Evidence for Different Addition Mechanisms in the Bromochlorination of 3-*tert*-Butylcyclohexene with Bromine Chloride and with Monopyridinebromine(I) Chloride

Giuseppe Bellucci,* Giovanni Ingrosso, Franco Marioni, Ettore Mastrorilli, and Ivano Morelli

Istituto di Chimica Organica dell'Università di Pisa, 56100 Pisa, Italy

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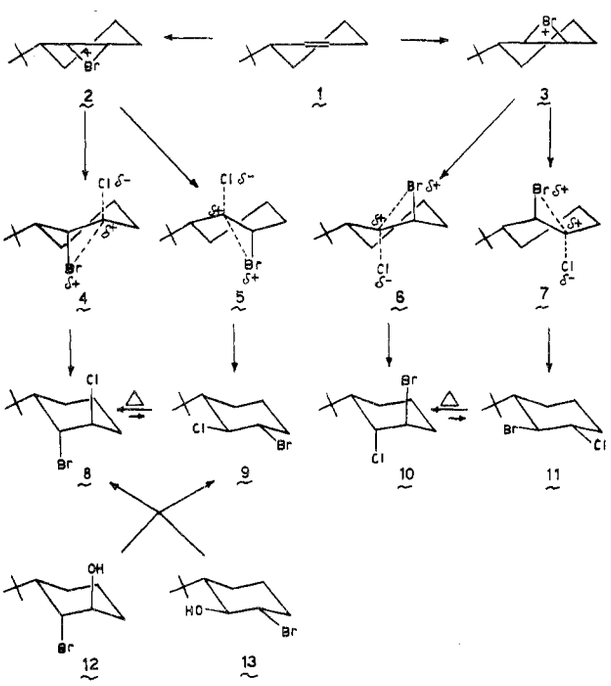
The bromochlorination of 3-*tert*-butylcyclohexene has been investigated in several solvents and with different halogenating reagents. The distribution of the four possible trans bromochlorides, which has been determined through a mixed glpc–ir method of analysis, is in accordance with ionic two-step mechanisms. The stereoselectivity of the electrophilic attack by bromine ranges between 64 and 79% anti to the *tert*-butyl group with preformed bromine chloride, but practically disappears when monopyridinebromine(I) chloride in chloroform is used as the reagent. The nucleophilic attack is directed preferentially at C_1 on both of the bridged intermediates formed in the electrophilic step; however, while the regioselectivity of the attack by chloride syn to the *tert*-butyl group is constant under all examined conditions, that of the anti attack is strongly dependent both on the solvent and on the reagent. The results obtained with bromine chloride are consistent with an addition mechanism involving the rate- and product-determining formation of epibromonium ion intermediates; those found with pyridinebromine chloride suggest instead that the steric course of the addition be controlled mainly during the nucleophilic rather than during the electrophilic step.

Previous work[1–3] on bromine addition to cyclohexene derivatives in low-polarity nonprotic solvents had shown a marked influence of the ring substituents, the solvent, and the brominating agent on the steric course of the halogenation of both nonconjugated and conjugated substrates. While the latter compounds can give both anti and syn dibromo adducts in ratios depending on the reaction conditions,[2] the former ones undergo exclusive anti addition, affording mixtures of diaxial and diequatorial trans dibromides. It was also shown[1] that alkyl substituents in the allylic position favor the formation of the diequatorial adducts, this effect being, however, markedly reduced by a basic solvent like ethyl ether or by the use of pyridine perbromide and pyridinium hydrobromide perbromide as the brominating agents, or even by the mere presence of tertiary amines in the reaction medium. The product distribution of the addition of free bromine in nondonor solvents was rationalized on the basis of the usual bromination mechanism,[4] involving the rate-determining formation of epibromonium ion intermediates followed by a fast nucleophilic anti attack by bromide (or tribromide) ions to give the dibromo adducts. The decrease in the ratio of diequatorial to diaxial dibromides observed when bromine is coordinated by a base was attributed[1] to a change in the rate-determining step of the reaction, which would instead occur through a fast, reversible electrophilic step followed by a slow nucleophilic attack on the intermediates. Under these conditions both the stereo- and the regioselectivity of the addition would be determined mostly by substituent effects during the nucleophilic rather than during the electrophilic step. This type of behavior was actually observed for electrophilic additions to cyclohexene derivatives of several nonsymmetrical reagents such as NBS–H_2O (but not preformed BrOH),[5,6] IOH,[7] IN_3,[7] IOAc,[8] and $Hg(OAc)_2$,[9] which permit us to distinguish between the direction of the electrophilic and that of the nucleophilic attack, but, of course, this approach cannot be directly applied to the addition of bromine, for which only indirect evidence based on the analogy with other reactions could be given.[1,3] The possibility of a mechanism of the latter type has been, however, recently inferred[10] from kinetic evidence for the bromination of acyclic alkenes in trifluoroacetic acid. In order to obtain more significant information about the halogenation mechanisms of cycloalkenes in low-polarity nonprotic solvents, we undertook a study of the addition of an intehalogen, bromine chloride, and chose 3-*tert*-butylcyclohexene (1) as the first substrate, since previous work had shown[5,11,12] that an allylic *tert*-butyl group exerts a strong directive effect on both the electrophilic and the nucleophilic step of the additions.

Results

The bromochlorination of 3-*tert*-butylcyclohexene (1) was performed with a variety of reagents, including bromine chloride preformed from molecular bromine and chlorine, *N*-bromosuccinimide (NBS) in the presence of hydrogen chloride, and monopyridinebromine(I) chloride. Mixtures of all expected trans bromochlorides 8–11 (Scheme I) were obtained in every case, appreciable

Scheme I



amounts of trans dibromides and trans dichlorides being formed only with the first reagent. Column chromatogra-

Table I
Products Distribution, Stereoselectivity, and Regioselectivity Found in the Bromochlorinations of 1

Bromochlorinating reagent (solvent)	Ratio of bromochlorides to dibromides plus dichlorides	Distribution of bromochlorides, % 8	9	10	11	Stereoselectivity of the electrophilic attack syn/anti ratio	Regioselectivity of the nucleophilic attack C_1/C_2 ratio: Cis intermediate	Trans intermediate
BrCl (CCl_4)	90:10	16	5	13	66	21:79	76:24	84:16
BrCl ($CHCl_3$)	80:20	18	15	11	56	33:67	55:45	84:16
BrCl (CH_2Cl_2)	80:20	20	16	11	53	36:64	56:44	83:17
BrCl (C_6H_6)	85:15	18	15	10	57	33:67	55:45	85:15
BrCl (Et_2O)	90:10	21	7	12	60	28:72	75:25	83:17
BrCl + HCl (CH_2Cl_2)	85:15	22	9	12	57	31:69	71:29	83:17
NBS + HCl (CH_2Cl_2)	95:5	22	8	12	58	30:70	73:27	83:17
C_5H_5NBrCl (CCl_4)	>95:<5	38	2	10	50	40:60	95:5	83:17
C_5H_5NBrCl ($CHCl_3$)	>95:<5	50	2	8	40	52:48	96:4	83:17

phy of these mixtures allowed isolation of large amounts of pure **11**, while it was not possible to separate **8** and **10** from each other nor to isolate pure **9**. Thermal equilibration of **11** caused its conversion into **10** by 1,2-interchange,[13] the equilibrium being shifted to about 98% in favor of the latter. The other couple of bromochlorides (**8** and **9**) was prepared by treating both bromohydrins **12** and **13** with thionyl chloride; a 70:30 ratio of **8** to **9** was obtained from **12** and a 63:37 ratio from **13**. The 1,2-interchange of halogens occurring in these transformations was not unexpected, since the tendency of vicinal bromine to participate in displacement reactions on bromohydrins through epibromonium ions or SNi′ mechanisms is known.[14] Pure **8** and **9** could be separated from their mixtures, but **8** was more conveniently obtained after thermal equilibration, which changed the ratio of **8** to **9** to about 97:3.

The relative position of bromine and chlorine with respect to the *tert*-butyl group and the relative configurations of these bromochlorides were inferred from the method of obtainment and from their nmr spectra. Thus, both products arising from **12** and **13** must have bromine cis to the *tert*-butyl group as in the starting bromohydrins, this halogen atom being therefore vicinal to the alkyl substituent in the diaxial and in a 1,3 relationship to it in the diequatorial isomer. In the 60-MHz nmr spectrum of the major product obtained from **12** and **13** the two protons α to the halogens gave overlapping narrow signals ($W_{1/2}$ = 4.5 Hz), indicating a diaxial disposition of the two halogen atoms as in **8**; on the other hand, the minor isomer showed for the α protons a broad, complicated pattern of signals at higher field, as expected for **9**. The nmr spectra provided also safe configurational assignments for the other couple of bromochlorides, since the thermodynamically stable isomer and its partner showed patterns respectively very similar to those of **8** and **9** and consistent with the relative configurations **10** and **11**.[15]

A complete analysis of the mixtures of bromochlorides formed in the additions to **1** was not possible by glpc alone, but a mixed glpc–ir method solved the analytical problem (see Experimental Section). The results obtained by this method of analysis are summarized in Table I, which also includes the ratios of bromochlorides to trans dibromides and dichlorides formed in the various conditions.

It can be seen from Table I that the distribution of the individual bromochlorides is affected both by the reagent and by the solvent. Furthermore, the amount of trans dibromides and dichlorides formed in the additions of free bromine chloride depends on the solvent. It must also be observed that the total amounts of the diaxial adducts (**8** + **10**) and those of the diequatorial ones (**9** + **11**) are fairly constant in all mixtures obtained with preformed bromine chloride, but the total percentage of the former compounds increases when pyridinebromine chloride is used as the halogenating agent, in analogy with the results previously reported for the bromination reactions.[1]

Discussion

It is well known[16,17] that bromine is the electrophilic and chlorine the nucleophilic species in the polar additions of bromine chloride to alkenes. A two-stage mechanism, similar to that involved in the bromination, is generally assumed. On this basis, the course of the additions of bromine chloride to **1** can be illustrated as in Scheme I. It must be pointed out that this scheme is a rough simplification, since it does not consider the formation of charge transfer complexes between the interhalogen and the olefin, which, in analogy with the bromine additions,[18–20] could be involved as the precursors of the epibromonium ions **2** and **3**. Furthermore, the latter intermediates, which in the scheme are simply represented as free ions, in the nonpolar solvents employed are very probably ion-paired species, the nature of the negative counterion depending on the reaction order in electrophile.

The stereoselectivity of the electrophilic attack relative to the *tert*-butyl group and regioselectivity of the nucleophilic one on the ionic intermediates in the various additions of bromine chloride to **1** are given in Table I.

The data of Table I show that in the addition of preformed bromine chloride to **1** under all examined conditions the attack by positive bromine is directed preferentially anti to the alkyl substituent. This is consistent with the most generally accepted mechanism of electrophilic additions to alkenes,[21] involving an irreversible, rate-limiting electrophilic step leading to cationic intermediates, followed by a fast nucleophilic attack to give the final adducts. Under these conditions the stereoselectivity of the addition must be determined by steric and electronic effects of the substituents during the electrophilic stage. In the case of additions to **1**, the strong steric effect of the allylic *tert*-butyl group, hindering syn attack, should cause the preferential formation of products arising from anti electrophilic attack by bromine, as is actually found with preformed bromine chloride. The range of anti stereoselectivity observed in the various solvents is possibly due to a different polarization of the interhalogen and/or to slight solvent effects on the rates of attack on the two faces of the double bond.

The regioselectivity of the nucleophilic attack on the trans intermediate **3** is remarkably constant under all examined conditions (Table I) and very similar to that found in other electrophilic additions to **1** involving epibromonium ion intermediates.[5] The high preference for attack on C_1 is consistent with the expectation, supported also by the course of opening reactions of *trans*-3-*tert*-butyl-1,2-epoxycyclohexane,[5,11b] that the strong repulsive interaction between the attacking nucleophile and the *tert*-butyl group[22]

raises the energy of transition state 6 with respect to 7 so much as to reverse the usual preference for antiparallel over parallel opening of cyclohexene epibromonium ions.[23] The nucleophilic attack on the cis intermediate 2 occurs preferentially at C_1, through the chair-like transition state 4; however, in the addition of preformed bromine chloride this regioselectivity is much lower than expected on the basis of other additions to 1 involving electrophilic bromine as well as of opening reactions of *cis*-3-*tert*-butyl-1,2-epoxycyclohexane,[5,11b] surprisingly high percentages of parallel attack on C_2 anti to the *tert*-butyl group being found particularly in chloroform, dichloromethane, and benzene as the solvents. The latter results show that also more subtle factors than direct steric or inductive effects of ring substituents can play a considerable role in determining the mode of opening of cyclohexene epihalonium ions.

The steric course of the addition performed with NBS in the presence of hydrogen chloride is identical with that found when free bromine chloride is added in the presence of the same acid and is completely different from that observed with NBS in DMSO–water,[5] which gives 78% of the diaxial bromohydrin 12 through 2. This difference suggests that in the NBS–HCl reaction, in contrast with the NBS–DMSO–water addition, bromine is not directly transferred from nitrogen to the alkene, but free bromine chloride is formed before the electrophilic attack.

A definite change in product distribution is brought about when pyridinebromine chloride is used as the halogenating reagent. The inspection of Table I shows that this change is due first to an increased syn stereoselectivity of the electrophilic attack by bromine and second to a decreased percentage of parallel opening on C_2 of the cis intermediate formed in the electrophilic step. The unlikely possibility that pyridinebromine chloride acts as a donor of electrophilic chlorine rather than bromine can safely be ruled out, since the trans chloronium ion would give mostly the diequatorial adduct 9, which on the contrary is produced in a very small amount. Also the hypothesis that the coordination of the halogen molecule by the base may reduce the effective size of electrophilic bromine so much as to cause a practically random attack on the two faces of the double bond of 1 in spite of the presence of the bulky alkyl substituent seems very unlikely. In fact, all examined one-step additions (like epoxidation[11a] and hydroboration[12]) and two-step additions involving an irreversible electrophilic step (like addition of preformed hypochlorous and hypobromous acid and acetyl hypobromite[5,11b]) to 1 show a definite preference for anti electrophilic attack, independently of the different sizes of the various reagents. The change in steric course when pyridinebromine chloride is used as the reagent may instead be rationalized by the assumption of a change in the addition mechanism.

The present stage of knowledge about the nature and chemical behavior of this reagent does not allow definite conclusions to be drawn about its addition mechanism. However, it can be observed that both the stereoselectivity and the regioselectivity found in the bromochlorination of 1 with pyridinebromine chloride in chloroform tend to approach those expected from an addition mechanism of the type already proposed for the bromination with pyridine perbromide[1] and other additions showing a preference for syn electrophilic attack to a much higher degree.[6] The latter mechanism would involve a reversible electrophilic step leading to bridged cationic intermediates, followed by a slow, rate-determining nucleophilic attack to give products. Under these conditions, if the nucleophilic attacks are sufficiently slower than the formation of the intermediates 2 and 3 (or some equivalent species) and their reversal to the alkene, the overall steric course of the bromochlorination of 1 would mostly depend on the rates of the four competitive nucleophilic steps leading to the adducts 8–11. Since antiparallel attack on C_1 of the cis intermediate through a chair-like transition state like 4 would be less energy demanding than both antiparallel attack on C_2 of the trans intermediate (a chair-like transition state of type 6 being destabilized by repulsive interaction between the attacking nucleophile and the *tert*-butyl group) and parallel attacks (involving energetically less favorable boat-like transition states like 5 and 7), 8 should therefore be the main product. This actually occurs in the addition of pyridinebromine chloride in chloroform and to a smaller degree in carbon tetrachloride.

In conclusion, while more evidence, particularly of kinetic type, is definitely desirable and is being sought in order to better define mechanistic aspects, the present results fit well with the previously acquired ones into a picture that requires two different ionic mechanisms of addition for different electrophilic reagents.

Experimental Section

Nmr spectra were registered with a Geol C-60 HL spectrometer from *ca.* 30% (w/w) $CDCl_3$ solutions using TMS as internal standard. Glpc analyses were performed on a Fractovap C. Erba instrument, fitted with a 2-*m* glass column, 2.5 mm i.d., packed with 1% neopentyl glycol succinate on sylanized Chromosorb W 80–100 mesh. Ir spectra were registered on liquid films with a Perkin-Elmer Model 257 double-beam grating spectrophotometer.

3-*tert*-Butylcyclohexene was obtained from 2-*tert*-butylcyclohexanone tosylhydrazone with butyllithium.[11a] Bromine chloride was prepared[24] by mixing equimolar amounts of carbon tetrachloride solutions of bromine and chlorine and used after several hours. Monopyridinebromine(I) chloride was prepared by slowly adding the calculated volume of a carbon tetrachloride solution of bromine chloride to a slight excess of dry pyridine in the same solvent;[25] the white cyrstalline precipitate was immediately used without further purification. Dichloromethane was refluxed over P_2O_5 and rectified. Chloroform was purified by washing with 2 *N* NaOH, concentrated H_2SO_4, and water, drying with K_2CO_3, and distillation and was immediately used. Carbon tetrachloride was Rudi Pont spectroanalyzed reagent grade. Benzene was washed with H_2SO_4, refluxed on sodium, and distilled. Ethyl ether was freed from peroxides by washing with a solution of ferrous sulfate. $MgSO_4$ was always used as the drying agent. Evaporations were made *in vacuo* (rotary evaporator) at 30°. Petroleum ether refers to the fraction of boiling range 40–60°.

***r*-1-Chloro-*t*-2-bromo-*t*-3-*tert*-butylcyclohexane (8) and *r*-1-Bromo-*t*-2-chloro-*c*-3-*tert*-butylcyclohexane (9). A.** Thionyl chloride (7.5 ml) was added at 0° to bromohydrin 13[5] (3.0 g), and the mixture was left in a sealed vessel at room temperature for 2 hr and then poured onto ice and extracted with ether. The extract was washed with water and saturated aqueous $NaHCO_3$, dried, and evaporated to give a crude residue (2.6 g) consisting of a mixture of 8 and 9 in a ratio of 63:37. A portion of this mixture (1.0 g) was chromatographed through a 40 × 1.8 cm column of neutral silica gel (Schuchardt, grade I), petroleum ether being used as the eluent; 25-ml fractions were collected. Fractions 4–8 contained 0.50 g of pure 8: $n^{25}D$ 1.5072; nmr δ 0.96 (*t*-Bu, s, 9 H), 4.60 ppm (–CHBr– and –CHCl–, 2 overlapping m, $W_{1/2}$ = 4.5 Hz, 2 H); ir 665, 680 cm^{-1}.

Anal. Calcd for $C_{10}H_{18}BrCl$: C, 47.36; H, 7.15; Br, 31.50; Cl, 13.98. Found: C, 47.45; H, 7.25; Br, 31.70; Cl, 14.00.

Fractions 12–16 gave 0.28 g of pure 9: $n^{25}D$ 1.5135; nmr δ 1.08 (*t*-Bu, s, 9 H), 3.65–4.32 ppm (–CHBr– and –CHCl–, 2 overlapping m, 2 H); ir 680, 740, 770 cm^{-1}.

Anal. Calcd for $C_{10}H_{18}BrCl$: C, 47.36; H, 7.15; Br, 31.50; Cl, 13.98. Found: C, 47.25; H, 7.10; Br, 31.40; Cl, 13.80.

Another portion (1.0 g) of the above mixture was heated in a sealed vial for 6 hr at 165°. Glpc analysis showed that the original ratio of 8 to 9 was changed to 97:3, which remained unchanged after further heating. Percolation of this crude product through a silica gel column yielded pure 8.

B. Treatment of bromohydrin 12[5] with thionyl chloride as described under A gave a 70:30 mixture of 8 and 9.

The ratios of 8 to 9 obtained from both bromohydrins 12 and 13 did not change after reaction times ranging between 30 min and 48

hr, showing that the products were stable in the reaction conditions.

***r*-1-Chloro-*t*-2-bromo-*c*-3-*tert*-butylcyclohexane (11).** A solution of *N*-bromosuccinimide (6.5 g, 36.5 mmol) in dichloromethane (100 ml) was slowly added to a solution of 1 (4.0 g, 29 mmol) in 100 ml of the same solvent cooled at 0° and saturated with dry hydrogen chloride. The acid was bubbled until the end of the addition. The reaction mixture was then washed with water, saturated aqueous $NaHSO_3$, and water, dried, and evaporated to give 7.0 g of a crude mixture consisting of ~95% of bromochlorides and 5% of trans dibromides and dichlorides. Glpc analysis showed that the bromochlorides consisted of 34% of the diaxial adducts **8** and **10** (unseparated), 58% of **11**, and 8% of **9**. This mixture was chromatographed on a 65 × 1.8 cm column of neutral silica gel with petroleum ether as the eluent, and 25-ml fractions were collected. Fractions 5 and 6 contained mixtures of **8** and **10** (2.0 g) uncontaminated by the other adducts; ir analysis showed for both of them a **8** to **10** ratio of 64:36. Fractions 8–11 gave 2.5 g of pure **11**: $n^{25}D$ 1.5140; nmr δ 1.08 (*t*-Bu, s, 9 H), 3.84–4.37 ppm (–CHBr– and –CHCl–, 2 overlapping m, 2 H); ir 635, 690, 730, 780 cm^{-1}.

Anal. Calcd for $C_{10}H_{18}BrCl$: C, 47.36; H, 7.15; Br, 31.50; Cl, 13.98. Found: C, 47.20; H, 7.05; Br, 31.65; Cl, 14.10.

High yields of pure **11** were also obtained by column chromatography of all mixtures obtained by addition of preformed bromine chloride or pyridinebromine chloride, as described below.

***r*-1-Bromo-*t*-2-chloro-*t*-3-*tert*-butylcyclohexane (10).** A sample of **11** (1.0 g) was heated in a sealed vial for 5 hr at 165°, after which time glpc analysis showed that it was transformed into **10** in a 98% yield. A 2% amount of **11** remained unchanged also after further heating. Percolation of this crude product through a silica gel column gave pure **10**: $n^{25}D$ 1.5070; nmr δ 0.96 (*t*-Bu, s, 9 H), 4.62 ppm (–CHBr– and –CHCl–, 2 overlapping m, $W_{1/2}$ = 4.0 Hz, 2 H); ir 650, 695 cm^{-1}.

Anal. Calcd for $C_{10}H_{18}BrCl$: C, 47.36; H, 7.15; Br, 31.50; Cl, 13.98. Found: C, 47.25; H, 7.05; Br, 31.70; Cl, 14.10.

Additions of Bromine Chloride. A. With BrCl. A 10% excess of 1 *M* solution of BrCl in CCl_4 was added dropwise to a stirred solution of 1.0 g of 1 in 25 ml of the appropriate solvent at 0°. After the addition was complete, the reaction mixture was stirred for 10 min, and then washed with saturated aqueous $NaHSO_3$ and water, dried, and evaporated. The reaction in dichloromethane in the presence of hydrogen chloride was performed by bubbling the acid during the addition of the interhalogen.

B. With C_5H_5NBrCl in CCl_4. A 20% excess of solid C_5H_5NBrCl (1.75 g) was added to a solution of 1 (1.0 g) in CCl_4 (20 ml) at 0°. After stirring for 45 min most of the solid was dissolved and the reaction mixture was washed with saturated aqueous $NaHSO_3$, aqueous 2 *N* HCl, and water, dried, and evaporated.

C. With C_5H_5NBrCl in $CHCl_3$. A solution of C_5H_5NBrCl (1.75 g) in 17 ml of $CHCl_3$ was added within 20 min to a stirred solution of 1 (1.0 g) in 20 ml of the same solvent at 0°. After 10 min the reaction mixture was treated as described under B.

Three or more experiments were carried out for every procedure. The crude reaction mixtures were subjected to glpc. Under the conditions employed (column 80°, evaporator 130°, detectors 130°, nitrogen flow 45 ml/min) the bromochlorides, in contrast with the dibromides, did not undergo thermal interconversion on the gas chromatographic columns and the trans dibromides and dichlorides present in some reaction mixtures did not interfere with their determination; however, while the diequatorial adducts **9** and **11** were well separated from each other and from the diaxial isomers **8** and **10**, the latter two gave a single peak. The relative retention times of all possible adducts follow: *r*-1,*t*-2-dichloro-*t*-3-*tert*-butylcyclohexane, 1; **8** and **10** (unseparated), 1.75; *r*-1,*t*-2-dibromo-*t*-3-*tert*-butylcyclohexane, 3.05; *r*-1,*t*-2-dichloro-*c*-3-*tert*-butylcyclohexane, 3.60; **11**, 4.70; **9**, 6.20; *r*-1,*t*-2-dibromo-*c*-3-*tert*-butylcyclohexane, 7.60. Thus, glpc analysis gave the percentage of trans dibromides and dichlorides, the single percentages of the diequatorial bromochlorides (**9** and **11**), and the total percentage of the diaxial ones (**8** and **10**). The reaction mixtures were thereafter rapidly chromatographed over silica gel. The first eluted fractions, consisting of mixtures of **8** and **10** free from the other adducts, were subjected to ir analysis utilizing the bands at 650 and 695 cm^{-1}, typical of **10**, and those at 665 and 680 cm^{-1}, typical of **8**, by comparison with a calibration curve obtained with the pure reference compounds. No fractionation of **8** and **10** occurred, since identical ratios of **8** to **10** were obtained from three or more consecutive fractions. The single percentages of the diaxial bromochlorides were then deduced on the basis of their total percentage obtained by glpc and of the **8** to **10** ratio obtained by ir analysis. The values listed in Table I were reproducible within ±2%.

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Registry No.—**1**, 14072-87-8; **8**, 51821-11-5; **9**, 51821-12-6; **10**, 51830-05-8; **11**, 51830-06-9; **13**, 38512-63-9; BrCl, 13863-41-7; C_5H_5NBrCl, 51821-13-7.

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