A mixture of 38.00 g (0.30 mol) of *p*-chlorotoluene, 80 mL (0.63 mol) of trimethylchlorosilane, and 8.00 g (0.33 mol) of magnesium metal in 500 mL of dry THF was heated to reflux under nitrogen in a round-bottomed flask equipped with a condenser and a magnetic stirrer. The reaction mixture was stirred at reflux for 18 h, at the end of which most of the magnesium had been consumed and a thick gray precipitate had formed. The reaction mixture was cooled to room temperature and poured into 300 mL of water. After the magnesium salts had dissolved, 200 mL of ether was added and the layers were separated. The organic layer was washed with water and dried over $MgSO_4$, and the solvent was removed under reduced pressure. The resulting crude yellow liquid was distilled to yield 37.21 g (75%) of *p*-(trimethylsilyl)-toluene (**1a**) as a colorless liquid: bp 92–94 °C (33 mm) [lit.[8] bp 192 °C (748 mm)]; ^1H NMR ($CDCl_3$) δ 7.30 (d, J = 8 Hz, 2 H, aromatic), 7.19 (d, J = 8 Hz, 2 M aromatic), 2.32 (s, 3 H, CH_3), 0.22 (s, 9 H, $Si(CH_3)_3$).

Under conditions identical with those above, 38.00 g (0.30 mmol) of *m*-chlorotoluene was converted to 38.16 g (77%) of *m*-(trimethylsilyl)toluene (**1b**) as a colorless liquid: bp 92–94 °C (33 mm) [lit.[8] bp 188 °C (748 mm)]; ^1H NMR ($CDCl_3$) δ 7.16 (m, 4 H, aromatic), 2.36 (s, 3 H, CH_3), 0.28 (s, 9 H, $Si(CH_3)_3$).

Preparation of *p*-(Trimethylsilyl)benzyllithium (2a) with Alkyllithiums/THF. Method A. In a typical experiment, 1.00 g (6.08 mmol) of **1a** was dissolved in 10 mL of dry THF under nitrogen and cooled to −30 °C. Then 2.9 mL (6.67 mmol) of 2.3 M *tert*-butyllithium in pentane was added slowly over 5 min. The solution was allowed to warm to −20 °C and was stirred at this temperature for 1 h. The bright orange solution was then allowed to come to room temperature and was quenched with excess trimethylchlorosilane (1.55 mL, 12.2 mmol). The volume of the solution was doubled with ether, the mixture was transferred to a separatory funnel, washed with water (3 × 20 mL), and dried over $MgSO_4$, and the solvent was removed under reduced pressure. The mixture was analyzed by gas chromatography on a 7 ft × 0.25 in. column of 5% Carbowax 20M on 80/100 mesh Chromosorb G at a temperature of 107 °C. The mole ratio of [*p*-(trimethylsilyl)benzyl]trimethylsilane (**4**) to **1a** was determined (after correction for the relative detector response) to be 0.79:1. This corresponded to a 44% yield of *p*-(trimethylsilyl)benzyllithium (**2a**) based on the amount of **1a** used. No derivatives resulting from polylithiation[4] were detected by either GC or ^1H NMR analysis of the crude mixture. Samples of **1a** and **4** were obtained by preparative gas chromatography and identified by their ^1H NMR spectra. The spectrum of **4** was identical with that reported by West.[4]

In a similar manner, several experiments were conducted, varying the reaction time, quantity of THF used, or employing 1.18 M *sec*-butyllithium in hexane in place of *tert*-butyllithium. Experimental conditions and results are summarized in Table I.

Method B. In a typical experiment, 10.5 mL (12.4 mmol) of 1.18 *sec*-butyllithium in hexane was added to 1.00 g (6.08 mmol) of **1a** stirred at −8 °C under nitrogen, followed by 2.0 mL (24 mmol) of THF added dropwise over 1 min. The bright orange reaction mixture was allowed to warm up to 8 °C over a period of 4 h and then was quenched with excess trimethylchlorosilane (2.5 mL, 20 mmol). The color of the reaction mixture faded immediately on addition of the trimethylchlorosilane. Workup was identical with that in method A. By gas chromatographic analysis of the resulting reaction mixture, the ratio of **4** to **1a** was determined to be 7.89:1, corresponding to an 89% yield of lithio salt **2a** based on the amount of **1a** used. Conditions and results for similar experiments using method B are summarized in Table I.

Preparation of [*p*-(Trimethylsilyl)phenyl]acetic Acid (3a). To a solution of 51.5 mL (60 mmol) of 1.18 M *sec*-butyllithium in hexane and 5.00 g (30 mmol) of **1a** at −10 °C under nitrogen was added 10 mL (123 mmol) of dry THF over a period of 5 min. The rate of addition was controlled to maintain the temperature of the reaction mixture below −5 °C. After addition was completed, the reaction mixture was allowed to warm slowly to room temperature over 1.5 h, stirred for an additional 2 h, and then quenched by pouring over crushed dry ice with vigorous stirring. After the excess dry ice had sublimed, the residual solid was dissolved in 250 mL of 10% KOH. The aqueous solution was washed with ether (1 × 100 mL), acidified with concentrated HCl, and then extracted with ether (3 × 100 mL). The combined ethereal extracts were dried over $MgSO_4$ and evaporated under reduced pressure. The resulting crude yellow oil was distilled and, after a small forerun, yielded 4.18 g (67%) of **3a** as a pale yellow oil which rapidly solidified on cooling: bp 116 °C (0.10 mm); mp 52–54 °C (lit.[2] mp 40 °C); ^1H NMR ($CDCl_3$) δ 11.90 (s, 1 H, OH), 7.34 (d, J = 8, Hz, 2 H, aromatic), 7.10 (d, J = 8 Hz, 2 H, aromatic), 3.50 (s, 2 H, CH_2), 0.22 (s, 9 H, $Si(CH_3)_3$); IR ($CDCl_3$) 3000 (OH), 1710 cm^{-1} (C=O). Anal. Calcd for $C_{11}H_{16}O_2Si$: C, 63.41; H, 7.74. Found: C, 63.45; H, 7.56.

Preparation of [*m*-(Trimethylsilyl)phenyl]acetic Acid (3b). To a solution of 74.7 mL (85.4 mmol) of 1.14 M *sec*-butyllithium in hexane and 7.00 g (42.6 mmol) of *m*-(trimethylsilyl)toluene (**1b**) at −10 °C under nitrogen was added 14 mL (172 mmol) of dry THF over a period of 5 min. After the addition was completed, the reaction mixture was allowed to warm slowly to room temperature over 1 h, stirred for an additional 15 min, and then quenched by pouring over crushed dry ice with vigorous stirring. The reaction was processed as above. The resulting yellow oil was distilled to yield 5.27 g (59%) of **3b** as a pale yellow oil which solidified slowly on standing: bp 122–125 °C (0.25 mm); mp 33–34 °C (lit.[2] mp 33 °C); ^1H NMR ($CDCl_3$) δ 11.88 (s, 1 H, OH), 7.32 (m, 4 H, aromatic), 3.58 (s, 2 H, CH_2), 0.25 (s, 9 H, $Si(CH_3)_3$); IR (NaCl) 2950 (OH), 1700 cm^{-1} (C=O).

In a similar experiment 18 mL (221 mmol) of dry THF was added to a solution of 165 mL (110 mmol) of 1.5 M *tert*-butyllithium in pentane and 9.00 g (55 mmol) of **1b** over 10 min at −30 °C. The resulting solution was allowed to warm to room temperature and then quenched by pouring over dry ice. Workup as before afforded 6.34 g (55%) of **3b** identical with that obtained above.

Registry No. **1a**, 3728-43-6; **1b**, 3728-44-7; **2a**, 74542-26-0; **3a**, 5112-65-2; **3b**, 5112-64-1; **4**, 2415-91-0; *p*-chlorotoluene, 106-43-4; *m*-chlorotoluene, 108-41-8.

Halogenations of Conjugated Dienes. Bromination and Chlorination of *cis*- and *trans*-3-Methyl-1,3-pentadienes

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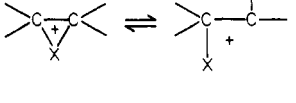
It is well-known that halogen additions to many alkenes are stereospecific and form only anti products.[1] The preference for anti addition is rationalized on the basis of the involvement of cyclic halonium ion intermediates in the reactions. Thus, the study of electrophilic addition becomes a tool for observing the behavior of halonium ions and their ion pairs, with the added interest that these can be generated in aprotic solvents of widely varying polarities. Previous studies[2] have revealed that halonium ions are marginally stable in comparison to open carbocations.



(1) For a recent review of electrophilic addition, see G. H. Schmid and D. G. Garrett, "The Chemistry of the Double Bonded Functional Groups", Supplement A, S. Patai, Ed., Wiley, London, 1977.

(2) See, e.g., S. P. McManus and P. E. Peterson, *Tetrahedron Lett.*, 2753 (1975), and F. Freeman, *Chem. Rev.*, **75**, 452 (1975), and references contained in these articles.

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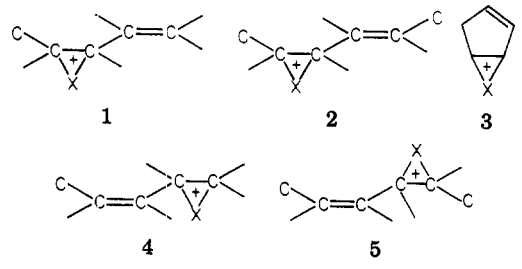
Table I. Bromination and Chlorination of *cis*- and *trans*-3-Methyl-1,3-pentadienes

entry	reaction[a]	3,4-adducts[b] % threo	3,4-adducts[b] % erythro	1,2-adducts[c] % cis	1,2-adducts[c] % trans	% 1,4-adduct[d]	% anti addn for 3,4-adduct	% stereochem retained in 1,2-adduct	% yield[e]
1	**6a**, Br_2, pentane	19.5	2.5	11	5	62	89	69	86
2	**6a**, Br_2, CCl_4	12	4	9	4	71	75	69	93
3	**6a**, Br_2, CH_2Cl_2	4	3	7	6	80	57	54	78
4	**6a**, Br_2, CH_3NO_2	7	1	10	17	65	87	37	46
5	**6b**, Br_2, pentane	1.5	5.5	1.5	33	58.5	78	96	74
6	**6b**, Br_2, CCl_4		3		26	71		99	84
7	**6b**, Br_2, CH_2Cl_2			1	29	70		97	74
8	**6b**, Br_2, CH_3NO_2		2	2	33	63		94	53
9	equilibrated[f] dibromides in CH_2Cl_2	0.5	2	10.5	18	65.5			
10	**6a**, Cl_2, pentane	10.5	4.5	4	1	80	70	80	49[g]
11	**6a**, Cl_2, CCl_4	7.5	4	4	1	83.5	65	80	51[g]
12	**6a**, Cl_2, CH_2Cl_2	8.5	9.5	8.5	2.5	71	47	77	42[g]
13	**6b**, Cl_2, pentane	2.5	10		20	67.5	80	99	25[g]
14	**6b**, Cl_2, CCl_4	2	9	1	18	70	82	95	59[g]
15	**6b**, Cl_2, CH_2Cl_2	3.5	9	5	37.5	45	72	88	42[g]
16	**6a**, Br_2, 2,6-Lu[h]	14	1	41	3	42	93	93	52
17	**6a**, Br_2, Py[h]	23.5		46	3.5	27	>99	93	43
18	**6a**, Br_2, 3,5-Lu[h]	41		45	4	10	>99	92	40
19	**6b**, Br_2, 6-Lu[h]		3		70	27		>99	56
20	**6b**, Br_2, Py[h]		3.5		74	22.5		>99	40
21	**6b**, Br_2, 3,5-Lu[h]		9		80	11	95	>99	42

[a] Reported results were obtained for reactions in which the halogen added was equal to 50% of the diene but runs at 25% and 80% completion gave product ratios which did not differ significantly. [b] Products from bromination are *threo*-3,4-dibromo-3-methylpentene (**10a**) and *erythro*-3,4-dibromo-3-methylpentene (**10b**) and from chlorination are *threo*-3,4-dichloro-3-methylpentene (**11a**) and *erythro*-3,4-dichloro-3-methylpentene (**11b**). [c] Products from bromination are 4,5-dibromo-3-methyl-*cis*-2-pentene (**12a**) and 4,5-dibromo-3-methyl-*trans*-2-pentene (**12b**) and from chlorination are 4,5-dichloro-3-methyl-*cis*-2-pentene (**13a**) and 4,5-dichloro-3-methyl-*trans*-2-pentene (**13b**). [d] The product from bromination is 1,4-dibromo-3-methyl-*trans*-2-pentene (**14**) and from chlorination is 1,4-dichloro-3-methyl-*trans*-2-pentene (**15**). [e] Yields were repeatable to ±5%. [f] Samples rich in either **12a** or **14** give a mixture of the same composition after being kept in sealed tubes for 6 months at room temperature. [g] The yields from chlorination include a chlorine substitution product, 2-(1-chloroethyl)-1,3-butadiene (**16**), obtained in the following percentages in comparison to the total dichlorides: **6a**, pentane, 33%; **6a**, CCl_4, 35%; **6a**, CH_2Cl_2, 31%; **6b**, pentane, 17%; **6b**, CCl_4, 22%; **6b**, CH_2Cl_2, 14%. [h] The amines are Py = pyridine, 2,6-Lu = 2,6-lutidine; 3,5-Lu = 3,5-lutidine.

Structural changes which stabilize carbocations thus favor open ions with the result that electrophilic addition may become nonstereospecific. Substitution of aromatic groups (styrenes) and vinyl groups (conjugated dienes) are examples of such changes.[1]

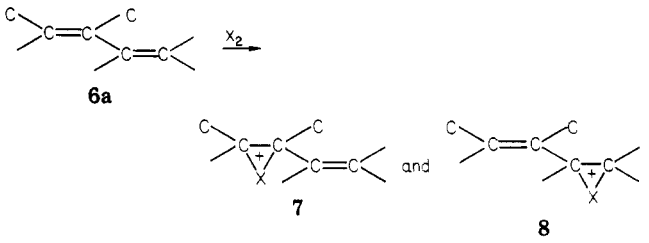
In previous studies on halogen addition to conjugated dienes we have made some observations on halonium ion stabilities.[3] Structures **1**–**5** represent ions which were encountered.[4] Halonium ion **1**, is significantly more stable

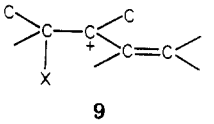


than **2** or **3** as exhibited by the virtually stereospecific anti bromine and chlorine addition obtained with the 1,3-pentadienes[4a,c] in contrast to only stereoselective anti addition with cyclopentadiene[4c,d] and the 2,4-hexadienes.[4b,c] The stability of ions **4** and **5** was sufficient that isomerization of the cis double bond did not occur.

We wished to extend these observations on halonium ions by exploring the bromination and chlorination of the 3-methyl-1,3-pentadienes (*cis*-**6a** and *trans*-**6b**). The halonium ions resulting from **6a** are represented by structures **7** and **8** in Scheme I. Ion **7** is similar to **1** except that the positive charge in **7** could reside on a tertiary center (structure **9**). This would probably have the effect of diminishing bridging to the halogen.

Scheme I





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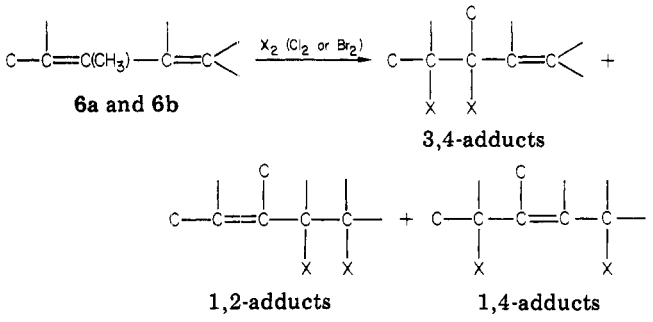
Ion **8** differs from ions **4** and **5** in that two cis methyl groups would constitute the driving force for isomerization,

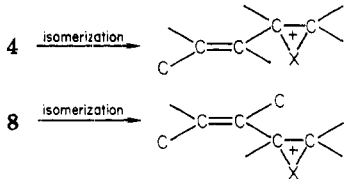
(3) We do not mean to imply that there are no significant differences between the intrinsic stabilities of chloronium ions and bromonium ions. These differences have been noted; see, e.g., F. Freeman, *Chem. Rev.*, **75**, 454 (1975).

(4) (a) V. L. Heasley, G. E. Heasley, S. K. Taylor, and C L. Frye, *J. Org. Chem.*, **35**, 2967 (1970); (b) 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); (c) G. E. Heasley, V. L. Heasley, P. D. Davis, D. C. Hayse, D. M. Ingle, G. R. McClung, K. D. Rold, D. K. Strickland, and T. S. Ungermann, *ibid.*, **41**, 334 (1976); (d) G. E. Heasley, V. L. Heasley, J. M. Bundy, S. Arnold, A Gipe, D. McKee, R. Orr, S. L. Rodgers, and D. F. Shellhamer, *ibid.*, **43**, 2793 (1978).

Scheme II



in contrast to 4 and 5 where the distal methyl encounters the carbon atom of the dienic system. Scheme II shows



the products to be expected from bromination or chlorination of **6a,b**. Data on the dihalides formed from chlorination and bromination in several solvents is presented in Table I.

Results and Discussion

We would like to call attention to several aspects of our results. First, as concerns the formation of the 3,4-adduct, we observe that the addition is nonstereospecific with both Br_2 and Cl_2 in all of the solvents, but anti addition predominates over syn addition with one exception (chlorination of **6b** in dichloromethane). The results suggest that the halonium ions obtained by 3,4-attack (7) are weakly bridged to the 3 carbon. The predominance of anti addition suggests that bridged ions are at least partly involved, perhaps in equilibrium with open ions. Since bromination and chlorination of the 1,3-pentadienes was stereospecific, we conclude that halonium ion 7 is in fact less stable than 1 and that bridging to the tertiary center in 7 is weaker than that to the secondary center in 1. The changes in stereoselectivity with different solvents closely resemble the results with the 2,4-hexadienes where halonium ion 2 is an intermediate.

We were somewhat surprised to observe that formation of the 1,2-adduct from the cis diene (**6a**) involves considerable isomerization of the carbon–carbon π bond. By contrast, the π bond in the 1,2-adduct from the trans diene (**6b**) shows little isomerization. These results contrast with those from the chlorination and bromination of *cis*-piperylene and *cis,cis*-2,4-hexadiene (intermediates 4 and 5) where no isomerization occurred. The variation in isomerization in the bromination of **6a** is consistent with the polarity of the solvent, changing from a low of 31% isomerization in pentane and carbon tetrachloride to a high of 63% in nitromethane. Furthermore, the extent of isomerization appears to be greater for bromination than for chlorination (entries 1–4 compared with 10–12). Perhaps the ion pair from chlorine is more reactive than the ion pair from bromine and collapses to product before rotation becomes significant.[5]

Table II. Percentage of 1,4-Dihalide Addition Product Obtained from Several Dienes

	bromination		chlorination	
diene	CH_2Cl_2	CCl_4	CH_2Cl_2	CCl_4
butadiene	76[a]	43.5[b]	43.5[b]	43.5[b]
isoprene	83[a]	73[a]	75[d]	
cis-1,3-pentadiene	79.5[a]	56[c]	43[e]	40[e]
trans-1,3-pentadiene	70[a]	64.5[c]	32[e]	49[e]
cis,cis-2,4-hexadiene	81[f]	66[f]	55[e]	55[e]
cis,trans-2,4-hexadiene	74[f]	69[f]	53[e]	70[e]
trans,trans-2,4-hexadiene	73[f]	71[f]	52[e]	65[e]
6a	80	71	71	83.5
6b	70	71	45	70

[a] Reference 4d. [b] Reference 8. [c] Reference 4a. [d] G. E. Heasley et al., unpublished results. [e] Reference 4c. [f] Reference 4b.

The major product in all the halogenations of **6a** and **6b** is the 1,4-adduct. Table II compares the percentage of 1,4-dihalide obtained from **6a,b** with the chlorinations and brominations of several other dienes in dichloromethane and carbon tetrachloride. Some general trends appear. The amount of 1,4-addition with bromine in methylene chloride is high and strikingly similar for all of the dienes. In every case but one (**6b**) the percentage of 1,4 bromine addition is significantly greater in dichloromethane than in the less polar solvent, carbon tetrachloride. Another observation is that all of the dienes give more 1,4-addition in dichloromethane with bromine than they do with chlorine. Undoubtedly, several factors influence the mechanisms of collapse of the ion pairs and, therefore, determine the ratios of 1,2 to 1,4 products. Such factors may involve differences in the symmetry of bridging in the halonium ions and differences in anion structures[5] and reactivities.

We were also interested in studying the effect of the presence of amines on these brominations since we have recently found that amines dramatically alter the stereochemistry and product ratios in the bromination of dienes. Results of these reactions are shown in Table I (entries 16–21). As previously observed,[4d] both 3,4- and 1,2-additions become essentially 100% stereoselective, and the extent of 1,4-addition decreases sharply. Changes in addition product ratios for the different amines are consistent with the probable stabilities of their bromine complexes as suggested previously. The present study fails to provide new insights into the mechanism of the amine effect.

Experimental Section

Reaction Conditions. The dienes **6a,b** were obtained from Chemical Samples Co. in 99% purity. Reaction conditions were selected which have been found in previous studies to assure ionic rather than radical reactions of halogens.[4b,c,9,10] Reactions were carried out in the dark at 0–5 °C with the diene at 0.02 mol fraction with respect to solvent. In chlorinations the solvent was saturated with oxygen to further prevent radical reactions. Halogen was added to consume 50% of the diene. In a typical bromination 0.098 g of bromine was added neat from a fine dropper to a well-stirred solution of 0.10 g of **6a** in 5.8 mL of carbon tetrachloride. Chloride was added as a 1 M solution in carbon tetrachloride.

(5) A major difference between chlorination and bromination could lie in the fact that the counter ion derived from bromine under these conditions is a complex anion[6] (Br_3^- or possibly larger), whereas, there is some evidence that the chlorination mechanism may involve only a single molecule and hence form ion pairs with the simple chloride ion.[7] On the other hand, more complex kinetic orders for chlorination in very nonpolar solvents have not been ruled out conclusively.

(6) A. Modro, G. H. Schmid, and K. Yates, *J. Org. Chem.*, **42**, 3673 (1977).
(7) Reference 1, p 755.
(8) V. L. Heasley, G. E. Heasley, R. A. Loghry, and M. R. McConnell, *J. Org. Chem.*, **37**, 2228 (1972).
(9) M. L. Poutsma, *J. Am. Chem. Soc.*, **87**, 2172 (1965); *J. Org. Chem.*, **31**, 4167 (1966).
(10) V. L. Heasley and S. K. Taylor, *J. Org. Chem.*, **34**, 2779 (1969).

Brominations in the presence of amines were done at an amine to bromine mole ratio of 5:1. In a typical run a solution of 0.098 g of bromine, 0.24 g of pyridine, and 3.8 mL of dichloromethane was stirred at ice temperature for a few minutes and then 0.1 g of diene was added.[11] The amine was removed by extraction with cold hydrochloric acid.

Stability of Products. Several observations support our conclusion that the products obtained in the brominations and chlorinations are kinetically controlled and not equilibrated. (1) Reactions mixtures were analyzed directly by VPC with no intermediate workup. Product mixtures which varied widely in composition (and hence cannot be equilibrated mixtures) were not found to change in composition in dilute solution when stored in the refrigerator for the brief times required to complete analysis—a few days at most. Complete equilibration at room temperature required several months (entry 9, Table I). (2) Stability of the dibromides to conditions of the bromination reaction itself was demonstrated by the following experiment. Diene **6a** was brominated according to entry 17 (Table I) to give a mixture of **10a**, **12a** (with a trace of **12b**), and **14**. Solvent and excess **6a** were removed and then **6b** and dichloromethane were added along with *p*-dibromobenzene as internal standard. This mixture was analyzed by VPC after which bromine was added (conditions of entry 7). The mixture was analyzed again by VPC and the ratio of **10a** and **12a** to the internal standard was found to be the same before and after the bromination (bromination of **6b** in dichloromethane produces only traces of **10a** and **12a**), showing their stability to the reaction conditions. (3) The lack of sensitivity to hydrogen chloride produced in significant amounts by concomitant substitution in the chlorination reaction was demonstrated by an experiment done to test the effect of amines on chlorination. Chlorination of **6a** and **6b** in dichloromethane in the presence of a 10 mol excess (over chlorine) of pyridine gave dichloride product mixtures which did not differ significantly from those obtained in dichloromethane.

Analysis and Identification. Analyses of mixtures of dibromides and dichlorides were accomplished by VPC under the following conditions: 10 ft × 6 mm (o.d.) glass column packed with 2.5% SE-30 on 80–100 Chromosorb W at a temperature of 60 °C for the dibromides and 40 °C for the dichlorides. Retention times of the dibromides were (min) **10a**, 9.4, **10b**, 10.5, **12a**, 13.8, **12b**, 16.0, and **14**, 26, and of the dichlorides were (min) **16**, 3.6, **11a**, 6.6, **11b**, 7.8, **13a**, 11.8, **13b**, 13.9, and **15**, 22.2.

All of the compounds formed in the chlorination and bromination reactions were isolated by preparative VPC except for the erythro dibromide, **10b**, which was formed in such small amounts that it could not be readily obtained. Its presence was inferred because of a peak in the chromatogram very close to that of **10a**. Structures of isolated compounds were assigned on the basis of their NMR spectra. Distinctions between erythro–threo and cis–trans isomers were made on the assumptions that the major 3,4-isomer produced in the less polar solvents arises from anti addition and that the major 1,2-adduct from the trans diene has the trans structure. Proton NMR spectra (60 MHz in CCl_4 obtained with a Varian T-60A or EM-360A, parts per million downfield from $(CH_3)_4Si$) follow.

Bromination Products. 10a: 1.90 (d, 3, CH_3, $J_{4,5}$ = 6.4 Hz), 2.07 (s, 3, $CH_3CBrC{=}C$), 4.42 (q, 1, CHBr, $J_{4,5}$ = 6.4 Hz), 5.28 (d of d, 1, *cis*-HC=CH(**H**), $J_{1,2}$ = 10.2, $J_{1,1'}$ = 1.2 Hz), 5.40 (d of d, 1, *trans*-HC=C**H**(H), $J_{1',2}$ = 17, $J_{1,1'}$ = 1.2 Hz), 6.18 (d of d, 1, **H**C=CH_2, $J_{1,2}$ = 10.2, $J_{1',2}$ = 17 Hz). **12a**: 1.72 (d, 3, CH_3C-H=C, $J_{1,2}$ = 6.0 Hz), 1.78 (s, 3, $CH_3C{=}C$), 3.72 and 3.73 (d, 2, CH_2Br, J = 6.2 and 10.5 Hz), 5.2 (d of d, 1 CHBr, $J_{4,5(4,5')}$ = 6.2 and 10.5 Hz), 5.58 (q, 1, CH=C, $J_{1,2}$ = 6.0 Hz). **12b**: 1.67 (d, 3, $CH_3CH{=}C$, $J_{1,2}$ = 7.0 Hz), 1.70 (s, 3, $CH_3C{=}C$), 3.72 and 3.73 (2 d, 2, CH_2Br, J = 6.2 and 9.0 Hz), 4.72 (d of d, 1, $J_{4,5}$ and $J_{4,5'}$ = 6.2 and 9.0 Hz), 5.75 (br q, 1, CH=C, $J_{1,2}$ = 7.0 Hz). **14**: 1.78 (d, 3, CH_3CHBr, $J_{4,5}$ = 6.8 Hz), 1.87 (s, 3, $CH_3C{=}C$), 3.93 (d, 2, CH_2Br, $J_{1,2}$ = 8.0 Hz), 4.67 (q, 1, CHBr, $J_{4,5}$ = 6.8 Hz), 5.87 (t, 1, C=CH, $J_{1,2}$ = 8.0 Hz).

Chlorination Products. 11a: 1.60 (d, 3, CH_3CHCl, $J_{4,5}$ = 6.4 Hz), 1.80 (s, 3, $CH_3CCl{=}C$), 4.17 (q,1, CHCl, $J_{4,5}$ = 6.4 Hz), 5.33 (d of d, 1, *cis*-HC=CH(**H**), $J_{1,2}$ = 10.0, $J_{1,1'}$ = 1.4 Hz), 5.47 (d of d, 1, *trans*-HC=C**H**(H), $J_{1',2}$ = 16.4, $J_{1,1'}$ = 1.4 Hz), 6.13 (d of d, 1, C**H**=CH_2, $J_{1,2}$ = 10, $J_{1',2}$ = 16.4 Hz). **11b**: 1.65 (d, 3, CH_3CHCl, $J_{4,5}$ = 6.8 Hz), 1.73 (s, 3, CH_3CCl), 4.10 (q, 1, CHCl, $J_{4,5}$ = 6.8 Hz), 5.22 (d of d, 1, CH=CH(**H**), $J_{1,2}$ = 10.5, $J_{1,1'}$ = 1.5 Hz), 5.38 (d of d, 1, CH=C**H**(H), $J_{1',2}$ = 16.5 Hz, $J_{1,1'}$ = 1.5 Hz), 6.08 (d of d, 1, C**H**=CH_2, $J_{1,2}$ = 10.5, $J_{1',2}$ = 16.5 Hz). **13a**: 1.72 (d, 3, CH_3CH, $J_{1,2}$ = 5.2 Hz), 1.77 (s, 3, $CH_3C{=}C$), 3.68 and 3.73 (2 d, 2, CH_2Cl, J = 6.4 and 9.2 Hz), 4.98 (d of d, 1, CHCl, $J_{4,5}$ = 6.4 and 9.2 Hz), 5.58 (br q, 1, CH=C, $J_{1,2}$ = 5.2 Hz). **13b**: 1.68 (s, 3, $CH_3C{=}C$), 1.73 (d, 3, CH_3, $J_{1,2}$ = 5.0 Hz), 3.65 and 3.67 (2 d, 2, J = 6.4 and 8.8 Hz), 4.40 (d of d, 1, CHCl, $J_{4,5}$ = 6.4 and 8.8 Hz), 5.63 (q, 1, CH=C, $J_{1,2}$ = 5.0 Hz). **15**: 1.58 (d, 3, CH_3CHCl, $J_{4,5}$ = 6.5 Hz), 1.82 (s, 3, $CH_3C{=}C$), 4.02 (d, 2, CH_2Cl, $J_{1,2}$ = 8.0 Hz), 4.45 (q, 1, CHCl, $J_{4,5}$ = 6.5 Hz), 5.67 (t, 1, C=CH, $J_{1,2}$ = 8.0 Hz). **16**: 1.65 (d, 3, CH_3CHCl, J = 7.3 Hz), 4.58 (q, 1, CHCl, J = 7.3 Hz), 4.93–5.47 (m, CH=C**H**$_2$ and C=C**H**$_2$), 6.22 (d of d, 1, CH=CH_2, J = 11.3 and 18.0 Hz).

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(11) We also carried out brominations in which the bromine–amine solution was added last to the dienes dissolved in dichloromethane. Product ratios did not differ significantly.

Syntheses of Muscone and Exaltone by Three-Carbon Ring Expansion

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Muscone (1) and exaltone (cyclopentadecanone) (2) are naturally occurring 15-membered cyclic ketones with a musk odor. Numerous syntheses of these cyclic ketones have been reported.[1] One important approach is the three-carbon ring expansion of easily available cyclododecanone. These attempts utilize mostly bicyclo[10.3.0]-1(12)-pentadecen-13-one (3) as a precursor, and several methods for the synthesis of this ketone and its expansion reactions have been reported.[2]

Our new method utilizes bicyclo[10.3.0]-1(15)-pentadecen-14-one (4) (Scheme I). We have previously developed a new synthetic method for 1,4-diketones and their cyclization to give cyclopentenones.[3] The method is based on the allylation of ketones and subsequent oxidation of the terminal double bond with the system $PdCl_2$–CuCl–O_2 to give 1,4-diketones, which are subjected to aldol condensation. Application of this method to cyclododecanone is expected to afford the bicyclic ketone 4. Thus, allylation of the β-keto ester 5 obtained from cyclododecanone by ethoxycarbonylation using diethyl carbonate gave 6, which was oxidized with $PdCl_2$–CuCl–O_2 in aqueous DMF to give the 1,4-diketone 7 in 72% yield from 5 (Scheme II). Aldol cyclization of the 1,4-diketone 7 using KOH in EtOH gave

(1) For references to recent synthetic activity, see (a) C. Fehr and G. Ohloff, *Helv. Chim. Acta*, **62**, 2655 (1979); (b) G. Büchi and H. Wüest, *ibid.*, **62**, 2661 (1979); (c) K. H. Schulte-Elte, A. Hauser, and G. Ohloff, *ibid.*, **62**, 2673 (1979); (d) J. Tsuji, T. Yamada, M. Kaito, and T. Mandai, *Tetrahedron Lett.*, 2257 (1979); (e) W. E. Fristad, D. S. Dime, T. R. Bailey, and L. A. Paquette, *ibid.*, 1999 (1979); (f) S. R. Wilson and R. N. Misra, *J. Org. Chem.*, **43**, 4903 (1978).

(2) (a) G. Ohloff, J. Becker, and K. H. Schulte-Elte, *Helv. Chim. Acta*, **50**, 705 (1967); (b) A. Eschenmoser, D. Felix, and G. Ohloff, *ibid.*, **50**, 708 (1967); (c) R. W. Gray and A. S. Dreiding, *ibid.*, **60**, 1969 (1977); (d) M. Baumann, W. Hoffmann, and N. Müller, *Tetrahedron Lett.*, 3585 (1976).

(3) J. Tsuji, I. Shimizu, and K. Yamamoto, *Tetrahedron Lett.*, 2975 (1976).

0022-3263/80/1945-5209$01.00/0