Radical Chlorination of Tetracyclo[3.3.0.0^{2,7}.0^{4,6}]octane and Tetracyclo[3.3.0.0^{2,4}.0^{3,7}]octane with *tert*-Butyl Hypochlorite

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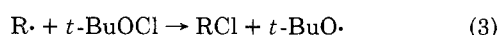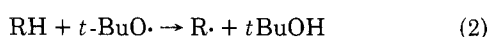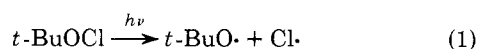*Department of Chemistry, Oregon State University, Corvallis, Oregon 97331*

Photochlorination of tetracyclo[3.3.0.0^{2,7}.0^{4,6}]octane (2) with *tert*-butyl hypochlorite in carbon tetrachloride results in C-3 methylene (58%) and C-1 bridgehead substitution (16%) leading to 3-chloro- and 1-chlorotetracyclo[3.3.0.0^{2,7}.0^{4,6}]octane, which are accompanied by three minor monochloride components. Radical chlorination of tetracyclo[3.3.0.0^{2,4}.0^{3,7}]octane (3) with *tert*-butyl hypochlorite proceeds via C-1 and C-6 hydrogen abstraction generating a mixture of monochlorides consisting of 1-chlorotetracyclo[3.3.0.0^{2,4}.0^{3,7}]octane (50%), *endo*-6-chlorotetracyclo[3.3.0.0^{2,4}.0^{3,7}]octane (28%), and an equimolar mixture of *exo*-6-chlorotetracyclo[3.3.0.0^{2,4}.0^{3,7}]octane and *exo*-8-chlorotetracyclo[3.3.0.0^{2,7}.0^{4,6}]octane (22%). The successful competition of bridgehead (in the [2.1.1] system) with cyclopropylcarbinyl abstraction in the case of tetracyclo[3.3.0.0^{2,7}.0^{4,6}]octane and bridgehead (in the [2.2.1] system) with trishomocyclopropenyl abstraction in the chlorination of tetracyclo[3.3.0.0^{2,4}.0^{3,7}]octane appear to be dependent upon the antiperiplanarity of the bridgehead C–H bond and a transannular cyclopropane C–C bond.

Earlier studies in this laboratory characterized the interesting carbene insertion pathways of bivalent intermediate **1** that lead to the formation of tetracyclo[3.3.0.0^{2,7}.0^{4,6}]octane (**2**) and tetracyclo[3.3.0.0^{2,4}.0^{3,7}]octane (**3**).[1] Subsequently, Coates and Yano[2] have synthesized the [3.3.0.0^{2,7}.0^{4,6}] system using a Wolff rearrangement of diazodeltacyclanone (**4**) and discovered that solvolysis of **5** in aqueous diglyme–NaBH$_4$ generates a mixture of the two tetracyclooctanes **2** and **3**. Recently, we have reported on an improved photochemical synthesis of tetracyclooctane **3**, which employs the [$_\pi 2_s + _\pi 2_s$] intramolecular valence isomerization of diene **6**.[3]
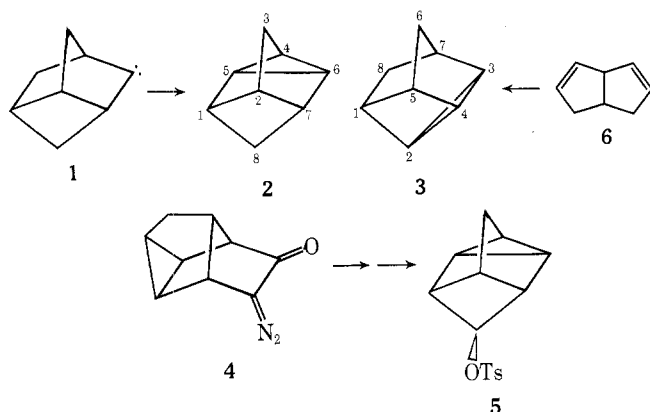

With several routes to tetracyclooctanes **2** and **3** available, we initiated a study of radical substitution of these interesting substrates with the goals of providing a useful method of introducing a functional group and exploring the nature of hydrogen abstraction and radical rearrangement in the [3.3.0.0^{2,7}.0^{4,6}] (**2**) and [3.3.0.0^{2,4}.0^{3,7}] (**3**) ring systems. Initial experiments using chlorine as the chain transfer agent, however, failed to give monochlorides, since the rate for substitution was at least 100 times less than the rate for electrophilic addition to the cyclopropane moiety in either ring system. As a consequence, we turned to the chlorinating agent *tert*-butyl hypochlorite, which provides a radical substitution route described by the initiation and propagation steps of eq 1–3,[4] since it does not add to three-membered rings.[5]

$$t\text{-BuOCl} \xrightarrow{h\nu} t\text{-BuO} \cdot + \text{Cl} \cdot \qquad (1)$$

$$\text{RH} + t\text{-BuO} \cdot \rightarrow \text{R} \cdot + t\text{BuOH} \qquad (2)$$

$$\text{R} \cdot + t\text{-BuOCl} \rightarrow \text{RCl} + t\text{-BuO} \cdot \qquad (3)$$

Photochlorination of tetracyclo[3.3.0.0^{2,7}.0^{4,6}]octane (**2**) with *tert*-butyl hypochlorite in carbon tetrachloride yielded two major and three minor monochlorides in a ratio of 7:16:3:58:8, as determined by vapor phase chromatographic analysis. Mass spectral analysis revealed parent ion masses corresponding to a molecular formula of C$_8$H$_9$Cl for the major monochlorides, and lack of olefinic absorptions in ir and NMR spectra indicated that both isomers were tetracyclic.

The 16% component contained no protons α to chlorine in the NMR, establishing it as a bridgehead chloride. Substitution at C-2 and C-4 was ruled out because there are two distinct geminal couplings of 6 and 12 Hz in the NMR spectrum of this component. Of the two remaining bridgehead positions, C-5 was excluded since the endo C-8 proton (identifiable because of its distinct 6-Hz geminal coupling in both this monochloride and in parent hydrocarbon **2**) appears 70 Hz downfield from its chemical shift position in parent hydrocarbon **2**; thus it seems reasonable to assign the 1-chloro structure **8** to this component.[6]

The most abundant product of the photochlorination of **2** was readily identified as 3-chlorotetracyclo[3.3.0.0^{2,7}.0^{4,6}]octane (**7**) by observation of a proton α to chlorine in the NMR spectrum of **7** at δ 4.05 in addition to at least three other unique protons. Substitution at C-8 would yield a structure containing only two unique protons other than the one α to chlorine.
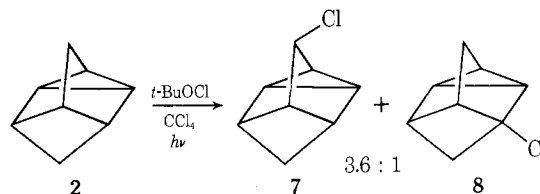

Verification of these two product structures was attempted by subjecting them to free-radical reduction by treatment with tri-*n*-butyltin hydride using azobisisobutyronitrile (AIBN) initiation. Although **8** gave no reduction, the major chloride **7** gave 3% of parent hydrocarbon **2** and 97% of a mixture of bicyclo[3.3.0]octadienes **13** and **14**. The latter two products may arise by either of the fragmentation reactions outlined in Scheme I.

Photochlorination of tetracyclo[3.3.0.0^{2,4}.0^{3,7}]octane (**3**) with *tert*-butyl hypochlorite in carbon tetrachloride yielded four monochlorides which appeared upon VPC analysis as three components in a ratio of 50:28:22. Ir and NMR spectral analyses in conjunction with mass spectral mea-

Scheme I
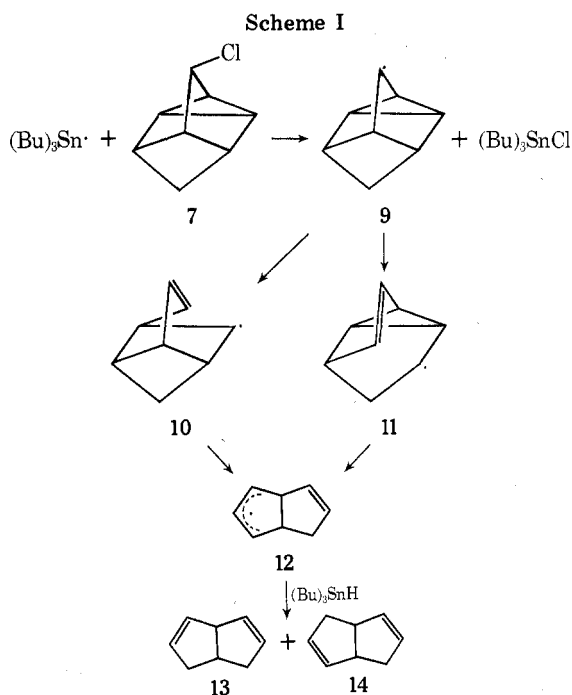
surements, which revealed parent ion masses of 140 and 142 (C_8H_9Cl), suggested that all components were tetracyclic.

Treatment of the 50% monochloride with tri-n-butyltin hydride (AIBN, 100°) yielded only parent hydrocarbon **3** in 10% yield. Lack of any protons α to chlorine and the presence of at least three magnetically nonequivalent protons in the NMR spectrum of this component identified it as a bridgehead chloride in the [3.3.0.0^{2,4}.0^{3,7}] system other than those derived by C-3 or C-7 substitution. Comparison of the NMR spectrum of this monochloride to that of parent hydrocarbon **3** reveals that the proton at C-3 is shifted downfield only 10 Hz in the chloride and has an unaltered splitting pattern, except for the loss of the C-1-H–C-3-H splitting of 0.9 Hz. These observations establish that the structure of this product is 1-chlorotetracyclo[3.3.0.0^{2,4}.-0^{3,7}]octane (**18**). The 28% product resulting from the photochlorination of **3** yielded parent hydrocarbon **3** (73%) and a mixture of bicyclooctadienes **13** and **14** (27%) upon reduction with tri-n-butyltin hydride (AIBN, 100°). Since the NMR spectrum of this chloride contains one proton α to chlorine (δ 3.47), the observed fragmentation must arise from radical **16** via a mechanism similar to that observed in the [3.3.0.0^{2,7}.0^{4,6}] ring system (Scheme II).

Scheme II
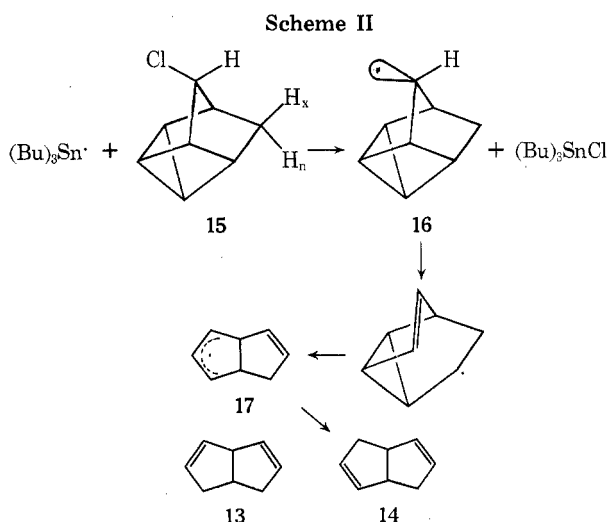
Elucidation of the stereochemistry of the chlorine atom in monochloride **15** was effected by observation of a 14 ± 4% nuclear Overhauser enhancement in the NMR signal of the exo C-8 proton (H_x) relative to the endo C-8 proton (H_n) as a result of irradiation of the proton α to chlorine.[8] Supporting this assignment is the observation of a singlet for the proton α to chlorine in the NMR spectrum of **15**. In the parent hydrocarbon, the exo C-6 and C-8 protons appear as singlets, whereas the endo C-6 and C-8 protons are coupled to the unique bridgehead proton by 2.3 Hz.[10]
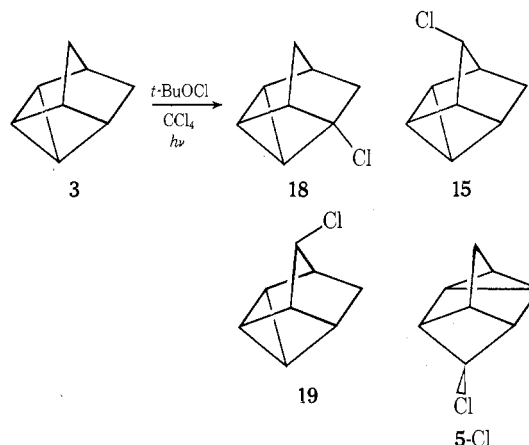

Vapor phase chromatographic and NMR analyses revealed that the 22% product from the photochlorination of **3** was actually a mixture of two isomers in approximately equal proportions. The presence of two protons α to chlorine (a singlet at δ 3.95 and a doublet with J = 2 Hz at δ 3.72) indicated that at least one of these isomers must be a rearrangement product, since in hydrocarbon **3** there are only two diastereotopic secondary positions and substitution at one of these led to chloride **15**. Reduction of the 22% chloride mixture with tri-n-butyltin hydride yielded hydrocarbon **2** (70%), hydrocarbon **3** (10%), and a mixture of dienes **13** and **14** (20%) when conducted at 60° with photoinitiation, whereas at 100° without irradiation, **3** was the major product (70%) with minor amounts of **2** (10%) and diene mixture **13** + **14** (20%) also observed. This interesting result suggests that both [3.3.0.0^{2,7}.0^{4,6}] and [3.3.0.0^{2,4}.0^{3,7}] ring systems are present in this mixture. Recalling the trishomocyclopropenyl relationship between hydrocarbons
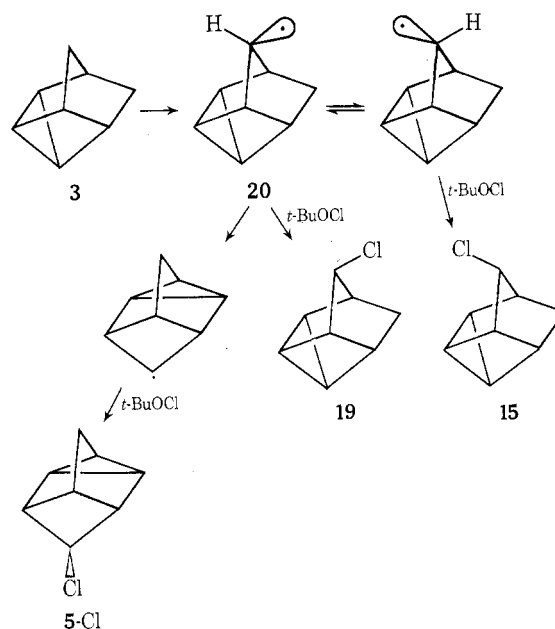
2 and **3**, a logical choice for the composition of this mixture would be *exo*-6-chlorotetracyclo[3.3.0.0^{2,4}.0^{3,7}]octane (**19**) and *exo*-8-chlorotetracyclo[3.3.0.0^{2,7}.0^{4,6}]octane (**5-Cl**), the latter having been formed by rearrangement of initially formed radical **20**, or by rearrangement after product formation, either in the reaction solution or during VPC collection. The tri-*n*-butyltin hydride reductions performed on the mixture of **19** and **5-Cl** suggest that indeed a radical–radical rearrangement is involved.

Discussion

The predominant feature of interest that emerges from a consideration of the results of radical chlorination of tetracyclooctanes **2** and **3** is the important role played by abstraction of hydrogen from bridgehead positions. Abstraction of hydrogen from C-1 in **2** represents abstraction from the bridgehead position of bicyclo[2.1.1]hexane, a previously unprecedented radical reaction pathway.[11] This process takes place in competition with abstraction from C-3, a cyclopropylcarbinyl position in which the transition state may approach the idealized bisected geometry for a cyclopropylcarbinyl radical[12] (i.e., **21**) and from C-8 (maximum 7%), a trishomocyclopropenyl position similar to that of the C-8 position in *endo*-tricyclo[3.2.1.0^{2,4}]octane where anchimeric assistance to *tert*-butoxy radical abstraction ≥100 ± 18 (40°) is observed.[13] Thus in C-8 abstraction a transition state similar in nature to **22** might be anticipated.

21   22
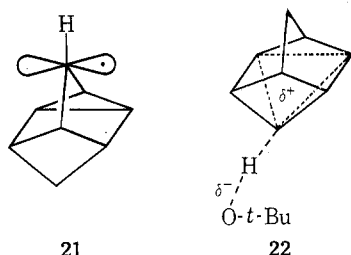
The major monochloride in radical chlorination of tetracyclooctane **3** results from *tert*-butoxy hydrogen abstraction at C-1 (equivalent to C-5), which represents bridgehead abstraction in a bicyclo[2.2.1]heptane system.[14] This reaction pathway is followed in close competition with abstraction at C-6, a trishomocyclopropenyl position, again analogous to C-8 abstraction in the *endo*-tricyclo[3.2.1.0^{2,4}]octane ring system.

The bridgehead abstractions observed for radical chlorination of tetracyclic **2** and **3** are similar to those we have uncovered in *tert*-butyl hypochlorite chlorination of *exo*-tricyclooctane **23** and *exo,exo*- and *exo,endo*-tetracyclononanes (**24** and **25**)[13] and serve to emphasize the importance of the fused cyclopropane rings in tetracyclic **2** and **3**, even though a bisected cyclopropylcarbinyl radical conformation in the transition state is not possible. Antiperiplanarity of

23   24   25
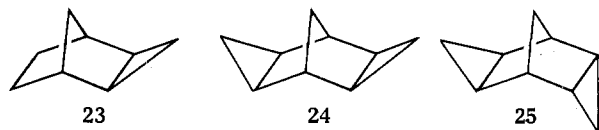
the C-5–C-6 transannular bond with C-1-H(C-7-H) in **2** and C-2-C-3 with C-1-H (C-4-C-3 with C-5-H) in **3** appear to be the important features in rate enhancement at these bridgehead positions. In both cases a consideration of models reveals that the divergence from antiperiplanar alignment is approximately 8°, using a value of 8.5° for the angle that the maximum electron density of the C–C bond of cyclopropane makes with the internuclear direction.[15] Dependence on antiperiplanarity is emphasized by the total lack of bridgehead substitution at C-7 in tetracyclic **3**,

in which case the C-7-H and transannular bond C-3–C-4 are much farther from antiperiplanar alignment (38°).

Experimental Section

Product ratios and percentage yields calculated from chromatographic data are based on relative peak areas and were corrected, when necessary, for differences in molecular weight by the method of Eastman.[16] Peak areas were determined by electronic integration using a Hewlett-Packard Model 3373-B integrator unless stated otherwise.

Reduction of Chlorides with Tri-*n*-butyltin Hydride. Chloride reductions reported were conducted in two ways.

Method A. Thermal Initiation. A mixture of alkyl halide, ca. 1.5 equiv of tri-*n*-butyltin hydride, a catalytic amount of azobisisobutyronitrile (AIBN), and cyclohexane was sealed under N$_2$ in a Pyrex ampule and heated to 100° in an oil bath. The resulting solutions were invariably colorless.

Method B. Photoinitiation. A mixture of required reactants was prepared as in the thermal initiation procedure above, and heated to 60° in an oil bath with irradiation from a 275-W sunlamp at a distance of about 8 in. for 5 h. The resulting solutions were consistently yellow, and were analyzed as individually reported. *tert*-Butyl hypochlorite was prepared by a standard procedure,[17] distilled, and either used at once or stored in the dark at −20° in sealed, degassed ampules. Tri-*n*-butyltin hydride was prepared and distilled by the method of Kuivila[18] and stored at 5° in the dark.

Chlorination of Tetracyclo[3.3.0.0^{2,7}.0^{4,6}]octane (2) with *tert*-Butyl Hypochlorite. A 4-*m* solution of 75.0 mg (0.71 mmol) of **2** and 90 μl (1 equiv) of *t*-BuOCl in CCl$_4$ was irradiated in a sealed Pyrex tube at 39.85 ± 0.15° (standardized) with a 275-W sunlamp at a distance of 8 in. for 1 h. To the resulting solution was added 10.0 mg (0.084 mmol) of cyclohexyl chloride as an internal reference, and the mixture was analyzed by VPC on columns A, B, and C. No less than six components in addition to the cyclohexyl chloride and unreacted hydrocarbon were observed in the ratio of 7:16:3:58:8:8 in an overall yield of 34%. Components eluting after these peaks, although numerous, amounted to no more than 5% in yield. The first five components had parent *m/e* 140 and 142, corresponding to tetracyclic monochlorides. The last peak has *m/e* 174, 176, and 178 as well as ions at *m/e* 139 and 141, which corresponded to parent tetracyclic dichloride and P − Cl masses.

The 7% component, in addition to exhibiting *m/e* peaks corresponding to C$_8$H$_9$Cl, had ir absorptions at ν 3085, 3001, 2879, 1447, 1342, 1269, 1194, 1090, 1050, 1083, and 1021 cm^{-1}. The 3% component also had a molecular weight corresponding to a molecular formula of C$_8$H$_9$Cl and had ir absorptions at ν 3103, 2031, 2959, 2880, 1338, 1264, 966, 944, and 700 cm^{-1}. These two components were not identified further.

The 16% component was identified as 1-chlorotetracyclo[3.3.0.0^{2,7}.0^{4,6}]octane (**8**) by the spectral analysis summarized below and detailed in the discussion: ir (CCl$_4$) ν 3078, 3001, 2966, 2890, 2863, 1445, 1318, 1268, 1194, 1160, 1090, 1066, 990, 944, 918, and 874 cm^{-1}; NMR (100 MHz, CCl$_4$) δ 2.40 (d, *J* = 6 Hz, 1H, exo C-8), 2.35–2.15 (m, 3 H, C-2, C-7, and endo C-8), 1.95–1.65 (m, 4 H,

C-4, C-5, C-6, and syn C-3), 1.52 (d, J = 12 Hz, 1 H, syn C-3).

Anal. Calcd for C_8H_9Cl: m/e 140.039. Found: m/e 140.039.

The major product was identified as 3-chlorotetracyclo[3.3.0.0^{2,7}.0^{4,6}]octane (7) by a combination of spectral and chemical evidence outlined below, in the following experiment, and in the discussion: ir (CCl$_4$) ν 3085, 2994, 2891, 1339, 1318, 1276, 1249, 1229, 1205, 1147, 1047, 1037, 982, 961, 939, 847, and 650 cm^{-1}; NMR (100 MHz, CCl$_4$) δ 4.05 (t, J = 1.6 Hz, 1 H, C-3), 2.75 (m, 1 H, C-2), 2.45 (m, 1 H, C-4), 2.15 (m, 1 H, C-7, anti to chlorine), 2.00 (m, 2 H, C-1, syn to chlorine, and exo C-8), 1.80 (m with a protruding doublet with coupling of 7 Hz, 3 H, C-5, C-6, and endo C-8).

Anal. Calcd for C_8H_9Cl: C, 68.34; H, 6.45. Found: C, 68.22; H, 6.62.

The 8% monochloride, in addition to a mass corresponding to a molecular formula C_8H_9Cl, had the following ir absorptions: ν 3085, 2983, 2959, 2873, 1617, 1450, 1320, 1287, 1267, 1219, 1195, 1039, 948, 912, 854, 847, 828, 706, 681, and 654 cm^{-1}.

Reduction of 3-Chlorotetracyclo[3.3.0.0^{2,7}.0^{4,6}]octane (7) by Tri-n-butyltin Hydride. Chloride 7 (8 mg) was reduced by method A using a 24-h reaction time. Subsequent dilution of the product mixture with pentane and analysis by VPC on column D revealed two volatile peaks in the ratio of 3:97, and no chloride. The minor product had a VPC retention time equal to that of parent hydrocarbon 2, but was not characterized further. The major product was identified as a 78:22 mixture of 2,7- and 2,6-cis-bicyclo[3.3.0]octadiene (13 and 14) by comparison of ir and NMR spectral data with those of authentic samples.[19]

Attempted Reduction of 1-Chlorotetracyclo[3.3.0.0^{2,7}.0^{4,6}]octane (8) by Tri-n-butyltin Hydride. Treatment of chloride 8 by method A for 5 days resulted in an essentially quantitative recovery of starting material and no hydrocarbon production as determined by VPC analysis.

Chlorination of Tetracyclo[3.3.0.0^{2,4}.0^{3,7}]octane (3) with tert-butyl Hypochlorite. A 4-m solution of 0.141 g (1.33 mmol) of hydrocarbon 3 and 159 μl (ca. 1 equiv) of t-BuOCl in CCl$_4$ was irradiated in a sealed Pyrex ampule at 39.85 ± 0.15° (standardized) with a 275-W sunlamp at a distance of 8 in. for 1 h. To the resulting solution was added 10.5 mg of cyclohexyl chloride as an internal reference and the mixture was analyzed by VPC on columns A, B, and C. Three peaks, each with parent peaks at m/e 140 and 142 corresponding to monochlorides, were observed in the ratio of 50:22:28 in an overall yield of 28%. The 22% component had a peak shape indicating that it was a mixture of two components. Dichlorides were not observed in greater than 10% overall yield.

The major component was identified as 1-chlorotetracyclo[3.3.0.0^{2,4}.0^{3,7}]octane (18) by a combination of spectral and chemical analysis described below, in the discussion section, and in the following tri-n-butyltin hydride reduction: ir (CCl$_4$) ν 3104, 3020, 2982, 2891, 1439, 1343, 1248, 1250, 1220, 1058, 1020, and 682 cm^{-1}; NMR (100 MHz, CCl$_4$) δ 2.73–2.43 (m, 4 H, C-2, C-4, C-5, and C-7), 2.02–1.83 (m, 1 H, C-3), 1.69 (d, J = 10 Hz, 1 H, exo C-8), 1.23 (d, J = 10 Hz, 1 H, exo C-6), 0.92 (d, J = 10 Hz, 2 H, endo C-6 and C-8).

Anal. Calcd for C_8H_9Cl: m/e 140.039. Found: m/e 140.040.

The 22% component, although a mixture, was treated as a single component, since preparative VPC separation proved unsuccessful. This peak was assigned as a mixture of endo-6-chlorotetracyclo[3.3.0.0^{2,4}.0^{3,7}]octane (19) (chloride B in the NMR assignments below) and exo-8-chlorotetracyclo[3.3.0.0^{2,7}.0^{4,6}]octane (5-Cl) (chloride A in the NMR assignments below) by a combination of spectral and chemical evidence outlined below, in the following reduction experiments, and in the discussion section: ir (CCl$_4$, collective) ν 3096, 3030, 2976, 2890, 1448, 1287, 1261, 973, 951, 911, 701, and 656 cm^{-1}; NMR (100 MHz, CCl$_4$) δ 3.95 (s, $W_{1/2}$ = 2 Hz, 1A H, endo C-8), 3.72 (d, J = 2 Hz, 1B H, exo C-6), 2.99 (broad m, $W_{1/2}$ = 8 Hz, 1B H, C-7), 2.58 (broad s, $W_{1/2}$ = 9 Hz, 2B H, C-1 and C-5), 2.53–2.38 (m, 2A H, C-1 and C-7, and 1B H, C-4), 2.20–2.05 (m, 1A H, C-2), 2.04–1.85 (m, protruding doublet, J = 9 Hz, 2B H, exo C-8 and C-2), 1.95–1.65 (m, 1A H, C-4, and 1B H, C-3), 1.52–1.40 (m, 4A H, C-3, C-5, and C-6), 1.37 (d, J = 9 Hz, 1B H, endo C-8).

Anal. Calcd for C_8H_9Cl: m/e 140.039. Found: m/e 140.036.

The 28% component was identified as exo-6-chlorotetracyclo[3.3.0.0^{2,4}.0^{3,7}]octane (15) by spectral analysis, a nuclear Overhauser experiment, and tri-n-butyltin hydride reduction described below and in the discussion: ir (CCl$_4$) ν 3104, 3058, 3010, 2915, 1444, 1297, 1279, 954, 688, and 652 cm^{-1}; NMR (100 MHz, CCl$_4$) δ 3.47 (s, $W_{1/2}$ = 5 Hz, 1 H, C-6), 2.58–2.45 (m, 1 H, C-7), 2.43–2.08 (m, 4 H, C-1, C-2, C-4, and C-5), 2.00–1.76 (m, 1 H, C-3), 1.28 (doublet of doublets, J = 10, ca. 2 Hz, 1 H, exo C-8), 1.04 (d, J = 10 Hz, 1 H, endo C-8).

Anal. Calcd for C_8H_9Cl: m/e 140.039. Found: m/e 140.040.

Reduction of 1-Chlorotetracyclo[3.3.0.0^{2,4}.0^{3,7}]octane (18) by Tri-n-butyltin Hydride. Using method A, 7.12 mg of chloride 18 was heated for 5 days. Dilution of the resulting solution with pentane followed by preparative VPC isolation, using column D, of the single volatile component, in addition to a large amount of unreacted chloride (estimated to be 90%), identified this product as parent hydrocarbon 3 by comparison of an ir spectrum and VPC retention time with those of an authentic sample.

Reduction of exo-6-Chlorotetracyclo[3.3.0.0^{2,4}.0^{3,7}]octane (15) by Tri-n-butyltin Hydride. Application of method A for 24 h gave approximately 80% conversion of 7.0 mg of chloride 15 to two volatile components in the ratio of 100:37 which were isolated by preparative VPC using column D. The ir spectrum of the major product was identical with that of an authentic sample of hydrocarbon 3. The minor product had an ir spectrum identical with that of 2,6-cis-bicyclo[3.3.0]octadiene (14). It was estimated that as much as 20% of the 2,7 isomer 13 could have been present.

Reduction of the Mixture of endo-6-Chlorotetracyclo[3.3.0.0^{2,4}.0^{3,7}]octane (19) and exo-8-Chlorotetracyclo[3.3.0.0^{2,7}.0^{4,6}]octane (5-Cl) by Tri-n-butyltin Hydride. Method A. Reduction of 6.0 mg of a mixture of chlorides 19 and 5-Cl for 5 days, followed by VPC analysis using column D, revealed three volatile peaks in the ratio of 10:70:20, having retention times equal to 2, 3, and 13 and/or 14, respectively. Preparative VPC followed by ir analysis confirmed the identity of the major product as hydrocarbon 3.

Method B. Reduction of 7.0 mg of a mixture of chlorides 19 and 5-Cl, followed by VPC analysis using column D, revealed three components in the ratio of 70:10:20 having retention times equal to 2, 3, and 13 and/or 14, respectively. Preparative VPC followed by ir analysis identified the 70% component as hydrocarbon 2, and the 20% component as 2,6-diene 14, which could have contained up to 30% of the 2,7 isomer 13.

References and Notes

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