Bromochlorination of Conjugated Dienes with Dichlorobromate(1-) Ion

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Synopsis. The reactions of some conjugated dienes with tetrabutylammonium dichlorobromate (1-) (**1**) were found to give the bromochloroalkenes in good yields, 1,2-addition predominating. Appreciable *anti*-Markownikoff adduct was obtained from 1,3-butadiene. An $AdEC_2$-type mechanism is suggested.

The ratio of 1,2- to 1,4-addition of bromine (and bromine chloride) to conjugated dienes has been shown to be markedly dependent on the brominating (and bromochlorinating) agents employed.[1,2] The predominance of 1,2-addition was observed for the reaction with a tribromide ion.[2,3] However, no studies have been carried out on the reaction with tetrabutylammonium dichlorobromate (1-) (**1**) as a bromochlorinating agent. We have reported that the additions of **1** to alkenes are strikingly different from that of molecular bromine chloride (BrCl).[4,5] In this paper, we will report the bromochlorination of some conjugated dienes with **1**.

Results and Discussion

The reaction of **1** with 1, 3-butadiene (**2a**), 2-methyl-1, 3-butadiene (**2b**), *cis*- and *trans*-1,3-pentadienes (**2c** and **2d**), and cyclopentadiene (**2e**) in dichloromethane gave the corresponding bromochloroalkenes in good yields (Table 1). In the cases of **2b** and **2e**, a small amount of 1, 4-dichloro adducts (**6**) was isolated.

TABLE 1. REACTIONS OF DIENES WITH **1**[a]

Dienes	1,2-Adduct[b]		1,4-Adduct[b]		Yield/%[c]
	3	**4**	**5**	**6**	
2a	99.0[d]		1.0		98
2b	78.6	11.0	9.2	1.2	98
2c	66.2	29.4	4.4		99
2d	87.1	5.1	7.8		99
2e	93.2		0.9	5.9[e]	93

a) Reactions were carried out with 30 mmol of **1**, 36 mmol of diene, and 100 ml of CH_2Cl_2 at −12 °C. b) The products are identified as follows: from **2a**, 4-bromo-3-chloro-1-butene (**3a**), 3-bromo-4-chloro-1-butene (**3a′**), *trans*-1-bromo-4-chloro-2-butene (**5a**); from **2b**, 4-bromo-3-chloro-3-methyl-1-butene (**3b**), 4-bromo-3-chloro-2-methyl-1-butene (**4b**), 1-bromo-4-chloro-2-methyl-2-butene (**5b**),1,4-dichloro-2-methyl-2-butene (**6b**); from **2c** and **2d**, *cis*- and *trans*-5-bromo-4-chloro-2-pentenes (**3c** and **3d**), *threo*- and *erythro*-4-bromo-3-chloro-1-pentenes (**4c** and **4d**), *trans*-1-bromo-4-chloro-2-pentene (**5c**=**5d**); from **2e**, *trans*-4-bromo-3-chlorocyclopentene (**3e**), *cis*-3-bromo-5-chlorocyclopentene (**5e′**), *cis*- and *trans*-3,5-dichlorocyclopentenes (**6e′** and **6e**). Percentages are normalized to 100%. c) Based on **1**. Total bromochloralkene yields determined by GLC using 1,2-dibromobutane as an internal standard. d) **3a**:**3a′**=84:16. e) **6e**:**6e′**=35:65.

Furthermore, in all cases, the yield of 1, 4-bromochloro adducts (**5**) decreased by the prolonged reaction time, producing **6**. It was shown that **6** is also formed upon treatment of **5** with tetrabutylammonium chloride in CH_2Cl_2. Therefore, it probably arises by the halogen-exchange reaction of 5 with generating chloride ions in the reaction system. Control experiments showed that all the 1, 2-bromochloro adducts (**3** and **4**) are stable under the reaction conditions.

A common characteristic of the present reaction is the highly selective formation of the 1, 2-bromochloro adducts. Moreover, the addition to the 3, 4-bond in **2c**, **2d**, and **2e** gave completely *anti*-stereospecific products (**4c**, **4d**, and **3e**).

In the case of **2a**, the reaction gave a mixture of 4-bromo-3-chloro-1-butene (**3a**) and 3-bromo-4-chloro-1-butene (**3a′**) as the 1, 2-adducts.

$$\underset{\textbf{2a}}{CH_2{=}CHCH{=}CH_2} + \textbf{1} \longrightarrow \underset{\textbf{3a}, 84\%}{CH_2BrCHClCH{=}CH_2} + \underset{\textbf{3a′}, 16\%}{CH_2ClCHBrCH{=}CH_2}$$

Fig. 1.

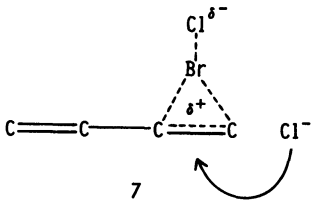
When the reaction of **2a** with **1** was carried out in the presence of a free radical inhibitor, 2,6-di-*t*-butyl-4-methylphenol or oxygen, the product composition did not change within experimental errors. This result indicates that the lack of regiospecificity cannot be ascribed to a radical process.[6]

The reaction of **2a** with **1** was investigated in a variety of solvents. The reaction in chloroform, dichloromethane, 1,2-dichloroethane, acetic anhydride, and nitromethane gave nearly the same ratio of **3a** and **3a′** (84:16) within an experimental error (±1%). The amount of the 1,4-adduct (**5a**) was less than 2% in all the solvents employed. A similar solvent independency on the regiochemistry has been previously observed for the reaction of 1-phenylpropenes with **1**.[5]

In contrast to the present results, the high preference of 1,4-addition has been observed for the reaction of BrCl (and Br_2) with conjugated dienes.[1,2,7] Furthermore, dependence of the 1,2- *vs.* 1,4-addition of Br_2 to **2a** on solvent polarity has been reported.[7] We have also found that BrCl reacted with **2a** to give a mixture of **3a** and **5a** (**3a**:**5a**=27:73). None of the *anti*-Markownikoff adduct (**3a′**) was detected by ^{13}C-NMR analysis of the product mixture.

Thus, the addition to dienes appeared to be very different in reactions with **1** and with BrCl. Therefore, the present reaction cannot be explained on the basis of any accepted mechanism involving a bromonium ion intermediate for the addition of BrCl (and Br_2).[2,3] We would like to suggest another possible mechanism

which involves the attack of chloride ions on a three-center bound π complex-type intermediate (**7**) with little delocalization of the positive charge across the allylic system: a similar mechanism has been suggested for the addition of **1** to alkenes.[4,5]



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Experimental

The NMR and mass spectra were recorded on a JEOL JNM FX-60Q and JMS-D-300 mass spectrometer, respectively. The GLC analyses were performed on a Yanako G-180 Gas Chromatograph with a Silicone SE-30 (2.5%)-Chromosorb WAW DMCS (2 m) column at 50°C with helium as a carrier gas (35 ml/min). All the organic starting materials were distilled before use.

Reaction of **2a** *with* **1**. Details of the reaction have been reported previousiy.[4] To a solution of **2a** (3.0 ml, 36 mmol) in CH_2Cl_2 (100 ml) was added **1** (11.8 g, 30 mmol) at −12°C over 20 min with stirring. After the usual work-up, distillation afforded 3.83 g (75.3%) of a mixture of **3a** and **3a'**: Bp 46—48°C/26 mmHg (1 mmHg=133.322 Pa); MS M$^+$ at m/z=168, 170, 172 (100:132:35); Found: m/z 167.9330. Calcd for C_4H_6BrCl: M, 167.9342. ^{13}C-NMR showed a 84:16 mixture of **3a** and **3a'**, respectively. ^{13}C-NMR ($CDCl_3$) (an asterisk indicates **3a'**) δ=35.0, 47.0*, 51.1*, 60.2, 119.7, 135.2, 135.5*. Although attempts to separate **3a** and **3a'** were unsuccessful, these assignments were supported for dibromo and dichloro analogs as follows: 3,4-dichloro-1-butene, ^{13}C-NMR ($CDCl_3$) δ=47.3, 60.1, 119.7, 134.8; 3,4-dibromo-1-butene, ^{13}C-NMR ($CDCl_3$) δ=34.5, 50.5, 119.8, 136.0. The structure of the minor 1,4-adduct (**5a**) was verified by comparison of the spectra of the sample prepared by the reaction of **2a** with BrCl.[2] **5a**, ^{1}H-NMR ($CDCl_3$) δ=3.90—4.10 (4H, m, CH_2Br and CH_2Cl), 5.90—6.01 (2H, m, CH=CH); ^{13}C-NMR ($CDCl_3$) δ=30.9, 43.5, 130.3 (2C).

Reaction of **2b—e** *with* **1**. The reactions were carried out similarly to those of **2a**. The relative amounts of the products were determined by the peak areas of GLC (Table 1). All the reaction products were identified by comparing GLC and NMR spectra with the authentic samples prepared by the reaction of BrCl with these dienes.[1,2] The ^{1}H-NMR spectra of the products correspond well with those reported in the literatures.[1,2]

Reaction of **2a** *with* **1** *Under Various Conditions*. When **2a** was treated with **1** in CH_2Cl_2 as described above, O_2 was bubbled during the reaction. ^{13}C-NMR analysis of the residue showed an 85:15 mixture of **3a** and **3a'**, respectively. The reaction was carried out with 12 mmol of **2a**, 10 mmol of **1**, and 3 mmol of 2,6-di-*t*-butyl-4-methylphenol in CH_2Cl_2 (50 ml). After the usual work-up, ^{13}C-NMR analysis of the residue showed an 86:14 mixture of **3a** and **3a'**, respectively.

To 12 mmol of **2a** in 50 ml of the solvent ($CHCl_3$, CH_2Cl_2, CH_2ClCH_2Cl, $(CH_3CO)_2O$, and CH_3NO_2) was added 10 mmol of **1** at −12°C over 5 min with stirring. After the usual work-up, the residues were subjected to GLC and ^{13}C-NMR analyses. In all cases, GLC analysis showed over 98% of the 1, 2-adducts. ^{13}C-NMR analysis showed nearly the same ratio of **3a** and **3a'** (84:16) within an experimental error (±1%).

Halogen Exchange Reaction. To 5 mmol of **5a** in CH_2Cl_2 (25 ml) was added 10 mmol of tetrabutylammonium chloride and the mixture was allowed to stand for 24 h at 0°C with stirring. After the usual work-up, GLC analysis showed the composition to be: **5a**, 5%; *trans*-1,4-dichloro-2-butene (**6a**), 95%. Similar treatment of **5b—e** and **5e'** with chloride ions gave over 95% of the corresponding 1,4-dichloro compounds.

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