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Reactions of Molecular Bromine Chloride and Amine–Bromine Chloride Complexes with Cyclopentadiene

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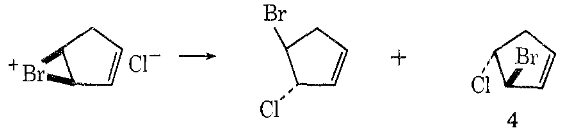
A survey of the literature reveals that there has been one study of the addition of bromine chloride to an allene,[1] and many investigations of the addition of this electrophile to olefins,[2a–e] but that no studies on the addition of bromine chloride to conjugated dienes have been undertaken. Earlier studies[2b–e] established that molecular bromine chloride adds to olefins via a bromonium ion–chloride ion ion pair, in which the rate-determining step involves formation of this ion pair. In the most recent investigation,[2a] Bellucci et al. compared the addition of bromine chloride with that of pyridine–bromine chloride complex, and concluded that the second, product-determining step is rate determining in the case of the complex.[3]

It seemed to us that it would be of interest to investigate the reaction of these halogenating agents with the conjugated diene cyclopentadiene. We chose cyclopentadiene because it offered the possibility of both cis and trans 1,2 and 1,4 addition, and because we had recently studied the additions of chlorine[4] and bromine[5] to this diene. In the present study we were particularly interested in comparing the addition of bromine chloride with amine–bromine chloride complexes, since if these reagents do involve different rate-determining steps they would likely produce a different mixture of stereoisomeric bromochlorocyclopentenes.

The possibility of anti-Markovnikov addition was also considered, since chloride ion could add to either of the carbons (bonded to bromine) as illustrated in the following reaction.



1 Markovnikov

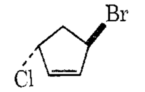
4 anti-Markovnikov

Delocalization of the charge (resulting in unsymmetrical bridging, i.e., weaker bonding between carbon 3 and bromine) is probable here since a secondary carbonium ion would result.[6] Extensive delocalization should favor cis attack of chloride ion (as in the case of the chlorination of cyclopentadiene[4]) to give cis 1,2 addition as shown below.

5

Results and Discussion

The addition of bromine chloride and amine–bromine chloride complexes to cyclopentadiene resulted in the formation of only three isomeric bromochlorocyclopentenes: *trans*-4-bromo-3-chlorocyclopentene (1), *trans*-3-bromo-5-chlorocyclopentene (2), and *cis*-3-bromo-5-chlorocyclopentene (3). The ratios and yields of these isomers formed under various conditions are shown in Table I.



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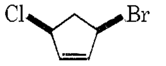


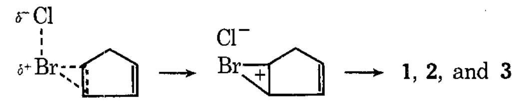
3

The data in Table I show that all of the amine–bromine chloride complexes react with cyclopentadiene to give very similar mixtures of bromochlorocyclopentenes, and that the product composition from the complexes is considerably different from that of bromine chloride. In particular, bromine chloride gives significantly more cis 1,4 addition

Table I
Addition of Bromine Chloride and Amine–Bromine Chloride Complexes to Cyclopentadiene

			Bromochlorocyclopentenes			
Halogenating agent	Solvent	Temp, °C	1	2	3	Yield, %
BrCl	C_5H_{12}	−15	34	18	48	78
BrCl	CH_2Cl_2	−15	22	15	63	68
BrCl	CCl_4	−15	25	12	63	76
			27	15	58	
Pyridine–BrCl	C_5H_{12}	−15	53	21	26	81
Pyridine–BrCl	CH_2Cl_2	−15	90	4	6	78
Pyridine–BrCl	CCl_4	−15	51	22	27	86
BrCl	CH_2Cl_2	25	25	15	60	64
Pyridine–BrCl	CH_2Cl_2	25	79	10	11	72
Quinoline–BrCl	CH_2Cl_2	25	63	16	21	83
3,5-Lutidine–BrCl	CH_2Cl_2	25	83	9	8	74
2,6-Lutidine–BrCl	CH_2Cl_2	25	73	13	14	108

(**3**), and the complexes give more trans 1,2 addition (**1**). In the case of bromine chloride the transition state (rate-determining step) leading to the ion pair can be described as follows.

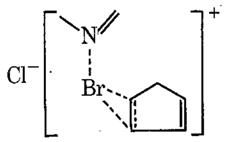


In proceeding from the transition state to the ion pair the chloride ion has been generated above the bromine atom. Collapse to product (apparently a rapid reaction) can occur with least reorientation of the ion pair by cis attack of the chloride ion on the 1 carbon atom to give **3** (cis 1,4 addition), since all that is required is that the chloride ion move over to the adjacent π lobe. Trans 1,4 addition (to give **2**) would require the most extensive reorientation. The product ratios seem to reflect the energy requirements for reorientation of the ion pair.

In the case of the amine–bromine chloride complexes the structure of the electrophile is uncertain,[7] but we suspect that it is the $C_5H_5N^+Br$ ion (in the case of pyridine) whose formation is shown in the following reaction.

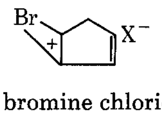
$$C_5H_5N-\overset{\delta+}{Br}\cdots\overset{\delta-}{Cl} \rightleftharpoons C_5H_5N^+-Br\ Cl^-$$

On the basis of the studies by Bellucci et al.[2a,8] and related studies of our own,[9] we suspect that the electrophile and cyclopentadiene react to form an ion pair in which bonding is maintained between the nitrogen and the halogen atom, as shown below.



In this ion pair the chloride ion will certainly not be formed above the plane of the cyclopentadiene ring (as occurred with BrCl) because of steric interaction with the ring of the amine and the adjacent π bond, but will be situated along the charged "side" of the cation (location of the anion will depend on the charge distribution). The unusually rapid attack at carbon 3 may occur because the chloride is situated close to this carbon in the ion pair and attack at this position requires least reorientation of the ion pair. On the other hand, the product-determining step may be rate determining (as suggested by Bellucci et al. for the cyclohexenes), and attack occurs at carbon 3 because the activation energy is lower for attack at this carbon than at carbons 4 or 1 (cis or trans). Our data simply do not allow us to choose between these alternatives.

It is also of interest to compare the additions of bromine chloride and bromine[5] to cyclopentadiene, since both of these additions involve identical bromonium ions in the intermediate ion pairs, as shown below



where X^- is Cl^- from bromine chloride, and Br^- (undoubtedly Br_3^- also, depending on conditions) in bromination. A summary of the previous study on bromination (averaging the percentages in the three solvents) is: *trans*-3,4-dibromocyclopentene (38%); *trans*-3,5-dibromocyclopentene (25%); and *cis*-3,5-dibromocyclopentene (37%). In comparison with bromine chloride addition (an average of the results), bromination gives approximately 20% less cis 1,4 addition, and 10% more trans 1,2 and 10% more trans 1,4 addition. We interpret these differences in the following manner. The large bromide ion (or larger tribromide ion) experiences steric hindrance (interaction with the nonbonded electrons of the bromine in the bromonium ion) as it approaches the 3 carbon atom, leading to cis 1,4 addition.[10] This type of interference is not experienced during attack at the 1 carbon (trans) or at the 3 carbon (trans). On the other hand, the chloride ion, being considerably smaller, experiences no steric hindrance during attack at any of the three positions.

The principal difference that surfaces in a comparison of the additions of bromine chloride and chlorine to cyclopentadiene relates to the fact that chlorination gives (averaging the results from the three solvents) extensive cis 1,2 addition (55%). Absence of cis attack[11] by the chloride ion (from bromine chloride) at the 3 carbon to give **5** can result from either steric hindrance between the bromine atom (in the bromonium ion) and the incoming chloride ion, or from sufficiently high electron density between the bromine and the 3 carbon atom to discourage attack at this position. From our experience with the bromination of the 2,4-hexadienes[5,12] we would anticipate extensive delocalization of charge in the bromonium ion of cyclopentadiene. Therefore we conclude that steric hindrance between the bromine atom and chloride ion is probably the primary factor involved in the failure of the chloride ion to undergo cis 1,2 attack.

No anti-Markovnikov product was observed.[11] Absence of this product implies that attack at the allylic carbon and the vinyl carbon is much faster than at the secondary 4 carbon, both in the cases of bromine chloride and the amine–bromine chloride complexes. This result is somewhat surprising inasmuch as carbons 3 and 4 are both secondary.[13]

Experimental Section

Materials. All solvents and reagents were obtained commercially in high purity, and were used without further purification unless indicated. Cyclopentadiene was prepared from its dimer. The amine–bromine chloride complexes were prepared according to the procedure of Williams.[14] Bromine chloride was prepared by adding an equimolar amount of bromine to a chlorine–carbon tetrachloride solution (0.5–1.0 *M*).

Reaction Conditions. The electrophiles were added to cyclopentadiene (mole fraction of 0.02 in diene) in the appropriate solvent (well stirred) and at the indicated temperature. The total reaction volumes varied from 10 to 25 ml. Sufficient halogen was added to consume 10–20% of the diene, and yields were based on the amount of halogen used. Each reaction was run at least twice and results were within ±2%.

The amine–bromine chlorides were insoluble in carbon tetrachloride or pentane and reacted slowly (approximately 1 hr to react at −15°). Reactions of the amine–bromine chlorides in dichloromethane and bromine chloride in all solvents occurred instantly.

Isolation of the Isomers. *trans*-4-Bromo-3-chlorocyclopentene (**1**) was isolated by fractional distillation, bp 50–55° (4 mm), from a large-scale addition of pyridine–bromine chloride[15] to cyclopentadiene. It was further purified by recrystallization from low-boiling petroleum ether at −70°.

cis-3-Bromo-5-chlorocyclopentene (**3**) was obtained by successive recrystallizations (−70°, low-boiling petroleum ether) of the product from the addition of pyridine–bromine chloride to cyclopentadiene in carbon tetrachloride. Separation of the cis isomer from the other isomers is possible, since the cis isomer has a higher melting point.

All attempts to isolate pure *trans*-3-bromo-5-chlorocyclopentene (**2**) failed.

Establishment of the Structures of the Isomers. Gas chromatographic analyses of the products from the addition of bromine chloride and the amine–bromine chlorides to cyclopentadiene showed only three peaks (other than dichlorides and dibromides) under all analysis conditions (various column packings and temperatures). The three peaks had retention times of 4.4, 5.4, and 8.1 min under the following conditions: 6 ft × 0.25 in. column packed with 2.5% SE-30 on 60–80 mesh Chromosorb W (AW-DMCS) at 50° at a flow rate of 55 ml/min (N_2).

The compounds responsible for peaks 1 and 3 were assigned the structures of **1** and **3** primarily on the basis of NMR analyses of the pure isomers. The spectra assigned to **1** and **3** closely resembled those of the corresponding cyclopentadiene dibromides[5] and dichlorides.[4] Thus, the compound assigned structure **1** exhibited two absorptions assignable to methine hydrogens, a doublet (5.5 Hz) at 4.48 ppm (adjacent to methylene) and a broad singlet at 5.06 ppm (adjacent to vinyl). Absorptions for the methylene hydrogens also occur separately, a doublet at 2.76 ppm and a doublet of doublets at 3.35 ppm. The absorptions centered at 2.76 and 3.35 ppm each exhibit the geminal coupling at 18 Hz with the additional splitting of 5.5 Hz occurring in the 3.35-ppm absorption. The compound assigned structure **3** was identified particularly by absorptions of its methylene hydrogens. A pair of well-separated double triplets (2.57 and 3.14 ppm) was observed. The double triplet at 2.57 showed a small coupling (2.5 Hz) and that at 3.14 a larger coupling (6.6 Hz) consistent with their trans and cis vicinal relationship to the methine hydrogens, respectively (both double triplets show the geminal coupling of 16 Hz). The methine hydrogens have nearly the same chemical shift in **3** and appear as an unresolved multiplet. The 60-MHz spectral data (CCl_4) for **1** and **3** are summarized as follows: **1**, δ 2.76 [br d, 1, *cis*-C(Br)C(**H**)H, $J_{5,5'} = 18$ Hz], 3.35 (dd, 1, *trans*-C(Br)C(**H**)H, $J_{5,5'} = 18$, $J_{4,5} = 5.5$ Hz], 4.48 [d, 1, $CH_2C(\mathbf{H})Br$, $J_{4,5} = 5.5$ Hz], 5.06 [br s, 1, CH=CHC(**H**)Cl], 5.99 [br s, 2, CH=CH); **3**, δ 2.57 [dt, 1, *cis*-C(Cl,Br)C(**H**)H, $J_{4',4} = 16$, $J_{4',3(5)} = 2.5$ Hz], 3.14 [dt, 1, *trans*-C(Cl,Br)C(**H**)H, $J_{4,4'} = 16$, $J_{4,3(5)} = 6.6$ Hz], 4.92 (m, 2, CHBr and CHCl), 6.06 (m, 2, CH=CH)

The compound responsible for peak 2 was assigned the structure *trans*-3-bromo-5-chlorocyclopentene (**2**) on the basis of the following information. NMR analysis: Although a pure sample of **2** was not obtained, an NMR spectrum was prepared of a mixture of **2** (30%) and **1**, which indicated absorptions at 2.8, 5.0, and 6.0 ppm. These absorptions are consistent with the spectrum expected for **2** on the basis of that observed for the corresponding dibromide[5] and dichloride.[4] In particular, the spectrum in the methylene region showed absorptions clustered near 2.8 ppm which would be consistent with the near chemical shift equivalency expected for the methylene hydrogens. Unambiguous synthesis: We have shown previously[4] that *cis*-3,5-dichlorocyclopentene and *trans*-3,5-dichlorocyclopentene can be prepared from the corresponding dibromides by treatment with lithium chloride in DMSO. Therefore, when *trans*-3,5-dibromocyclopentene was treated with a *limited* (equimolar) amount of lithium chloride, VPC analysis showed that **3** was the only isomeric bromochlorocyclopentene that was formed. (*cis*-3,5-Dichlorocyclopentene and unreacted dibromide were also present.) Correspondingly, treatment of *cis*-3,5-dibromocyclopentene with limited lithium chloride gave a compound which had an identical retention time with that of **2**. (The expected dichloride and dibromide mixture was also formed.) By analogy to the reaction of the trans dibromide, we conclude that *trans*-3-bromo-5-chlorocyclopentene (**2**) is formed in the reaction of the cis dibromide. Formation upon rearrangement of **1** and **3**: When authentic **1** and **3** were refluxed in ether, containing a catalytic amount of zinc bromide, the compound assigned structure **2** was formed in largest amounts (percentages): **1** (15), **2** (46), and **3** (38). Previous experience with the equilibration of the dibromides from cyclopentadiene and 1,3-cyclohexadiene suggests that **2** should be the thermodynamically stable isomer, since in our previous studies the trans 1,4-dibromides were more stable.

Stability of the Products to Reaction and Analysis Conditions. When the amine–bromine chlorides react with cyclopentadiene, pyridine is formed. It seemed possible that pyridine might react with the bromochlorocyclopentenes and thus distort the composition of the product. We established that this did not occur by stirring a mixture of **1**, **2**, and **3** (of known composition) with pyridine under reaction conditions and observing that no change in composition or material balance occurred.

We made this assumption that rearrangement of the isomers did not occur during VPC analysis of the bromochlorocyclopentenes, since we previously confirmed that rearrangement did not occur under identical conditions with many similar systems (dibromides and dichlorides of butadiene, isoprene, piperylene, isomer 2,4-hexadienes, and cyclopentadiene).

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Registry No.—**1**, 54384-85-9; **2**, 54384-86-0; **3**, 54384-87-1; BrCl, 13863-41-7; pyridine–BrCl, 21300-57-2; quinoline–BrCl, 54384-82-6; 3,5-lutidine–BrCl, 24068-43-7; 2,6-lutidine–BrCl, 24068-41-5; cyclopentadiene, 542-92-7.

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(3) Bellucci and coworkers have suggested that the rate-determining step for other amine–halogen complexes (e.g., $C_5H_5NBr_2$) is also the product-forming step. See P. Barili, G. Bellucci, F. Marioni, I. Morelli, and V. Scartoni, *J. Org. Chem.*, **37**, 4354 (1972).

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(6) We found that there was sufficient delocalization of charge in the intermediate bromonium ions in the case of the 2,4-hexadienes to give a nonstereospecific addition, but not with piperylene, since delocalization in the former involves formation of a secondary carbonium ion, whereas the latter would involve a primary carbonium ion.

(7) X-Ray defraction studies on pyridine–iodine chloride show that the N–I–Cl bonding system is linear with the N–I bond being nearly a typical covalent bond and the N–Cl bond being much longer than anticipated for a covalent bond, suggesting that charges have developed as shown below.

$$C_5H_5\overset{\delta+}{N}—I\cdots\overset{\delta-}{Cl}$$

For a detailed discussion of the bonding in these charge-transfer complexes see O. Hassel and C. Romming, *Q. Rev., Chem. Soc.*, **16**, 1 (1962). The following ionization of pyridine (py) bromine chloride in polar solvents has been confirmed: $2pyBrCl \rightleftharpoons py_2Br^+ BrCl_2^-$. See S. G. W. Ginn, I. Haque, and J. L. Wood, *Spectrochim. Acta, Part A*, **24**, 1531 (1968). Conceivably the electrophile is the py_2Br^+ ion. Also the undissociated charge-transfer complex may be sufficiently electrophilic to attack the π bond.

(8) This type of bonding in the ion pair is suggested by Bellucci and coworkers[2a] in the case of the substituted cyclohexenes. We see no reason to expect different behavior on the part of the electrophile with cyclopentadiene.

(9) In a recent study of ours on the reaction of olefins with Br_2, NBS, and NBA in a mixture of CH_3OH and DMSO, we found that the greater nucleophilicity (toward opening of the bromonium ion) of DMSO became apparent with the N–Br systems. We interpreted these results as meaning that with NBS and NBA there is bonding between nitrogen and bromine in the bromonium ions, and that the stronger nucleophile DMSO is more effective in this energy-demanding (rate-determining) step than is CH_3OH. See V. L. Heasley, G. T. Heasley, R. A. Skidgel, and D. Strickland, *J. Org. Chem.*, **39**, 3953 (1974).

(10) We have already suggested that steric hindrance between the bromide ion and the bromine atom of the bromonium ion accounts for the fact that there is less cis 1,4 addition with cyclopentadiene than 1,3-cyclohexadiene.[5]

(11) Neither products **4** or **5** were detected in the VPC or NMR analyses. It is possible that one or both of these compounds were present in small amounts and not detected. Unambiguous syntheses would provide the only method of unequivocally confirming their absence.

(12) In the case of the isomeric 2,4-hexadienes, the 1,2 addition was nonstereospecific.[5] On the basis of this observation we concluded that the bond between bromine and the adjacent allylic carbon (in the bromium ion) was sufficiently weak (resulting from delocalization of charge) to permit rotation around this C–C bond. Since delocalization can occur in cyclopentadiene to give a *secondary carbonium ion*, as with the 2,4-hexadienes, we conclude that there is unsymmetrical bridging in the bromonium ion of cyclopentadiene.

(13) Dalton and Davis observed only the Markovnikov product in the addition of BrOH (NBS in DMSO and H_2O) to the 2,4-hexadienes. Also they did not observe any 1,4 addition and concluded that the charge was localized on the allylic carbon, with weak bonding to bromine. See D. R. Dalton and R. M. Davis, *Tetrahedron Lett.*, 1057 (1972). Since all our solvents are far less polar we would anticipate much greater delocalization of charge with our system and, hence, greater equalization of reactivities at the two secondary carbons, 3 and 4.

(14) D. M. Williams, *J. Chem. Soc.*, 2783 (1931).

(15) **1** was isolated from the addition of pyridine–bromine chloride rather than from bromine chloride because the product from the former was not contaminated with dibromides.