# Stereoselective Free-Radical Rearrangements[1]

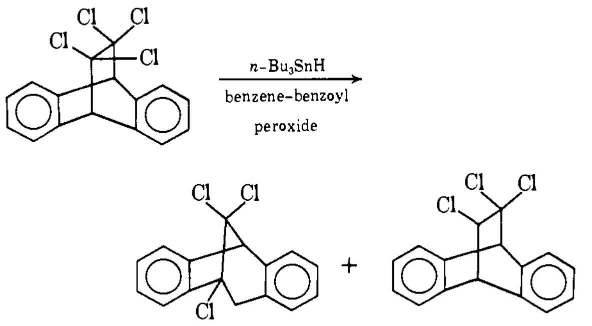
**Bruce B. Jarvis,* John P. Govoni, and Philip J. Zell**

*Contribution from the Department of Chemistry, University of Maryland, College Park, Maryland 20742.* *Received June 24, 1970*

**Abstract:** Free-radical additions of carbon tetrahalides to dibenzobicyclo[2.2.2]octatrienes give both unrearranged dibenzobicyclo[2.2.2]octadienes and dibenzobicyclo[3.2.1]octadienes. The amount of rearrangement increases with increasing reaction temperatures and decreasing concentration of chain-transfer reagent. The stereochemistry of the rearrangement is dependent upon the nature and concentration of the chain-transfer reagents as well as upon the substituents present on the olefin.

Molecular rearrangements involving free radicals[2] are far less common than the corresponding rearrangements involving carbonium ions. This accounts in part for the paucity of information about the stereochemical preference (if any) in free-radical rearrangements[3] compared with a wealth of data in carbonium ion systems.

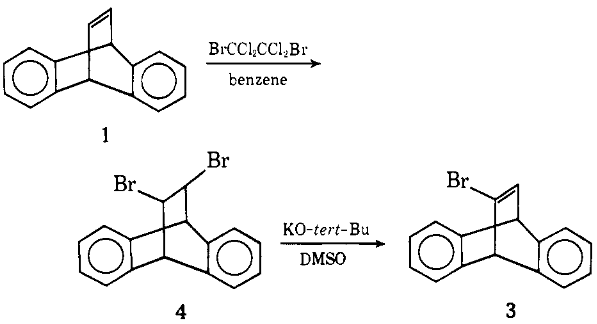
Carbonium ion rearrangements in the dibenzobicyclo[2.2.2]octadiene–dibenzobicyclo[3.2.1]octadiene system have been shown to be highly stereospecific.[4] However, only one example of a free-radical rearrangement in this system has been reported (eq 1),[5] and the compound was such that the stereochemistry of the rearrangement could not be examined. Since ionic additions to dibenzobicyclo[2.2.2]octatriene (**1**) are known to proceed with a high degree of stereoselectivity to give syn C-8 substituted dibenzobicyclo[3.2.1]-octadienes, analogous free-radical additions to **1** (or substituted **1**) also conceivably could lead to similar rearranged products. These reactions, then, would serve as a test for any stereochemical preference in such radical rearrangements.



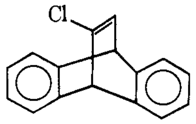
(1)

## Results and Discussion

The olefins **1**, **2**, and **3** were chosen to study so as to be able to determine the effect of an $\alpha$-halogen atom on the free-radical additions to this system. Olefins **1**[6] and **2**[7] are known compounds, but bromoolefin **3** has not been reported in the literature. The synthesis of **3** is outlined in eq 2. 1,2-Dibromotetrachloroethane has been successfully employed in the synthesis of vicinal dibromides from olefins which normally give Wagner–Meerwein rearranged products upon addition of molecular bromine.[8] Although carbon tetrachloride is the usual solvent for these reactions, we found that the reaction proceeds more readily in benzene solvent.



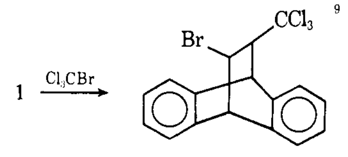
(2)



**2**

The free-radical reactions of **1**, **2**, and **3** with bromotrichloromethane ($Cl_3CBr$) and trichloromethanesulfonyl chloride ($Cl_3CSO_2Cl$) give 1 : 1 adducts of the olefins and carbon tetrahalides in high yields (see Chart I). The products were studied as a function of change in reaction temperature and concentration of chain-transfer reagent (Table I).

**Chart I**



**5**

Proof of structure for **7–20** (**5** and **6** are known compounds)[9] rests mainly on pmr spectral data and elemental analyses. The C-8 *syn*-trichloromethyl com-

---

[1] Taken in part from the M.S. Theses of J. P. Govoni and P. J. Zell, University of Maryland, 1970.

[2] (a) C. Walling in "Molecular Rearrangements," P. de Mayo, Ed., Interscience, New York, N. Y., 1963, Chapter 7; (b) R. Kh. Friedlina, *Advan. Free-Radical Chem.*, **1**, 211 (1965).

[3] A notable exception to this is found in W. Adam, Y. M. Chang, C. Wilkerson, and W. A. Zaidi, *J. Amer. Chem. Soc.*, **91**, 2111 (1969).

[4] (a) S. J. Cristol, F. P. Parungo, and D. E. Plorge, *ibid.*, **87**, 2870 (1965); (b) S. J. Cristol, R. J. Bopp, and A. E. Johnson, *J. Org. Chem.*, **34**, 3574 (1969).

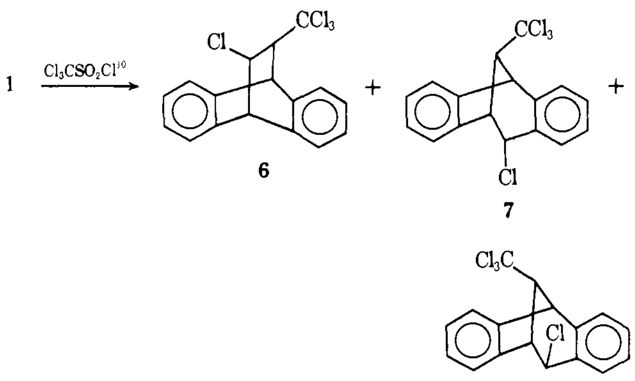
[5] B. B. Jarvis and J. B. Yount, III, *ibid.*, **35**, 2088 (1970).

[6] S. J. Cristol and W. Lim, *ibid.*, **34**, 1 (1969).

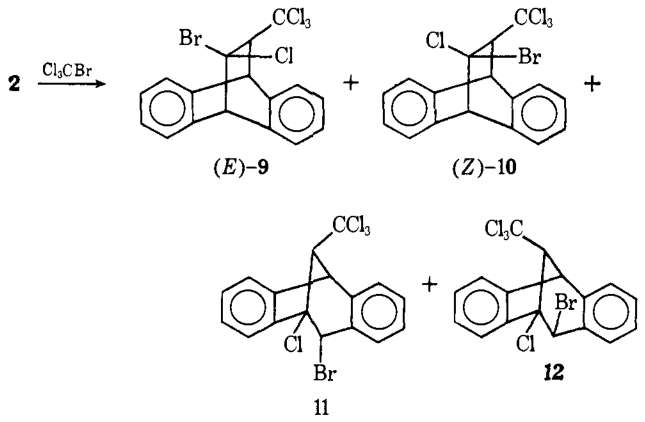
[7] S. J. Cristol and N. L. Hause, *J. Amer. Chem. Soc.*, **74**, 2193 (1952).

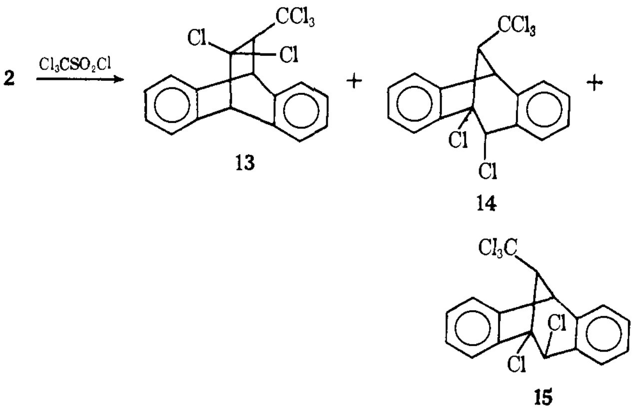
[8] J. W. Wilt and P. J. Chenier, *J. Org. Chem.*, **35**, 1562 (1970).

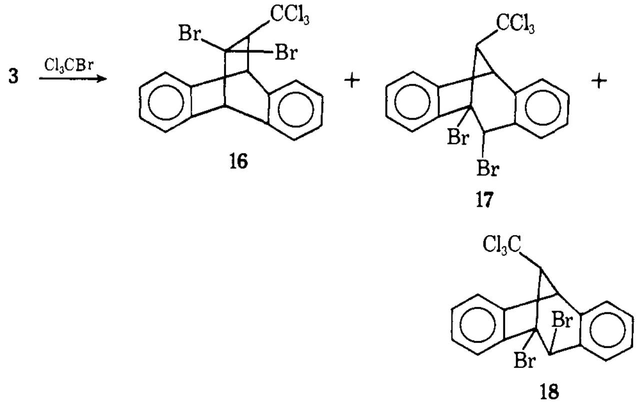
[9] B. B. Jarvis, *ibid.*, **33**, 4075 (1968).

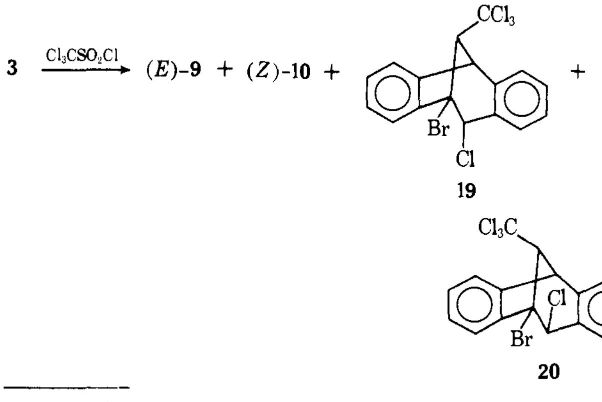


pounds 7,[11] **11**, **14**, **17**, and **19** show *ca.* a 3.5-Hz coupling between the hydrogen atom $\alpha$ to the trichloromethyl group and the benzhydryl proton,[12,13] while the anti epimers **8**, **12**, **15**, **18**, and **20** exhibit 0-Hz coupling between the C-8 and benzhydryl protons. In the dibenzobicyclo[2.2.2]octadiene adducts (*E*)-**9**, (*Z*)-**10**, **13**, and **16** there is *ca.* 1-Hz coupling between the bridge and bridgehead hydrogen atoms, a typical value for compounds of this structure.[14] The assignments of configuration of the *E* and *Z* isomers, (*E*)-**9** and (*Z*)-**10**, are based on both chemical-shift data for their pmr spectra and their behavior on column chromatography. In all the compounds reported in this work, the chemical shifts of the protons $\beta$ to a bromine atom appear downfield from those protons $\beta$ to a corresponding chlorine atom, *e.g.*, the chemical shift of hydrogen atom $\alpha$ to the $CCl_3$ group (and cis to a bromine atom) in **16** is found at $\tau$ 6.11 while the chemical shift of the proton $\alpha$ to the $CCl_3$ group (and cis to a chlorine atom) in **13** is located at $\tau$ 6.23. For (*E*)-**9**, the chemical shift of the proton $\beta$ and cis to the bromine atom is at $\tau$ 6.04 while the chemical shift of the proton in (*Z*)-**10** which is $\beta$ and cis to a chlorine atom is at $\tau$ 6.35. Furthermore, passage of a 3:1 mixture of (*E*)-**9**–(*Z*)-**10** over Woelm acid-washed alumina (activity I, elution with Skellysolve B) gives a mixture of recovered unreacted (*Z*)-**10** (one part) and a 1:1 mixture (three parts) of the rearranged exo chloride **15** and the endo epimer **21** (eq 3). (*exo*-**15** gives a 1:1 mixture of **15**–**21** when passed over Woelm acid-washed alumina.) Clearly, (*E*)-**9** undergoes a rearrangement accompanied by a bromide–chloride exchange reaction on chromatography. The fact that (*E*)-**9** gives only the anti epimers **15** and **21** is consistent with the stereospecific carbonium ion rearrangements in the system.[4] That (*Z*)-**10** fails to undergo rearrangement under the same reaction conditions (chromatography) agrees with a previous finding in our laboratories that on silver ion assisted solvolysis, the trichloride **22** gives only the *anti*-chloroacetates **23** and **24** (eq 4).[15] Apparently, the presence of a large group cis to the leaving group (bromide ion in the case of (*E*)-**9**) hinders ionization.[16,17]









---

[10] H. Goldwhite, M. L. Gidson, and C. Harris (*Tetrahedron*, **20**, 1613 (1964)) have investigated the general utility of this reagent for the addition of carbon tetrachloride to olefins.

[11] Because 7 is formed only in low yield (Table I) and proved to be inseparable from 6 and 8 by either column chromatography or fractional crystallization, 7 was never isolated. Its existence was inferred from the pmr spectra of the crude reaction mixtures (see Experimental Section).

[12] S. J. Cristol, J. R. Mohrig, and D. E. Plorde, *J. Org. Chem.*, **30**, 1956 (1965).

[13] A. R. Katritzky and B. Vallis, *Chem. Ind. (London)*, 2025 (1964).

[14] S. J. Cristol, T. W. Russell, J. R. Mohrig, and D. E. Plorde, *J. Org. Chem.*, **31**, 581 (1966).

[15] J. B. Yount, III, M.S. Thesis, University of Maryland, 1970.

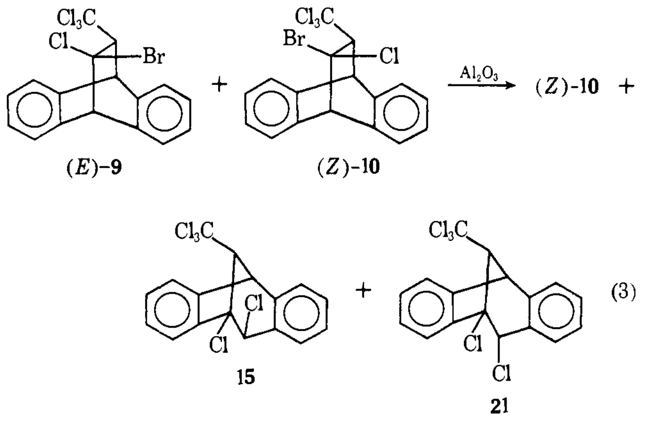
[16] Steric hindrance to ionization has been noted in a number of cases: P. von R. Schleyer, M. M. Donaldson, and W. E. Watts, *J. Amer. Chem. Soc.*, **87**, 375 (1965); H. C. Brown and S. Ikegami, *ibid.*, **90**, 7122 (1968); S. Ikegami, D. L. Vander Jagt, and H. C. Brown, *ibid.*, **90**, 7124 (1968); H. C. Brown, I. Rothberg, P. von R. Schleyer, M. M. Donaldson, and J. J. Harper, *Proc. Natl. Acad. Sci. U. S.*, **56**, (1966).

[17] When passed over Merck 71695 acid-washed alumina or Fisher A-540 alumina, (*E*)-**9** and (*Z*)-**10** undergo elimination of hydrogen halide to give a mixture of olefins.

**Table I.** Product Distributions from the Addition of $Cl_3CBr$ and $Cl_3CSO_2Cl$ to the Olefins **1**, **2**, and **3** in Chlorobenzene

| Olefin | [Addend] | Temp, °C | Products[a,b] |
|---|---|---|---|
| **1** | Neat $Cl_3CBr$ | 105 | 100% **5** |
| | | 50 | 100% **5** |
| **1** | 1 *M* $Cl_3CBr$ | 105 | 100% **5** |
| **1** | 0.15 *M* $Cl_3CBr$[d] | 105 | 80% **5** + 20% **4** |
| **1** | Neat $Cl_3CSO_2Cl$ | 132[c] | >95% **6** + trace of **8** |
| **1** | 2 *M* $Cl_3CSO_2Cl$ | 132 | 85% **6** + 5% **7** + 10% **8** |
| **1** | 1 *M* $Cl_3CSO_2Cl$ | 132 | 80% **6** + 5% **7** + 15% **8** |
| **1** | 0.15 *M* $Cl_3CSO_2Cl$[d] | 132 | 15% **6** + 15% **7** + 70% **8** |
| **2** | Neat $Cl_3CBr$ | 105 | 48% (*E*)-**9** + 19% (*Z*)-(**10** + 29% **11** + 4% **12** |
| | | 50 | 72% (*E*)-**9** + 24% (*Z*)-**10** + 4% **11** |
| **2** | 2 *M* $Cl_3CBr$ | 105 | 35% (*E*)-**9** + 14% (*Z*)-**10** + 41% **11** + 10% **12** |
| **2** | 1 *M* $Cl_3CBr$ | 105 | 28% (*E*)-**9** + 11% (*Z*)-**10** + 44% **11** + 17% **12** |
| **2** | 0.15 *M* $Cl_3CBr$[d] | 105 | Trace of **9** + **10** + 60% **11** + 40% **12** |
| **2** | Neat $Cl_3CSO_2Cl$ | 132[c] | 43% **13** + 43% **14** + 14% **15** |
| **2** | 2 *M* $Cl_3CSO_2Cl$ | 132 | 39% **13** + 44% **14** + 17% **15** |
| **2** | 1 *M* $Cl_3CSO_2Cl$ | 132 | 35% **12** + 45% **14** + 20% **15** |
| **2** | 0.15 *M* $Cl_3CSO_2Cl$[e] | 132 | Trace **13** + 50% **14** + 50% **15** |
| **2** | 2 *M* $Cl_3CSO_2Cl$ | 80 | 55% **13** + 33% **14** + 12% **15** |
| **3** | Neat $Cl_3CBr$ | 105 | 65% **16** + 30% **17** + 5% **18** |
| | | 50 | 95% **16** + 5% **17** |
| **3** | 2 *M* $Cl_3CBr$ | 105 | 25% **16** + 50% **17** + 25% **18** |
| **3** | 1 *M* $Cl_3CBr$ | 105 | 20% **16** + 52% **17** + 28% **18** |
| **3** | 0.15 *M* $Cl_3CBr$[d] | 105 | Trace **16** + 55% **17** + 45% **18** |
| **3** | Neat $Cl_3CSO_2Cl$ | 132[c] | 6% (*E*)-**9** + 22% (*Z*)-**10** + 52% **19** + 20% **20** |
| **3** | 2 *M* $Cl_3CSO_2Cl$ | 132 | 5% (*E*)-**9** + 18 (*Z*)-**10** + 55% **19** + 22% **20** |
| **3** | 1 *M* $Cl_3CSO_2Cl$ | 132 | 4% (*E*)-**9** + 14% (*Z*)-**10** + 56% **19** + 26% **20** |
| **3** | 0.15 *M* $Cl_3CSO_2Cl$[d] | 132 | *Ca.* 2% (*E*)-**9** + 7% (*Z*)-**10** + 52% **19** + 15% **20** |
| **3** | 2 *M* $Cl_3CSO_2Cl$ | 80 | 8% (*E*)-**9** + 25% (*Z*)-**10** + 52% **19** + 15% **20** |

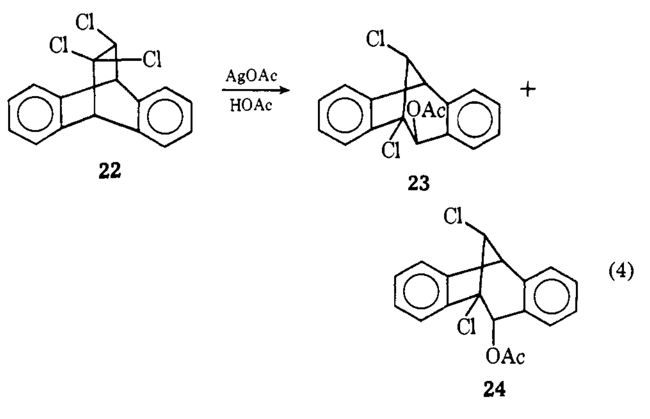
[a] The reactions were initiated with either benzoyl peroxide or uv light from a GE 275-W sunlamp. The product distribution was unaffected by the initiation source. All products were stable under the reaction conditions except the anti, exo substituted compounds **12**, **15**, **18**, and **20**. These compounds tended to isomerize to the endo epimers if allowed to stand under the reaction conditions for extended periods of time. Such isomerizations have been observed previously for similar compounds (S. J. Cristol, F. P. Parungo, D. E. Plorde, and K. Schwarzenbach, *J. Amer. Chem. Soc.*, **87**, 2879 (1965)). [b] The overall yields in these reactions are generally 80–90%. [c] Run in a sealed tube in a nitrogen atmosphere. [d] The conversion to 1:1 adducts at this concentration is poor (*ca.* 20–30%) due to formation of polymeric material. In order for the reaction to proceed at a reasonable rate, it was necessary to irradiate the solution with a sunlamp (GE 275-W). [e] At this concentration small amounts of the endo epimer of **15** (**21**) (*ca.* 5%) and *syn*-8-*endo*-4,5-trichlorodibenzobicyclo[3.2.1]octadiene (*ca.* 5%) are formed. It was shown that **15** partially isomerized to the endo epimer **21** under the reaction conditions. The trichloride presumably arises from the ionic addition of chlorine (formed from radical recombination reactions) to **2**.



(*E*)-**9** (*Z*)-**10**

**15** **21**

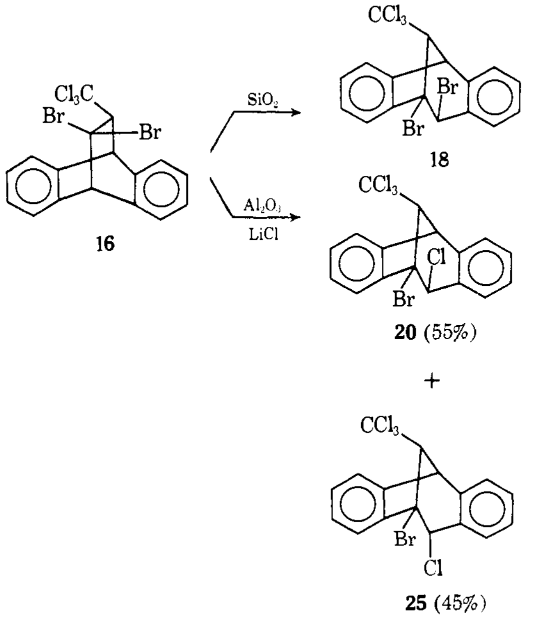
(3)



**22** **23** **24**

(4)

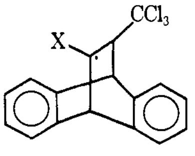
The [2.2.2] isomers (*E*)-**9** and (*Z*)-**10** are relatively stable to chromatography over silica gel, but the dibromide **16** rearranges to **18** when passed slowly over silica gel. If Woelm acid-washed alumina is used in place of silica gel, a mixture of rearranged bromides and chlorides results (see Experimental Section). However, **16** can be completely converted to a mixture of **20** and



**16** **18** **20** (55%) **25** (45%)

**25** when chromatographed over a mixture of Woelm acid-washed alumina and lithium chloride.

Interestingly, addition of $Cl_3CBr$ to the chloroolefin gives (*E*)-**9** as the major unrearranged adduct while addition of carbon tetrachloride (*via* $Cl_3CSO_2Cl$) to the bromoolefin **3** results in (*Z*)-**10** as the major unrearranged product. Both additions go preferentially trans. This shows that in the chain-transfer step to radical **26**, the chain-transfer reagent ($Cl_3CBr$ or $Cl_3CSO_2Cl$) prefers to approach from a side opposite to the bulky trichloromethyl group.[18] However, this is also a function of the steric requirements of the chain-transfer reagent. Reduction of a mixture of (*E*)-**9** and (*Z*)-**10** with tri-*n*-butyltin hydride gives **6** in high yield. In this case the chain-transfer reagent (*n*-$Bu_3SnH$)[19] approaches **26** from the side cis to the bulky trichloromethyl group. Addition of thiols to the chloroolefin **2** gives predominately cis addition accompanied by no observable amount of rearranged products.[20]

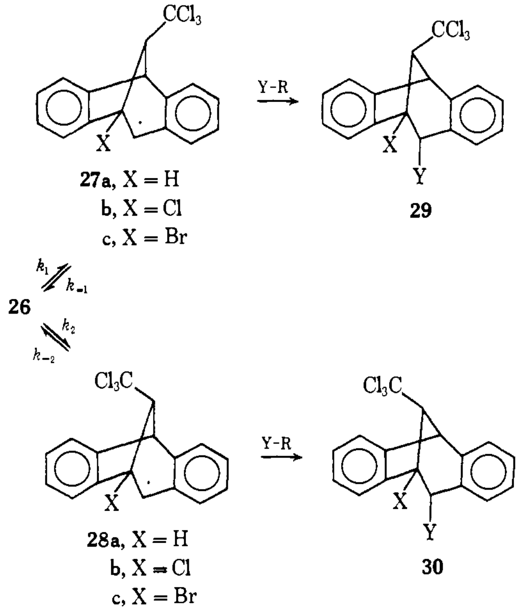


**26a**, X = H
**b**, X = Cl
**c**, X = Br

A number of trends are clearly discernible from Table I. The tendency toward rearrangement increases with (a) increasing temperature, (b) decreasing concentration of chain-transfer reagent ($Cl_3CSO_2Cl$ or $Cl_3CBr$), (c) on going from $Cl_3CBr$ to $Cl_3CSO_2Cl$, and (d) on going from olefin **1** to the vinyl halides **2** and **3**.[21] These results are typical for radical-rearrangement reactions.[2] The longer the lifetime of the first-formed radical **26**, the more opportunity there will be for rearrangement to the more stable benzylic radical. The lifetime of radical **26** can be increased in a number of ways, *e.g.* (a) dilution of chain-transfer reagent, (b) placement of groups $\alpha$ (or $\beta$) to the radical center that might either stabilize the radical and/or sterically inhibit chain transfer, or (c) make use of a poorer chain-transfer reagent that would react more slowly with **26** ($Cl_3CBr$ appears to be a better chain-transfer reagent than $Cl_3CSO_2Cl$). What is striking about the data in Table I is not that the amount of rearrangement is a function of the above factors but that the ratio of anti–syn epimers also appears to change in a similar systematic fashion, *i.e.*, anti–syn increases (a) upon dilution of chain-transfer reagent, (b) in going from $Cl_3CBr$ to $Cl_3CSO_2Cl$, and (c) in going from olefin **1** to olefins **2** and **3**.

Since the ratio of anti–syn epimers increases with decreasing concentrations of chain-transfer reagent, this indicates that the rearranged radicals **27** and **28** are formed reversibly[23] (Scheme I). That radical **27** gives only endo substitution but **28** tends to yield exo substitution is due to blockage of the C-4 exo position by the bulky *syn*-8-trichloromethyl group in **27** while in **28** chain transfer is able to take place from the stereoelectronically more favored exo side.[4,11,24] It also may be for this reason that the amount of anti products **8**, **12**, **15**, **18**, and **20** increases with increasing dilution of chain-transfer reagent (Y–R). As [Y–R] decreases this allows time for **27** to be converted to **28**. Chain transfer to **28** should be faster than chain transfer to **27** since the stereoelectronically more favored exo position is blocked in **27**.

**Scheme I**



**27a**, X = H
**b**, X = Cl
**c**, X = Br

**29**

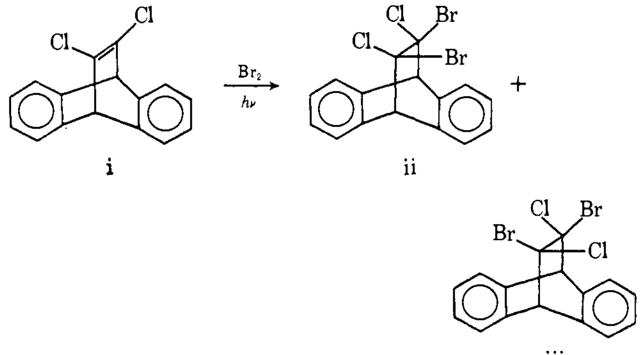
**28a**, X = H
**b**, X = Cl
**c**, X = Br

**30**

R = $CCl_3$ for Y = Br
R = $SO_2CCl_3$ for Y = Cl

---

(18) Free-radical addition of bromine to the dichloroolefin i gives the cis dibromide ii as the major product: B. B. Jarvis and T. H. Yang, unpublished results.



(19) H. G. Kuivila, *Accounts Chem. Res.*, **1**, 299 (1968).

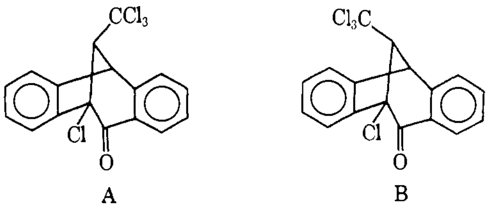
(20) Lack of rearrangement of radicals analogous to **26b** in this reaction is no doubt due to the high propensity of thiols to chain transfer. See S. J. Cristol, R. Caple, R. M. Sequeira, and L. O. Smith, Jr., *J. Amer. Chem. Soc.*, **87**, 5679 (1965).

(21) The bromo radical **26c** consistently gives more rearranged products than does the chloro radical **26b**. This may be due either to the greater stabilizing effect of an $\alpha$-bromine atom compared to an $\alpha$-chlorine atom[22] or to higher steric hindrance to chain transfer associated with the more bulky **26c**.

(22) R. H. Martin, F. W. Lampe, and R. W. Taft, *J. Amer. Chem. Soc.*, **88**, 1353 (1966).

(23) M. Julia and M. Maumy, *Bull. Soc. Chim. Fr.*, 2427 (1969).

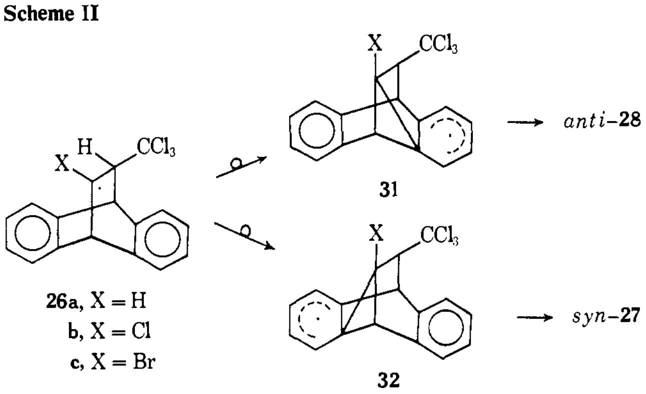
(24) Reduction of ketone A with lithium aluminum hydride gives only the exo alcohol (endo hydride attack) whereas ketone B gives only the endo alcohol (exo attack); B. B. Jarvis and J. P. Govoni, submitted for publication.



A B

In the case of **26b** and **26c** the fact that $k_1 > k_2$ (Scheme I) probably reflects the increased torsional strain[25] developed in the transition state leading to radical **31** (dihedral angle between X and $CCl_3$ groups in **31** is *ca.* 40°) compared with that developed in the transition state leading to radical **32** (dihedral angle between X and $CCl_3$ groups in **32** is *ca.* 80°) (Scheme II).

**Scheme II**



The kinetic pathway for the rearrangement of **26a** is less clear than for the rearrangements of **26b** and **26c**. Although the amount of *anti*-**8** increases upon dilution of the chain-transfer reagent ($Cl_3CSO_2Cl$) in the reaction of **1** with trichloromethanesulfonyl chloride, the anti product **8** appears to be favored over the syn product **7** at all concentrations. A number of explanations might be offered to account for the divergent behavior of **26a**, but without certain knowledge as to which is the kinetically preferred rearranged radical, **27a** or **28a**, any suggestions on our part would be undue conjecture.

## Experimental Section[26]

**Preparation of *trans*-7,8-Dibromodibenzobicyclo[2.2.2]octadiene (4).** Dibenzobicyclo[2.2.2]octatriene (**1**) (5 g; 24.6 mmol) and 12 g (36.9 mmol) of 1,2-dibromotetrachloroethane[8] were dissolved with stirring in 200 ml of benzene in a three-necked, round-bottomed flask (room temperature). The flask was flushed with nitrogen and a reflux condenser attached. The solution was irradiated with a GE sunlamp (275-W) and the solution temperature allowed to rise to 70–80°. After 2 hr, the reaction was shown by pmr spectroscopy to be one-third complete. Another 8 g (24.6 mmol) of 1,2-dibromotetrachloroethane was added and the reaction allowed to proceed. After another 5 hr, a pmr spectrum showed no trace of the starting material. The solvent was removed by rotary evaporation and the crude material redissolved in a minimum amount of Skellysolve B (bp 60–80°). The solution was chromatographed over 300 g of Fisher chromatography grade alumina (packed in Skellysolve B). Elution with Skellysolve B gave first unreacted 1,2-dibromotetrachloroethane followed by 7 g (74%) of *trans*-7,8-dibromodibenzobicyclo[2.2.2]octadiene (**4**), mp 123° (ethanol); pmr $\tau$ 5.6–5.9 (m, 4).

*Anal.* Calcd for $C_{16}H_{12}Br_2$: C, 52.78; H, 3.32. Found: C, 53.05; H, 3.50.

**Preparation of 7-Bromodibenzobicyclo[2.2.2]octatriene (3).** To a solution of 10 g (27.5 mmol) of **4** dissolved in 80 ml of dimethyl sulfoxide, 6.16 g (55.0 mmol) of potassium *tert*-butoxide was added. The brown solution was allowed to stir for 1.5 hr at room temperature. The solution was then transferred to a separatory funnel, and 100 ml of water was added. The subsequent white slurry was extracted with three 50-ml portions of ether. The ether extracts were combined and washed once with 50 ml of water, dried over anhydrous magnesium sulfate, and filtered. The ether was removed by rotary evaporation and the crude product recrystallized from ethanol, yielding 5.0 g (64%) of **3**: mp 156–157°; pmr $\tau$ 4.99 (d, 1, $J$ = 2.2 Hz), 5.08 (d, 1, $J$ = 6.3 Hz), vinyl-H (beneath the aromatic protons).

*Anal.* Calcd for $C_{16}H_{11}Br$: C, 67.84; H, 3.93. Found: C, 68.10; H, 3.97.

**General Procedure for the Addition of $Cl_3CBr$ and $Cl_3CSO_2Cl$ to the Olefins 1, 2, and 3.** The olefin (1 g) was added to a solution of 3–6 equiv of either $Cl_3CBr$ or $Cl_3CSO_2Cl$[27] at the desired concentration in chlorobenzene at a given temperature (the boiling point of chlorobenzene is 132°; the 50 and 80° temperatures were maintained by an oil bath). The reactions were initiated with 50–100 mg of benzoyl peroxide. For some of the more dilute reactions, it was necessary to periodically add more benzoyl peroxide. In the case of the 0.15 *M* reactions in chlorobenzene, the reactions proceeded at a reasonable rate only in the presence of a sunlamp (GE 275-W). The course of the reactions was followed by pmr spectroscopy. The final percentages of the products were determined as follows. At the end of the reaction, the solvent was removed by rotary evaporation, and the ratio of the products was determined by careful integration of peaks.[28] The products were isolated and weighed (*vide infra*). The figures in Table I are based on the average of three runs for each reaction. The following are sample reactions and the details of the isolation of the compounds.

**Addition of $Cl_3CBr$ (0.15 *M* in Chlorobenzene) to Olefin 1.** To 1.0 g (4.9 mmol) of **1** and 4.0 g (20.2 mmol) of $Cl_3CBr$ in 130 ml of chlorobenzene under nitrogen was added 100 mg of benzoyl peroxide. The flask was fitted with a water condenser and placed in an oil bath at 105°. The solution was irradiated with a sunlamp for 1 day. The solvent was removed by rotary evaporation and a pmr spectrum of the crude reaction mixture showed a mixture of **5** (80%) and what appeared to be the dibromide **4** (20%). From ethanol was crystallized 1.2 g (62%) of **5**, mp 133–135°.[9] The mother liquor yield 200 mg (10%) of **4**, mp 123°, undepressed with an authentic sample of **4**.

The reaction run at higher concentrations gave **5**[9] as the only observable product.

**Reaction of Olefin 1 with $Cl_3CSO_2Cl$. (a) High Concentration.** One gram (4.9 mmol) of **1**, 6.0 g (28 mmol) of $Cl_3CSO_2Cl$, and 50 mg of benzoyl peroxide were sealed under nitrogen in a glass tube. The tube was suspended above a solution of refluxing chlorobenzene (bp 132°) for 8 hr. A pmr spectrum of the crude reaction mixture showed the product to be almost entirely the unrearranged adduct **6** with a trace of rearranged **8** observable. Isolation by chromatography (silica gel, elution with 5% benzene in Skellysolve B) gave 1.5 g (85%) of **6**, mp 118–119°.[9]

**(b) Low Concentration.** One gram (4.9 mmol) of **1**, 5.0 g (23.3 mmol) of $Cl_3CSO_2Cl$, and 100 mg of benzoyl peroxide were dissolved in 150 ml of chlorobenzene under nitrogen. The solution stood at reflux for 2 days. (The solution was irradiated with a sunlamp (GE 275-W) and several 50-mg portions of benzoyl peroxide were added intermittently.) The reaction mixture was worked up as above (see Table I) to yield, after chromatography, 0.9 g (51%) of the rearranged adduct **8**, mp 137–138° from ethanol: pmr $\tau$ 5.62 (s, 1), 5.08 (s, 1), 4.77 (d, 1, $J$ = 2.0 Hz), 5.87 (d, 1, $J$ = 2.0 Hz).

*Anal.* Calcd for $C_{17}H_{12}Cl_4$: C, 56.99; H, 3.39. Found: C, 57.23; H, 3.47.

The syn,endo epimer **7** was present to a small extent in all the reaction mixtures. The material was inseparable by crystallization or chromatography from the other products, and its existence was inferred by pmr spectroscopy: a doublet at $\tau$ 4.22, $J_{45}$ = 4.8 Hz.[12,13]

**Addition of $Cl_3CBr$ to Chloroolefin 2.** A mixture of 1.5 g (6.2 mmol) of **2**,[22] 10 mg of benzoyl peroxide, and 10 ml of $Cl_3CBr$

---

[25] (a) P. von R. Schleyer, *J. Amer. Chem. Soc.*, **89**, 701 (1967); (b) C. L. Osborn, J. V. Van Auken, and D. J. Trecker, *ibid.*, **90**, 5806 (1968); (c) F. R. Jensen, J. H. Gale, and J. E. Rogers, *ibid.*, **90**, 5739 (1968); (d) B. B. Jarvis and J. B. Yount, III, *Chem. Commun.*, 1405 (1969).

[26] Melting points were determined on a Fisher-Johns apparatus and are uncorrected. Proton magnetic resonance spectra (carbon tetrachloride solutions) were measured with a Varian A-60D spectrometer with tetramethylsilane ($\tau$ 10.00) as the internal standard. $J$ values are "observed" ones. The pmr data are given only for the protons found outside the aromatic region. All the compounds exhibit a multiplet (8 H) from *ca.* $\tau$ 2.4 to 3.0 in their pmr spectra. Elemental analyses were performed by Dr. F. J. Kasler, University of Maryland.

[27] Eastman Organic Chemicals, red label. There was essentially no differences in the results between experiments in which the $Cl_3CSO_2Cl$ was taken directly from the bottle or when the $Cl_3CSO_2Cl$ was recrystallized a number of times from aqueous methanol.

[28] The more dilute reactions tended to give pmr spectra whose base lines were poor. This problem could be avoided by chromatographing the crude reaction mixture over silica gel (elution with 10% benzene in Skellysolve B) and collecting and combining the fractions. This appeared to remove any polymeric impurity that interfered with the integration of the pmr spectra of the resulting mixture of 1:1 adducts.

was held at reflux under nitrogen for 30 min. A pmr spectrum of the crude reaction mixture showed a mixture of 1:1 adducts: 75% of a 5:2 mixture of (*E*)-**9**–(*Z*)-**10**, respectively, and 25% of a 6:1 mixture of **11**–**12**, respectively. The $Cl_3CBr$ was removed by distillation, and the resulting yellow oil was crystallized from pentane to give 1.8 g of a 5:2 mixture of (*E*)-**9**–(*Z*)-**10**, respectively: mp 157–158°; pmr ((*E*)-**9**) $\tau$ 5.07 (s, 1), 5.13 (d, 1, $J_{18}$ = 1.2 Hz), 6.04 (d, 1, $J_{18}$ = 1.2 Hz); pmr ((*Z*)-**10**) $\tau$ 5.07 (s, 1), 5.13 (d, 1, $J_{18}$ = 1.2 Hz), 6.35 (d, 1, $J_{18}$ = 1.2 Hz). The mother liquor was chromatographed over 70 g of silica gel[29] (elution with 5% benzene in Skellysolve B). The first fractions were rich in the [2.2.2] isomers **9** and **10**, followed by **11** and lastly **12**. Crystallization from pentane gave 150 mg of **11**, mp 136–137° [pmr $\tau$ 3.72 (s, 1), 5.48 (d, 1, $J_{18}$ = 3.5 Hz), 5.80 (d, 1, $J_{18}$ = 3.5 Hz)], and 20 mg of **12**, mp 165–166° (pmr $\tau$ 4.48 (s, 1), 5.30 (s, 1), 5.57 (s, 1)).

The reaction of **2** with 0.15 *M* $Cl_3CBr$ was conducted in the same manner as the reaction of **1** with 0.15 *M* $Cl_3CBr$ (*vide supra*) (see Table I). The reaction of **2** with $Cl_3CBr$ (neat, sunlamp) at 50° gave a 3:1 mixture of (*E*)-**9**–(*Z*)-**10** and only a trace of **11**.

*Anal.* for 3:1 mixture of (*E*)-**9**–(*Z*)-**10**. Calcd for $C_{17}H_{11}BrCl_4$: C, 46.73; H, 2.54. Found: C, 46.50; H, 2.53.

*Anal.* for **11**. Calcd for $C_{17}H_{11}BrCl_4$: C, 46.73; H, 2.54. Found: C, 46.95; H, 2.57.

*Anal.* for **12**. Calcd for $C_{17}H_{11}BrCl_4$: C, 46.73; H, 2.54. Found: C, 46.95; H, 2.60.

**Addition of $Cl_3CSO_2Cl$ to Chloroolefin 2. (a) High Concentration.** A mixture of 1.0 g (4.2 mmol) of **2**, 5.0 g (23.3 mmol) of $Cl_3CSO_2Cl$, and 50 mg of benzoyl peroxide was sealed under nitrogen in a glass tube. The reaction was conducted in the same manner as in the case of olefin **1**. (The results are given in Table I.) The first fractions from the chromatography column were rich in the [2.2.2] adduct. These were combined and crystallized from ethanol to give 380 mg (25%) of unrearranged **13**: mp 154–156°; pmr $\tau$ 5.20 (s, 1), 5.13 (d, 1, $J_{18}$ = 1.2 Hz), 6.23 (d, 1, $J_{18}$ = 1.2 Hz). The next fractions were rich in *syn,endo*-**14**. These were combined and crystallized from pentane to give 300 mg (20%) of **14**: mp 136°; pmr $\tau$ 4.00 (s, 1), 5.47 (d, 1, $J_{18}$ = 3.8 Hz), 5.82 (d, 1, $J_{18}$ = 3.8 Hz). The next fractions were rich in *anti,exo*-**15**. These were combined and crystallized from ethanol to give 100 mg (7%) of **15**: mp 165–166°; pmr $\tau$ 4.77 (s, 1), 5.31 (s, 1), 5.68 (s, 1). The last fractions contained small amounts of *anti,endo*-**21** which was isolated by crystallization from pentane: 20 mg (1.5%); mp 200–201°; pmr $\tau$ 4.37 (s, 1), 5.31 (s, 1), 6.27 (s, 1). When **15** is heated at 132° (under nitrogen in a sealed tube) in the presence of $Cl_3CSO_2Cl$, a mixture of **15** and **21** results. No epimerization of **15** was observed in the absence of $Cl_3CSO_2Cl$.

*Anal.* for **13**. Calcd for $C_{17}H_{11}Cl_5$: C, 52.03; H, 2.83. Found: C, 52.00; H, 2.88.

*Anal.* for **14**. Calcd for $C_{17}H_{11}Cl_5$: C, 52.03; H, 2.83. Found: C, 51.80; H, 2.91.

*Anal.* for **15**. Calcd for $C_{17}H_{11}Cl_5$: C, 52.03; H, 2.83. Found: C, 51.97; H, 2.92.

*Anal.* for **21**. Calcd for $C_{17}H_{11}Cl_5$: 52.03; H, 2.83. Found: C, 51.75; H, 2.87.

**(b) Low Concentration.** Three grams (12.5 mmol) of **2**, 17.0 g (80 mmol) of $Cl_3CSO_2Cl$, and 100 mg of benzoyl peroxide were dissolved in 500 ml of chlorobenzene, and the reaction was conducted in the same manner as in the reaction of **1** with $Cl_3CSO_2Cl$ at high dilution. An 80% yield of 1:1 adducts was obtained and these products were carefully purified by chromatography over 300 g of silica gel (elution with 5% benzene in Skellysolve B). The compounds were eluted in the following order: *syn,endo*-**14**, *anti,exo*-**15**, *anti,endo*-**21** (*ca.* 5%), and *syn*-8-*endo*-4,5-trichlorodibenzobicyclo[3.2.1]octadiene (*ca.* 5%): mp 113–114° (from pentane); pmr $\tau$ 4.35 (s, 1), 5.10 (d, 1, $J_{18}$ = 5.0 Hz), 5.88 (d, 1, $J_{18}$ = 5.0 Hz).

*Anal.* Calcd for $C_{16}H_{11}Cl_3$: C, 62.06; H, 3.58. Found: C, 61.99; H, 3.73.

**Reactions of $Cl_3CBr$ and $Cl_3CSO_2Cl$ with Bromoolefin 3.** These reactions were conducted and worked up in the same manner as described in the reactions of the chloroolefin **2** (*vide supra*). The results are recorded in Table I. The physical data for the adducts obtained are as follows: for **16**, mp 184–185° (Skellysolve B); pmr $\tau$ 4.94 (s, 1), 6.11 (d, 1, $J_{18}$ = 1.2 Hz), 5.18 (d, 1, $J_{18}$ = 1.2 Hz); *Anal.* Calcd for $C_{17}H_{11}Br_2Cl_3$: C, 42.42; H, 2.30. Found: C, 42.42; H, 2.35; for **17**, mp 150–151° (Skellysolve B); pmr $\tau$ 3.67 (s, 1), 5.50 (d, 1, $J_{18}$ = 3.5 Hz), 5.75 (d, 1, $J_{18}$ = 3.5 Hz). *Anal.* Calcd for $C_{17}H_{11}Br_2Cl_3$: C, 42.42; H, 2.30. Found: C, 42.64; H, 2.37; for **18**, mp 164–165° (Skellysolve B); pmr $\tau$ 4.38 (s, 1), 5.30 (s, 1), 5.52 (s, 1); *Anal.* Calcd for $C_{17}H_{11}Br_2Cl_3$: C, 42.42; H, 2.30. Found: C, 42.30; H, 2.31; for **19**, mp 140–141° (Skellysolve B); pmr $\tau$ 3.97, (s, 1), 5.54 (d, 1, $J_{18}$ = 3.5 Hz), 5.80 (d, 1, $J_{18}$ = 3.5 Hz); *Anal.* Calcd for $C_{17}H_{11}BrCl_4$: C, 46.73; H, 2.54. Found: C, 46.55; H, 2.57; for **20**, mp 160–161° (Skellysolve B); pmr $\tau$ 4.67, (s, 1), 5.28 (s, 1), 5.62 (s, 1); *Anal.* Calcd for $C_{17}H_{11}BrCl_4$: C, 46.73; H, 2.54. Found: C, 46.80; H, 2.55.

**Rearrangement–Exchange of (*E*)-9 on Chromatography.** A mixture consisting of 0.60 g of (*E*)-**9** and 0.20 g of (*Z*)-**10** was passed over 30 g of Woelm acid-washed alumina (activity I, elution with Skellysolve B). Obtained from the column in their order of elution were 170 mg of (*Z*)-**10**, (mp 195–210°),[30] 300 mg of **15** (mp and mmp 163–164°) and 200 mg of **21** (mp and mmp 200–201°). There was no observable amount of (*E*)-**9** or syn-substituted isomers present. If lower activity alumina (*e.g.*, III or V) was used, the recovery was poor due probably to hydrolysis of the halides on the column.

**Reaction of the Mixture of (*E*)-9 and (*Z*)-10 with *n*-$Bu_3SnH$.** A solution of 300 mg of a 3:1 mixture of (*E*)-**9**–(*Z*)-**10**, respectively, 220 mg of *n*-$Bu_3SnH$,[31] and 5 mg of benzoyl peroxide in 8 ml of dry benzene (under nitrogen) was held at reflux for 4 hr. A pmr spectrum indicated the presence of **6** and tri-*n*-butyltin halide. Chromatography over 25 g of silica gel (elution with 5% benzene in Skellysolve B) first gave the tin halides followed by 200 mg of **6**, mp and mmp 118–119°.[9]

**Rearrangement of 16 on Chromatography.** **16** (1 g) was passed over 150 g of silica gel (elution with 3% benzene in Skellysolve B). A pmr spectrum of the resulting material showed **18** and a trace of starting material (**16**) present. Crystallization from Skellysolve B gave 0.85 g of **18**, mp 164–165°.

When **16** was passed over Woelm acid-washed alumina (ratio **16**–alumina was 1:50, elution with Skellysolve B), a mixture of what appeared to be rearranged bromides and chlorides (**18** and endo epimer of **18** and **20** and **25**) resulted. Passage of 0.80 g of **16** over a mixture of 35 g of Woelm acid-washed alumina (activity I) and 5 g of lithium chloride (anhydrous) resulted in complete conversion to a 55:45 mixture of **20**–**25**. From this mixture was crystallized (Skellysolve B) first 0.25 g of **25**, mp 204–205° (pmr $\tau$ 4.28 (s, 1), 5.26 (s, 1), 6.23 (s, 1); *Anal.* Calcd for $C_{17}H_{11}BrCl_4$: C, 46.73; H, 2.54. Found: C, 46.55; H, 2.57) followed by 0.20 g of **20**, mp 160–161°.

**Acknowledgment.** Financial support from the donors of the Petroleum Research Fund of the American Chemical Society (Grant No. 1050-G1) is gratefully acknowledged.

---

[29] If the material is allowed to stand on the chromatography column for long periods of time, *e.g.*, days, the (*E*)-**9** isomer rearranges to *anti*-**12** and the endo epimer of **12**.

[30] This seems to be a rather large melting range. Several recrystallizations (ethanol or Skellysolve B) did not markedly affect this large range. The material did appear to decompose slightly (turn yellow) on melting.

[31] H. G. Kuivila and O. F. Beumel, *J. Amer. Chem. Soc.*, **83**, 1246 (1961).