for 30 min, and the mixture was stirred for 1.5h until afading of the orange color took place. The reaction mixture was concentrated in vacuo, and to the residue obtained was added ether (50ml) and sodium sulfite solution (5%, 20ml); then, the ether extract was washed with water (20ml). The ether layer was dried on magnesium sulfate, filtered and evaporated to give residue which was

purified by column chromatography on silica gel using hexane as solvent and eluant. The first eluate gave **2c**; yield 0.10g (17%), and the second eluate gave 1-bromo-2-methoxy-2-phenylethane (**4c**) as colorless liquid; yield 0.42g(80%); Bp 108–109°C/20mmHg(Lit.,[16] Bp 66–65°C/2mmHg).

Reaction of 1d with BTMA Br_3 in dichloromethane-methanol. The procedure was similar to that described above. 1,2-Dibromo-2-phenylpropane (**2d**): colorless liquid (Lit.,[9] Bp 95–97/0.07mmHg); yield 5%. 1-Bromo-2-methoxy-2-phenyl-propane (**4d**): colorless liquid; yield 94%; ^{1}H NMR ($CDCl_3$) δ=1.75 (3H, s, CH_3), 3.19 (3H, s, OCH_3), 3.52 (1H, d, J=10.4Hz, -C*Ha*HbBr), 3.71 (1H, d, J=10.4Hz, -CHa*Hb*Br), 7.45 (5H, s, C_6H_5). Found: C, 52.31; H, 5.83%. Calcd for $C_{10}H_{13}OBr$: C, 52.42: H, 5.72%.

Reaction of 1h with BTMA Br_3 in dichloromethane-methanol. The procedure was similar to that described above. Compound **2h**: Colorless crystals; yield 31%. Methyl 2-bromo-3-methoxy-3-phenylpropionate (**4h**): colorless crystals; yield 58%; Mp 78–79°C (methanol-water (1:1)) (Lit.,[19] Mp 65–67°C); ^{1}H NMR ($CDCl_3$) δ=3.26 (3H, s, OCH_3), 3.90 (3H, s, $COOCH_3$), 4.31(1H, d, J=10.4Hz, Ph–C*H*-), 4.66 (1H, d, J=10.4Hz, -CHBr-), 7.52 (5H, s, C_6H_5). Found: C, 48.13; H, 4.76%. Calcd for $C_{11}H_{13}O_3Br$: C, 48.37; H, 4.80%.

Reaction of 1c with BTMA Br_3 in dichloromethane-acetic acid; Typical procedure using acetic acid: To a solution of **1c** (0.25g, 2.40mmol) in acetic acid (50ml) was added dropwise a solution of BTMA Br_3 (0.94g, 2.40mmol) in dichloromethane (20ml) for 30min, and the mixture was stirred for 1.5h until a fading of the orange color took place. The reaction mixture was concentrated in vacuo, and to the residue obtained was added hexane (50ml) and sodium sulfite solution (5%, 20ml); the hexane solution was washed with sodium hydrogensulfite (5%, 20ml) and then with water (20ml). The hexane layer was dried on magnesium sulfate, filtered and evaporated to give residue which was purified by column chromatography on silica gel using hexane as solvent and eluant. The first elate gave **2c**; yield 0.64g (79%); and the second eluate gave 1-acetoxy-2-bromo-1-phenyl-ethane (**5c**) as colorless liquid (Lit.,[21] oil); yield 0.08g (13%); ^{1}H NMR ($CDCl_3$) δ=2.14 (3H, s, $OCOCH_3$), 3.67 (1H, d, J=5.1Hz, C*Ha*HbBr), 3.69 (1H, d, J=7.50Hz, CHa*Hb*Br), 6.12 (1H, br.t, Ph-C*H*-), 7.48 (5H, s, C_6H_5). Found: C, 49.33; H, 4.54%. Calcd for $C_{10}H_{11}O_2Br$: C, 49.41; H, 4.56%.

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