

Bromination of Alkenes and Related Compounds by Use of Benzyltrimethylammonium Tribromide in Aprotic and Protic Solvents

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Bromination of Alkenes and Related Compounds by Use of Benzyltrimethylammonium Tribromide in Aprotic and Protic Solvents¹⁾

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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 Br₃) in aprotic solvents such as dichloromethane and chloroform gave 1,2-dibromo adducts in fairly good yields. The reaction of 1 with BTMA Br₃ 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 tribromide⁴⁾ 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 several alkenes by use of tetrabutylammonium tribromide (TBA Br₃). In this paper, we wish to report on the bromination of much more alkenes and related compounds (1) with benzyltrimethylammonium tribromide (BTMA Br₃), more effective brominating agent than TBA Br₃, in aprotic and protic solvents.

Results and Discussion

The reaction of 1 with BTMA Br₃ 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 Br₃ 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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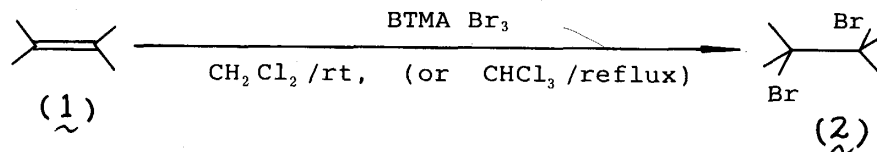
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Table 1. Bromination of **1** with BTMA Br₃ in Aprotic Solvent

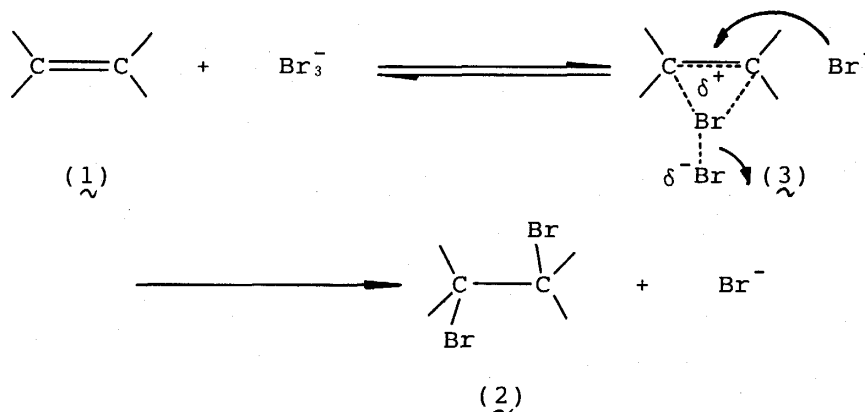
Substrate (1)	Reaction conditions		Solvent	Product (2)	Yield ^{a)} %	Mp (°C) or Bp (°C)/mmHg	
	temp (°C)	time (h)				Found	Reported
 (1a)	25	2	CH ₂ Cl ₂	 (2a) (dl-)	84	oil	110–112/23 ⁶⁾
 (1b)	25	2	CH ₂ Cl ₂	 (2b) (dl-)	91	oil	70/0.15 ⁷⁾
Ph-CH=CH ₂ (1c)	25	2	CH ₂ Cl ₂	Ph-CHBr-CH ₂ -Br (2c) (dl-)	98	73–75	72 ⁸⁾
Ph-(CH ₃)C=CH ₂ (1d)	25	2	CH ₂ Cl 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 ₂ Cl ₂	Ph-CHBr-CHBr-Ph (2e) (meso-)	83	238–240	237 ¹⁰⁾
Ph-CH=CH-CHO (1f) (E-)	25	10	CH ₂ Cl ₂	Ph-CHBr-CHBr-CHO (2f) (erythro-)	58	oil	45–48 ¹¹⁾
Ph-CH=CH-COOH (1g) (E-)	25	10	CH ₂ Cl 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 ₃ OCO-CH=CH-COOCH ₃ (1i) (E-)	reflux	24	CHCl ₃	CH ₃ OCO-CHBr-CHBr-COOCH ₃ (2i) (meso-)	53	64–65	61.5–62 ¹³⁾
CH ₃ OCO-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 Br₃ gave dl-1, 2-dibromocyclohexane (2a) and dl-1, 2-dibromocyclooctane (2b), respectively. The complete anti-selective dibromo addition of 1 with BTMA Br₃ 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.




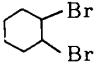
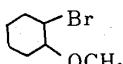
Scheme 2

Although the reaction of dimethyl fumarate (1i) with BTMA Br₃ 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 Br₃ 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 solvent-incorporated 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.


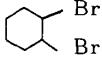
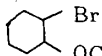
The regiochemistry of the reactions of 1 (1c-1h) with BTMA Br₃ in protic solvents is in particularly interesting. Recently, Negoro et al.²²⁾ reported that the bromochlorination of styrene derivatives with tetrabutylammonium dichlorobromate (TBA BrCl₂) in protic solvents (acetic acid and methanol) gave the corresponding bromo chloro adducts along with solvent-incorporated 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 Br₃ in Dichloromethane-Methanol

Substrate (1)	Reaction conditions		Product (2)	Yield ^{a)} %	Mp (°C) or Bp (°C)/mmHg	
	temp (°C)	time (h)			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 ₂ Br (2c)	17	73–75	72 ⁸⁾
			Ph-CH(OCH ₃)-CH ₂ Br (4c)	80	108–109/20	65–66/2 ¹⁶⁾
Ph-(CH ₃)C=CH ₂ (1d)	25	2	Ph-C(CH ₃)Br-CH ₂ Br (2d)	5	oil	95–97/0.07 ⁹⁾
			Ph-C(CH ₃)OCH ₃ -CH ₂ Br (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⁾

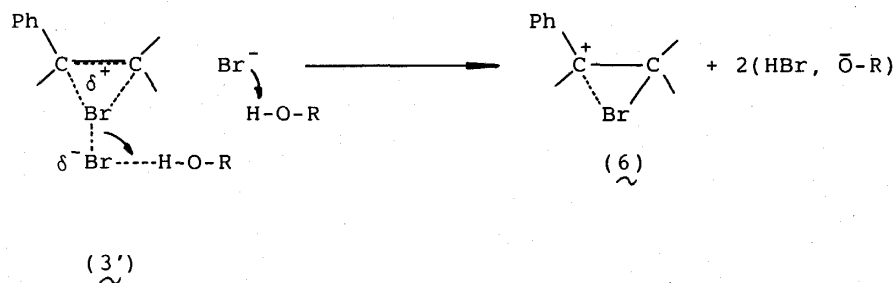
a) Yield of isolated product. b) Yield was based on ¹H NMR.

Table 3. Bromination of **1** with BTMA Br₃ in Dichloromethane-Acetic acid

Substrate (1)	Reaction conditions		Product (2)	Yield ^{a)} %	Mp (°C) or Bp (°C)/mmHg	
	temp (°C)	time (h)			Found	Reported
 (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 ₂ Br (2c)	79	73–75	72 ⁸⁾
			Ph-CH(OCOCH ₃)-CH ₂ Br (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.

Bromination by Use of Benzyltrimethyl ammonium Tribromide



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 Br₃ (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 Br₃ (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 Br₃ in dichloromethane-methanol. Typical procedure using methanol: To a solution of 1c (0.25g, 2.40 mmol) in methanol (50 ml) was added dropwise a solution of BTMA Br₃ (0.94g, 2.40 mmol) in dichloromethane (20 ml) for 30 min, and the mixture was stirred for 1.5h until fading of the orange color took place. The reaction mixture was concentrated in vacuo, and to the residue obtained was added ether (50 ml) and sodium sulfite solution (5%, 20 ml); then, the ether extract was washed with water (20 ml). 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 Br₃ 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%; ¹H NMR (CDCl₃) δ=1.75 (3H, s, CH₃), 3.19 (3H, s, OCH₃), 3.52 (1H, d, J=10.4Hz, -CHaHbBr), 3.71 (1H, d, J=10.4Hz, -CHaHbBr), 7.45 (5H, s, C₆H₅). Found: C, 52.31; H, 5.83%. Calcd for C₁₀H₁₃OBr: C, 52.42; H, 5.72%.

Reaction of 1h with BTMA Br₃ 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); ¹H NMR (CDCl₃) δ=3.26 (3H, s, OCH₃), 3.90 (3H, s, COOCH₃), 4.31(1H, d, J=10.4Hz, Ph-CH-), 4.66 (1H, d, J=10.4Hz, -CHBr-), 7.52 (5H, s, C₆H₅). Found: C, 48.13; H, 4.76%. Calcd for C₁₁H₁₃O₃Br: C, 48.37; H, 4.80%.

Reaction of 1c with BTMA Br₃ 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 Br₃ (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%); ¹H NMR (CDCl₃) δ=2.14 (3H, s, OCOCH₃), 3.67 (1H, d, J=5.1Hz, CHaHbBr), 3.69 (1H, d, J=7.50Hz, CHaHbBr), 6.12 (1H, br.t, Ph-CH-), 7.48 (5H, s, C₆H₅). Found: C, 49.33; H, 4.54%. Calcd for C₁₀H₁₁O₂Br: C, 49.41; H, 4.56%.

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