Electrophilic Additions to Dienes and the 1-Phenylpropenes with Pyridine–Halogen Complexes and Tribromides. Effects on Stereochemistry and Product Ratios

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Received November 15, 1977

Dibromide product ratios from bromination with molecular bromine, pyridine–bromine complexes, and tribromide salts for butadiene (**1**), isoprene (**2**), the piperylenes (**3a–b**), the 2,4-hexadienes (**4a–c**), cyclopentadiene (**5**), and the 1-phenylpropenes (**6a–b**) are reported. Bromine chloride addition with analogous reagents to **2**, **3a–b**, and **6a–b** is reported. The pyridine–halogen complexes and tribromide give much less 1,4-dihalide product from the dienes than does the molecular halogen. The proportion of 1,4 addition to dienes is suppressed further by an increase in amine concentration. Dienes **4a–b** and alkenes **6a–b**, which give nonstereospecific 1,2 addition with bromine and bromine chloride, approach 100% anti addition when the pyridine–halogen complexes or tribromide is used as the brominating agent. The stereochemistry of 1,4-bromine addition with dienes **4a–c** and **5** is primarily anti in the presence of amine, in contrast to being chiefly syn with molecular halogen in the absence of amine. Possible mechanistic differences between the halogenating agents are suggested.

Crystalline bromine complexes such as pyridine hydrobromide perbromide ($PyHBr_3$), pyridine dibromide ($PyBr_2$), and related amine–dibromides are readily prepared and have advantages over liquid bromine because of ease in handling. Significantly different results between molecular bromine and tribromide have been noted,[1] particularly in the bromination of ketones. Our attention was attracted to the complexes as potentially novel halogenating agents by the proposal that $PyHBr_3$, $PyBr_2$, and PyBrCl add halogen to certain alkenes by a mechanism ($AdEC_2$) in which the nucleophilic step is rate determining,[2] which is in contrast to the commonly accepted halogen addition mechanism,[3] where the formation of a cyclic halonium ion or halo carbonium ion is rate determining ($AdEC_1$). We felt that the above novel proposal could be explored by studying the halogenation of dienes with the halogen complexes. In a preliminary study we reported the addition of bromine chloride to cyclopentadiene, along with several amine–BrCl complexes, and noted striking differences between the two classes of reagents.[4] In particular the amount of 1,4 addition was greatly reduced with the complexes. In this paper we have extended the study to include a variety of dienes and alkenes whose stereochemistry of molecular halogen addition had been reported. The unsymmetrical dienes, isoprene and the piperylenes, were included because differences in bond reactivities between molecular BrCl and BrCl complexes could be determined.

Results

Competition between 1,4 and 1,2 Addition to Dienes. Table I shows the dibromide products[5] obtained from butadiene (**1**), isoprene (**2**), and the piperylenes, *trans*-**3a** and *cis*-**3b**. Dibromides[5] obtained from the 2,4-hexadienes, *trans,trans*-**4a**, *cis,trans*-**4b**, and *cis,cis*-**4c**, and from cyclopentadiene (**5**) are shown in Table II. Product ratios of dibromides obtained with molecular bromination are compared to those obtained with the amine–dibromide complexes, pyridine dibromide ($PyBr_2$), 3,5-lutidine dibromide (3,5-$LuBr_2$), and 2,6-lutidine dibromide (2,6-$LuBr_2$), and the tribromides, pyridine hydrobromide perbromide ($PyHBr_3$) and tetraethylammonium tribromide (Et_4NBr_3).

All of the dienes examined show increases in 1,2 addition when the amine dibromide or a tribromide is substituted for molecular bromine. In fact the 1,2 dibromide is the main product with the latter reagents with all of the dienes except isoprene, whereas with molecular bromine in methylene chloride all of these dienes yield predominately the 1,4-dibromide. Experiments were done to assure that the dibromide products were stable to the reaction conditions.

Data in Tables I and II show that the degree to which 1,4 addition is eliminated by the use of amine dibromides depends upon the concentration of excess amine and also upon the structure of the amine.[6] For example, the ratio of 1,2 to 1,4 addition with butadiene was 5.7 with pyridine dibromide alone and 24 in the presence of a fivefold excess of pyridine. The 1,2 to 1,4 dibromide ratio from isoprene is 0.45, 1.6, and 2.3 for $PyBr_2$, a fivefold pyridine excess, and a tenfold pyridine excess, respectively. Similar increases in 1,2 addition are observed with other amines for **1** and **2** and with dienes **4a,b** and **5** in Table II.

Stereochemistry of 1,2 Addition. Tables II and III present data on the effect of amines and tribromide in changing the stereochemistry of 1,2 and 1,4 addition. Data for the dienes **4a–c** and **5** are shown in Table II and data for the β-methylstyrenes, *trans*-**6a** and *cis*-**6b**, are shown in Table III. Scheme I shows possible stereochemical routes for formation of the products.

Scheme I

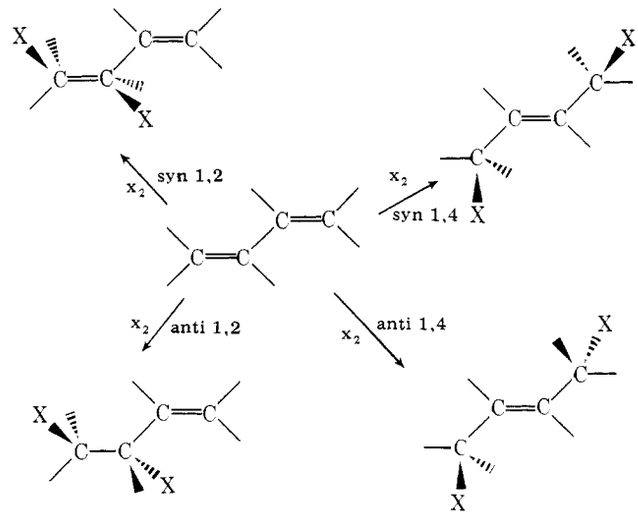

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Table I. Effects of Amines and Tribromides in Bromination of Butadiene, Isoprene, and the Piperylenes

Run	Diene	Registry No.	Brominating[a] agent	Added amine[b] (amine/Br_2)	Dibromides,[c,d] % I	II	III	IV	1,2/1,4 addn.
1	**1**	106-99-0	Br_2		24			76	0.32
2	**1**		$PyHBr_3$		88			12	
3	**1**		$PyBr_2$		85			15	5.7
4	**1**		$PyBr_2$	Py (1:1)	91			9	10
5	**1**		$PyBr_2$	Py (3:1)	95			5	19
6	**1**		$PyBr_2$	Py (5:1)	96			4	24
7	**1**		2,6-$LuBr_2$		71			29	2.4
8	**1**		2,3-$LuBr_2$	2,6-Lu (5:1)	87.5			12.5	7
9	**2**	78-79-5	Br_2		12.5	0.5	4	83	0.15
10	**2**		$PyHBr_3$		46	4.5	2.5	47	
11	**2**		$PyBr_2$		30	1	3	66	0.45
12	**2**		$PyBr_2$	Py (5:1)	58.5	3	1.5	37	1.6
13	**2**		$PyBr_2$	Py (10:1)	65	5	3	27	2.3
14	**2**		2,6-$LuBr_2$		22	0.5	2.5	75	0.29
15	**2**		2,6-$LuBr_2$	2,6-Lu (5:1)	44.5	3.5	2.0	50	0.92
16	**2**		2,6-$LuBr_2$	2,6-Lu (10:1)	50.5	3.5	2.5	43.5	1.17
17	**2**		3,5-$LuBr_2$		27	3	4	71	0.40
18	**2**		3,5-$LuBr_2$	3,5-Lu (10:1)	74	6	1	19	4.0
19[e]	**2**		Br_2	3,5-Lu (10:1)	71	10	2	17	4.3
20[e]	**2**		Br_2	Et_4NBr (5:1)	44.5	7	2.5	46	1.06
21	**3a**	2004-70-8	Br_2		30			70	0.43
22	**3a**		$PyHBr_3$		63	1		36	1.8
23[e]	**3a**		Br_2	Py (5:1)	83.5	1.5		15	5.7
24	**3b**		Br_2		20	0.5		79.5	0.26
25	**3b**		$PyHBr_3$		63.5	8		28.5	2.5
26[e]	**3b**	1574-41-0	Br_2	Py (5:1)	79.5	11.5		9	10

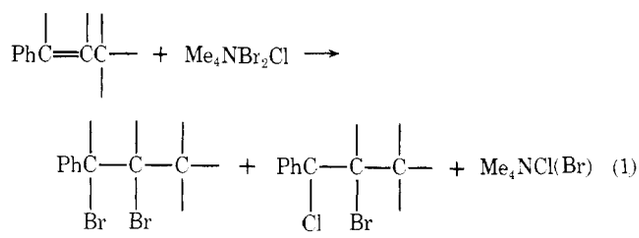
[a] The brominating agent (neat bromine, the solid amine dibromide, or solid pyridine hydrobromide perbromide ($PyHBr_3$)) was added last to a methylene chloride solution of the alkene and amine. The alkene was 0.02 mol fraction, with respect to the solvent. The temperature was 0–5 °C. [b] (Amine/Br_2) is the mole ratio of the amine to moles of available bromine. [c] The dibromides are identified as follows: From **1**, I = 3,4-dibromo-1-butene (Registry no. 10463-48-6) and IV = 1,4-dibromo-*trans*-2-butene (Registry no. 821-06-7); from **2**, I = 3,4-dibromo-3-methyl-1-butene (Registry no. 64251-92-9), II = 3,4-dibromo-2-methyl-1-butene (Registry no. 64251-93-0), III = 1,4-dibromo-2-methyl-*cis*-2-butene (Registry no. 16526-18-4), and IV = 1,4-dibromo-2-methyl-*trans*-2-butene (Registry no. 16526-19-5); from **3a** and **3b**, I = 4,5-dibromo-2-pentene (trans from **3a** (Registry no. 25296-35-9) and cis from **3b** (Registry no. 25356-03-0), II = 3,4-dibromo-1-pentene (erythro from **3a** (Registry no. 25296-34-8) and threo from **3b** (Registry no. 25356-02-9)); IV = 1,4-dibromo-*trans*-2-pentene (Registry no. 25296-22-4). The percentages are normalized to 100%. [d] Yields of total dibromides were determined by NMR on selected runs as follows: 9, 80%; 18, 33%. [e] The diene was added last in these runs to a solution in which bromine and the amine or bromine and tetraethylammonium bromide (run 20) had been allowed to equilibrate for a few minutes.

The 1,2 addition of molecular bromine to dienes **4a–c**[5d] and the alkenes **6a** and **6b**[3,7] previously had been found to be nonstereospecific, i.e., some syn addition was observed. The lack of complete anti addition to the above alkenes was interpreted as meaning that delocalization of positive charge into the neighboring vinylic or benzylic system weakens bridging to bromine and permits an open carbonium ion to form.[7,5d]

The data in Tables II and III show that when amine–dibromides or –tribromides are substituted for molecular bromine a much higher percentage of anti 1,2 addition is observed. For example, addition of solid $PyBr_2$ to the cis alkene, **6b**, results in 98% *threo*-dibromide in contrast to molecular bromination which is only 74% stereospecific. The reaction of **6b** with $PyHBr_3$ gave essentially 100% threo product. The dienes **4a–c** and **5** also show a marked trend in the direction of stereospecific anti addition when the complexes are employed as brominating agents. A further increase in anti addition was obtained when an excess of amine was used (e.g., run 2 vs. run 7 and run 10 vs. run 13, Table II).

The effect (restoration of anti addition) is more pronounced when the solid $PyBr_2$ is added than when the alkene is added last to an equilibrated solution of $PyBr_2$ (runs 2 vs. 3 and 10 vs. 11). In general the tribromides were more effective than dibromides in producing stereospecific 1,2 addition. The above differences can be explained on the basis of dissociation of the complexes (see eq 2, Discussion Section). Once dissolved, $PyBr_2$ would be able to equilibrate to free bromine. The tribromide salt would give less free bromine since its dissociation constant is reported[8] to be much smaller than that of $PyBr_2$.

Similar differences between the molecular halogen and halogen complexes was found with bromine chloride. We found (runs 6, 7, and 8 in Table III) that bromine chloride addition to **6a** and **6b** was nonstereospecific to about the same extent as bromine whereas addition of BrCl via PyBrCl was stereospecific (runs 9 and 10). We also prepared the trihalide salt, tetramethylammonium dibromochloride (Me_4NBr_2Cl) and studied its reaction with **6a** and **6b** (runs 11 and 12). The latter reaction gave both dibromides and bromochlorides (see eq 1) and the addition of each was nearly 100% stereospecific.



(1)

Stereochemistry of 1,4 Addition. The stereochemistry of 1,4 addition of bromine to dienes **4a–c** and **5** (see Scheme I) was previously examined.[5d] We reported that, although the 1,4 addition was nonstereospecific, there was a strong preference for syn addition. The data in Table II show that along with the total reduction in 1,4 (vs. 1,2) addition which occurs when the amine–dibromides and tribromide are substituted

Table II. Effects of Amines and Tribromide on Stereochemistry of 1,2- and 1,4-Bromine Addition to Dienes

Run	Diene	Brominating agent[a]	Added amine or salt[b]	Dibromides,[c,d] % Anti 1,2	Syn 1,2	Anti 1,4	Syn 1,4	1,2 addn. % anti	1,4 addn. % syn	1,2/1,4 addn.
1	**4a**[h]	Br_2	None	19.5[l]	4.5[m]	15[n]	61[o]	81	80	0.32
2	**4a**	$PyBr_2$	None	45	5.5	16	33.5	89	68	1.02
3	**4a**	$PyBr_2$[e]	None	67	4	13.5	15.5	94	53	2.45
4	**4a**	$PyHBr_3$	None	59.5	5	10	25.5	92	72	1.82
5	**4a**	Br_2	Et_4NBr (1:1)	93	1.5	3.5	2	98	36	17
6	**4a**	Br_2	Et_4NBr (1:5)	97	1	1.5	0.5	99	40	49
7	**4a**	$PyBr_2$	Py (1:5)	89	3	4.5	3.5	97	44	11.5
8	**4a**	3,5-$LuBr_2$	3,5-Lu (1:20)	92.5	4	2	1.5	96	43	28
9	**4b**[f,i]	Br_2	None	17.5	4	15.5	62	81	80	0.28
10	**4b**[f]	$PyBr_2$	None	51	4	14.5	26	93	64	1.47
11	**4b**[f]	$PyBr_2$[e]	None	74.5	1	11.5	9.5	98	45	3.8
12	**4b**[f]	$PyHBr_3$	None	63	2	12	19.5	97	62	2.2
13	**4b**[f]	$PyBr_2$	Py (1:5)	70.5	1	9.5	10	99	51	4.1
14	**4b**[f]	3,5-$LuBr_2$	3,5-Lu (1:20)	77		7	2	100	22	10
15	**4c**[j]	Br_2	None	14[p]	5[q]	5	76	74	94	0.23
16	**4c**	3,5-$LuBr_2$	3,5-Lu (1:20)	97.5		1.5	1	100	40	39
17	**5**[k]	Br_2	None	23.5[r]	*g*	14[s]	51[t]	*g*	78	0.54
18	**5**	Br_2	Py (1:1)	66	*g*	18	14	*g*	44	2.1
19	**5**	Br_2	Py (1:20)	88.5		8	3.5	100[u]	30	7.7
20	**5**	Br_2	3,5-Lu (1:20)	97		2	1	100	33	32
21	**5**	Br_2	Et_4NBr (1:1)	60.5	*g*	20.5	17.5	*g*	54	1.63
22	**5**	Br_2	Et_4NBr (1:5)	79		10.5	10.5	100	50	3.8

[a] The reaction conditions are the same as reported in Table I except that unless otherwise stated the diene was added last to a solution of the brominating agent (and amine, if added) which had been allowed to equilibrate for a few minutes. [b] The ratio in parentheses shows the mole ratio between available bromine and the amine or bromide salt. [c] See ref 5d for identification of the dibromides. [d] Percentages are normalized to 100%. Yields of total dibromides were determined by NMR on selected runs as follows: 1, 96%; 6, 107%; 8, 35%; 17, 71%; 20, 62%. [e] The solid $PyBr_2$ complex was added last to the solution of alkene. [f] The difference between the total dibromide percentages and 100% equals the percentage of 4,5-dibromo-*cis*-2-hexene which results from bromination of the trans bond in **4b**. [g] In runs 17, 18, and 21 there is an additional VPC peak in the bromination product in the amount 11.5, 1, and 1.5%, respectively, which was overlooked in our previous investigation of the bromination of **5**. We suspect that this compound may be *cis*-3,4-dibromocyclopentene but were unable to isolate the compound in sufficient amounts to prove its structure. A very dilute solution of the compound (along with about 50% of the other dibromides) was prepared from VPC collection. Upon standing at room temperature in the light for a day, the unknown peak in the above solution largely disappeared. However, significant increase of the other dibromide peaks (determined with an internal standard) did not accompany the loss of the unknown. [h] Registry no. 5194-51-4. [i] Registry no. 5194-50-3. [j] Registry no. 6108-61-8. [k] Registry no. 542-92-7. [l] Registry no. 42086-57-7. [m] Registry no. 42086-58-8. [n] Registry no. 42086-59-9. [o] Registry no. 66323-08-8. [p] Registry no. 42086-55-5. [q] Registry no. 42086-56-6. [r] Registry no. 66323-09-9. [s] Registry no. 42086-50-0. [t] Registry no. 17040-70-9. [u] Registry no. 42086-51-1.

Table III. Addition[a] of Bromine and Bromine Chloride to *cis*- and *trans*-β-Methylstyrenes in CH_2Cl_2

Run	Alkene	Reagent	Dibromides[b] Threo	Erythro	Bromochlorides[b] Threo[c]	Erythro[d]
1	**6a**[f]	Br_2	11[h]	89[i]		
2	**6b**[e]	Br_2	74.5	25.5		
3	**6a**	$PyBr_2$	2	98		
4	**6b**[g]	$PyBr_2$	98	2		
5	**6b**	$PyHBr_3$	100			
6	**6a**	BrCl			8.5[j]	91.5[k]
7	**6b**	BrCl (CCl_4)			75.5	24.5
8	**6b**	BrCl			79	21
9	**6a**	PyBrCl				100
10	**6b**	PyBrCl			100	
11	**6a**	Me_4NBr_2Cl		71		29
12	**6b**	Me_4NBr_2Cl	71.5	0.5	28	

[a] The reaction conditions are the same as those in Table I. The halogenating agent was added last to a solution of the alkene. [b] Product percentages are normalized to 100%. VPC response factors were determined for a dibromide isomer and a bromochloride isomer and were used to establish the mole ratio between dibromides and bromochlorides. Yields of products were determined by VPC and/or NMR and did not drop below 60% for any runs. [c] *threo*-2-Bromo-1-chloro-1-phenylpropane (7). [d] *erythro*-2-Bromo-1-chloro-1-phenylpropane (8). [e] Fahey and Schneider[3] report 74% threo and 26% erythro for the bromination of **6b** in methylene chloride. [f] Registry no. 873-66-5. [g] Registry no. 766-90-5. [h] Registry no. 21087-20-7. [i] Registry no. 21087-19-4. [j] Registry no. 66323-24-8. [k] Registry no. 4962-44-1.

for bromine, there is an accompanying decrease in the preference for syn-1,4 addition. Thus, the percentage of syn-1,4 addition drops from 80 to 68 for **4a** and from 80 to 64 for **4b** when the brominating agent is changed from neat bromine to a solution of pyridine dibromide (diene added last). Direct addition of the solid complex (runs 3 and 11) causes a greater reduction in the percentage of syn addition. Tribromides reduce the percentage of syn-1,4 addition in a similar manner as do the pyridine dibromides. When the dienes are added to bromine solutions containing an excess of amine (compared to bromine) the small amount of accompaning 1,4-dibromide (runs 7, 8, 13, 14, 16, 18, 19, and 20) usually contains an excess of the anti adduct.

Addition of Bromine Chloride to Dienes 2, 3a, and 3b. The results for bromine chloride addition to the dienes **2, 3a,** and **3b** using the molecular halogen itself and amine solutions of bromine chloride are presented in Table IV. The use of the unsymmetrical electrophile with these dienes permits the ratio of attack at each bond to be determined. Although the presence of amine caused a marked decrease in the amount of 1,4 addition, the relative reactivities of the two double bonds did not change drastically.

It should also be pointed out that the relative reactivities of the two double bonds in **2, 3a,** and **3b** are in line with those reported for a rather different electrophilic system (MeOCl or Cl_2 in methanol).[9]

Discussion

A satisfactory mechanistic interpretation of our data should

Table IV. The Reaction of Bromine Chloride with Isoprene and *cis*- and *trans*-1,3-Pentadiene in CH_2Cl_2 at 25 °C

Run	Diene	Added amine (amine/BrCl)	Bromochloride products, %[a] I	II	III	IV	III + IV
1	**2**	None	15.5	1	10	73.5	83.5
2	**2**	Py (5:1)	53.5	7	8.5	31	39.5
3	**2**	3,5-Lu (5:1)	58	8			34
4	**2**	2,6-Lu (5:1)	48.5	6			45.5
5	**3a**	None	38	0.5	60	1.5	61.5
6	**3a**	Py (1:1)	67	1			32
7	**3a**	Py (5:1)	68	1.5	30	0.5	30.5
8	**3a**	3,5-Lu (5:1)	81	1.5			17.4
9	**3a**	2,6-Lu (5:1)	74.5	1	23	1.5	24.5
10	**3b**	None	31.5	3.5	59.5	5.5	65
11	**3b**	Py (1:1)	67	10.5			22.5
12	**3b**	Py (5:1)	71.5	14.5	12	2	14
13	**3b**	3,5-Lu (5:1)	73.5	18.5			8
14	**3b**	2,6-Lu (5:1)	74.5	10.5			15

[a] The products are identified as follows: from **2**, I = 4-bromo-3-chloro-3-methyl-1-butene (Registry no. 66323-15-7) (**9**), II = 4-bromo-3-chloro-2-methyl-1-butene (Registry no. 66323-14-6) (**10**), III = 4-bromo-1-chloro-2-methyl-2-butene (Registry no. 66323-16-8) (**11**), IV = 1-bromo-4-chloro-2-methyl-2-butene (Registry no. 6323-17-9) (**12**); from **3a** and **3b**, I = 5-bromo-4-chloro-2-pentene (trans (Registry no. 66323-18-0) (**13**) from **3a** and cis (Registry no. 66323-19-1) (**14**) from **3b**), II = 4-bromo-3-chloro-1-pentene (erythro (Registry no. 66323-20-4) (**15**) from **3a** and threo (Registry no. 66323-21-5) (**16**) from **3b**), III = 4-bromo-1-chloro-*trans*-2-pentene (Registry no. 66323-22-6) (**17**), and IV = 1-bromo-4-chloro-*trans*-2-pentene (Registry no. 66323-23-7) (**18**). Product percentages are normalized to 100%. Total product yields, determined by means of VPC internal standards, varied between 69 and 100%.

be able to account for the following differences between additions employing the halogen complexes, amine dibromides and tribromide salts, and those of the free, molecular halogens: (1) Alkenes which give nonstereospecific 1,2 addition with free bromine (**4a–c**, and **6a,b**) and free bromine chloride (**6a,b**) give nearly stereospecific anti addition with the halogen complexes. (2) Conjugated dienes show greatly diminished 1,4 addition with the complexes in comparison to the free halogens. (3) The results with the amine dibromides are very similar to those with the trihalides, especially when an excess of amine is used.

First of all, we want to comment about our observations (Tables I and II) that the effects of the amines depend upon their concentration and structure. A reasonable explanation for the concentration effect is that the pyridine dibromide complexes are in equilibrium with free bromine

$$\text{Py:Br:Br} \rightleftharpoons \text{Py} + \text{Br:Br} \qquad (2)$$

Thus the addition of excess amine suppresses the concentration of molecular bromine.

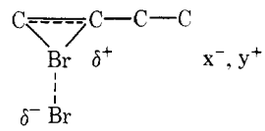
An alternative explanation for the effect of excess amine is that some other equilibrium involving amine is present, such as in eq 3.[10,11] In the latter case, tribromide ion might be the electrophile at high amine concentration.

$$2\text{PyBr}_2 \rightleftharpoons \text{Py}_2\text{Br}^+, \text{Br}_3^- \qquad (3)$$

The similarity in effects which have been observed between amine–dibromides and ammonium–tribromides could therefore be due to the fact that both brominate via tribromide ion or that both reagents simply limit the concentration of free bromine (see later discussion).

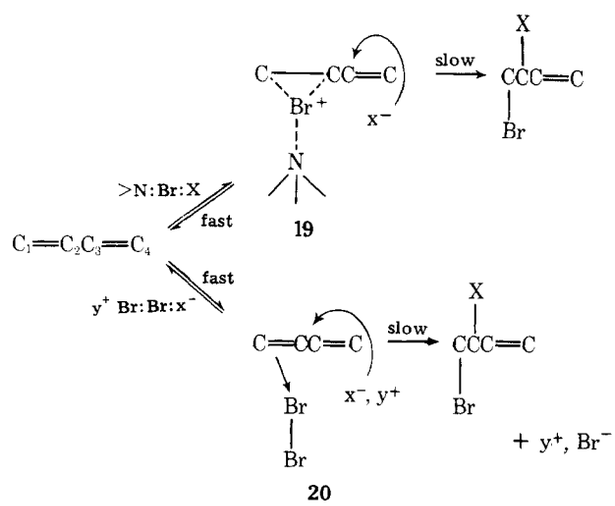
The three amines which were used differ in their capacity to suppress 1,4 addition of bromine to the dienes. In bromination of **1**, $PyBr_2$ gives 85% 1,2-dibromide compared to 71% with 2,6-$LuBr_2$ and with a fivefold excess of each amine, the percentages of 1,2-dibromide are 96 and 87.5, respectively (Table I). In bromination of **2** the effectiveness of the amines in suppressing 1,4 addition varies in the order 3,5-Lu > Py > 2,6-Lu (Table I). The differences between these amines are probably due to the relative stabilities of their bromine complexes and therefore the extent to which each dissociates into free bromine as discussed above.[12,13]

We turn now to a mechanistic discussion of the differences between molecular halogens and their amine and tribromide complexes. One possible explanation for these differences is that there is a fundamental mechanistic change, similar to that proposed by Bellucci[2] for his work on *tert*-butylcyclohexenes, involving a type $AdEC_1$ addition mechanism with the free halogens and a type $AdEC_2$ with the complexes. As shown in Scheme II, the $AdEC_2$ mechanism would involve a rate-determining attack by halide ion on a bromonium–amine complex (**19**) derived from the amine–dibromide[2] or on the alkene–halogen charge transfer complex (**20**) obtained from the trihalide.[14–16] Conceivably both intermediates **19** and **20** are charge-transfer complexes or perhaps **20** could be viewed as a bromonium ion with significant charge on carbon, e.g.,



Intermediates **19** and **20** are similar in that both have a nucleophile (>N: or $Br:^-$) associated with the electrophilic bromine in the intermediate thus reducing the extent to which the positive charge would be localized on the carbon atoms and

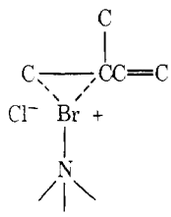
Scheme II



also permiting reversibility of intermediate formation ($AdEC_2$).

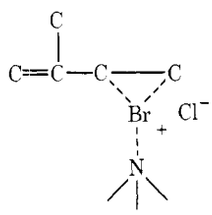
Scheme II can be used to account for some of our observations. Since **19** and **20** are π complexes or bromonium ions with a smaller amount of charge on carbon, they would be expected to yield anti products when attacked by halide ion. Also, with minimal concentration of charge on carbon, charge dispersal to the number 4 carbon of the neighboring vinylic system would be diminished and, hence, 1,4 addition would be reduced. It is not clear why 1,4 addition becomes more anti than syn. Possibly the preferred stereochemistry of S_N2' attack is anti and that what we are seeing is a change from a S_N1' mechanism (molecular halogenation, $AdEC_1$) to a more pure S_N2' mechanism (halogenation with the complexes, $AdEC_2$).[17]

Although Scheme II accounts for some of the facts of this study, it seems questionable at other points. For example, if the mechanisms of Scheme II are operative, we might expect that the products formed from the unsymmetrical dienes, **2** and **3a,b,** might show considerable differences between molecular bromine chloride and the pyridine complexes. In the case of 2,6-$LuBr_2$ considerable steric hindrance should be experienced for attack on the 3,4 bond in **3a** and **3b** and the 1,2 bond in **2.** Yet we see no significant diminution in the relative amount of attack on the more highly substituted double bond in going from BrCl to 2,6-$LuBr_2$. We would expect that this would be particularly noticeable in attack on the 1,2 bond in **2,** where attack by halide on the intermediate **19** would require nucleophilic substitution on a tertiary carbon (structure **21**).



21

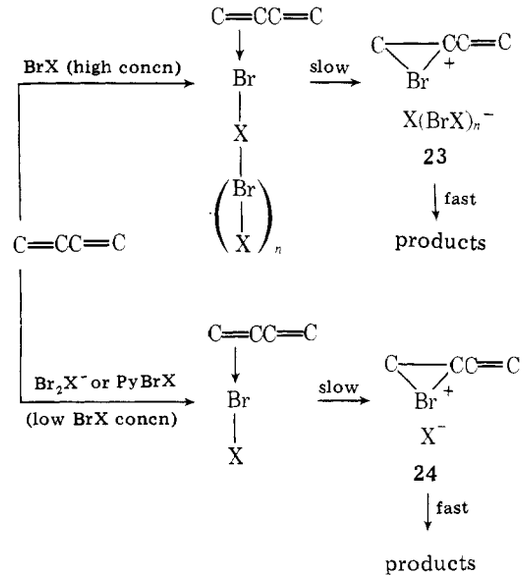
Again we observe no significant decrease in attack at the 1,2 bond when the amine–bromochlorides are the reagents. Indeed there is relatively more 1,2 addition (in comparison to 1,4 addition) resulting from attack on the intermediate **21** than from the intermediate obtained from attack at the 3,4 bond of **2,** i.e., structure **22** (compare runs 1 and 2, Table IV).



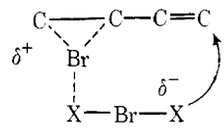
22

In our opinion the data presented here do not provide conclusive evidence either for or against an $AdEC_2$ mechanism in the reaction of the amine–dibromides and –tribromide. Let us suggest another possible explanation for the results obtained with these reagents.[18] Perhaps the differences between the reaction of free halogens and the halogen complexes result from the fact that with the molecular halogens two or more halogen molecules participate in the transition state (second order), whereas reactions with the halogen complexes limit the availability of halogen and impose a first-order mechanism. In other words, the function of the complexes (amine–dibromides and –tribromide) would be to limit the concentration of free halogen. The two mechanisms are compared in Scheme III.

Scheme III



The structures of the anions in the intermediates (**23** and **24**) constitute the real differences between the mechanisms. Whereas in **23** the anion would be a trihalide or polyhalide, in **24** it would be a simple halide ion. Therefore, ion-pair **24** should be much less stable than ion-pair **23** and would quickly collapse to the anti-1,2 adduct before opening of the bromonium ion could occur. The greater stability of the anion in **23** would result in an ion pair of longer lifetime, thus permiting bromonium ion ring opening and the accompanying syn-1,2 addition. Possibly the differences between the anions could account for the large amounts of syn-1,4 addition with the molecular halogen. The complex anion in **23** may interact with the number 4 carbon atom simultaneously with the development of the bromonium ion (structure **25**). On the other hand, the highly unstable character of ion-pair **24** and the relatively small size of the anion might prevent it from yielding much 1,4 adduct.



25

Attempts to test our hypothesis that product ratios are affected significantly by halogen concentration have not been encouraging. In a series of experiments on bromination of the 2,4-hexadienes we found that the use of very dilute bromine did indeed have a striking effect on product compositions in the same manner as the complexes, i.e., stereospecific anti-1,2 addition, greatly reduced 1,4 addition, and lower proportion of syn-1,4 addition. However, the effects were observed only when the solvent was carbon tetrachloride or pentane. There was very little detectable effect of dilution in the more polar solvents, methylene chloride and nitromethane. When bromination of β-methylstyrene was attempted with very dilute bromine, the rate of reaction decreased enormously and there was little change in the stereoselectivity (compared to more concentrated bromine).

Definitive answers to the mechanistic questions raised here may await kinetic studies since little kinetic work has been done in the aprotic, nonpolar solvents in which electrophilic additions are often done.

Finally, we would suggest that results presented here can be used to advantage in synthesis, since the proper selection of halogenation conditions permits isolation of a variety of

pure isomers. For example, the 1,4-dibromide of butadiene is easily obtained by bromination with neat bromine in dichloromethane (followed by crystallization), whereas the 1,2-dibromide can be isolated in high purity when the amine–dibromide or –tribromide is used. Also, essentially pure 1,2-dibromide stereoisomers, e.g., from the 1-phenylpropenes or 2,4-hexadienes, are obtained under the latter bromination conditions. Tribromides, e.g., Et_4NBr_3 which is easily prepared in situ (see footnote *e*, Table I), afforded much higher yields than did the amine–dibromides.[19]

Experimental Section

The alkenes and dienes were obtained commercially and distilled before use. The amines and solvents were used without further purification. The amine–dibromides were prepared by the method described by Bellucci.[2a] Pyridine hydrobromide perbromide ($PyHBr_3$) was prepared by the Fieser method.[1a]

Tetramethylammonium dibromochloride (Me_4NBr_2Cl) was prepared from tetramethylammonium chloride by an adaptation of the procedure used to make $PyHBr_3$. Its melting point was 59–65 °C.

Brominations of Dienes 1, 2, 3a,b, 4a–c, 5. The specific conditions for bromination of the dienes are described in Tables I and II. A typical reaction (run No. 6, Table I) follows: To a mixture of 0.15 mL (0.0015 mol) of isoprene and 0.15 mL (.0019 mol) of pyridine in 4.7 mL (0.073 mol) of dichloromethane at 0–5 °C there was added with stirring 0.089 g (0.00037 mol) of solid pyridine dibromide. After 5 min the reaction mixture was extracted with cold, 10% hydrochloric acid and then shaken with sodium bicarbonate solution. The HCl extraction was done in all runs in which amine was present in the product.

The analysis of the dibromide mixtures was done by VPC as described previously,[5a–d] except that glass columns were used instead of stainless steel.

Yields were obtained on selected runs by NMR after stripping of the solvent and unreacted diene (benzene was used as internal standard).

To assure that the product compositions were uneffected by the reaction conditions, i.e., were kinetically determined, certain control experiments were performed. The absence of reactions between the amines and dibromide products is shown by the following experiment (also done on the bromination product from **4a**): The dibromide mixture from bromination of **2** (run 9, Table I) was stirred with a tenfold excess of 3,5-lutidine for 5 min under the conditions of the typical reaction described above. After removal of the amine by HCl extraction, the product was analyzed by VPC and was found to be the same as before treatment with the amine. The quantity of dibromide was reduced by 22% (NMR) but this may be attributed in part to loss in the extraction and solvent stripping procedure. A similar experiment with the dibromide product (run 1, Table II) of **4a** using a 20-fold excess of 3,5-lutidine showed no effect on the dibromide composition within experimental error.

Control experiments were performed on the dibromide products from **2** and **4a**, similar to those reported previously,[5d] which showed that the dibromides were not rearranged under the conditions of molecular bromination.

Additions to 1-Phenylpropenes (6a,b). The reaction conditions are described in Table I. Mixtures of *erythro*- and *threo*-dibromides were analyzed by VPC and/or NMR as reported previously.[3,7] *threo*-2-Bromo-1-chloro-1-phenylpropane (**7**) and *erythro*-2-bromo-1-chloro-1-phenylpropane (**8**) were separated from each other and from the *erythro*- and *threo*-dibromides by VPC (2.5% SE-30 on 60–80 CW (DMCS), 6 ft × 0.25 in. ss, 100 °C). Retention times for **7**, **8**, the *erythro*-dibromide, and the *threo*-dibromide are respectively 25.2, 22.4, 36.0, and 40.2 min. Pure samples of **7** and **8** were obtained by reaction of the respective alkenes with PyBrCl followed by fractionation. The NMR spectra (Varian T-60, in CCl_4) follow: **7**, 1.88 (d, 3, CH_3, J_{23} = 6.4 Hz), 4.33 (d of q, 1, CHBr, J_{12} = 9.0, J_{23} = 6.4 Hz), 4.90 (d, 1, CHCl, J_{12} = 9.0 Hz), 7.32 [m (narrow), 5, C_6H_5]; **8**, 1.62 (d, 3, CH_3, J_{23} = 6.4 Hz), 4.42 (d of q, 1, CHBr, J_{23} = 6.4, J_{12} = 6.0 Hz), 5.03 (d, 1, CHCl, J_{12} = 6.0 Hz), 7.33 [m (narrow), 5, C_6H_5].

Reaction of Isoprene (2) with Bromine Chloride. The reactions were done at 25 °C, with the diene at 0.02 mol fraction with respect to the solvent dichloromethane. In the reactions using excess amine, the diene was added last to a solution of the amine and bromine chloride. A typical reaction follows: Pyridine (0.58 g 0.0073 mol) and 1 mL of 1.4 M (0.0015 mol) bromine chloride solution (in CCl_4) were dissolved in 12 mL of dichloromethane and a solution of 0.50 g (0.0073 mol) of **2** in 12 mL of dichloromethane was added rapidly with stirring. After 5 min the solution was extracted with cold, 10% hydrochloric acid. Control experiments with excess amine as described for **2** and **4a** above did not effect the bromochloride mixture.

Mixtures of the bromochlorides from **2** were analyzed by VPC under the following conditions: 3% OV-17 on 80–100 CW (DMCS), 70 °C, 6 ft × 0.25 in., ss. Retention times of **9**, **10**, **11**, and **12** are respectively 6.5, 8.5, 32, and 32 min.

The pure bromochlorides were obtained as follows and identified by their NMR spectra reported below. Peaks 1 and 2 (**9** and **10**) were separated and collected by VPC (OV-17). Compound **12** was obtained by recrystallization from a crude reaction product (reaction of **2** with $BrCl$–CCl_4) from pentane at low temperatures. Isomer **11** was obtained via the following independent synthesis:

$$2 \xrightarrow{\text{HOCl (ether)}^{20}} \xrightarrow{PBr_3{}^{21}} \mathbf{11}$$

The crude mixture obtained from this sequence was distilled and **11** was obtained from the mixture by VPC collection (5% DC-550). The compound obtained (**11**) in this way had very similar (but different) NMR spectrum to **12**. Mixtures of **11** and **12** could not be separated by VPC on liquid phases such as SE-30, FFAP, DEGS, dinonyl phthalate, and β,β-dioxypropionitrile. The determination of ratios of **11** and **12** produced in reaction mixtures was accomplished by VPC collection of peak 3 (**11** and **12**) and then analysis by 100 MHz NMR which separated the up-field line of the C_4 methylene doublet of **11** from the other methylene absorptions of **11** and **12**.

The NMR (60 MHz, CCl_4) spectra of the bromochlorides from **2** follow: **9**, 1.80 (s, 3, CH_3), 3.63 (s, 2, CH_2Br), 5.1–5.5 (m, 2, C=CH_2), 5.98 (dd, 1, C**H**=CH_2, J_{12} = 16.4, J_{12}, = 10.4 Hz); **10**, 1.82 [s (br), 3, CH_3], 3.42–3.72 (m, 2, CH_2), 4.50 (dd, 1, CHCl, J = 5.0, J' = 9.6 Hz), 4.93–5.20 (m, 2, C=CH_2); **11**, 1.87 (s, 3, CH_3), 3.83 (d, 2, CH_2Br, J_{34} = 8.6 Hz), 4.00 (s, 2, CH_2Cl), 5.83 (t, 1, C=CH, J_{34} = 8.6 Hz); **12**, 1.87 (s, 3, CH_3), 3.93 (s, 2, CH_2Br), 4.02 (d, 2, CH_2Cl, J_{34} = 7.2 Hz), 5.79 (t, 1, C=CH, J_{34} = 7.2 Hz).

Reaction of the Piperylenes (3a and 3b) with Bromine Chloride. The reaction conditions are the same as for **2** described above. The mixtures of piperylene bromochlorides were analyzed by VPC [2.5% SE-30 on 80–100 CW (DMCS), 5 ft × 0.25 in. ss, 70 °C] with retention times of 3.8, 4.6, and 6.6 min for (**13** and **14**), (**15** and **16**), and (**17** and **18**), respectively. Pure isomers were identified by their NMR spectra reported below. Pure compounds were obtained from reaction mixtures rich in a particular isomer. Pure **14** was isolated by fractional distillation (bp 50 °C (7 Torr)). Isomers **13**, **15**, **16**, and **18** were isolated by VPC collection (SE-30 or DC-550). Compound **17** was synthesized from **3a** by the procedure used to prepare **11** as described above and was obtained pure by VPC collection.

Since attempts to separate the 1,4 adducts (**17** and **18**) were unsuccessful the ratio between the two was obtained as follows: Peak 3 containing **17** and **18** was collected by VPC (5% DC-550) from a particular reaction mixture. Since the methyl groups absorb in the NMR at 1.80 and 1.57 ppm for **17** and **18**, respectively, their ratio could be obtained. However, small amounts of 4,5-dibromo-2-pentene, a consistent impurity in the bromine chloride reaction, also absorbed at 1.80 ppm. Its composition in the mixture was determined by VPC and its NMR integration was subtracted from that of **17**.

The NMR spectra of the bromochlorides from **3a** and **3b** (60 MHz, CCl_4) follow: **13**, 1.77 (d, 3, CH_3, J_{12} = 5.2 Hz), 3.40 (dd, 1, BrC**H**(H), J_{45} = 9.0, $J_{55'}$ = 10.0 Hz), 3.65 (dd, 1, BrCH(**H**), $J_{45'}$ = 5.0, $J_{55'}$ = 10.0 Hz), 4.42 (ddd, 1, CHCl, $J_{45'}$ = 5.0, J_{45} = 9.0 Hz), 5.22–6.0 (m, 2, CH=CH); **14**, 1.75 (d, 3, J_{12} = 5.2 Hz), 3.42 (dd, 1, BrC**H**(H), $J_{4,5}$ = 8.8, $J_{5,5'}$ = 10.0 Hz), 3.67 (dd, 1, BrCH(**H**), $J_{45'}$ = 5.2 Hz, $J_{55'}$ = 10.0 Hz), 4.87 (ddd, 1, CHCl, $J_{45'}$ = 5.0, J_{45} = 9.2, J_{34} = 9.2 Hz), 5.18–5.90 (m, 2, CH=CH); **15**, 1.82 (d, 3, CH_3, J_{45} = 6.4 Hz), 3.9–4.5 (m, 2, CHBrCHCl), 5.13–6.0 (m, 3, CH=CH_2); **16**, 1.70 (d, 3, CH_3, J_{45} = 6.4 Hz), 4.28 (d of q, 1, CHBr, J_{45} = 6.4, J_{34} = 3.6 Hz), 4.58 (dd, 1, CHCl, J_{34} = 6.6, J_{23} = 6.6 Hz), 4.22–5.53 (m, 2, C=CH_2), 5.73–6.33 (m, 1, CH=C); **17**, 1.80 (d, 3, CH_3, J_{45} = 6.6 Hz), 3.98 (apparent d, 2, J_{12} = 6.0 Hz), 4.53 (apparent quintet, 1, CHBr, $J_{4,5}$ = 6.5 Hz), 5.62–6.00 (m, 2, CH=CH); **18**, 1.57 (d, 3, CH_3, J_{45} = 6.4 Hz), 3.73–3.93 (m, 2, CH_2), 4.23–4.67 (m, 1, CHCl), 5.63–5.92 (m, 2, CH=CH).

Acknowledgment. Support for this work was provided by the Research Corporation, the donors of the Petroleum Research Fund, administered by the American Chemical Society, the Research Associates of Point Loma College, and a Science-Alumni group of Bethany Nazarene College. We are grateful to Oklahoma University for their assistance in obtaining NMR spectra.

Registry No.—Br_2, 7726-95-6; $PyHBr_3$, 66323-10-2; $PyBr_2$, 6081-86-3; 2,6-$LuBr_2$, 35120-69-5; 3,5-$LuBr_2$, 35120-70-8; Py, 110-86-1;

2,6-Lu, 108-48-5; 3,5-Lu, 591-22-0; Et_4NBr, 71-91-0; BrCl, 13863-41-7; BrCl(CCl_4), 66323-11-3; PyBrCl, 21300-57-2; Me_4NBr_2Cl, 66323-12-4; Et_4NBr_3, 66323-13-5.

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(1) (a) L. F. Fieser and M. Fieser, "Reagents for Organic Synthesis", Wiley, New York, N.Y., 1967, pp 967–970, and references therein; (b) V. W. Armstrong, N. H. Chishti, and R. Ramage, *Tetrahedron Lett.*, 373 (1975); (c) D. V. C. Avang and S. Wolfe, *Can. J. Chem.*, **47**, 706 (1969).

(2) (a) P. L. Barili, G. Bellucci, F. Marioni, I. Morelli, and V. Scartoni, *J. Org. Chem.*, **37**, 4353 (1972); (b) P. L. Varili, G. Bellucci, F. Marioni, I. Morelli, and V. Scartoni, *ibid.*, **38**, 3472 (1973); (c) G. Bellucci, G. Ingrosso, F. Marioni, E. Mastrorilli, and I. Morelli, *ibid.*, **39**, 2562 (1974).

(3) E.g., see R. C. Fahey and H. J. Schneider, *J. Am. Chem. Soc.*, **90**, 4429 (1968), and references therein.

(4) V. L. Heasley, C. N. Griffith, and G. E. Heasley, *J. Org. Chem.*, **40**, 1358 (1975).

(5) The kinetically determined dibromide products of these dienes have been determined previously. From **1**, (a) V. L. Heasley, G. E. Heasley, R. A. Loghry, and M. R. McConnell, *J. Org. Chem.*, **37**, 2228 (1972); L. F. Hatch, P. O. Gardner, and R. E. Gilbert, *J. Am. Chem. Soc.*, **81**, 5943 (1956). From **2**, (b) V. L. Heasley, C. L. Frye, R. T. Gore, Jr., and P. S. Wilday, *J. Org. Chem.*, **33**, 2342 (1968). From **3a** and **3b**, (c) V. L. Heasley, G. E. Heasley, S. K. Taylor, and C. L. Frye, *ibid.* **35**, 2967 (1970). From **4a–c**, (d) G. E. Heasley, V. L. Heasley, S. L. Manatt, H. A. Day, R. V. Hodges, P. A. Kroon, D. A. Redfield, T. L. Rold, and D. E. Williamson, *ibid.*, **38**, 4109 (1973). From **5**, ref 5d and 5e, G. Heublein and M. Helbig, *Tetrahedron*, **29**, 3247 (1973).

(6) This is in contrast to a report by Bellucci[2a] who reported that the structure of the amine or their concentrations had no significant effect on product ratios.

(7) J. H. Rolston and K. Yates, *J. Am. Chem. Soc.*, **91**, 1469 (1969).

(8) R. E. Buckles and J. P. Yuk, *J. Am. Chem. Soc.*, **75**, 5048 (1953), report a p*K* of 5.9 for Me_4NBr_3 in CH_2Cl_2 in comparison to a p*K* of 0.99 reported (ref 13c) for $PyBr_2$ in CCl_4.

(9) G. E. Heasley, V. L. Heasley, V. M. McCully, R. T. Wiegman, and R. A. Skidgel, *J. Org. Chem.*, **41**, 644 (1976).

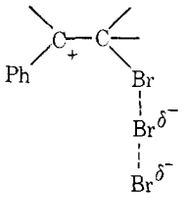
(10) The literature concerning the structures of the amine dihalogen charge transfer complexes in the solid and in solution is confusing. Hassel and Romming (ref 11a) cite X-ray crystallographic studies to support a linear amine–dihalide structure in the solid state. But, on the basis of infrared and Raman spectral data, Ginn et al. (ref 11b) conclude that $PyBr_2$ is present as a Py_2Br^+, Br_3^- salt in the solid state, as the nonionized PyBr–Br complex in nonpolar solvents, and as an equilibrium mixture of PyBr–Br with Py_2Br^+, Br_3^- in more polar solvents (e.g., CH_2Cl_2) and in the presence of excess pyridine. In a paper on the role of pyridine in the bromination of aromatic compounds, Ganesan and Jabeen (ref 11c) accept earlier conclusions by Popov and Rygg (ref 11d) that $PyBr_2$ readily gives rise to the species $PyBr^+$ and Br^-. Bellucci[2a] apparently assumes that $PyBr^+$, Br^- is the electrophilic agent in brominations with $PyBr_2$.

(11) (a) O. Hassel and C. H. R. Romming, *Q. Rev., Chem. Soc.*, **16**, 1 (1962); (b) S. G. W. Ginn, I. Haque, and J. L. Wood, *Spectrochim. Acta, Part A*, **24**, 1531 (1968); (c) R. Ganesan and Zahera J., *J. Indian Chem. Soc.*, **49**, 205 (1972); (d) A. I. Popov and R. H. Rygg, *J. Am. Chem. Soc.*, **79**, 4622 (1957).

(12) Formation constants for pyridine–halogen complexes have not been determined in methylene chloride. Formation constants ($\times 10^3$) for the BrCl complexes[13a] in CCl_4 of PyBrCl, 1.2, 2,6-LuBrCl, 1.5, and 3,5-LuBrCl, 6.8, compared to formation constants for the ICl complexes[13b] ($\times 10^5$) of PyICl, 4.8, and 2,6-LuICl, 0.89. The 2,6-Lu complexes are of lower stability than the 3,5-Lu complexes, evidently because of greater steric interactions in the former. Given the greater size of chlorine over bromine, it seems likely that 2,6-$LuBr_2$ might be less stable than $PyBr_2$. The few constants for the dibromides which have been reported[13c] ($PyBr_2$, 9.7, 3,4-$LuBr_2$, 15.4) show that the bromine complexes are much less stable than the BrCl or ICl complexes.

(13) (a) T. Surles and A. I. Popov, *Inorg. Chem.*, **8**, 2049 (1969); (b) A. I. Popov and R. H. Rygg, *J. Am. Chem. Soc.*, **79**, 4622 (1957); (c) G. G. Aloisi, G. Beggiato, and U. Mazzucato, *Trans. Faraday Soc.*, **66**, 3075 (1970).

(14) Bellucci has suggested[2a] that the reason that $PyBr_2$ and $PyHBr_3$ give similar results is because $PyHBr_3$ is converted to $PyBr_2$ but that would not be possible for Et_4NBr_3 which gives results similar to $PyBr_3$ in our study. Concerning the mechanism of bromination by Br_3^- Rolston and Yates[15] found a much less negative ρ value for bromination of a series of substituted styrenes by tribromide than for bromination by molecular bromine (−2.02 for Br_3^- vs. −4.21 for Br_2) and concluded that much less positive charge was developed on the α carbon in the transition state (we might note that the transition state proposed by these workers, see structure below, could not be consistent with our stereochemical results). Du Bois[16] has concluded that tribromide reacts by an electrophilic attack by Br_3^- in reactive alkenes compared to a nucleophilic attack by Br^- on the Br_2 charge transfer



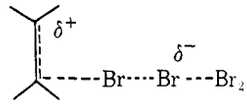
complex when the alkene is of low reactivity. On the basis of these reports, we would expect that our alkenes would probably react with Br_3^- by the $AdEC_1$ mechanism.

(15) J. H. Rolston and K. Yates, *J. Am. Chem. Soc.*, **91**, 1483 (1969).

(16) J. E. Dubois and X. Q. Huynh, *Tetrahedron Lett.*, 3369 (1971).

(17) G. Stork and A. F. Kreft, *J. Am. Chem. Soc.*, **99**, 3851, 3850 (1977), report considerable variation in the stereochemistry of S_N2' attack, depending upon the nature of the nucleophile and other conditions. Theoretical calculations [R. L. Yates, N. D. Epiotis, and F. Bernardi, *J. Am. Chem. Soc.*, **97**, 6615 (1975)] predict that the stereochemistry of the S_N2' reaction should be controlled by nonbonded attraction and repulsion forces. Thus the nucleophile should approach syn to the leaving group when the nucleophile is negatively charged, and the anti approach should be favored when the nucleophile is uncharged. Bordwell, *Acc. Chem. Res.*, **3**, 281 (1970), has stressed the lack of evidence for the S_N2' mechanism and has found that many reactions which appear to be S_N2' actually proceed via ion pair mechanisms.

(18) Wilson, *J. Chem. Soc., Perkin Trans. 2*, 141 (1976), has also suggested that variations in stereospecificity of bromine addition to styrenes with changes in bromine concentration could be explained by the fact that the higher order (in Br_2) mechanism would proceed directly to an open carbonium ion (structure below) whereas the unimolecular reaction would yield



a cyclic bromonium ion.

(19) Lower yields were obtained with the amine dibromides (in comparison to molecular bromine), particularly in the presence of a large excess of amine. Although we showed that this was not caused by a reaction of the amine with the dibromide products, we did not establish the reason for the loss in material balance. One possibility is that the pyridines, themselves, are brominated in competition with the alkenes.

(20) See ref 1a, p 487.

(21) A. Valette, *Ann. Chim. (Paris)*, **3**, 644 (1948).