and little dibromonitromethane (**2**) would be formed. In the case of slow addition there would be ample time for **8** to give **1** and the hypobromite would preferentially react with the more reactive **1** than nitromethane.[7]

Experimental Section

Reaction Conditions. To a stirred solution of 0.004 mol of olefin in 11.2 ml of nitroalkane maintained at ice-bath temperatures was added 2 ml (1.2 M) of *tert*-butyl hypobromite–carbon tetrachloride solution. (The concentrations of the alkyl hypobromites solutions varied somewhat depending on the preparation.) The reactions were essentially instantaneous but stirring was continued for a short time. Slow addition of the hypobromite was done with a dropping funnel or a dropping pipet. Rapid addition simply involved letting the hypobromite solution run in directly from a volumetric pipet. The reaction products were analyzed directly by VPC. The synthesis of methyl hypobromite has been described previously;[1] we used this same procedure to make *tert*-butyl hypobromite. As was the case with the alkyl hypochlorites, no reaction occurred between the alkyl hypobromites and the nitroalkanes unless the olefins were present.

Identification of Products. Bromonitromethane (**1**) and tribromonitromethane (**3**) were synthesized unambiguously by addition of the appropriate amount of bromine to a solution of nitromethane and base, and were identified by comparison of their infrared spectra with the reported spectra for these compounds.[8] Dibromonitromethane (**2**) was prepared as described for **1** and **3**, and its structure was confirmed from its infrared spectrum (absorption bands, cm^{-1}), C–H, 2400; $-NO_2$, 1325 and 1575; C–Br, 600 and 675; and from its boiling point; reported,[9] 58–60 °C (13 mm) [175 °C (760 mm)]; found, 50 °C (5.5 mm) [180 °C (760 mm)]. 1-Bromonitroethane (**4**) and 1,1-dibromonitroethane (**5**) were synthesized unambiguously as previously described.[10] The ir spectrum of **4** also compared favorably with the reported spectrum.[7] The compound responsible for peak 4 was isolated from the reaction product (hypobromite, olefin, and nitroethane) by preparative VPC; the ir spectrum of the collected compound was identical with that of the unambiguously synthesized **4**, with the exception of a small carbonyl absorption (contaminant) in the later. Compounds **1**, **2**, **3**, and **5** were confirmed as products by comparisons of the retention times of the peaks assigned to them with the retention times of the authentic compounds. Styrene dibromide was prepared by addition of bromine to styrene. β-Bromostyrene was synthesized unambiguously by the decarboxylation of 2,3-dibromocinnamic acid.[11] The synthesis of 2-bromo-1-methoxy-1-phenylethane has been described previously.[12] 2-Bromo-1-*tert*-butoxy-1-phenylethane was isolated by preparative VPC and identified by its NMR spectrum:[13] δ 1.20 [s, 9, $C(CH_3)_3$], 3.35 (d, 2, CH_2), 4.65 (t, 1, CH), 7.35 (s, 5, C_6H_5).

Analysis Procedure. Compounds **1**, **2**, and **3** were separated on a 4 ft × 0.25 in. column packed with 2% DNP on Chromosorb W (60/80 mesh) DCMS at 65 °C (flow rate 60 ml/min He); under these conditions the retention times (min) were respectively 3.3, 6.5, and 13.0. The internal standard was *p*-bromochlorobenzene. Compounds **4** and **5** were separated as described for the bromonitromethanes with the exception that the column was 8 ft; the retention times (min) were respectively 4.8 and 9.1. The internal standard was *o*-bromotoluene. Compounds **6**, **7**, 2-bromo-1-methoxy-1-phenylethane, and styrene dibromide were separated on the same column as used for the bromonitromethanes (column temperature 100 °C) with the following retention times (min), respectively: 4.6, 11.7, 6.9, and 15.8.

Acknowledgment. Support for this work was provided by the donors of the Petroleum Research Fund, administered by the American Chemical Society, by the Research Corporation, and by the Atlantic Richfield Foundation.

Registry No.—**1**, 563-70-2; **2**, 598-91-4; **3**, 464-10-8; **4**, 563-97-3; **5**, 7119-88-2; **6**, 103-64-0; **7**, 57951-57-2; nitromethane, 75-52-5; nitroethane, 79-24-3; methyl hypobromite, 28078-73-1; *tert*-butyl hypobromite, 1611-82-1; styrene dibromide, 7436-90-0; bromine, 7726-95-6; styrene, 100-42-5; 2-bromo-1-methoxy-1-phenylethane, 13685-00-2.

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(3) V. L. Heasley, G. E. Heasley, D. M. Ingle, P. D. Davis, and T. L. Rold, *J. Org. Chem.*, **38**, 2549 (1973).

(4) For a discussion of the role of olefins as catalysis in the reactions of alkyl hypochlorites with nitromethane, see ref 2.

(5) It is conceivable that the addition product could result from addition of Br_2 (formed by decomposition of the alkyl hypobromite) to styrene in the presence of *tert*-butyl alcohol (from the reaction of hypobromite with nitroethane) or by solvolysis of styrene dibromide in the presence of *tert*-butyl alcohol. We eliminated these possibilites by bromination of styrene in a mixture of nitroethane–*tert*-butyl alcohol and by solvolysis of styrene dibromide in the same solution, and determining that no addition product was formed.

(6) In our earlier study[1] on the addition of alkyl hypobromites to 1-hexene and styrene in dichloromethane, we also observed dibromide formation. At that time, we absolutely confirmed, using ultraviolet spectroscopy, that no more than a trace of molecular bromine was present in the hypobromite solutions. In the present study, more dibromides were formed when oxygen was passed through the reaction solution.

(7) At the moment of addition the concentration of hypobromite is high with rapid addition. It is conceivable that under these conditions the reaction occurs by a mechanism which is second order in hypobromite involving an anion of the structure (R–O–Br–O–R)$^-$; this would be analogous to bromination with molecular bromine in which the tribromide ion (Br_3^-) is involved. However, at this time we see no way of accounting for the difference in products between the two methods of addition on the basis of the structure of the anion.

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(13) The corresponding radical addition product (1-bromo-2-*tert*-butoxy-1-phenylethane) was prepared as described by Walling et al. [*J. Am. Chem. Soc.*, **87**, 1715 (1965)] and its spectrum was compared with that of **7**. The spectra were essentially identical except for differences in chemical shifts.

Chlorination of Cyclopentadiene and 1,3-Cyclohexadiene with Iodobenzene Dichloride and Trichloramine

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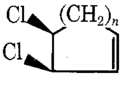
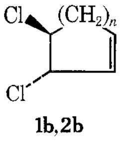
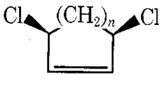
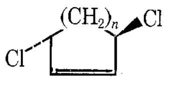
It has recently been shown that trichloramine reacts with olefins to give vicinal dichlorides by a radical mechanism,[1] and that iodobenzene dichloride and olefins also form vicinal dichlorides by either an ionic or radical mechanism depending on the conditions.[2] Since we had recently established the structures of the stereoisomeric dichlorides that result from chlorination of cyclopentadiene (**1**)[3] and 1,3-cyclohexadiene (**2**),[4] we felt that it would be of interest to compare the product ratios from these chlorinating agents with those from molecular chlorine with the object being to obtain information on the bonding in the intermediate radicals and ion pairs. The products from reaction of the dienes with antimony pentachloride are also included for comparison purposes.[5]


1a, 2a


1b, 2b


1c, 2c


1d, 2d

The structures of the dichloride products are shown

Table I. Chlorinations of Cyclopentadiene and 1,3-Cyclohexadiene

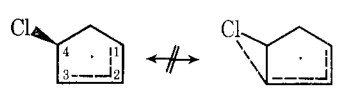
			Dichlorides, %								Yield, %	
Entry	Chlorinating agent	Solvent	**1a**	**1b**	**1c**	**1d**	**2a**	**2b**	**2c**	**2d**	1	2
1	Cl_2	CH_2Cl_2	38	25	18	9	14	58	21	7	52	38
2	Cl_2	CCl_4	27	23	39	11	8	22	69	1	60	28
3	Cl_2	C_5H_{12}	13	29	29	28	15	49	33	3	68	34
4[a]	Cl_2	Neat	25	26	34	15					40	
5[b]	$PhICl_2$	CH_2Cl_2	10	17	24	49	3	39	18	40	43	67
6[b]	$PhICl_2$	CCl_4	5	21	41	33	<1	24	28	45	55	96
7[b]	$PhICl_2$	C_5H_{12}	7	17	44	32	3	36	28	32	74	74
8[a,c]	$PhICl_2$	CH_2Cl_2	1	44	29	26	0	46	10	44	85	90
9[a]	$PhICl_2$	Neat	0	41	30	29	1	49	9	41	59	88
10	NCl_3	CH_2Cl_2	19	37	26	18	9	47	20	24	54	99
11	NCl_3	CCl_4	14	36	26	24	8	41	31	20	71	92
12[b]	NCl_3	CCl_4	11	38	25	26						
13	NCl_3	C_5H_{12}	12	33	25	30	9	45	23	23	68	99
14[a]	NCl_3	Neat	12	38	25	25	6	46	19	29	55	58
15	$SbCl_5$	CH_2Cl_2	7	12	52	29					27	
16	$SbCl_5$	CCl_4	6	22	38	34	2	40	16	42	96	65
17	$SbCl_5$	C_5H_{12}	19	21	27	33					71	

[a] The reactants were illuminated with ultraviolet light and flushed with N_2. [b] 2,6-Dimethyl-4-*tert*-butylphenol was added (1 M) as an inhibitor. [c] The solution was 0.5 mol fraction in diene.

below where n = 1 and 2 for cyclopentadiene (**1**) and 1,3-cyclohexadiene (**2**), respectively.

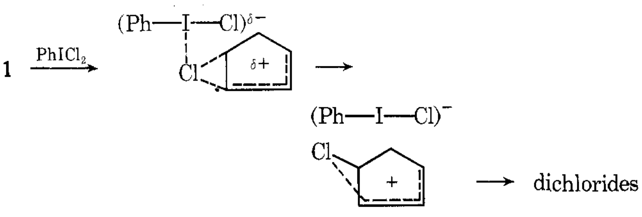
The amounts of the products and the corresponding reaction conditions are summarized in Table I. The following general observations can be made: (a) all three chlorinating agents give more trans 1,4-dichlorides than does molecular chlorine—this is particularly dramatic with 1,3-cyclohexadiene; (b) in most cases there is a decrease in amount of cis 1,2 addition with all of the chlorinating agents which is most notable with iodobenzene dichloride; and (c) the yields of the dichlorides (**2a–d**) from 1,3-cyclohexadiene are greatly improved with iodobenzene dichloride, trichloramine, and antimony pentachloride.

Entry 14 describes reaction conditions which are most conducive to a radical reaction: pure diene (molecule-induced homolysis); absence of an inhibitor (O_2 removed by N_2); and ultraviolet illumination. Product ratios (entries 10–13) under all of the different reaction conditions are essentially identical with those from entry 14, suggesting that trichloramine reacts with dienes **1** and **2** only by a radical mechanism.[6] The intermediate radical (**3**) apparently has little bridging between the chlorine and the adjacent allylic system since trichloramine does give considerable cis 1,2 addition. The electron density in **3** may be somewhat lower at C_3, and hence less stable and more reactive, since trans 1,2-dichloride **1b** is the major product under radical conditions, or the product ratios from the reaction of radical intermediate **3** with the chain-carrying species (NCl_3, NCl_2, NCl, etc.) simply may reflect a steric preference.[7] If chlorine reacts with cyclopentadiene (**1**) by a radical mechanism (entry 14),[8] the radical intermediate from molecular chlorine should be identical with **3** from trichloramine, but since the product ratios are different the intermediate must exhibit a steric preference in its reaction with the different chlorine donors. This is further exemplified by iodobenzene dichloride, which, under radical conditions (entry 9), shows similar reactivity to trichloramine except for the fact that it gives little cis 1,2 addition to either dienes **1** or **2**. Apparently the large iodobenzene dichloride molecule experiences severe steric hindrance as it approaches C_3 (cis) in both of the intermediate radicals. The radical intermediate from 1,3-cyclohexadiene also shows a slight preference for trans attack at C_3 in the chain-propagating step with both trichloramine and iodobenzene dichloride (entries 10–14 and 8–9, respectively).



3

We feel that a comparison of the ionic addition products from the reaction of iodobenzene dichloride (entries 5, 6, and 7)[9,10] and chlorine (1, 2, and 3) with dienes **1** and **2** raises an interesting question concerning the structure of the ion pair from iodobenzene dichloride. The results in Table I show that iodobenzene dichloride gives considerably more trans 1,4 addition to both **1** and **2** than does molecular chlorine. We suggest that this difference can be explained on the basis of a consideration of the respective ion pairs. In the reaction of iodobenzene dichloride the ion pair (**4**, shown with diene **1**)[11] would involve the large anion (Ph–I–Cl⁻) which would experience steric hindrance as it approached C_3 in a cis direction (cis 1,2 addition), but could undergo trans attack freely at the same carbon. On the other hand, the small chloride ion in the corresponding ion pair from molecular chlorine apparently experiences little steric hindrance during attack at any of the positions. Steric hindrance also appears to be involved in cis attack of the large anion at C_1 since there is a significant reduction in cis 1,4 addition for both dienes in going from chlorine to iodobenzene dichloride; this is particularly dramatic for diene **2**. (The results for diene **1** in pentane are, for unknown causes, exceptions to these comparisons.) Tanner and Gidley[2] do not discuss the structure of the anion in the ion pair but show chloride ion and the iodobenzene molecule in their ion pair. It is conceivable that our results could be explained on the basis that the chloride ion and the iodobenzene molecule remain in close proximity in the ion pair and that the large iodobenzene molecule effectively blocks cis attack by chloride ion at carbons 1 and 3.

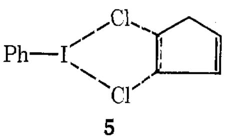


4

The steric requirements of the large anion ($Ph{-}I{-}Cl^-$) can also be used to explain the fact that Cristol et al.[11] obtained trans addition of chlorine in the reaction of acenaphthylene with iodobenzene dichloride. Tanner and Gidley[2] concluded that this reaction must be going by a radical mechanism since ionic addition of molecular chlorine to acenaphthylene gave only cis addition. However, the large anion from iodobenzene would probably prefer to add trans while the small chloride ion could add cis.

The increase in trans 1,4 addition and the decrease in cis 1,2 addition in the reaction between **1** and antimony pentachloride has also been rationalized on the basis of a large anion ($SbCl_4^-$ or $SbCl_6^-$) in the ion pair.[5]

The small amount of cis 1,2 addition (**1a, 2a**) which does occur in the reaction of **1** and **2** with iodobenzene dichloride is probably not the result of a concerted, molecular process (**5**, shown with diene **1**) since cis 1,2-dichloride formation with this chlorinating agent in the case of other olefins has been interpreted in other ways,[2] or simply has not been observed.[11,12] The cis 1,4-dichlorides (**1c** and **2c**) can not be formed by a concerted cis 1,4 addition since this suprafacial addition would be forbidden with iodobenzene dichloride as has been explained with antimony pentachloride.[13]



5

Experimental Section

Materials. Both iodobenzene dichloride[14] and trichloramine[15] were prepared as described in *Organic Syntheses.* Antimony pentachloride was obtained from Alfa Products.

Reaction Conditions. Reactions were carried out under nitrogen (unless oxygen was required as an inhibitor) and at the following temperatures: trichloramine and antimony pentachloride, −10 °C; and iodobenzene dichloride, room temperature. The dienes were dissolved in the appropriate amount of solvent to give a mole fraction of 0.02. The chlorinating agents were added to a stirred solution of the dienes in such amounts to consume 10 and 20% of the diene in dilute and neat solutions, respectively. The method of addition of the chlorinating agent depended on the reaction conditions: with dilute solutions, antimony pentachloride and iodobenzene dichloride were added as ca. 5% solution in the appropriate solvent; and in neat reactions, antimony pentachloride was added neat, and iodobenzene dichloride as a solid. Under all conditions trichloramine was added as a solution (0.6–0.7 M) in the appropriate solvent. The approximate volumes of dilute reaction mixtures are (ml): CH_2Cl_2, 22; CCl_4, 32; and C_5H_{12}, 38.

Identification and Analysis of Products. The cyclopentadiene dichlorides have already been reported,[3] and the procedures for establishing the structures of the cyclohexadiene dichlorides are described elsewhere.[4] The dichlorides from both dienes were analyzed by VPC under the following conditions: (cyclopentadiene), 7 ft × 0.125 in. column (SS) at 62 °C packed with β,β-oxydipropionitrile (2.5%) on 80–100 mesh Chromosorb W (AWDMCS) with retention times (min) of 4.4, 7.4, 20.6, and 22.6 for **1b, 1d, 1c,** and **1a,** respectively; and (cyclohexadiene),[16] 6 ft × 0.125 in. column (SS) at 57 °C packed with SE-30 (2.5%) on 80–100 mesh Chromosorb W (AWDMCS) with retention times (min) of 5.8, 7.2, 7.9, and 9.2 for **2b, 2d, 2c,** and **2a,** respectively. The stability of the dichlorides under these reaction and analysis conditions have been discussed elsewhere.[3–5]

Acknowledgment. Support for this work was provided by the Research Corporation, the donors of the Petroleum Research Fund, administered by the American Chemical Society, and the Atlantic Richfield Foundation.

Registry No.—**1a,** 51502-28-4; **1b,** 31572-43-7; **1c,** 31572-45-9; **1d,** 31572-44-8; **2a,** 53921-00-9; **2b,** 53920-98-2; **2c,** 54112-34-4; **2d,** 53920-99-3; cyclopentadiene, 542-92-7; 1,3-cyclohexadiene, 592-57-4; iodobenzene dichloride, 932-72-9; trichloroamine, 10025-85-1.

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(2) D. D. Tanner and G. C. Gidley, *J. Org. Chem.*, **33,** 38 (1968).
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(4) G. E. Heasley, V. L. Heasley, D. Strickland, G. McClung, D. M. Ingle, P. D. Davis, T. S. Ungermann, K. D. Rold, and D. Hayse, *J. Org. Chem.*, in press.
(5) The mechanisms of the reactions of antimony pentachloride with olefins and dienes (including cyclopentadiene) is discussed in the following article: V. L. Heasley, G. E. Heasley, K. D. Rold, D. Titterington, C. Leach, D. McKee, and B. Gipe, unpublished work. A study on the reaction of butadiene with antimony pentachloride has recently been reported.[13]
(6) Molecular oxygen also had no effect on the product ratios. Field and Kovacic (ref 1) observed that solvents had no effect on the meso/*dl* ratio in the reaction between *cis*-2-butene and trichloramine, and that inhibitors did not affect the reactions with cyclohexene.
(7) We observed in a separate study that radical addition of methyl hypochlorite to isoprene resulted primarily in 1,4 addition ($CH_3OC{-}C{-}C{=}C{-}C{-}Cl$) although the main contributor to the intermediate resonance system must be the tertiary radical ($CH_3OC{-}C{-}C{-}C{=}C$). Apparently steric preference is involved in the attack of the radical on methyl hypochlorite.
(8) Although this chlorination was done under radical conditions, we feel that the addition may be occurring primarily by an ionic mechanism since the product ratios are so similar to the ionic reactions. Under the conditions of entry 4 cyclohexane was chlorinated to give chlorocyclohexane confirming a radical component to the reaction, but it may be a minor one. At least there is no major change in product composition in going from radical to ionic conditions as was observed by Poutsma in the chlorination of butadiene [M. L. Poutsma, *J. Org. Chem.*, **31,** 4167 (1966)].
(9) Tanner and Gidley[2] found that in their reactions with iodobenzene dichloride *sym*-tri-*tert*-butylphenol was ineffective as a radical inhibitor. In our case 2,6-dimethyl-4-*tert*-butylphenol was much more effective at retarding rate and altering product composition than oxygen. However, the concentration of the phenol that we used was approximately 300 times greater than was used by Tanner and Gidley.
(10) Our evidence for the ionic addition of the chlorines from iodobenzene dichlorides to **1** and **2** under the conditions described in entries 5, 6, and 7 is as follows. (a) There is a significant change in product ratios between ionic conditions (entries 5, 6, and 7) and radical conditions (8 and 9) with an increase in trans 1,2 addition (**1b** and **2b**) under radical conditions which correlates with the radical addition of trichloramine. (b) The inhibitor, 2,6-dimethyl-4-*tert*-butylphenol, greatly retarded the rate of reaction of iodobenzene dichloride. Under radical conditions the reaction is complete in a few minutes whereas with the inhibitor a couple of days is required for complete reaction. (c) In a separate study butadiene reacted with iodobenzene dichloride in the presence of the inhibitor to give the ratio of dichlorides expected from ionic addition, and in the absence of the inhibitor (and in the presence of N_2 and ultraviolet illumination) the ratio of dichlorides indicated radical addition. [For a discussion of the ratio of dihalides expected from ionic and radical additions to butadiene see the studies on the chlorination[8] and bromination [V. L. Heasley and S. K. Taylor, *J. Org. Chem.*, **34,** 2779 (1969)] of this diene.] Further evidence confirming the ionic addition of iodobenzene dichloride in the presence of the inhibitor came from a comparison of the rates of addition to butadiene and cyclopentadiene (**1**). The latter was found to be immensely faster; this appears reasonable on the basis of the relative stabilities of the allylic cation (chloronium ion) intermediates.
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(16) During the course of the present study it was determined that dichlorides **2a–d** could be separated under simpler conditions (a shorter column) than was reported in an earlier study.[4]

A Convenient Synthesis of 2,3,12,13-Tetrathia[4.4]metacyclophanes and 2,3,12,13-Tetrathia[4.4]paracyclophanes

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The potential of tetrathia[4.4]cyclophanes as useful synthetic precursors of bridged aromatic ring systems has been