4992 *J. Org. Chem.* 1981, *46*, 4992-4998

Bridged Polycyclic Compounds. 87. Radical Rearrangements in Some Bicyclooctadienyl, Tricyclooctenyl, Bicyclononatrienyl, and Tricyclononadienyl Systems[1]

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Received July 3, 1981

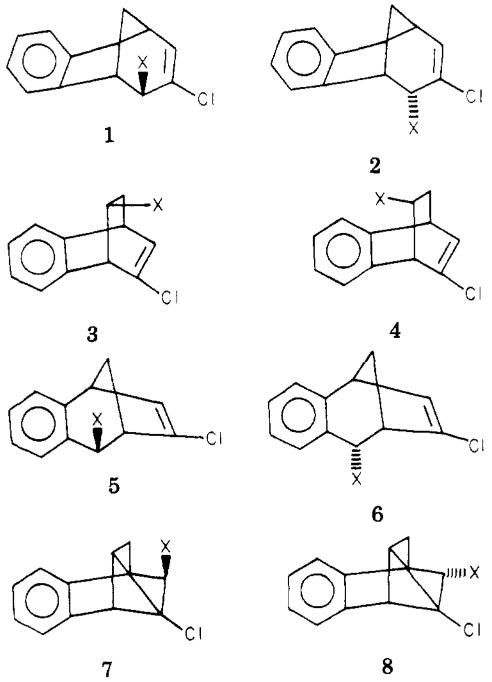
Chlorides and *S*-methyl xanthates of alcohols in the chlorobenzobicyclo[3.2.1]octadienyl systems **1** and **2**, the chlorobenzobicyclo[2.2.2]octadienyl system **3**, the chlorobenzotricyclo[3.2.1.0^{2,7}]octenyl systems **7** and **8**, the chlorodibenzobicyclo[3.2.2]nonatrienyl systems **23–25**, the chlorodibenzotricyclo[3.3.1.0^{2,8}]nonadienyl system **26** and the dibenzobicyclo[2.2.2]octadienyl system **30** have been treated with tri-*n*-butyltin and/or triphenyltin hydrides. Replacement of the functional group (chlorine or xanthate) by hydrogen proceeds through a radical intermediate which may, depending upon its nature and/or experimental conditions, rearrange before capture by hydrogen transfer. Comparison of these radical intermediates with each other and with corresponding carbocations is discussed briefly. The intervention of an alkoxythiocarbonyl radical in the xanthate reduction has been demonstrated.

Members of our research group have been interested in certain photochemically induced rearrangements and attendant solvolyses.[2] It has been proposed that these reactions involve carbenium ion intermediates, and the corresponding ionic ground-state reactions have also been studied. In many reactions, and particularly in photoinduced or photosensitizer-induced ones, the nature of the reactive intermediate(s) may not be known. Cases where radicals have markedly different fates from cations (or from other reactive intermediates) may be particularly useful in understanding such processes. It was therefore of interest to study reactions involving radical intermediates analogous to the cations produced in the ground-state and those presumably produced from excited-state progenitors. This paper reports a study of radical rearrangements in some systems in whose chemistry and photochemistry we have been interested.

One of the systems in which work has been reported[2b,c] or is in progress is the chlorobenzobicyclooctadienyl and chlorobenzotricyclooctenyl systems represented by **1–8** (Chart I). In those reports and in other work,[3] it was shown, *for a variety of nucleofugal groups X,* that carbenium ion processes have a large energy barrier separating the anti allylic systems represented by formulas **1–3** from the syn benzylic cyclopropylcarbinyl systems represented by formulas **4–8**. Thus, for example, acetolysis of the methanesulfonates of **1**, **2**, or **3** leads largely to **1**-OAc, which in acidified acetic acid is rapidly interconverted with **2**-OAc and is more slowly converted to an equilibrium mixture of acetates of **1–3**, with **3**-OAc predominating and without any measurable amounts of the acetates of **4–8**. On the other hand, acetolysis of the *syn*-methanesulfonate **4**-OMs gives a mixture of benzylic acetates **5** and **6**, whose acid-catalyzed equilibration[3] leads to **7**, **8**, and **4**-OAc without formation of the acetates of **1**, **2**, or **3**. Photoreactions of **1** or **2** (X = Cl, OMs, $OCOCHCl_2$) showed[2b,c] a similar barrier in solvolysis or rearrangement.

These results were interpreted with the assumption that the allylic ion **9** (Chart II) is the lowest lying one formed in the manifold from the anti allylic systems but that the benzo-bridged ion **10** is only slightly higher in energy, so that it was accessible in the equilibration studies. The ions **11** and **12**, which would mix the two systems, must be too high in energy to have been accessible in those studies, while the benzylic ion **13** and its companion cyclopropylcarbinylhomoallylic ion **14** were utilized in the **4–8** interconversions.

Chart I



As a source of free radicals analogous to these carbocations, reaction[4] of the corresponding chlorides with tri-*n*-butyltin hydride or triphenyltin hydride, initiated with azobis(isobutyronitrile), seemed most useful, and, indeed, the reaction of **1**-Cl with Bu_3SnH has already been reported.[2b] However, *certain of the starting chlorides* (e.g., **2**, **7**, and **8**) were difficult to obtain, although their alcohols are readily available.[2b] We therefore made use of a procedure reported recently by Barton and co-workers,[5] in which *S*-methyl xanthates replace chlorides in the tin

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(1) Paper 86: Cristol, S. J.; Strom, R. M.; Stull, D. P. *J. Org. Chem.* **1978**, *43*, 1150.

(2) See for example: (a) Cristol, S. J.; Stull, D. P.; Daussin, R. D. *J. Am. Chem. Soc.* **1978**, *100*, 6674. (b) Cristol, S. J.; Strom, R. M. *Ibid.* **1979**, *101*, 5707. (c) *Ibid.* **1980**, *102*, 5577.

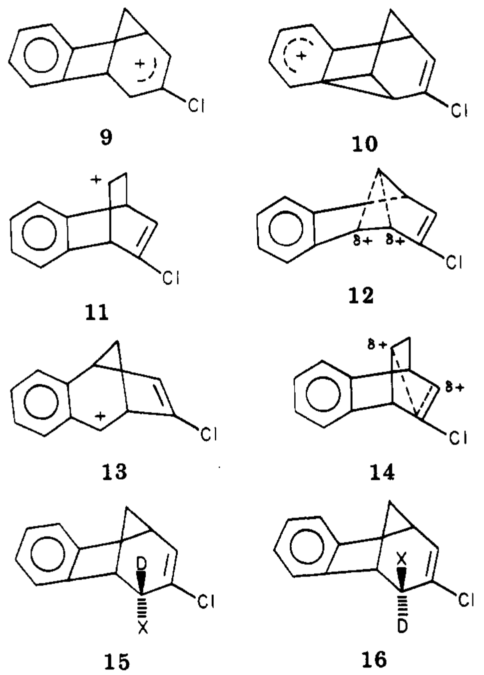
(3) Dickenson, W., personal communication.

(4) (a) Kuivila, H. G.; Menapace, L. W.; Warner, C. R. *J. Am. Chem. Soc.* **1962**, *84*, 3584. (b) Kuivila, H. G.; Menapace, L. W. *J. Org. Chem.* **1963**, *28*, 2165. (c) Menapace, L. W.; Kuivila, H. G. *J. Am. Chem. Soc.* **1964**, *86*, 3047. (d) Warner, C. R.; Strunk, R. J.; Kuivila, H. G. *J. Org. Chem.* **1966**, *31*, 3381.

(5) Barton, D. H. R.; McCombie, S. W. *J. Chem. Soc., Perkin Trans. 1* **1975**, 1574.

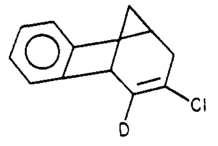
0022-3263/81/1946-4992$01.25/0

Chart II



hydride reduction. The reaction path, like that of the chloride, involves the formation of R· and its reaction with tin hydride, and the reaction is an extremely useful method for the transformation of secondary alcohols into hydrocarbons. We comment briefly below on the mechanism of reaction.

Treatment of 1-Cl with an excess of 0.09 M Bu_3SnH in benzene at 60 °C has been reported[2b] to give only 1-H; that is, rearrangement to 3, 5, or 7 (or epimeric) species was not observed. Similarly, when the *S*-methyl xanthate of the *exo*-deuterio endo alcohol 15-OH was treated with 0.08 M Bu_3SnH in benzene at 72 °C, only allylic species were produced. The product mixture (^2H NMR analysis) comprised 7% 15-H, 45% 16-H, and 48% 17. The results are thus consistent with the intermediacy of the classical allylic radical 18, which does not rearrange to 19 (the corresponding transformation of 1-X to 3-X is observed photochemically[2b,c] and which suffers hydrogen atom transfer from Bu_3SnH about 6 times more readily to its exo face than to its endo face. We assume that the selectivity has a steric and/or stereoelectronic basis.



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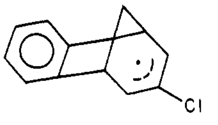

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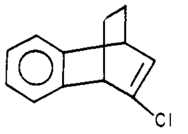

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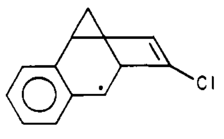

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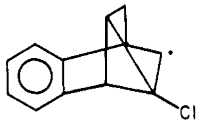
The failure of the probably more stable disubstituted allylic radical 18 to rearrange to the secondary radical 19 seemed reasonable, and, indeed, the reverse reaction might be anticipated. For carbocationic processes, it has been shown[2b,c] that solvolyses of 3-Cl and 3-OMs lead to 1-X derivatives and that the cation 9 is more stable than 11 (see above), and one would expect the same trend for the radicals. We therefore undertook the reduction of 3-Cl with dilute (0.04 M) Bu_3SnD. Under these conditions, no 3-D, 4-D, 1-D or 2-D was observed. Instead, migration of the chloroethenyl group occurred, and the *exo*-deuterio benzylic isomer 5-D was produced, along with a trace of dechloro-5-D. That radical 19 was in fact first produced in the reaction of the trialkyltin radical with 3-Cl was demonstrated by conducting the reduction of 3-Cl in neat triphenyltin hydride. This hydride is reported[6] to transfer hydrogen atoms somewhat faster than does tri-*n*-butyltin hydride. Under these conditions, hydrogen transfer was faster than rearrangement, and, within the limits of our analytical method, reaction led only to 3-H which, in the presence of the excess hydride, was converted to the dechloro analogue.

It has been reported[2b,c] that 3-OMs acetolyzes significantly faster than its epimer 4-OMs, although the opposite is true for the dechloro analogue.[7] Thus, in these carbenium-ion intermediate reactions, homoallylic participation of the double bond to give a delocalized cyclopropylcarbinyl cation, which is normally superior to participation of a benzene ring,[7-9] giving a bridged phenonium ion, is rendered inferior because of the adverse carbon–chlorine bond dipole *β* to the carbenium ion site (viz., 14). On the other hand, radical 19 on rearrangement gives products derived from 20 rather than from 18, as the electronegativity of the chlorine atom has only a negligible effect in radical stabilization. It may be assumed that 21 and 22 are intermediates in the pathway to 20 and 18, respectively, and the course of the reaction makes it clear that 21 is on a lower energy path than 22. Experiments described below are consistent with this interpretation.



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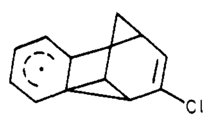

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We attempted to capture radical 21 by study of 7 and 8 progenitors. Attempts to prepare 7-Cl and 8-Cl by triplet sensitization of 1-Cl and 2-Cl, while not completely unsuccessful, gave poor results. Alcohols 1 and 2, on the other hand, are readily transformed to 7-OH and 8-OH by irradiation in good yield and with clean stereochemistry. These were readily converted to *S*-methyl xanthates, which were in turn treated with 0.7–0.8 M tri-*n*-butyltin deuteride. No 7-D or 8-D could be observed. Instead, the product of both reactions, within our detection limits, was entirely 5-D. Rearrangement of 21 to 20 thus is faster than capture under these conditions, a fact consistent with the failure to see tricyclic products from the reduction of 3-Cl. We thought we might capture 21 by reduction of 8-OCS_2CH_3 with neat triphenyltin hydride, as described above with 3-Cl. The experiment was unsuccessful, as it led to the methyl ether 8-OMe instead.

Barton and McCombie[5] proposed that the reduction of xanthates to hydrocarbons involved the propagation steps shown in eq 1–3. The formation of 8-OMe from 8-

$$R'_3Sn\cdot + ROC(S)SCH_3 \rightarrow RO\text{–}\dot{C}{=}S + R'_3SnSCH_3 \qquad (1)$$

$$RO\dot{C}{=}S \rightarrow R\cdot + COS \qquad (2)$$

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(6) (a) Carlsson, D. J.; Ingold, K. U. *J. Am. Chem. Soc.* **1968**, *90*, 1055, 7047.

(7) Tanida, H.; Tori, K.; Kitahonoki, K. *J. Am. Chem. Soc.* **1967**, *89*, 3212.

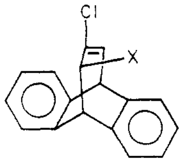
(8) Bartlett, P. D.; Giddings, W. P. *J. Am. Chem. Soc.* **1960**, *82*, 1240.

(9) (a) Cristol, S. J.; Nachtigall, G. W. *J. Am. Chem. Soc.* **1968**, *90*, 7132. (b) Cristol, S. J.; Noreen, A. L.; Nachtigall, G. W. *Ibid.* **1972**, *94*, 2187.

$$R\cdot + R'_3SnH \rightarrow RH + R'_3Sn\cdot \qquad (3)$$

OCS_2CH_3 is consistent with the stepwise process, if one assumes that the methyl group in the ether arises by capture of the ROCS· species to give the thioformate **8**-OC(S)H which is then further reduced to **8**-OMe. An experiment in which the *S*-methyl group in the xanthate ester was replaced by a trideuteriomethyl group, and which led only to the triprotiomethyl ether **8**-OCH_3, fits this explanation. No experiments with intermediate hydride concentrations were carried out to see if conditions could be found in which radical **21**, once produced, could be captured.

We then decided to look at the dibenzobicyclononatriene–dibenzotricyclononadiene systems **23**–**26**, whose ground-state cationic and photochemical reactions had been studied extensively in this laboratory,[1,2a,10,11] but whose radical interconversions have not been investigated in detail. It has been reported[2a] that bromination of **23**-H with *N*-bromosuccinimide gave only **23**-Br, while bromination of **24**-H gave **23**-Br, as well as **24**-Br and **25**-Br. However, as those authors noted, the question of whether radical **27** rearranged to **28** was left unanswered, in view of the fact that **24**-Br and **25**-Br are transformed fairly readily to the more stable **23**-Br by ground-state heterolytic rearrangement.



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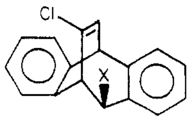

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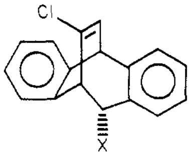

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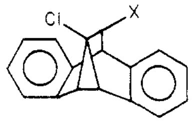

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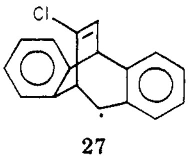

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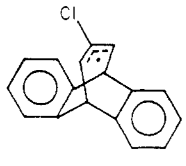

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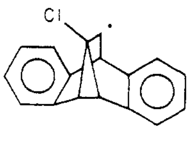

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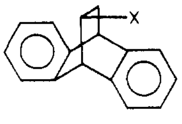
When **26**-Cl was treated with 0.13 M tri-*n*-butyltin hydride (AIBN initiation), no unrearranged **26**-H was found. Instead, just as with the **7** and **8** xanthate reductions, the cyclopropylcarbinyl radical **29** rearranged to its homoallyl isomer **27**, which in the presence of the fairly concentrated hydride was reduced to **24**-H (**23**-H and **26**-H were not observed under these conditions). Use of 0.15 M tributyltin deuteride with **26**-Cl gave a 1:1 mixture of **24**-D and **25**-D, showing that radical **27** is, within the limits of our analysis, close to symmetrical with regard to hydrogen atom transfer.

The rearrangement of these radicals is, of course, a unimolecular process, while hydrogen atom transfer is bimolecular. Thus the latter reaction depends upon hydride concentration (see below for quantitative results). We therefore decided to utilize highly dilute solutions of hydride to see if, under such conditions,[12] rearrangement might be observed. Reduction of **23**-Cl with tributyltin hydride under conditions where the hydride was added at a rate approximating that of its rate of consumption gave only **23**-H. Thus the allylic radical **28** did not rearrange to the benzylic radical **27**. On the other hand, when a 1:1 mixture of **24**-Cl and **25**-Cl was treated with tributyltin hydride under similar high-dilution conditions, about equal amounts of **23**-H and **24**-H were produced.[13] Clearly then, the benzylic radical **27** rearranges to the allylic radical **28**. It has been shown previously[1,2a,10,11] that the benzylic ion is the most stable one in the manifold of ions in this system. This experiment shows that this is not true for the corresponding radicals. We attribute this to the destabilizing effect of the chlorine atom which is β in the allylic ion and which has a position γ to the benzylic position (and obviously a still more remote position when delocalization in the benzylic cation is considered).

As described above, treatment of **3**-Cl with neat triphenyltin hydride gave **3**-H, while treatment with 0.04 M tributyltin deuteride gave **5**-D, presumably via radicals **19** → **21** → **20**, with that path being favored over the alternate path **19** → **22** → **18**. Put another way, radical rearrangement via chloroethenyl participation was more favored than that via benzo participation. We thought it would be interesting to compare the rate of chloroethenyl migration in **19** with that of benzo migration in some other radical. For this reason we studied the effect of variation in concentration of tributyltin hydride on the ratio of **3**-H to **5**-H from **3**-Cl and that of **30**-H to **31**-H from **30**-Cl.[14]



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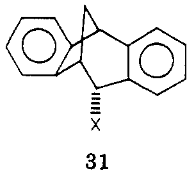

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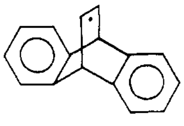

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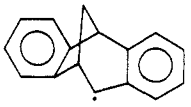

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In the experiments we conducted, a large excess (ca. tenfold) of hydride (over a range of concentration of 0.13–1.3 M) was used, so as to approximate pseudounimolecular conditions. **3**-Cl, **3**-H, and **5**-H (plus their dechloro analogues) were detected by ^1H NMR spectroscopy. Similarly, reduction of **30**-Cl with tributyltin hydride (0.017–0.17 M) was followed by measurements of **30**-H and **31**-H by ^1H NMR spectroscopy. From the data collected, the ratio of the rate constant for rearrangement to that of hydrogen atom transfer was calculated to be 0.41 for

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[10] Cristol, S. J.; Sequeira, R. M.; Mayo, G. O. *J. Am. Chem. Soc.* **1968**, *90*, 5564.

[11] Cristol, S. J.; Mayo, G. O.; Lee, G. A. *J. Am. Chem. Soc.* **1969**, *91*, 214.

[12] For early examples of such a technique, see: (a) Seubold, F. *J. Am. Chem. Soc.* **1953**, *75*, 2532. (b) Cristol, S. J.; Brindell, G. D.; Reeder, J. A. *Ibid.* **1958**, *60*, 635.

[13] Experiments designed to show that the benzylic chlorides **24**-Cl and **25**-Cl did not rearrange to the more stable allylic chloride **23**-Cl in the course of the experiments were conducted (see Experimental Section).

[14] It was known, from previous work in this laboratory,[15] that radical **32** rearranges to **33**.

[15] Opitz, R. J. Ph.D. Dissertation, University of Colorado, 1980.

radical **19** and 0.055 for radical **32**. As Carlsson and Ingold[16] have shown that there is little variation in the reactivity of alkyl radicals toward tributyltin hydride and as **19** and **32** are both secondary radicals with approximately identical steric requirements, it seems safe to assume that hydrogen atom transfer rate constant values are approximately equal for these two radicals. If that is assumed, the rearrangement rate constant ratios for **19** and **32** are 0.41/0.055 or 7.5. Correcting for the fact that **32** has two benzo rings for migration, one gets a value of 15 for the migration aptitude of the chloroethenyl group over that of the benzo group, a value consistent with the result for **19** itself.

Conclusion

The fates of radicals produced from compounds **1**–**3** and from compounds **23**–**25** are quite different from those of the cations produced from similar progenitors and also are different from those of species produced photochemically in polar solvents. We conclude, therefore, that the photochemical processes[2] do not involve radical intermediates.

Experimental Section

General Methods. ^{1}H NMR spectra were taken in deuteriochloroform with a Varian Associates EM-390 spectrometer. ^{2}H NMR spectra were taken with a JEOL PS-100 Fourier transform instrument. Mass spectra were obtained on a Varian-MAT Model CH5 mass spectrometer. Gas chromatography–mass spectrometry analyses were performed on a Hewlett-Packard Model 5980A instrument utilizing a 10-ft glass capillary column. Carbon and hydrogen analyses were done by Galbraith Laboratories. Melting points were measured with a Thomas-Hoover capillary melting point apparatus and are corrected. Dry benzene was obtained by distillation of thiophene-free, reagent-grade benzene from calcium hydride or lithium aluminum hydride (LAH). Dry tetrahydrofuran (THF) was obtained by distillation of reagent-grade THF from LAH. Organotin hydride reagents were prepared by reduction of the appropriate organotin chloride with LAH.[17] Tri-*n*-butyltin deuteride was used as obtained from Alfa Chemicals.

Gas–Liquid Phase Chromatography. All gas–liquid phase chromatography (GLC) was done by using a 4 ft × $^1/_8$ in. (i.d.) aluminum column packed with 20% SE-30 on Chromosorb P (100–120 mesh). Analytical GLC was performed with a Hewlett-Packard Model 5750 chromatograph using a flame-ionization detector and a Hewlett-Packard Model 3380S integrator. The injector, detector, and column were set at 225, 350, and 225 °C, respectively.

Sample collection was performed on an Aerograph Model A-90-P3 chromatograph, with a thermal-conductivity detector and a Honeywell recorder. Here the injector, detector, and column were set at 210, 250, and 190 °C, respectively.

High-Pressure Liquid Chromatography. Sample collection by high-pressure liquid chromatography was performed by using a Waters Associates Model 6000A pump, Model U6K injection system, and two 30 cm × 4 mm (i.d.) μ-Porasil columns connected in series. Hexane was used as the eluting solvent. Detection was by ultraviolet absorption at 254 nm, with a Beckman model 25 UV spectrophotometer equipped with a Waters microcell apparatus.

^{1}H NMR Spectra of the Observed Reduction Products. Product ratios were determined by ^{1}H NMR spectroscopy except where otherwise indicated. Those portions of each spectrum which were used for the purpose of analysis are as follows.

3-Chloro-6,7-benzobicyclo[3.2.1]octa-3,6-diene (1-H). This compound has previously been synthesized and its NMR spectrum characterized.[2b] The chemical shifts of *exo*-H-4, *endo*-H-4, and H-2 are 2.85, 2.24, and 6.25 ppm, respectively.

5-Chloro-2,3-benzobicyclo[2.2.2]octa-2,5-diene (3-H). The ethylenic proton (H-3) of this compound displays the characteristic doublet of doublets noted previously for all 3-X analogues[2b] ($J_{3,4}$ = 7 Hz, $J_{3,1}$ = 2 Hz). The chemical shift for 3-H is 6.4 ppm, falling 0.3-ppm upfield of the analogous proton on 3-Cl.

6-Chloro-2,3-benzobicyclo[3.2.1]octa-2,6-diene (5-H). The ethylenic proton (H-7) of this compound exhibits the characteristic doublet noted earlier for all 5-X compounds[2b] ($J_{7,1}$ = 3 Hz) at δ 6.1. The other features of the **5**-D spectrum are as follows: δ 7.1 (m, 4, aromatic H), 3.4 (dd, 1, H-1, $J_{1,7}$ = 3 Hz, $J_{1,8_{anti}}$ = 5 Hz), 2.9 (d, 1, H-5, $J_{5,8_{anti}}$ = 9 Hz), 2.9 (s, 1, H-4$_{endo}$), 2.5 (m, 1, H-8$_{anti}$), 2.0 (d, 1, H-8$_{syn}$, $J_{8_{syn},8_{anti}}$ = 10 Hz). The *endo*-H-4 proton usually has a small or zero coupling constant with H-5, whereas a 5–6-Hz coupling constant is generally associated with *exo*-H-4. This fact leads to the conclusion that the deuterium in **5**-D, obtained by the reduction of **3**-Cl with tributyltin deuteride, was in the exo position.

2,3-Benzobicyclo[2.2.2]octa-2,5-diene. The ^{1}H NMR spectrum of this compound in CCl_4 has been published by Tanida and co-workers.[18] The spectrum, run in $CDCl_3$, displays a triplet at δ 6.5 for the ethylenic protons.

2,3-Benzobicyclo[3.2.1]octa-2,6-diene. The ^{1}H NMR spectrum of the corresponding acetate, run in CCl_4, has been published by Tanida and co-workers.[7] The ^{1}H NMR spectrum of the hydrocarbon labeled at C-4 with deuterium is analogous. It exhibits the following features: δ 7.1 (m, 4, aromatic H), 6.3 (dd, 1, H-7, $J_{7,1}$ = 5 Hz, $J_{7,5}$ = 2 Hz), 5.8 (dd, 1, H-6, $J_{6,7}$ = 5 Hz, $J_{6,5}$ = 2 Hz), 3.3 (dd, 1, H-1, $J_{1,7}$ = 2 Hz, $J_{1,8_{anti}}$ = 2 Hz), 3.0 (m, 1, H-5), 2.6 (m, 1, H-2$_{endo}$), 2.2 (m, 1, H-8$_{anti}$), 1.9 (d, 1, H-5$_{syn}$, $J_{8_{syn},8_{anti}}$ = 9 Hz). Deuterium was observed in the *exo*-H-2 position as a singlet at 2.91 ppm in the decoupled ^{2}H NMR spectrum, which is downfield of the *endo*-2-H proton.

2,3:5,6-Dibenzobicyclo[2.2.2]octa-2,5-diene (30-H). The ^{1}H NMR spectrum of this compound in CCl_4 has been published.[19] In $CDCl_3$, a broad singlet is observed at δ 4.3 for the bridgehead protons.

2,3:6,7-Dibenzobicyclo[3.2.1]octa-2,6-diene (31-H). The ^{1}H NMR spectrum of this compound, in CCl_4, has previously been published.[20] In $CDCl_3$, a doublet is observed at δ 3.85 for the H-1 bridgehead proton ($J_{1,8_{anti}}$ = 4 Hz).

Preparation of *O*-(*exo*-2-Deuterio-3-chloro-6,7-benzobicyclo[3.2.1]octa-3,5-dien-*endo*-2-yl) *S*-Methyl Xanthate (15-OCS_2CH_3). *n*-Butyllithium (1.08 mL, 2.17 M in hexanes; 2.34 mmol) was added to a stirred solution of 462 mg (2.23 mmol) of **15**-OH[1] in 10 mL of dry THF under a nitrogen atmosphere. This mixture was stirred for 30 min, and 238 mg (3.12 mmol) of carbon disulfide was added. After 3 h, 443 mg (3.12 mmol) of methyl iodide was added. After an additional 3 h, the solution was poured into 10 mL of water. The layers were separated, and the aqueous layer was extracted with 34 mL of ether. The combined organic portions were dried ($MgSO_4$), treated with decolorizing charcoal, and filtered. Evaporation of solvent gave 1.46 g of a yellow oil. The crude product was applied to a preparative TLC plate (silica gel; 2 mm) and eluted with 35:65 THF/hexanes. One band was isolated (R_f 0.43), which weighed 428 mg (65%). The ^{1}H NMR spectrum ($CDCl_3$) was consistent with that anticipated for **15**-OCS_2CH_3: δ 7.2 (m, 4, aromatic H), 6.6 (d, 1, H-4, $J_{4,5}$ = 8 Hz), 4.1 (m, 1, H-1), 3.5 (m, 1, H-5), 2.7 (d, 1, H-8$_{syn}$, $J_{8_{syn},8_{anti}}$ = 11 Hz), 2.5 (s, 3, CH_3), 2.4 (m, 1, H-8$_{anti}$). The mass spectrum showed a one deuterium atom excess. This was exclusively at H-2 (^{2}H NMR spectrum).

Reduction of 15-OCS_2CH_3 with Tri-*n*-butyltin Hydride. A solution of 118 mg (0.395 mmol) of **15**-OCS_2CH_3, 231 mg (0.793 mmol) tri-*n*-butyltin hydride, 17.0 mg (0.104 mmol) of azobis(isobutyronitrile) (AIBN) and 10 mL of dry benzene was heated at reflux for 17 h. After addition of 5 mL of CCl_4 (to react with excess hydride), the solvents were distilled. The ^{1}H NMR spectrum was consistent with that of **2**-H[2b] containing some deuterium, and the ^{2}H NMR spectrum showed deuterium to be in the H-2 (ethylenic), *exo*-H-4, and *endo*-H-4 positions in a ratio of 48:7:45, as found by the cut and weigh method of integration.

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Reduction of *anti*-2-6-Dichloro-7,8-benzobicyclo[2.2.2]octa-5,7-diene (3-Cl) with Tri-*n*-butyltin Deuteride. A solution of 400 mg (1.178 mmol) of 3-Cl,[2b] 621 mg (2.13 mmol) of tri-*n*-butyltin deuteride, and 30 mg (0.178 mmol) of AIBN in 25 mL of dry benzene was heated at reflux for 18 h. It was then quenched with CCl_4. The solvents were removed and replaced with 2 mL of CH_2Cl_2. GC/MS analysis of this mixture revealed two components which did not contain tin and which had molecular weights of 191 and 157. Quantitative gas chromatography showed the ratio of these components (191 to 157) to be 96:4. The relative response factor of the 191 peak to the 157 peak was 1.22. GC collection of these components was performed. ^1H NMR spectra of these products showed them to be *exo*-4-deuterio-2,3-benzobicyclo[3.2.1]octa-2,6-diene (M_r = 157) and *exo*-4-deuterio-6-chloro-2,3-benzobicyclo[3.2.1]octa-2,6-diene (5-D; M_r = 191). ^2H NMR spectra showed the deuterium of both products to be exclusively in the exo position at C-4. Apparently, with the very dilute hydride, replacement of the second (ethylenic) chlorine atom occurred by attack of the ethylenic radical on the solvent, as demonstrated by mass spectrometry and ^1H and ^2H NMR spectroscopy. An analogous result was reported recently[21] in the reduction of *trans*-β-bromostyrene.

Preparation of *O*-(7-Chloro-3,4-benzotricyclo[3.2.1.0^{2,7}]octa-3-en-*syn*-6-yl) *S*-Methyl Xanthate (8-OCS_2CH_3). *n*-Butyllithium (2.35 mL, 2.17 M in hexanes; 5.10 mmol) was added to a stirred solution of 1.00 g (4.85 mmol) of 8-OH[2b] in 15 mL of dry THF under nitrogen at 0 °C. After 30 min, 517 mg (6.79 mmol) of carbon disulfide was added. After 3 h at room temperature, 964 mg (6.79 mmol) of methyl iodide (or trideuteriomethyl iodide, 984 mg, 99.8% D) was added. The mixture was stirred for an additional 12 h. At this time, the solution was decanted into 0.25 mL of H_2O, treated with decolorizing charcoal, and filtered. Distillation of solvents left a yellow oil, which was applied to a preparative TLC plate (silica gel) and eluted with 35:65 THF/hexanes. One band was removed (R_f 0.40) and the product isolated by washing with ether, giving 1.01 g (75%) of a pale yellow oil with a ^1H NMR spectrum ($CDCl_3$) consistent with that expected for 8-OCS_2CH_3: δ 6.9–7.5 (m, 4, aromatic H), 6.0 (dd, 1, H-6, $J_{6,5}$ = 5 Hz, $J_{6,2}$ < 0.5 Hz), 3.8 (dd, 1, H-5, $J_{5,6}$ = 5 Hz, $J_{5,8_{anti}}$ = 5 Hz), 2.9 (d, 1, H-2, $J_{2,1}$ = 9 Hz), 2.4 (ddd, 1, H-8_{anti}, $J_{8_{anti},8_{syn}}$ = 12 Hz, $J_{8_{anti},5}$ = 5 Hz, $J_{8_{anti},1}$ = 3 Hz), 2.2 (d, 1, H-8_{syn}, $J_{8_{syn},8_{anti}}$ = 12 Hz). A pure sample was collected by high-pressure liquid chromatography. Anal. Calcd for $C_{14}H_{13}ClOS_2$: C, 56.65; H, 4.41. Found: C, 56.83; H, 4.44.

Reduction of 8-OCS_2CH_3 with Tri-*n*-butyltin Deuteride. A solution of 109 mg (0.368 mmol) of 8-OCS_2CH_3, 216 mg (0.739 mmol) of tri-*n*-butyltin deuteride, and 26.5 mg (0.161 mmol) of AIBN in 10 mL of dry benzene was heated at reflux for 11 h, after which 5 mL of CCl_4 was added. Gas chromatographic separation of the chloro hydrocarbon gave a product whose ^1H NMR spectrum was consistent with that of 5-D. The ^2H NMR spectrum showed all deuterium to be in the *exo*-4-position.

Preparation of *O*-(7-Chloro-3,4-benzotricyclo[3.2.1.0^{2,7}]oct-3-en-*anti*-6-yl) *S*-Methyl Xanthate (7-OCS_2CH_3). A solution of 230 mg (1.12 mmol) of 7-OH[2b] in 3.5 mL of dry ether was slowly added to 221 mg of sodium hydride (57% oil dispersion, 5.25 mmol) in 3.5 mL of ether. The mixture was heated under reflux for 3 h. Carbon disulfide (490 mg, 6.44 mmol) was added, and heating was resumed for an additional 3 h. Methyl iodide (949 mg, 6.69 mmol) was then added, and the mixture was heated for another 12 h. At this point enough water was added to dissolve the solid material present. This mixture was poured into 25 mL of saturated sodium chloride solution. The layers were separated, and the aqueous layer was extracted with two 25-mL portions of ether. The combined organic portions were dried ($MgSO_4$). Evaporation of volatiles gave a brown oil, which was purified by preparative TLC (silica gel). Elution with 47:53 ether/hexanes gave 240 mg (73%) of a yellow oil: ^1H NMR ($CDCl_3$) δ 7.2 (m, 4, aromatic H), 5.5 (s, 1, H-6), 3.4 (d, 1, H-5, $J_{5,8_{anti}}$ = 5 Hz), 2.8 (d, 1, H-2, $J_{2,1}$ = 8 Hz), 2.6 (s, 3, CH_3), 2.6 (ddd, 1, H-8_{anti}, $J_{8_{anti},8_{syn}}$ = 12 Hz, $J_{8_{anti},5}$ = 5 Hz, $J_{8_{anti},1}$ = 3 Hz), 2.3 (m, 1, H-1), 1.1 (d, 1, H-8_{syn}, $J_{8_{syn},8_{anti}}$ = 12 Hz). A pure sample was collected by high-pressure liquid chromatography. Anal. Calcd for $C_{14}H_{13}ClOS_2$: C, 56.65; H, 4.41. Found: C, 56.47; H, 4.61.

Reduction of 7-OCS_2CH_3 with Tri-*n*-butyltin Deuteride. A solution of 88.8 mg (0.299 mmol) of 7-OCS_2CH_3, 244 mg (0.834 mmol) of tri-*n*-butyltin deuteride, and 25.2 mg (0.154 mmol) of AIBN in 10 mL of dry benzene was heated at reflux for 10.5 h. Excess hydride was destroyed with 5 mL of CCl_4. Gas chromatographic separation and collection of the chloro hydrocarbon fraction was carried out. The ^1H NMR spectrum of this fraction was that of 5-D, and the ^2H NMR spectrum showed all the deuterium to be at the *exo* position at C-4.

Reduction of 3-Cl with Neat Triphenyltin Hydride. A mixture of 77 mg (0.34 mmol) of 3-Cl and 1.353 g of triphenyltin hydride was heated at 75 °C with stirring until a solution was obtained. AIBN (25 mg, 0.15 mmol) was added. The solution was heated for 25 h at 55 °C and at 85 °C for 10 h. Excess hydride was destroyed with 35 mL of CCl_4. Most of the $(C_6H_5)_3SnCl$ was crystallized from an ethanolic solution, giving 393 mg of a yellow oil which was eluted on a preparative TLC plate (silica gel) with 70:30 hexanes/ether. A fraction (R_f 0.5) weighing 54 mg was isolated from that plate. The ^1H NMR spectrum of that fraction was identical with the published[18] spectrum of 2,3-benzobicyclo[2.2.2]octadiene (dechloro-3-H).

Reduction of 8-OCS_2CH_3 with Neat Triphenyltin Hydride. A mixture of 243 mg (0.821 mmol) of 8-OCS_2CH_3, 1.477 g (4.21 mmol) of triphenyltin hydride, and 25 mg (0.15 mmol) of AIBN was stirred at 65 °C for 18 h. Excess hydride was destroyed with 5 mL of CCl_4. The product mixture was adsorbed onto 25 g of neutral alumina (Woelm) and eluted first with 560 mL of hexanes, which was discarded, and then with 150 mL of 80:20 hexanes/methylene chloride. Evaporation of the solvent left 863 mg of white solid, which was dissolved in 25 mL of ether and stirred with 25 mL of saturated KF solution[22] for 12 h. The crystalline material was filtered, and the layers were separated. The aqueous layer was extracted with ether (2 × 25 mL). The combined organic portions were dried ($MgSO_4$), filtered, and condensed to yield 316 mg of a pale yellow oil. GC/MS analysis of this mixture showed that the product not containing tin and that had arisen from 8-OCS_2CH_3 had a molecular weight of 220. It was determined that this product was 8-OCH_3 by comparison of the ^1H NMR spectrum of the product mixture with that of an authentic sample of 8-OCH_3 (see below).

Preparation of 7-Chloro-*syn*-6-methoxy-3,4-benzotricyclo[3.2.1.0^{2,7}]oct-3-ene (8-OCH_3). *n*-Butyllithium (725 μL, 2.17 M in hexanes; 1.58 mmol) was added to a solution of 206 mg (1.00 mmol) of 8-OH in 10 mL of dry THF under nitrogen. After 45 min at room temperature, 270 mg (1.90 mmol) of methyl iodide was added. After an additional 30 min, the solution was poured into 10 mL of water. The layers were separated, and the aqueous layer was extracted with 35 mL of ether. The combined organic portions were dried ($MgSO_4$), treated with decolorizing carbon, and filtered. Solvent distillation left 202 mg (92%) of a clear oil. This sample was further purified by elution from a dry-packed silica gel column with hexanes. A clear oil was obtained upon evaporation of the solvent, which crystallized upon cooling. Recrystallization from *n*-hexane gave 8-OMe: mp 79–79.5 °C; ^1H NMR ($CDCl_3$) δ 7.2 (m, 4, aromatic H), 3.9 (dd, 1, H-6, $J_{6,5}$ = 5 Hz, $J_{6,2}$ < 0.5 Hz), 3.3 (dd, 1, H-5, $J_{5,6}$ = 5 Hz, $J_{5,8_{anti}}$ = 5 Hz), 3.2 (s, 3, CH_3), 2.7 (d, 1, H-2, $J_{2,1}$ = 8 Hz), 2.2 (ddd, 1, H-8_{anti}, $J_{8_{anti},8_{syn}}$ = 12 Hz, $J_{8_{anti},5}$ = 5 Hz, $J_{8_{anti},1}$ = 3 Hz), 2.0 (m, 1, H-1), 1.1 (d, 1, H-8_{syn}, $J_{8_{syn},8_{anti}}$ = 12 Hz). Anal. Calcd for $C_{13}H_{13}ClO$: C, 70.75; H, 5.94. Found: C, 70.52; H, 5.86.

Reduction of 8-OCS_2CD_3 with Triphenyltin Hydride. A mixture of 173 mg (0.577 mmol) of 8-OCS_2CD_3, 1.37 g (3.91 mmol) of triphenyltin hydride, and 20.0 mg (0.122 mmol) of AIBN was heated for 18 h at 65 °C. Excess hydride was destroyed with 5 mL of CCl_4. Column chromatography over Woelm neutral alumina with hexane elution was used. Evaporation of solvent was followed by extraction with 20 mL of ethanol. The ethanol was evaporated, giving 194 mg of a clear oil which had a ^1H NMR spectrum consistent with that of 8-OCH_3. The ^2H NMR spectrum showed no deuterium incorporated in the methoxy group.

Treatment of 1,9-Dichloro-3,4-dibenzotricyclo[3.3.1.0^{2,8}]nona-3,6-diene (26-Cl) with Tri-*n*-butyltin Hydride. The

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tricyclic chloride **26**-Cl[10] (109 mg, 0.38 mmol) was dissolved in 4.0 mL of benzene. Tri-*n*-butyltin hydride (140 μL, 0.53 mmol) and 25 mg of AIBN were added. The reaction mixture was heated at reflux for 14 h and was then quenched by the addition of 3 mL of chloroform. After 3 h at reflux, the solvent was removed by distillation, leaving 306 mg of a light yellow solid. Analysis by ^{1}H NMR spectroscopy showed that the solid included the tricyclic chloride **26**-Cl and the hydrocarbon **24**-H in a ratio of approximately 1:1. The remainder of the product mixture was largely tri-*n*-butyltin chloride. Preparative TLC (silica gel with 3% THF/hexanes) gave two bands. Band 1 (R_f 0.39) was 33 mg of 6-chloro-2,3:8,9-dibenzobicyclo[3.2.2]nona-2,6,8-triene (**24**-H): mp 121–122 °C (lit.[23] mp 142–144.5 °C); ^{1}H NMR, as reported for **24**-H[2a]; mass spectrum, *m/e* 252 (M). Band 2 (R_f 0.22) was 60 mg of the tricyclic chloride **26**-Cl; mp 196–198 °C.

Treatment of 26-Cl with Tri-*n*-butyltin Deuteride. The tricyclic chloride **26**-Cl (117 mg, 0.40 mmol) was dissolved in 4.0 mL of benzene. Tri-*n*-butyltin deuteride (159 μL, 0.60 mmol) and 25 mg of AIBN were added. The solution was heated at reflux for 14 h. After the addition of 2.0 mL of chloroform, the reaction mixture was heated at reflux for 2 h. Evaporation of the solvent gave 327 mg of a light yellow oil. The oil consisted of **26**-Cl, **24**-D, **25**-D, and tri-*n*-butyltin chloride (^{1}H NMR analysis). The oil was dissolved in methylene chloride and placed on a preparative TLC plate (silica gel). Elution with 3% THF/hexanes gave two bands. Band 1 (R_f 0.35) was 56 mg of a 1:1 mixture of **24**-D and **25**-D: ^{1}H NMR ($CDCl_3$) δ 2.92 (0.5 H, m) 3.77 (0.5 H, dd, J = 1.8, 3.2 Hz), 4.26 (1 H, d, J = 7 Hz), 6.68 (1 H, dd, J = 1.8, 7 Hz), 6.8–7.5 (8 H, m). ^{2}H NMR spectroscopy confirmed that **24**-D and **25**-D were present in a ratio of 1:1. Band 2 (R_f 0.20) was 40 mg of **26**-Cl.

Reduction of 3,4-Dichloro-6,7:8,9-dibenzobicyclo[3.2.2]nona-2,6,8-triene (23-Cl) with Tributyltin Hydride. To a refluxing solution of 146 mg (0.5 mmol) of **23**-Cl[2a] in 250 mL of benzene was added dropwise, over a period of 2.5 h, a solution of 265 μL (1.00 mmol) of tributyltin hydride and 15 mg of AIBN in 50 mL of benzene. The reaction was carried out under nitrogen, and the solution was heated at reflux for 12 h. Hydride was destroyed by treatment for 1 h with 3 mL of carbon tetrachloride, after which the solvents were removed by distillation. The ^{1}H NMR spectrum of the residue had absorbances, in addition to the broad multiplet between δ 0.2 and 2 assignable to tri-*n*-butyltin chloride, identical with those[2a] for 3-chloro-6,7:8,9-dibenzobicyclo[3.2.2]nona-2,6,8-triene (**23**-H); absorbances[2a] assignable to the isomeric **24**-H were absent.

Reduction of 4,6-Dichloro-2,3:8,9-dibenzobicyclo[3.2.2]nona-2,6,8-trienes 24-Cl and 25-Cl with Tributyltin Hydride. To a refluxing solution of 146 mg (0.5 mmol) of a 1:1 mixture of **24**-Cl and **25**-Cl[1] in 350 mL of benzene was added dropwise, over a period of 2 h, a solution of 265 μL (1.0 mmol) of tributyltin hydride and 10 mg of AIBN in 50 mL of benzene. The solution was held at reflux under nitrogen for an additional 12 h, with three 10-mg portions of AIBN being added at 2 h intervals. After addition of 3 mL of carbon tetrachloride, the solvents were removed by distillation. ^{1}H NMR analysis of the product showed that both **23**-H and **24**-H[2a] were present. Expansion of the ethylenic proton peaks at δ 6.47 (for **23**-H) and δ 6.68 (for **24**-H) and integration by the cut and weigh procedure indicated that 46% of **23**-H and 54% of **24**-H were present.

Reduction of a Mixture of 23-Cl, 24-Cl, and 25-Cl with Insufficient Tributyltin Hydride. When the mixture (0.5 mmol) of **24**-Cl and **25**-Cl was treated with 0.05 mmol of tin hydride as above, equal amounts of the two dichlorides remained, and no absorbances assignable to **23**-Cl were observed in the ^{1}H NMR spectrum of the product mixture. This experiment suggested that the benzylic chlorides were not rearranging to the allylic chloride in the course of the reaction. As a further test of the possibility that the chlorides were interconverting but that **23**-Cl was so reactive that it did not accumulate, a mixture containing 50% **23**-Cl, 25% **24**-Cl, and 25% **25**-Cl was treated with half the equivalent amount of tributyltin hydride in the usual fashion. Integration of the ^{1}H NMR spectrum of the product showed that about 28% of the allylic chloride **23**-Cl had reacted and that 11% of the sum of **24**-Cl and **25**-Cl had reacted. Thus **23**-Cl was about 2.5–3 times as reactive as **24**-Cl or **25**-Cl. This reactivity difference is not great enough to account for the failure to see **23**-Cl in the reactions of **24**-Cl and **25**-Cl described above.

Table I. Effect of Tin Hydride Concentration on Ratio of Rearranged and Unrearranged Reduction Products. Calculation of Rate Constant Ratios

			fraction of product		
expt	reactant	[Bu_3SnH], M	rearranged	unrearranged	k_r/k_t,[a] M
1	**3**-Cl	0.129	0.70	0.30	0.30
2	**3**-Cl	0.200	0.66	0.34	0.39
3	**3**-Cl	0.821	0.36	0.64	0.46
4	**3**-Cl	1.280	0.28	0.72	0.50
					av 0.41
5	**30**-Cl	0.017	0.74	0.26	0.048
6	**30**-Cl	0.035	0.64	0.36	0.062
7	**30**-Cl	0.100	0.34	0.66	0.052
8	**30**-Cl	0.173	0.25	0.75	0.058
					av 0.055

[a] Ratio of the rate constant for rearrangement of the radical (**19** → **20** or **32** → **33**) to the rate constant of hydrogen transfer from tributyltin hydride to radical **19** or to **32**.

Preparation of *O*-(5,6:7,8-Dibenzobicyclo[2.2.2]octa-5,7-dien-2-yl) *S*-Methyl Xanthate (30-OCS_2CH_3). **30**-OCS_2CH_3 was prepared, by using the method described above for **7**-OH, from **30**-OH:[24] mp 116–117 °C; ^{1}H NMR δ 7.3 (m, 8, aromatic H), 5.9 (ddd, 1, H-7, $J_{7,1}$ = 3 Hz, $J_{7,8_{trans}}$ = 9 Hz, $J_{7,8_{cis}}$ = 3 Hz), 4.8 (d, 1, H-1, $J_{1,7}$ = 3 Hz), 4.4 (t, 1, H-4, $J_{4,8}$ = 3 Hz), 2.5 (ddd, 1, H-8_{trans}, $J_{8_{trans},8_{cis}}$ = 13 Hz, $J_{8_{trans},7}$ = 9 Hz, $J_{8_{trans},4}$ = 3 Hz), 2.3 (s, 3, CH_3), 1.7 (ddd, 1, H-8_{cis}, $J_{8_{cis}}$, $J_{8_{cis},8_{trans}}$ = 13 Hz, $J_{8_{cis},7}$ = 3 Hz, $J_{8_{cis},4}$ = 3 Hz). Anal. Calcd for $C_{18}H_{16}OS_2$: C, 69.20; H, 5.16. Found: C, 69.50; H, 5.42.

Reduction of 30-OCS_2CH_3 with Tributyltin Hydride. A solution of 84.4 mg (0.271 mmol) of **30**-OCS_2CH_3, 157 mg (0.540 mmol) of tributyltin hydride, and 25 mg (0.15 mmol) of AIBN in 13.6 mL of dry benzene was heated at reflux for 14.5 h. The reaction was then quenched with 10 mL of CCl_4. After removal of the solvents by distillation, the reaction mixture was analyzed by ^{1}H NMR spectroscopy and found to contain a 68:32 ratio of **30**-H to **31**-H.

Tri-*n*-butyltin Hydride Reduction of 3-Cl. Concentration Study. A solution of **3**-Cl (0.5 mmol) in enough benzene to make the appropriate concentration of tri-*n*-butyltin hydride (5 mmol) was heated at reflux and the hydride added all at once. The solutions were heated at reflux for 20 h, with AIBN added in 5-mg increments every 2 h for the first 6 h. The excess hydride was destroyed with 5 mL of carbon tetrachloride. The solvent was removed by distillation and the residue analyzed by ^{1}H NMR spectroscopy. The products contained **3**-H, **5**-H, and their dechloro analogues, as the excess hydride removed both the aliphatic and the aromatic chlorine atoms when the more concentrated hydride solutions were used. The region of the spectra between δ 5 and 7 was expanded, and the ratios of rearranged to unrearranged products were determined by the cut and weigh method of integration, using the absorbances at δ 5.8 and 6.2 for dechloro-**5**-H and those at δ 6.35 and 6.5 for dechloro-**3**-H.

The ratio of the rate constant for rearrangement, k_r, to that of hydrogen atom transfer, k_t, was computed from eq 4, which

$$k_r/k_t = [SnH]f_{BH}/f_{AH} \qquad (4)$$

may be readily derived and where f_{AH} and f_{BH} are the fractions of unrearranged and rearranged products, respectively, and [SnH] is the concentration of tin hydride. Data and results are given in Table I.

Tri-*n*-butyltin Hydride Reduction of 7-Chloro-2,3:5,6-dibenzobicyclo[2.2.2]octa-2,5-diene (30-Cl). Concentration Study. Solutions of 0.6 mmol of **30**-Cl[25] and a tenfold excess of

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(23) The melting point was incorrectly reported earlier[2a] and should have been 122–124 °C.

(24) Wawzonek, S.; Hallum, J. V. *J. Am. Chem. Soc.* **1953**, *18*, 288.

tributyltin hydride were made up in benzene to the concentrations reported in Table I and treated as described above for **3**-Cl. After the workup, ^{1}H NMR spectra in chloroform showed that the products were mixtures of **30**-H and **31**-H. The portion of each of the spectra between δ 3.5 and 4.5 was expanded, and ratios of **30**-H to **31**-H were determined by the cut and weigh method of integration. Data and results of computations of rate constant ratios are given in Table I.

Acknowledgment. We are indebted to the National Science Foundation for partial support of this research under Grants CHE-77-20854 and CHE-80-11933.

Registry No. **2**-H, 13351-27-4; **3**-Cl, 72182-74-2; **3**-H, 79134-73-9; dechloro-**3**-H, 7322-46-5; **5**-D, 79134-74-0; **5**-H, 79134-75-1; dechloro-**5**-H, 61836-97-3; **7**-OH, 72204-35-4; **7**-$\mathrm{OCS_2CH_3}$, 79134-76-2; **8**-OH, 72182-84-4; **8**-OMe, 79134-77-3; **8**-$\mathrm{OCS_2CH_3}$, 79199-35-2; **15**-OH, 64600-13-1; **15**-$\mathrm{OCS_2CH_3}$, 79134-78-4; **23**-Cl, 20852-67-9; **23**-H, 68661-36-9; **24**-Cl, 64600-09-5; **24**-D, 79134-79-5; **24**-H, 68661-37-0; **25**-Cl, 64626-00-2; **25**-D, 79199-36-3; **26**-Cl, 20851-78-9; **30**-Cl, 6476-45-5; **30**-H, 5675-64-9; **30**-OH, 1521-59-1; **30**-$\mathrm{OCS_2CH_3}$, 79134-80-8; **31**-H, 951-20-2; *exo*-4-deuterio-2,3-benzobicyclo[3.2.1]octa-2,6-diene, 79134-81-9.

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[25] Alder, K.; Rickert, H. F. *Justus Liebigs Ann. Chem.* **1939**, *543*, 1.

Notes

Approach to the Synthesis of Symmetrically Substituted Thianthrenes

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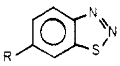
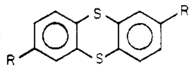
Received March 27, 1981

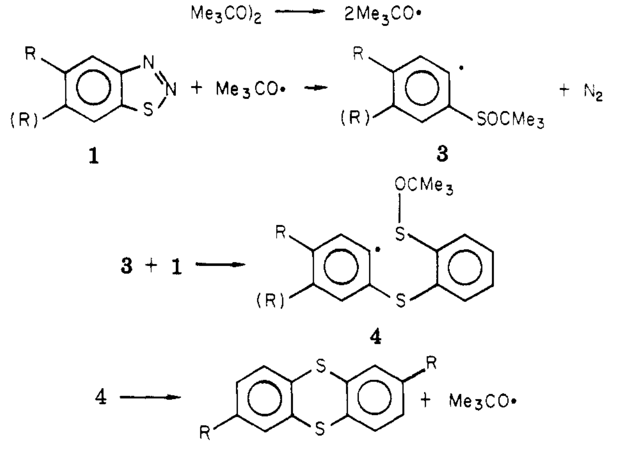
A number of thianthrene syntheses are available in the literature; thus, thianthrene can be obtained from reaction of benzene with sulfur monochloride,[1] from *o*-dichlorobenzene and $\mathrm{H_2S}$ at high temperature,[2] or by heating diphenyl disulfide in the presence of $\mathrm{AlCl_3}$.[3] As for substituted thianthrenes, apart from electrophilic substitution of the thianthrene nucleus,[1b] applicable only in few cases, their syntheses are accomplished by reaction of the appropriate bis(*o*-iodophenyl) disulfide with copper,[4] by thermal cyclization of substituted 2-mercaptophenyl phenyl sulfide,[5] and by aprotic diazotization of substituted 2-(phenylthio)phenyl 2-aminophenyl sulfide.[6]

The advantage of these methods derives from the possibility of obtaining asymmetrically substituted thianthrenes, but they suffer from the unavailability of starting materials. One of the oldest and most versatile reactions for synthesis of symmetrically substituted thianthrenes is the thermal elimination of nitrogen from 1,2,3-benzothiadiazole[7] at 200–220 °C, but, as we have recently reported,[8] this reaction leads to a complex mixture, from which thianthrene has to be separated by column chromatography and can be isolated only in ca. 20% yield.

Table I

R		mp, °C	yield, %	method
 **1**	 **2**			
H	H	157	65, 85	A
6-Cl	Cl	185–186	70	A
5-$\mathrm{CO_2Me}$	$\mathrm{CO_2Me}$	185–186	80	B
5-OMe	OMe	134–135	35	A
5-OMe	OMe	134–135	75	B

Scheme I



We now report a new method of synthesis of symmetrically substituted thianthrenes from the appropriate 1,2,3-benzothiadiazole (**1**). In this case nitrogen elimination from **1** is induced by *tert*-butoxy radicals at a relatively low temperature (80–110 °C), in agreement with the general behavior exhibited by **1** toward radical species.[9] The reaction is carried out by refluxing a benzene solution of **1** and di-*tert*-butyl peroxide for ca. 18 h (method A) or by refluxing a solution of **1** in di-*tert*-butyl peroxide for ca. 10 h (method B); thianthrene (**2**) is obtained as the only identified product in good yield (see Table I) and with a

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[1] (a) K. Fleischer and J. Stemmer, *Justus Liebigs Ann. Chem.*, **422**, 265 (1921). (b) See also D. S. Breslow and H. Skolnik in "The Chemistry of Heterocyclic Compounds, Multisulfur and Sulfur and Oxygen Five and Six-Membered Heterocycles", Wiley-Interscience, London, 1966, Part 2, p 1155. (c) H. E. Buckholtz and A. C. Bose, German Patent 2 739 217; *Chem. Abstr.* **89**, 43440 (1978). (d) "Organic Syntheses", Collect. Vol. II, Wiley, New York, 1943, p 242.

[2] M. G. Voronkov, E. N. Deryagine, L. G. Klochkova, G. M. Ivanova, and A. S. Nakhmanovic, USSR Patent 462 468, *Chem. Abstr.* **85** 33032 (1976).

[3] J. J. B. Deuss, *Recl. Trav. Chim. Pays-Bas*, **27**, 145 (1908); **28**, 136 (1909). See also footnote 1b.

[4] H. J. Berber and S. Smiles, *J. Chem. Soc.*, 1141 (1928).

[5] N. M. Collinane and C. G. Davies, *Rev. Cl. Trav. Chim. Pays-Bas* **55**, 881 (1936).

[6] L. Benati, P. C. Montevecchi, A. Tundo, and G. Zanardi, *J. Chem. Soc., Perkin Trans. 1* 1272 (1974).

[7] (a) P. Jacobson and E. Ney, *Chem. Ber.*, **22**, 904 (1889). (b) P. Jacobson and H. Janssen, *Justus Liebigs Ann. Chem.*, **277**, 218 (1893). (c) See also footnote 1b.

[8] L. Benati, P. C. Montevecchi, and G. Zanardi, *J. Org. Chem.*, **42**, 575 (1977).

[9] L. Benati, P. C. Montevecchi, A. Tundo, and G. Zanardi, *J. Chem. Soc., Perkin Trans. 1*, 1276 (1974); *J. Org. Chem.*, **41**, 1331 (1976).

0022-3263/81/1946-4998$01.25/0