Both groups attribute smooth curvature in log rate constant vs. log a_{H_2O} plots to variation in log (f_{SH^+}/f_{S^*}).
(31) Note that we are taking a *ratio* of activity coefficients and then the log of that ratio which greatly helps to even out nonlinear behavior.
(32) E. Högfeldt, *Acta Chem. Scand.*, **14**, 1597, 1627 (1960).
(33) F. A. Long and M. A. Paul, *Chem. Rev.*, **57**, 935 (1957).
(34) A parallelism between J_+ and J_0 was assumed, like that between H_+ and H_0 (e.g., ref 21, p 93), as there seems to be no measured J_+ scale.
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(36) W. M. Schubert and P. C. Myhre, *J. Am. Chem. Soc.*, **80**, 1755 (1958).
(37) E. Buncel, *Acc. Chem. Res.*, in press.

Radical Chlorination of *exo*- and *endo*-Tricyclo[3.2.1.$0^{2,4}$]octane and *exo,exo*- and *exo,endo*-Tetracyclo[3.3.1.$0^{2,4}$.$0^{6,8}$]nonane with *tert*-Butyl Hypochlorite[1]

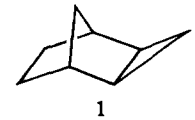
Peter K. Freeman,* Timothy D. Ziebarth, and R. S. Raghavan

Contribution from the Department of Chemistry, Oregon State University, Corvallis, Oregon 97331. *Received August 7, 1974*

Abstract: Irradiation of *exo*-tricyclo[3.2.1.$0^{2,4}$]octane and *tert*-butyl hypochlorite at 40° in CCl_4 generates a mixture of monochlorides which consists of *exo*-6-chloro-, *endo*-6-chloro-, and 1-chloro-*exo*-tricyclo[3.2.1.$0^{2,4}$]octane in a ratio of 67:12:17. In contrast, radical chlorination of *endo*-tricyclo[3.2.1.$0^{2,4}$]octane with *tert*-butyl hypochlorite results in a mixture of monochlorides consisting of *anti*-8-chloro-*endo*-tricyclo[3.2.1.$0^{2,4}$]octane, *endo*-2-chlorotricyclo[3.3.0.$0^{4,6}$]octane, and two incompletely characterized components in a 66:27:5:2 ratio. Analogous radical chlorination of *exo,exo*-tetracyclo[3.3.1.-$0^{2,4}$.$0^{6,8}$]nonane with *tert*-butyl hypochlorite yields 1-chloro- and 2-chlorotetracyclo[3.3.1.$0^{2,4}$.$0^{6,8}$]nonane in a ratio of 71:22, while photochlorination of *exo,endo*-tetracyclo[3.3.1.$0^{2,4}$.$0^{6,8}$]nonane with *tert*-butyl hypochlorite gives 1-chloro- and 6-chloro-*exo,endo*-tetracyclo[3.3.1.$0^{2,4}$.$0^{6,8}$]nonane and *endo*-9-chloro-*exo*-tetracyclo[4.3.0.$0^{2,4}$.$0^{5,7}$]nonane in a ratio of 44:35:21. Abstraction at C-8 in the *endo*-tricyclooctane and C-9 in the *exo,endo*-tetracyclononane system is suggested to be due to anchimeric assistance to hydrogen abstraction, and the stereoselectivity of the rearranged radicals in both cases is discussed in terms of transannular interaction of cyclopropane.

In recent years, there has been considerable interest in the characterization of radical intermediates which are structurally related to bridged carbonium ion intermediates, such as the 2-norbornyl,[2] 5- and 7-norbornenyl[2,3] and cholesteryl.[4] The reactions of these radical intermediates have, in all cases to date, been easily explained in terms of rearranging classical intermediates, rather than by invoking bridged delocalized intermediates.

Since in an earlier study we found that radical chlorination of bicyclo[3.1.0]hexane with *tert*-butyl hypochlorite results in substitution at C-2 and C-3, producing a ratio of *cis*-3- to *trans*-3-chlorobicyclo[3.1.0]hexane of 2:1,[5] in spite of the steric shielding of the cis face of the ring skeleton by the cyclopropane methylene, it appeared to be of considerable interest to carry out additional studies on 3-bicyclo[3.1.0]hexyl radical intermediates. A consideration of the anchimeric assistance found in the solvolyses of *exo*-5-norbornenyl (10^4),[6] *anti*-7-norbornenyl (10^{11}),[7] and *endo-anti*-tricyclo[3.2.1.$0^{2,4}$]oct-8-yl (10^{14})[8] substrates suggested that our investigation should focus attention on hydrogen abstraction from the *endo*-tricyclo[3.2.1.$0^{2,4}$]-octane ring system (**2**). On this basis, we have chosen to consider radical chlorination reactions of *exo*- and *endo*-tricyclo[3.2.1.$0^{2,4}$]octane (**1** and **2**) and *exo,exo*- and *exo,endo*-tetracyclo[3.3.1.$0^{2,4}$.$0^{6,8}$]nonane (**3** and **4**) with *tert*-butyl hypochlorite.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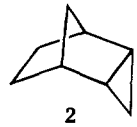
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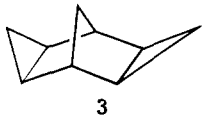
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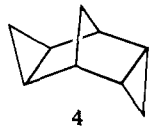
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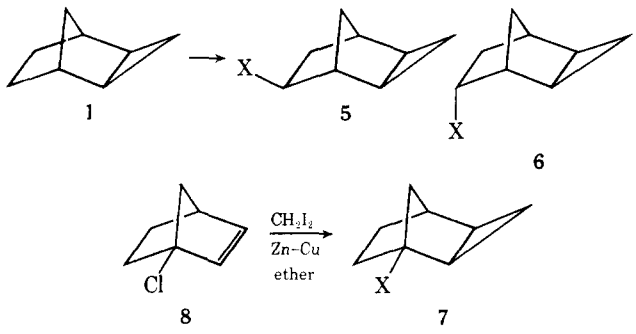
Results

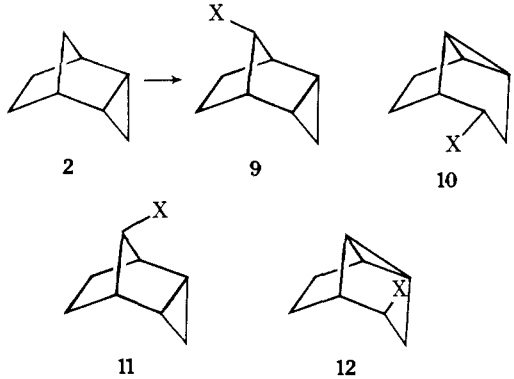
Irradiation of a 2:1 molar ratio of *exo*-tricyclo[3.2.1.$0^{2,4}$]octane and *tert*-butyl hypochlorite at 40° in CCl_4 produced a 27% yield of monochlorides, which consisted of *exo*-6-chloro- (**5**-Cl), *endo*-6-chloro- (**6**-Cl), and 1-chloro-*exo*-tricyclo[3.2.1.$0^{2,4}$]octane (**7**-Cl) in a ratio of 67:12:17 with an unidentified component present to an extent of 3%. No dichlorides were detectable by VPC. Structural identification was based upon the reduction of the product chlorides to a single hydrocarbon, parent structure **1**, with tributyltin hydride (AIBN initiation, 95°), spectral analysis of the three major product components, and independent syntheses. The infrared and NMR spectral data of the 67% component were identical with those of an authentic sample of **5**-Cl prepared by addition of hydrogen chloride to *exo*-tricyclo[3.2.1.$0^{2,4}$]octene-**6**. The NMR spectrum of the 12% component [τ 5.88 (doublet of triplets, J = 9, 3.5 Hz, 1 H), 7.55 (m, 1 H), 7.71 (m, 1 H), 7.95 (m, 1 H), 8.65 (m, 2 H), 8.85–9.4 (m, 3 H), 9.6 (m, 1 H), 9.95 (quartet, J = 7 Hz, 1 H)] is consistent with that expected for the endo-6 isomer (**6**-Cl), and NMR and infrared comparison with a standard prepared by treatment of **5**-OH with triphenylphosphine and CCl_4[9] verified this assignment. Since the NMR spectrum of the 17% component exhibits no absorption for hydrogen α to chlorine, only one bridgehead hydrogen at τ 7.84, and an unsubstituted fused cyclopropane (C_3H_4) unit [τ 8.94 (triplet of doublets, J = 7, 3 Hz, 1 H), 9.13 (triplet of doublets, J = 7, 3 Hz, 1 H), 9.37 (overlapping pair of triplets, J = 7, 3 Hz, 1 H), 9.87 (quartet, J = 7 Hz, 1 H)], the correct structure must be that of bridgehead chloride **7**-Cl. As a second check on the ring skeleton, reduction of an isolated sample of the 17% component with tributyltin hydride (AIBN initiation) produced tricyclooctane **1** as the sole hydrocarbon, reinforcing the structural assignment. An independent synthetic route to

7-Cl was developed using Simmons–Smith addition of methylene to 1-chloronorbornene (**8**), [10]which generated 7-Cl, identical with that formed in the radical chlorination, accompanied by iodide 7-I and ether 7-OEt.



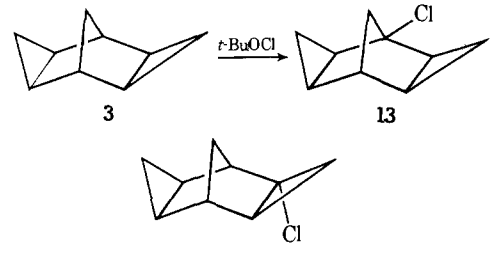
1 5 6 8 7

In the case of the *endo*-tricyclooctane ring system, irradiation of *endo*-tricyclooctane **2** and *tert*-butyl hypochlorite at 40° in CCl_4 produced a 33% yield of monochlorides, which consisted of four components in a ratio of 66:27:5:2, with no significant amount of dichlorides detectable by VPC. The infrared and NMR [τ 6.28 (m, 1 H), 7.60 (m, 2 H), 7.86–8.13 (m, 2 H), 8.19–8.42 (m, 2 H), 8.51–8.67 (m, 2 H), 9.17–9.37 (m, 2 H)] spectra of the 66% component were consistent with a structural assignment of *anti*-8-chloro-**9**-Cl. The rate of solvolysis in 80% aqueous acetone at 25° ($k = 6.10 \times 10^{-4}$ sec^{-1}; ratio of rate constants for **9**-Cl/ *anti*-7-norbornenyl chloride = 10^3)[11] as well as the solvolytic products (hydrolysis, **10**-OH exclusively; methanolysis in the presence of $CaCO_3$, **10**-OCH_3 exclusively) supports the assignment. The 27% component exhibited retention time and infrared and NMR spectra identical with those of an authentic sample of rearranged *endo*-**10**-Cl.[12] The 5% component (A) was not completely characterized, but analysis of the NMR spectrum [τ 6.05 (1 H, a doublet of triplets, J_s = 11, 4 Hz, with additional 1 Hz splitting), 7.48–7.82 (2 H), 7.90–8.14 (2 nonequiv H), 8.14–8.34 (1 H), 8.34–8.53 (1 H), 8.53–8.82 (2 H), 8.82 (1 H, doublet of triplets), 8.97–9.26 (1 H)] demonstrates that it is not the *syn*-7-chloro epimer **11**-Cl and most likely not the exo-rearranged chloride **12**-Cl [**12**-OH exhibits a simple doublet for hydrogen α to hydroxyl at τ 6.31 (J = 3.5 Hz)]. The 2% component (B) could not be obtained in sufficient quantity to be successfully identified.



2 9 10 11 12

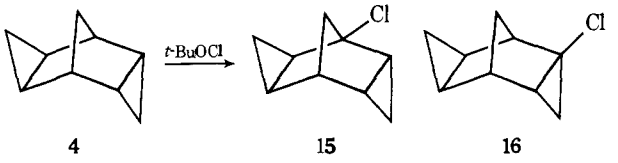
Photochlorination of a 4 *m* solution of *exo,exo*-tetracyclononane **3** with 1 equiv of *tert*-butyl hypochlorite in CCl_4 at 40° gave predominantly two monochlorides in a ratio of 71:22, in 9% yield, four additional components in the monochloride region accounting for a total of 7% of the known monochloride composition, and large amounts of acetone, 1,1-dimethyl-2-chloroethanol, and unreacted **3.** Dichlorides accounted for no more than 10% of the volatile products of the reaction. The ratio of the two major products was unchanged upon dilution of the chain transfer reagent and upon reduction of the initial *tert*-butyl hypochlorite:**3** concentration ratio. Both the major products gave solely hydrocarbon **3** in separate reactions with tributyltin hydride (AIBN initiation, 100°). The 71% component was inert when treated with alcoholic silver nitrate at 80° for 2 days. Lack of downfield protons in the NMR spectra of both major products suggests that they are tertiary chlorides [100-MHz NMR, 71% component: τ 7.81 (s, $w_{1/2}$ = 5 Hz, 1 H), 8.50–8.80 (m, 4 H), 8.93 (doublet of triplets, J = 3.5, 7 Hz, 2 H), 9.14 (s, $w_{1/2}$ = 4 Hz, 2 H), and 9.60 (doublet of triplets, J = 7 Hz, 2 H); 22% component: τ 7.56 (s, $w_{1/2}$ = 5.5 Hz, 1 H), 7.73 (s, $w_{1/2}$ = 5.5 Hz, 1 H), 8.38 (m, 1 H), 8.50–9.15 (complex m, 4 H), 9.24 (doublet of triplets, J = 3.5, 7 Hz, 1 H), 9.48 (s, $w_{1/2}$ = 5 Hz, 2 H), and 9.66 (doublet of triplets, J = 7, 7 Hz, 1 H)]. Since there are only two unique tertiary positions in **3,** the 71 and 22% products are readily assigned structures **13** and **14** corresponding to C-1 and C-2 substituted **3,** respectively, based on the observation of at least five unique protons in the NMR spectrum of the 22% component.



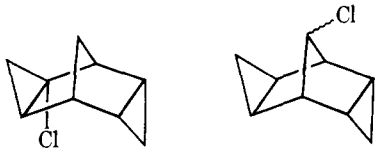
3 13 14

Reaction of 1 equiv of **4** with a 4 *m* solution of *tert*-butyl hypochlorite in CCl_4 at 40° with photoinitiation gave three major monochlorides in a ratio of 35:21:44, in 27% yield, two unidentified monochlorides in 3% yield, and large amounts of acetone, 1,1-dimethyl-2-chloroethanol, and unreacted **4**. Heavier components eluting with longer VPC retention times were found to be dichlorides by mass spectral analysis but were not formed in greater than 6% yield. Both the 35 and the 44% monochlorides gave exclusively **4** upon reduction with tributyltin hydride (AIBN, photoinitiation, 60°) and had NMR spectra lacking absorptions characteristic of protons α to chlorine [100-MHz NMR, 35% component: τ 7.55 (broad s, 1 H), 7.60–7.80 (m, 1 H), 7.80–8.05 (m, 1 H), 8.20–8.90 (m, 4 H), 8.90–9.60 (m, 3 H), and 9.81 (doublet of triplets, J = 7, 7 Hz, 1 H); 44% component: τ 7.82 (broad m, 1 H), 8.02–8.70 (m, with protruding doublet of J = 7 Hz, 5 H), 8.90–9.15 (m, 1 H), 9.15–9.45 (m, 7 Hz coupling evident, 3 H), and 9.80 (doublet of triplets, J = 7, 7 Hz, 1 H)]. These observations suggest that these two monochlorides are tertiary chlorides in the exo,endo-[3.3.1.$0^{2,4}$.$0^{6,8}$] system. Of the three unique tertiary positions in **4,** only substitution of either type of cyclopropyl methine hydrogen would leave two bridgehead protons at C-1 and C-5, as observed in the NMR spectrum of the 35% component. This product must therefore be **16** rather than **17** since the four-line pattern at τ 9.81, characteristic of the fused *exo*-cyclopropane moiety in the *exo*-tricyclo[3.2.1.$0^{2,4}$]octane system,[8c,13,14] is still present. The 44% component also has the *exo*-cyclopropane moiety intact but has only one absorption in its NMR spectrum characteristic of a norbornyl bridgehead proton, thus indicating its structure to be **15.** The 21% product, although a C_9H_{11} monochloride lacking olefinic absorptions in ir and NMR spectra [100-MHz NMR τ 5.95 (doublet of triplets, J = 4, 8.5 Hz, 1 H), 7.36 (doublet of doublets, J = 4.5, 4.5 Hz, 1 H), 7.53–7.60 (m, 2 H), 8.20–8.50 (m, 3 H), 8.55–8.95 (m, 2 H), 9.55 (doublet of triplets, J = 4, 7 Hz, 1 H), and 9.92

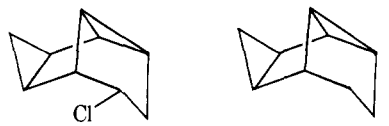
(doublet of triplets, J = 4, 7 Hz, 1 H)], did not contain the exo,exo- or the exo,endo-[3.3.1.$0^{2,4}$.$0^{6,8}$] skeleton, as evidenced by formation of a hydrocarbon other than **3** or **4** upon tributyltin hydride reduction (AIBN, photoinitiation, 60°). The NMR spectrum of this hydrocarbon [100-MHz NMR τ 7.26 (triplet, J = 4 Hz, 1 H), 8.74 (doublet of triplets, J = 3.5, 6 Hz, 1 H), 9.23 (m, 1 H), 9.52 (doublet of triplets, J = 3.5, 7 Hz, 1 H), 9.85 (quartet, J = 3.5 Hz, 1 H), and 7.70–8.95 (m, 7 H)] is consistent with proposed structure **20,** as is the spectrum of the 21% monochloride with structure **19,** by comparison of these two spectra with the spectra of known related compounds **10**-Cl and **10**-H, prepared by tributyltin hydride reduction of **10**-Cl.



4 15 16



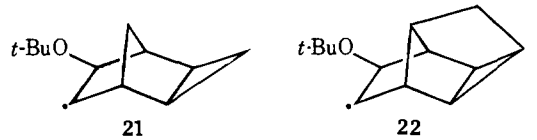
17 18



19 20

Discussion

In viewing the hydrogen abstraction reactions of **1,** the predominant abstraction at C-6 leads to a mixture of epimers with an exo:endo ratio (5.6) rather similar to that observed for the reaction of the 2-norbornyl radical with *tert*-butyl hypochlorite (7).[15] The normal exo:endo C-6 ratio and lack of skeletal rearrangement argue against any delocalization involving either the C-2–C-4[16] or C-2–C-3[17] cyclopropane bonds in the intermediate radical. This result is in complete harmony with the lack of participation found for cyclopropane in the analogous *tert*-butoxy-substituted radicals **21** and **22** which undergo chain transfer with *tert*-butyl hypochlorite to give mixtures of *cis*-di-*exo*- and *trans*-*tert*-butoxy chlorides.[18] The bridgehead abstraction leading to **7** was initially a surprise in view of the previously reported lack of reactivity at this position in radical halogenations of norbornane[19–21] and norbornene[22,23] but is in harmony with the reactivity patterns of **3** and **4** (vide infra).



21 22

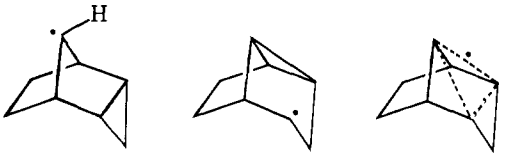
In sharp contrast to the radical substitution pattern found for *exo*-tricyclooctane **1,** attack of *tert*-butoxy radical on *endo*-tricyclooctane **2** occurs to an extent of 93% or greater at bridge position C-8. Since neither *anti*-8-chloride **9**-Cl nor rearranged **10**-Cl undergoes epimerization or skeletal rearrangement during the reaction conditions or VPC analysis, it seems reasonable to assume that *endo*-**10**-Cl is a primary product, and the question arises as to whether the products are generated via a rapid equilibrium of radicals (**23** ⇌ **24**) or a single delocalized radical **25.** The dilution experiments listed in Table I demonstrate that, at high concentrations of chain transfer agent the first formed radical

Table I. The Reaction of *tert*-Butyl Hypochlorite with 2 in CCl_4 at 40°

Run	Concn of 5, m	Concn of *t*-BuOCl, m	Product composition, % 9-Cl[a]	10-Cl[a]	A[a]	B[a]
1	1.56	0.68	66	27	5	2
2	1.56	0.49	63	28	6	3
3	1.56	0.26	32	41	11	16
4	0.73	0.18	11	56	15	18

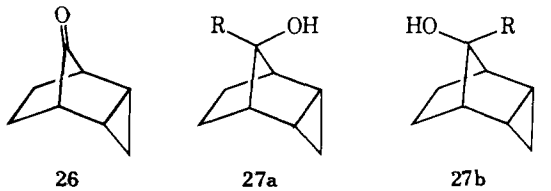
[a] Possible error is ±3%.

intermediate is trapped before there is much rearrangement to the second radical intermediate, while at low concentrations of *tert*-butyl hypochlorite, the reverse is the case. Thus, on this basis, an equilibrium (**23** ⇌ **24**) is favored over **25.** However, in addition, one must explain the regiospecificity for C-8 abstraction and the stereoselectivity of radicals leading to C-8 unrearranged (anti:syn ≥ 66/2) and C-2 rearranged (endo:exo ≥ 27/2) products (run 1). The



23 24 25

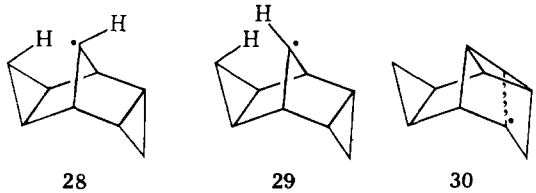
high preference for C-8 abstraction may reasonably be ascribed to abstraction of the anti C-8 hydrogen with the generation of a transition state in which the electronegative *tert*-butyl radical induces some carbonium ion character on the tricyclooctyl moiety.[24] Thus, the evidence suggests trishomocyclopropenyl anchimeric assistance to hydrogen abstraction in the transition state. Such assistance is, in fact, borne out in competition experiments of *endo*-tricyclooctane **2** and norbornane which reveal that the relative rates of hydrogen abstraction in *tert*-butyl hypochlorite chlorination give a rate ratio of **2** at C-8 to norbornane at C-7 ≥ 100 ± 18 at 40°, assuming all the C-8 abstraction on tricyclooctane **2** is anti. Once the anti C-8 hydrogen is removed, a localized pyramidal radical similar in structure to **23** might be formed.[25] Some interaction of the transannular cyclopropane bond is possible but not necessary for the simplest rationalization since a combination of competition of chain transfer with inversion and greater steric access to the anti side might explain the stereoselectivity. This view is reinforced by the facts that $LiAlH_4$ reduction of *endo*-tricyclo[3.2.1.$0^{2,4}$]octan-8-one (**26**) gives **11**-OH:**9**-OH in a ratio of 67:33,[8] addition of anisylmagnesium bromide to **26** leads to a 51:5.4 ratio of **27a** (R = anisyl):**27b** (R = anisyl),[26a] and the addition of methyllithium to **26** results in formation of syn alcohol **27a** (R = CH_3) as the sole product.[26b] However, steric access to the C-2 position of radical **24** would be expected to be highly biased toward exo approach ($LiAlH_4$ reduction of the related ketone, tricyclo[3.3.0.$0^{4,6}$]octan-2-one, yields entirely endo 2-alcohol).[8c] Thus, the evidence suggests that radical **23** rearranges to a second intermediate, which possesses some degree of transannular interaction of the cyclopropane bond with the radical center, hence protecting the exo face from attack.



26 27a 27b

The generality of the interesting facets of radical abstraction reactions revealed in the *tert*-butyl hypochlorite chlorination of *exo*- and *endo*-tricyclooctanes **1** and **2** is emphasized in the outcome of the radical substitution reactions of *exo,exo*- and *exo,endo*-tetracyclononanes **3** and **4.** The results of *tert*-butyl hypochlorite chlorination of *exo,exo*-**3** reveal that norbornyl bridgehead abstraction is not an isolated peculiarity of *exo*-tricyclooctane **2** but may, in favorable cases, represent the major reaction pathway.[27] The predominant abstraction from the C-1 bridgehead position of tetracyclic **3** and lack of C-9 substitution suggest enhanced reactivity in **3** at C-1 bridgehead relative to C-1 norbornane toward hydrogen abstraction by *tert*-butoxy radical.[28] An inspection of models does suggest that the O···H···C_9 elements of the abstraction transition state may be distorted from colinearity;[29] however, the relative rates of abstraction at C-9 and C-8 for *exo,endo*-tetracyclic **4** and *endo*-tricyclic **2** reveal that any deviation from colinearity does not significantly affect the rate (vide infra). The formation of endo chloride **14** represents an interesting demonstration that radical abstraction reactions may take place on the endo face of norbornane in this instance,[30] in spite of the resistance of cyclopropyl hydrogens to free-radical abstraction.[31]

The behavior of the *exo,endo*-tetracyclononane system (**4**) toward hydrogen abstraction reinforces the results with the simpler *endo*-tricyclooctane ring system since a trishomocyclopropenyl radical rearrangement has occurred in both. Failure to observe formation of a chloride resulting from chain transfer at a radical center at C-9 is not surprising since the *exo*-cyclopropane would mitigate to a greater degree against chain transfer with intermediate **28** than against hydrogen abstraction from the C-9 position of exo,endo tetracyclic **4** and would, in addition, hinder inversion of the pyramidal radical to **29.**[32] Thus, hydrogen abstraction at C-9 results in product chloride arising solely from rearranged radical represented by **30.** The stereochemical consequences of this trishomocyclopropenyl rearrangement are nicely analogous to those observed for *endo*-tricyclooctane with chain transfer occurring from endo side, the side opposite to that expected for a classical radical, and thus suggest some degree of trishomocyclopropenyl delocalization for radical **30.** Anchimeric assistance to abstraction at C-9 was anticipated and is reflected in relative rate studies of *tert*-butyl hypochlorite chlorination of *exo,endo*-tetracyclononane **4** and norbornane, which reveal a rate ratio of **4** at C-9 to norbornane at C-7 = 75 ± 14. Thus the steric shielding of abstraction of the C-9 hydrogen, anti to the *endo*-cyclopropane ring, by the syn C-3 hydrogen is not very significant.



28 29 30

Observation of C-1 substitution in radical chlorination of **4** is consistent with the norbornyl bridgehead substitution uncovered for *exo*-tricyclooctane **1** and *exo,exo*-tetracyclononane **3** and apparently is due to the presence of the fused cyclopropane rings. Although the developing cyclopropylcarbinyl radicals in the case of C-1 abstraction from *exo*-tricyclooctane **1** and *exo,exo*- and *exo,endo*-tetracyclononanes **3** and **4** are restricted to nonbisected geometries,[33] anti periplanarity of the C-1–H bond with respect to the $[0^{2,4}]$ or $[0^{6,8}]$ bridges in **1, 3,** and **4** may permit electron delocalization from these strained C–C bonds.

Experimental Section

All melting points were determined using a Büchi melting point apparatus and are corrected. All boiling points are uncorrected. Infrared spectra were recorded on a Beckman Model IR-8 infrared spectrophotometer. NMR spectra were recorded on a Varian Associates A-60 or HA-100 NMR spectrometer. Routine mass spectra were obtained using an Atlas CH7 mass spectrometer, while high resolution mass spectra were determined by the Department of Chemistry, University of Oregon, Eugene, Ore., 97403, on a CEC 110B instrument. Elemental analyses were performed by Alfred Bernhardt, Mikroanalytisches Laboratorium, 5251 Elbach über Engelskirchen, West Germany, or Dornis U. Kolbe, 433 Mulheim a.d. Ruhr, West Germany. VPC analyses were carried out using an F & M Model 700 chromatograph equipped with dual columns and thermal conductivity detectors or a Varian Aerograph Series 1200 chromatograph equipped with a flame ionization detector. Injector and detector ports were generally operated at 200°, except when analyzing and collecting alkyl halides, when the temperature was reduced to 120° and the injector port lined with Pyrex glass tubing. The following columns were employed:

(A) 29 ft × 0.25 in. aluminum containing 13% TCEP on 30–60 Chromosorb P(AW).

(B) 18 ft × 0.25 in. aluminum containing 15% QF-1 on Anakrom 70–80 ABS.

(C) 12 ft × 0.25 in. aluminum containing 13% TCEP on Chromosorb 30–60 P(AW).

(D) 8 ft × 0.25 in. 15% Carbowax 20M plus 2% XF-1112 on 30–60 Chromosorb P(AW).

(E) 32 ft × 0.25 in. aluminum containing 20% Carbowax 20M plus 2% XF-1150 on Anakrom 70–80 ABS.

(F) 18 ft × 0.125 in. stainless steel containing 10% UCW-98 (methyl vinyl) on 80–100 Diatoport S.

(G) 28 ft × 0.25 in. aluminum containing 9% FFAP on Anakrom 70–80 ABS.

(H) 17 ft × 0.25 in. 10% TCEP on 70–80 Anakrom ABS.

(I) 20 ft × ⅛ in. 13% TCEP on 30–60 Chromosorb P(AW).

Photochlorination of *exo*-Tricyclo[3.2.1.$0^{2,4}$]octane with *tert*-Butyl Hypochlorite. To a solution of 10.6 g (0.0931 mol) of the exo hydrocarbon[34] in 20 ml of reagent grade carbon tetrachloride in a 50-ml flask, provided with a magnetic stirrer and a reflux condenser, was added 5.05 g (0.0465 mol) of *tert*-butyl hypochlorite and the flask placed in a 40 ± 2° oil bath. The solution was irradiated with a 300-W Sylvania light bulb for 20 min from a distance of 1 in. The solution was stirred for an additional 5 min after discontinuance of irradiation. The solution, which was yellow to start with, was now colorless because of the color of the *tert*-butyl hypochlorite having been discharged. After partial removal of solvent by distillation, the products were analyzed by VPC (column A, 135°, 75 ml/min) and found to be composed of four monochlorides in the ratio 4:17:67:12 in the order of increasing retention times in a total yield of 27%. No dichlorides were detectable by VPC. The 4% component was too small to permit its isolation and characterization. The other three components were isolated by VPC collection, and each was found to show only one peak on reinjection, thus indicating stability to interconversion on the column under conditions of analysis.

The 67% component was identified as *exo*-6-chloro-*exo*-tricyclo[3.2.1.$0^{2,4}$]octane on the basis of spectral comparison with the data of an authentic sample synthesized by two independent methods: ir (neat) 3080 (w), 3020 (m) (both assignable to cyclopropyl C–H stretching), 750 (m), and 733 (s) (both attributable to C–Cl stretching); NMR (100 MHz, CCl_4) τ 6.45 (an apparent triplet of a doublet, J = 6.5, 2.2 Hz, 1 H, the α-chloro proton), 7.6 (envelope, 1 H, the bridgehead proton), 8.05 (a doublet of a doublet of a doublet, J = 13, 7, 2.5 Hz, 1 H, the endo-C-7 proton), 8.8 (doublet, J = 10.5 Hz, 1 H, the anti-C-8 proton), 9.1 (multiplet of a doublet, J = 10.5 Hz, 1 H, the syn-C-8 proton), 9.45 (complex multiplet, 3 H the cyclopropyl protons on C-2, C-4, and the syn-C-3 proton), and 9.9 (multiplet, 1 H, the anti-C-3 proton); mass spectrum *m/e* parent peaks at 142 and 144.

Anal. Calcd for $C_8H_{11}Cl$: C, 67.38; H, 7.78. Found: C, 67.36; H, 7.89.

The 12% component was assigned the structure *endo*-6-chloro-*exo*-tricyclo[3.2.1.$0^{2,4}$]octane on the basis of its spectral data. This assignment was confirmed by an independent synthesis of this

compound: ir (neat) 3105 (w), 3040 (m) (both assignable to cyclopropyl C–H stretching), 1034 (m) (cyclopropane ring deformation), 757 (s), and 732 (m) (both assignable to C–Cl stretching); NMR (100 MHz, CCl_4) τ 5.88 (an apparent triplet of a doublet, J = 9, 3.5, 3.5 Hz, 1 H, the α chloro proton), 7.55 (unresolved multiplet, 1 H, the bridgehead proton β to chlorine), 7.71 (envelope, 1 H, the remaining bridgehead proton), 7.95 (multiplet, 1 H, the endo-C-7 proton), 8.53–8.8 (multiplet, 2 H, the exo-C-7 proton and the cyclopropyl proton on C-4), 8.85–9.4 (multiplets, 3 H, the cyclopropyl proton on C-2 and the C-8 protons), 9.6 (an overlapping pair of triplets, J = 3 Hz, 1 H, the syn-C-3 proton), and 9.94 (quartet, J = 7 Hz, 1 H, the anti-C-3 proton); mass spectrum *m/e* parent peaks at 142 and 144.

Anal. Calcd for $C_8H_{11}Cl$: C, 67.38; H, 7.78. Found: C, 67.19; H, 7.78.

The 17% component was identified as 1-chloro-*exo*-tricyclo[3.2.1.$0^{2,4}$]octane on the basis of its spectral data and an independent synthesis: ir (neat) 3100 (w), 3030 (w) (cyclopropyl C–H stretching), 1035 (w), 1000 (s) (cyclopropane ring deformation), and 733 (s) (C–Cl); NMR (100 MHz, CCl_4) τ 7.84 (unresolved multiplet, 1 H, the bridgehead proton), 8.1–8.60 (complex overlapping multiplets, 4 H, the exo- and the endo protons on C-6 and C-7), 8.67 (doublet J = 11 Hz, 1 H, the anti-C-8 proton), 8.89 (doublet, J = 11 Hz, 1 H, the syn-C-8 proton), 8.90–9.24 (complex multiplets, 2 H, the C-2 and C-4 protons), 9.37 (a five-peak signal with a spacing of 3 Hz between each pair of peaks, 1 H, the syn-C-3 proton), and 9.87 (a four-peak signal with a spacing of 7 Hz between each pair of peaks, 1 H, the anti-C-3 proton); mass spectrum *m/e* parent peak at 142 and 144.

Anal. Calcd for $C_8H_{11}Cl$: C, 67.38; H, 7.78. Found: C, 67.20; H, 7.90.

Test for Stability of *exo*-6-Chloro-*exo*-tricyclo[3.2.1.$0^{2,4}$]octane to the Photochlorination Conditions. A pure sample of the title chloride (0.0385 g, 0.271 mmol) was dissolved in *tert*-butyl alcohol (0.117 g, 1.58 mmol), acetone (40 μl.), and carbon tetrachloride (50 μl.) and irradiated at 40° for 20 min. Analysis by VPC (column B, 140°, 60 ml/min) and ir revealed that the starting chloride had not suffered any detectable change.

Addition of Hydrogen Chloride to *exo*-Tricyclo[3.2.1.$0^{2,4}$]oct-6-ene. Hydrogen chloride gas was passed in a slow, steady stream through a solution of the exo olefin (1.49 g, 0.014 mol) in 6 ml of methylene chloride for 20 min. After removal of the solvent by rotary evaporation at room temperature, the products were analyzed by VPC (column C, 115–120°, 60 ml/min). Monochlorides accounting for 54% of the mixture were found to be present in a yield of 33%. The monochloride fraction consisted of two components in the ratio 48:52. The 52% component was the expected *exo*-6-chloro-*exo*-tricyclo[3.2.1.$0^{2,4}$]octane and was identical with the 67% component of the photochlorination of tricyclooctane **1** as observed by comparison of ir and NMR spectra. The 48% component was an olefinic chloride and was not completely characterized.

Reaction of *exo*-6-Hydroxy-*exo*-tricyclo[3.2.1.$0^{2,4}$]octane with Triphenylphosphine and Carbon Tetrachloride. The alcohol (0.0920 g, 0.74 mmol) was stirred with triphenylphosphine (0.273 g, 1.04 mmol) and carbon tetrachloride (3 ml) in a tightly stoppered flask for 24 hr. After removal of solvent and any volatile materials at reduced pressure (2 mm), the phosphorane ester was pyrolyzed at 90–130° (2.0 mm) and the pyrolysate collected in a receiver cooled by a bath of Dry Ice. Analysis of the pyrolysate (0.033 g) by VPC (column A, 150°, 60 ml/min) showed that the products were composed of four components in the ratio 3:15:64:18 in a yield of 31%. The 3% component was too small to permit its collection and identification.

The 64 and 18% components were the expected exo- and endo-6-chlorides and were identical respectively with the 67 and 12% components of the photochlorination products of *exo*-tricyclo[3.2.1.$0^{2,4}$]octane. The 15% component was identified as nortricyclylmethyl chloride on the basis of its spectral data: mass spectrum *m/e* parent peaks at 142 and 144; ir (neat) 3080 (s) (cyclopropyl C–H stretching), 800 (s) (nortricyclene ring), and 730 (s) (C–Cl stretching); NMR (100 MHz, CCl_4) τ 6.74 (complex multiplet, 2 H, the α-chloro protons), 8.05 (unresolved multiplet, 1 H, the bridgehead proton on the carbon γ to chlorine), 8.18 (complex multiplet, 1 H, the β-chloro proton), and 8.5–9.5 (complex multiplets, 7 H, the remaining protons).

Anal. Calcd for $C_8H_{11}Cl$: C, 67.38; H, 7.78. Found: C, 67.53; H, 7.96.

Simmons–Smith Reaction of 1-Chloronorbornene. To a refluxing solution of 1.00 g (7.8 mmol) of 1-chloronorbornene[10] in 10 ml of anhydrous ether, under nitrogen, were added in three aliquots, over a 36-hr period, a total of 9 g of methylene iodide and 3 g of zinc–copper couple (prepared from zinc dust and cupric acetate).[35] At the end of this period, the solution was diluted with pentane, washed with saturated NH_4Cl, and dried over K_2CO_3–Na_2SO_4. Removal of the pentane by distillation through a 10-cm Vigreux column yielded a residue which was analyzed by VPC using column D and was found to contain, in addition to a 10% recovery of starting chloride, three additional components in a yield ratio of 2:17:22. Aliquots removed during the course of the reaction indicated an even rate of buildup of the 2 and the 17% component, while the 22% component increased in area only near the end of the 36-hr reaction period. The products were isolated by preparative VPC and identified as described below. No other peaks in greater than 1% yield were observed.

The 2% component was identified as 1-ethoxy-*exo*-tricyclo[3.2.1.$0^{2,4}$]octane by analysis of the ir, NMR, and mass spectra: mass spectrum *m/e* 152; ir (CCl_4) ν 3098, 3030, 2983, 2890, 1602, 1462, 1389, 1343, 1320, 1297, 1208, 1190, and 1137 (very strong) cm^{-1}; NMR (100 MHz, CCl_4) τ 6.49 (quartet, J = 7 Hz, 1 H, ethoxy methylene), 6.61 (quartet, J = 7 Hz, 1 H, ethoxy methylene), 7.95 (broad s, $w_{1/2}$ = 8 Hz, 1 H, C-5), 8.10–8.35 (m, 1 H, exo C-7), 8.35–8.70 (m, 3 H, protruding peaks with J = 9 Hz, C-8 and endo C-7), 8.70–9.00 (m, 1 H, exo C-6), 8.85 (triplet, J = 7 Hz, 3 H, ethoxy methyl), 9.05–9.60 (m, 4 H, C-2, syn C-3, C-4, and endo C-6), 9.90 (doublet of triplets, J = 7, 7 Hz, 1 H, anti C-3).

Anal. Calcd for $C_{10}H_{16}O$: *m/e* 152.120. Found: *m/e* 152.120.

The 17% component was bridgehead 1-chloro-*exo*-tricyclo[3.2.1.$0^{2,4}$]octane, and spectral comparison demonstrated it to be identical with the 17% component obtained in the photochlorination of *exo*-tricyclooctane **1**.

The 22% component gave a yellow precipitate when treated with $AgNO_3$ in 80% aqueous acetone and formed *exo*-tricyclo[3.2.1.$0^{2,4}$]octane (**1**) upon treatment with tributyltin hydride at 80° for 12 hr. This evidence, in conjunction with the spectral data detailed below, defines this component as 1-iodo-*exo*-tricyclo[3.2.1.$0^{2,4}$]octane: ir (CCl_4) ν 3105, 1048, 2984, 2891, 1482, 1455, 1319, 1271, 1221, 1197, 1114, 1079, 1039, 995, 960, 943, 894, 869 cm^{-1}; NMR (100 MHz, CCl_4) τ 7.95–8.15 (m, 3 H, C-5 and C-8), 8.15–8.90 (m, 5 H, exo and endo C-6 and C-7, C-2), 9.00–9.25 (m, 1 H, C-4), 9.54 (doublet of triplets, J = 3.5, 7 Hz, 1 H, syn C-3), 9.83 (doublet of triplets, J = 7, 7 Hz, 1 H, anti C-3).

Anal. Calcd for $C_8H_{11}I$: C, 41.05; H, 4.74. Found: C, 40.85; H, 4.60.

Reduction of the Photochlorination Products of *exo*-Tricyclooctane 1 with Tributyltin Hydride. A mixture of the three monochlorides from the photochlorination of *exo*-tricyclo[3.2.1.$0^{2,4}$]octane was isolated by VPC collection (0.0880 g, 0.62 mmol) and treated with tributyltin hydride (ca. 170 μl., 0.1860 g, 0.64 mmol) and cyclohexane (80 μl.) in a small tube. Approximately 20 μl. was removed for later analysis as starting material. Two crystals of AIBN were added, and the tube was sealed and placed in a 95 ± 2° oil bath for 24 hr. VPC analysis (column B, 145°, 46 ml/min) showed the presence of only one hydrocarbon product in a yield of 60% (vs. cyclohexane internal standard). The hydrocarbon was identified as *exo*-tricyclo[3.2.1.$0^{2,4}$]octane by comparison of its VPC retention time, ir, and NMR spectra with those of an authentic sample.

Reduction of 1-Chloro-*exo*-tricyclo[3.2.1.$0^{2,4}$]octane with Tributyltin Hydride. About 8 μl. of the chloride (0.0090 g, 0.063 mmol) was reduced with tributyltin hydride (0.0310 g, 0.107 mmol). About 8 μl. of cyclohexane was added. About 3 μl. was withdrawn for later analysis. A crystal of AIBN was added and the tube sealed and placed in a 125–130° bath for 48 hr. After cooling to room temperature, the tube was opened and the contents analyzed by VPC (column B) and mass spectroscopy. The sole hydrocarbon product had VPC retention time and mass spectrum identical with those of an authentic sample of *exo*-tricyclo[3.2.1.$0^{2,4}$]-octane.

Photochlorination of *endo*-Tricyclo[3.2.1.$0^{2,4}$]octane with *tert*-Butyl Hypochlorite. A 1.56 *m* solution of the endo hydrocarbon in carbon tetrachloride (22.4 g of solution) was treated with *tert*-

butyl hypochlorite (1.43 g, 0.0132 mol, 0.68 ml) in a 50-ml flask provided with a magnetic stirrer and a reflux condenser. The flask was placed in an oil bath maintained at 40 ± 2° and irradiated for 20 min with a 300-W Sylvania light bulb from a distance of 1 in. The solution was stirred for 5 more min after discontinuance of irradiation. The solution became colorless because of the color of the *tert*-butyl hypochlorite having been discharged. After partial removal of solvent at reduced pressure, the products were analyzed by VPC (column A, 120°, 55 ml/min). Three peaks were seen in the monochloro region, the first two being poorly separated from each other and the last one being well separated from the first two. The first two peaks and the last peak were in the ratio 95:5. NMR analysis (100 MHz, CCl_4) in the α-chloro region of the first two peaks collected together showed that this was actually a mixture of three chlorides in the ratio 69.4:28.4:2.2. So the final analysis was that the photochlorination products consisted of four monochlorides in the ratio 66:27:2:5, estimated to be formed in a total yield of 33%. The 2% component did not lend itself to isolation and characterization.

The 66% component was isolated by repeated VPC collection and identified as *anti*-8-chloro-*endo*-tricyclo[3.2.1.$0^{2,4}$]octane on the basis of its spectral data: ir (neat) 3088 (w), 3020 (w) (all assignable to cyclopropyl C–H stretching), 785 (m), 760 (s), and 732 (m) (all assignable to C–Cl stretching); NMR (100 MHz, CCl_4) τ 6.28 (complex multiplet 1 H, the α-chloro proton), 7.63 (unresolved multiplet, 2 H, the bridgehead protons), 7.86–8.13 (complex multiplet, 2 H, the exo protons on C-6 and C-7), 8.19–8.42 (complex multiplet, 2 H the endo protons on C-6 and C-7), 8.51–8.67 (complex multiplet, 2 H, the two cyclopropyl methine protons) and 9.17–9.37 (complex multiplet, 2 H, the cyclopropyl methylene protons); mass spectrum *m/e* parent peaks at 142 and 144. The structure assignment was confirmed by the stereospecific methanolysis and hydrolysis of this chloride to *endo*-2-methoxy- and *endo*-2-hydroxytricyclo[3.3.0.$0^{4,6}$]octane.

Anal. Calcd for $C_8H_{11}Cl$: C, 67.38; H, 7.78. Found: C, 67.22; H, 7.92.

The 27% component was identified as the rearranged endo chloride, *endo*-2-chlorotricyclo[3.3.0.$0^{4,6}$]octane (**16**), by comparison of its ir and NMR spectra with those of an authentic sample supplied by Tanida.[12]

Anal. Calcd for $C_8H_{11}Cl$: C, 67.38; H, 7.78. Found: C, 67.58; H, 7.88.

The 5% component was not completely characterized. Its spectral data, however, showed that it could not be the rearranged exo chloride, the endo-syn-8 chloride, the endo-syn-3 chloride, the endo-anti-3 chloride, or the exo- or endo-6 chloride: ir (neat) 3120 (w), 3050 (m) (both assignable to cyclopropyl C–H stretching), 783 (s), 772 (s), and 725 (s) (all assignable to C–Cl stretching); NMR (100 MHz, CCl_4) τ 5.95 (triplet of a doublet, J = 11, 4 Hz, finer splitting of each of the lines to about 1 Hz was also observable, 1 H), 7.52 (envelope, 1 H), 7.66 (envelope, 1 H), 7.8–8.03 (complex multiplet, 2 H), 8.05–8.23 (complex multiplet, 2 H), 8.28–8.83 (complex multiplet, 3 H), and 8.88–9.13 (doublet of a quartet, J = 6.5, 2 Hz, 1 H); mass spectrum *m/e* 142 and 144.

Anal. Calcd for $C_8H_{11}Cl$: C, 67.38; H, 7.78. Found: C, 67.48; H, 7.67.

Tests of the Stability and Homogeneity of the Endo-anti-8 Chloride 9-Cl. A pure sample of the anti chloride (0.0245 g, 0.172 mmol) was dissolved in a solution containing anhydrous *tert*-butyl alcohol (0.059 g, 0.798 mmol), reagent grade acetone (25 μl.), and carbon tetrachloride (36 μl.) in a 10-ml flask provided with a magnetic stirrer and a reflux condenser, which was fitted with a calcium chloride tube. The flask was placed in a 40 ± 2° oil bath and irradiated for 20 min with a 300-W Sylvania light bulb from a distance of 1 in. VPC analysis (column A, 130°, 50–55 ml/min) showed only one monochloride peak, identical in retention time and NMR (100 MHz, CCl_4) spectrum with the starting anti chloride. Pure samples of the anti chloride were injected into several VPC columns of divergent polarity (columns A, B, E, F, and G). Only one peak was seen in each case. No detectable isomerization was observed on any of the columns tried.

Test of Stability of the Rearranged Endo Chloride 10-Cl. A pure sample of the title chloride (0.0190 g, 0.134 mmol) was dissolved in a solvent mixture containing *tert*-butyl alcohol (0.0880 g, 1.19 mmol), acetone (30 μl.), and carbon tetrachloride (40 μl.) and the resulting solution irradiated at 40° for 20 min by means of a 300-W Sylvania light bulb. After cooling to room temperature, the mixture was analyzed by VPC (column B, 140°, 60 ml/min). There was only one monochloride peak, which was found to have retention time and ir spectrum identical with those of the starting chloride.

Reduction of the Rearranged Endo Chloride 10-Cl with Tributyltin Hydride. A pure sample of the rearranged endo chloride (0.073 g, 0.51 mmol) was treated with tributyltin hydride (0.1560 g, 0.536 mmol) and ca. 50 μl. of cyclohexane in a small tube. Approximately 5 μl. was removed for later analysis. A crystal of AIBN was added and the tube sealed and placed in a 95 ± 2° oil bath for 12 hr. After cooling to room temperature, the tube was opened and analyzed by VPC (column B, 125°, 50 ml/min). There was only one hydrocarbon product, formed in a yield of 65% (vs. cyclohexane internal standard). The VPC retention time and ir and NMR spectra of this sole hydrocarbon product were identical with those of an authentic sample of tricyclo[3.3.0.$0^{4,6}$]octane.

Preparation of *exo,exo*- and *exo,endo*-Tetrachloro[3.3.-1.$0^{2,4}$.$0^{6,8}$]nonane (3 and 4). *exo,exo*- and *exo,endo*-tetracyclo[3.3.1.$0^{2,4}$.$0^{6,8}$]nonane (**3** and **4**) were prepared by addition of methylene to norbornadiene,[13,14] using the Simmons–Smith reaction.[34] Purification was achieved by chromatography on a 3-ft 10% silver nitrate on Silicar column with pentane elution. The di-exo isomer prepared in this manner was greater than 99% free of the exo,endo isomer. The sample of the exo,endo isomer **4** used in the following studies was 86% pure as determined by infrared and NMR analyses, the contaminant being a 14% impurity of the di-exo isomer **3**.

Photochlorination of *exo,exo*-Tetracyclo[3.3.1.$0^{2,4}$.$0^{6,8}$]nonane with *tert*-Butyl Hypochlorite in CCl_4. A 4 *m* solution of 187 mg (1.57 mmol) of hydrocarbon **3** and 187 μl. (ca. 1 equiv) of *t*-BuOCl in CCl_4 was sealed in a Pyrex ampoule and irradiated 1 hr at 39.85 ± 0.15° with a 275-W sunlamp at a distance of 8 in. VPC analysis of the resulting solution using column H and 9.8 mg of chlorocyclohexane as an internal reference indicated the presence of six volatile peaks, in the ratio of 0.5:22:3:0.5:71:3, in an overall yield of 9%. The same internal standard indicated that most of the starting hydrocarbon was unreacted. Heavier components comprised no more than 1% in total yield.

Both the 71 and the 22% components gave only parent hydrocarbon **3** upon reduction with tributyltin hydride (AIBN, 100°). This observation, coupled with the lack of a proton α to chlorine in the NMR spectrum of each isomer, indicated that both monochlorides resulted from tertiary C–H substitution. Since there are only two such positions in the di-exo-[3.3.1.$0^{2,4}$.$0^{6,8}$] ring system, the major isomer was readily identified as *exo,exo*-1-chlorotetracyclo-[3.3.1.$0^{2,4}$.$0^{6,8}$]nonane (**13**) since all protons appear in the NMR spectrum, in pairs except for a single downfield adsorption due to the C-5 bridgehead proton, and no precipitate was formed upon treatment of **13** with $AgNO_3$ at 80° for 2 days: mass spectrum *m/e* 154 and 156; ir (CCl_4) ν 3105, 3059, 2956, 1500, 1449, 1311, 1209, 1187, 1090, 1045, 991, 914, 836, and 706 cm^{-1}; NMR (100 MHz, CCl_4) τ 7.81 (s, $w_{1/2}$ = 5 Hz, 1 H, C-5), 8.50–8.80 (m, 4 H, C-2, C-4, C-6, and C-8), 8.93 (doublet of triplets, J = 3.5, 7 Hz, 2 H, syn C-3 and C-7), 0.86 (s, $w_{1/2}$ = 4 Hz, 2 H, C-9), and 9.60 (doublet of triplets, J = 7, 7 Hz, 2 H, anti C-3 and C-7).

Anal. Calcd for $C_9H_{11}Cl$: *m/e* 154.055. Found: *m/e* 154.055.

The 22% component was also readily identified as *exo,exo*-2-chlorotetracyclo[3.3.1.$0^{2,4}$.$0^{6,8}$]nonane (**14**) since there were at least five nonequivalent protons apparent in the NMR spectrum of this isomer: mass spectrum *m/e*, no parent ion observed, but a P − Cl peak at 119 was prominent; ir (CCl_4) ν 3104, 3049, 2994, 1502, 1449, 1314, 1271, 1250, 1194, 1128, 1088, 1046, 1040, 1011, 983, 939, 859 cm^{-1}; NMR (100 MHz, CCl_4) τ 7.56 (s, $w_{1/2}$ = 5.5 Hz, 1 H, C-1), 7.73 (s, $w_{1/2}$ = 5.5 Hz, 1 H, C-5), 8.38 (m, 1 H, C-4), 8.50–9.15 (complex m, 4 H, syn and anti C-3, C-6, and C-8), 9.24 (doublet of triplets, J = 3.5, 7 Hz, 1 H, syn C-7), 0.52 (s, $w_{1/2}$ = 5 Hz, 2 H, C-9), and 0.34 (doublet of triplets, J = 7, 7 Hz, 1 H, anti C-3).

Anal. Calcd for C_9H_{11}: *m/e* 119.086. Found: *m/e* 119.088.

Photochlorination of *exo,endo*-Tetracyclo[3.3.1.$0^{2,4}$.$0^{6,8}$]nonane with *tert*-Butyl Hypochlorite in CCl_4. A 4 *m* solution of 68 mg (0.58 mmol) of hydrocarbon **4**, containing a 16% impurity of the corresponding di-exo isomer **3** as determined by NMR analysis, and 69 μl. (ca. 1 equiv) of *t*-BuOCl in CCl_4 was sealed in a Pyrex ampoule and irradiated 1 hr at 39.85 ± 0.15° with a 275-W sun-

lamp at a distance of 8 in. VPC analysis of the resulting solution using column H and 5.6 mg of chlorocyclohexane as an internal reference indicated the presence of three major components which had parent-ion masses corresponding to tetracyclic $C_9H_{11}Cl$ monochlorides. The combined yield of these three products observed in a ratio of 35:21:44 was 27%. A small peak formed in 2% yield, which eluted just after the monochlorides, had large mass-spectral peaks at *m/e* 153 and 155, indicating that it was a dichloride of molecular formula $C_9H_{10}Cl_2$. Products eluting later on column H comprised no more than 20% of the total volatile chlorides. Unreacted hydrocarbon was collected, analyzed by NMR, and was found to contain 20% of the contaminating isomer **3**. No absorptions are found in either the ir or the NMR spectra of any of the three monochlorides which correspond to the distinguishing absorptions of the two monochloro derivatives **13** and **14** derivable from chlorination of the contaminating di-exo isomer **3**.

The 35% product had parent masses of 154 and 156, no olefinic absorptions in the ir or NMR spectra, and no protons α to chlorine in the NMR and gave exclusively parent hydrocarbon **4** upon reduction with tributyltin hydride (AIBN, photoinitiation, 60°), indicating that this component was a bridgehead monochloride in the exo,endo-[3.3.1.$0^{2,4}$.$0^{6,8}$] system. Observation of a single cyclopropyl proton at τ 9.81 and two unique bridgehead protons at τ 7.55 and ca. 7.70 in the NMR spectrum of this monochloride defines its structure as either 2- or 6-chloro-*exo,endo*-tetracyclo-[3.3.1.$0^{2,4}$.$0^{6,8}$]nonane. Analysis of this spectrum, presented in the discussion, indicates that this product is best represented as the C-6 substituted isomer **16**: mass spectrum *m/e* 154 and 156; ir (CCl_4) ν 3097, 3040, 2995, 1488, 1430, 1319, 1261, 1118, 1108, 1050, 1040, 1032, and 900 cm^{-1}; NMR (100 MHz, CCl_4) τ 7.55 (broad s, $w_{1/2}$ = 6 Hz, 1 H, C-1), 7.60–7.80 (m, 1 H, C-5), 7.80–8.05 (m, 1 H, endo C-7), 8.20–8.90 (m, 4 H, C-6, C-8, and both C-9), 8.90–9.60 (m, 3 H, syn C-3, C-4, exo C-7), 9.81 (triplet, J = 7 Hz, 1 H, anti C-3).

Anal. Calcd for $C_9H_{11}Cl$: *m/e* 154.055. Found: *m/e* 154.055.

The 44% product also had parent-ion masses of 154 and 156, no olefinic absorptions in ir or NMR spectra, and no protons α to chlorine in the NMR and gave exclusively parent hydrocarbon **4** upon reduction with tributyltin hydride (AIBN, photoinitiation, 60°). Observation of a single bridgehead proton at τ 7.82 and one cyclopropyl proton (a doublet of triplets, J = 7, 7 Hz) at 9.80 defines this product as *exo,endo*-1-chlorotetracyclo-[3.3.1.$0^{2,4}$.$0^{6,8}$]nonane (**15**): mass spectrum *m/e* 154 and 156; ir (CCl_4) ν 3105, 3040, 2994, 1487, 1437, 1316, 1193, 1080, 1042, 1019, 971, 901, and 704 cm^{-1}; NMR (100 MHz, CCl_4) τ 7.82 (broad m, $w_{1/2}$ = 9 Hz, 1 H, C-5), 8.02–8.70 (m, an apparent doublet protruding with J = 7 Hz, 5 H, C-6, endo C-7, C-8, and both C-9), 8.90–9.15 (m, 1 H, C-2), 9.15–9.45 (m, coupling of 7 Hz apparent, 3 H, syn C-3, C-4, exo C-7), 9.80 (doublet of triplets, J = 7, 7 Hz, anti C-3).

Anal. Calcd for $C_9H_{11}Cl$: *m/e* 154.055. Found: *m/e* 154.059.

The 21% product had parent-ion masses of 154 and 156, contained no olefinic absorptions in the ir and NMR spectra, but did have one proton α to chlorine in the NMR spectrum at τ 5.95 (a doublet of triplets with J = 4, 8.5 Hz). Reduction of the 21% component with tributyltin hydride (AIBN, photoinitiation, 60°) gave a single volatile product in quantitative conversion, as determined by VPC analysis on column I. Collection of this hydrocarbon followed by ir and NMR analyses demonstrated that the product was not **3** or **4** and led to the assignment of *exo*-tetracyclo[4.3.0.-$0^{2,4}$.$0^{5,7}$]nonane (**20**) for product hydrocarbon: ir (CCl_4) ν 3058, 2967, 2890, 1456, 1445, 1333, 1299, 1024, and 720 cm^{-1}; NMR (100 MHz, CCl_4) τ 7.26 (triplet, J = 4 Hz, 1 H, C-1), 8.74 (doublet of triplets, J = 3.5, 6 Hz, 1 H, C-4), 9.23 (m, 1 H, syn C-3), 9.52 (doublet of triplets, J = 3.5, 7 Hz, C-2), 9.85 (quartet, J = 3.5 Hz, 1 H, anti C-3), 7.70–8.95 (m, 7 H, hydrogens on C-5 to C-9).

The spectral analysis presented in the discussion led to the assignment of structure for this rearranged C_9H_{11} monochloride as *endo*-9-chloro-*exo*-tetracyclo[4.3.0.$0^{2,4}$.$0^{5,7}$]nonane (**19**): mass spectrum *m/e* 154 and 156; ir (CCl_4) ν 3059, 2965, 2899, 1449, 1338, 1296, 1276, 1234, 1027, 919, 908, 711, and 682 cm^{-1}; NMR (100 MHz, CCl_4) τ 5.95 (doublet of triplets, J = 4, 8.5 Hz, 1 H, C-9), 7.36 (doublet of doublets, J = 4.5, 4.5 Hz, 1 H, C-1), 7.53–7.60 (m, 2 H, exo and endo C-8), 8.20–8.50 (m, 3 H, C-5, C-6, and C-7), 8.55–8.95 (m, 2 H, C-2 and C-4), 9.42–9.69 (doublet of triplets, J = 4, 7 Hz, 1 H, syn C-3), 9.92 (doublet of triplets, J = 7, 4 Hz, 1 H, anti C-3).

Anal. Calcd for $C_9H_{11}Cl$: *m/e* 154.055. Found: *m/e* 154.056.

Relative Rates of Hydrogen Atom Abstraction. Relative rate data were obtained by the method of Walling and Jacknow.[36] Reference and chlorination runs, both performed in replicate, were prepared from single stock solutions of hydrocarbons in CCl_4 and were treated identically, except for the exclusion of *t*-BuOCl in the former. The solutions were prepared ca. 1 *m* in each hydrocarbon and *t*-BuOCl. Photolyses were carried out at 39.85 ± 0.15° (standardized) with irradiation from a 275-W sunlamp at a distance of 8 in. VPC analysis of the resulting solutions, performed by alternating analysis of reference and sample runs, gave relative peak areas for reference norbornane and polycyclic hydrocarbon. Per mole relative reactivities were calculated by the method of Huyser[37] using eq 1, where R = reference cyclohexane, H = polycyclic hydrocarbon, and the concentrations are the average of the concentrations determined in replicate. Errors were determined from standard deviations using standard propagating techniques.[38]

$$k/k_0 = \frac{\log [H]_0/[H]}{\log [R]_0/[R]} \quad (1)$$

Acknowledgments. The authors gratefully acknowledge the support of this work by the National Science Foundation and express their appreciation for an NSF Graduate Traineeship, 1971–1972 (T.D.Z.), and a Fulbright Travel Grant (R.S.R.).

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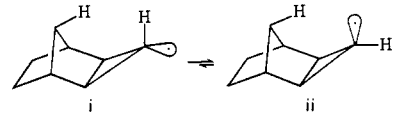

i ii

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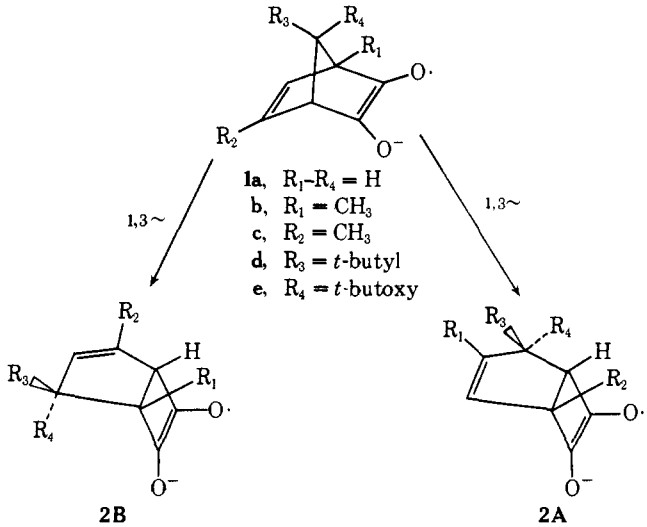
Aliphatic Semidiones. XXVIII. Formation of Bicyclo[3.2.0]hept-2-ene-6,7-semidiones from Bicyclo[3.2.0] and -[2.2.1] Precursors[1,2]

Glen A. Russell,* Kirk D. Schmitt, and John Mattox

Contribution from the Department of Chemistry, Iowa State University, Ames, Iowa 50010.
Received June 19, 1974

Abstract: The preparation of bicyclo[2.2.1]hept-5-ene-2,3-semidione and bicyclo[3.2.0]hept-2-ene-6,7-semidione are reported. In dimethyl sulfoxide solution containing potassium *tert*-butoxide, 3-hydroxybicyclo[2.2.1]hept-5-en-2-one yields the isomeric bicyclo[3.2.0] semidione. Under similar conditions, 3-*endo*-dimethyl-*tert*-butylsiloxybicyclo[2.2.1]hept-5-en-2-one yielded mainly the semidione in the bicyclo[2.2.1] system. It is argued that when rearrangement occurs it probably involves a symmetrical intermediate, possibly the enediol dianion. Once formed, the semidione radical anions do not seem to undergo rearrangement. 1- or 5-methylbicyclo[2.2.1]hept-5-en-2,3-acyloins each give mixtures of the two possible methyl substituted bicyclo[3.2.0]hept-2-ene-6,7-semidiones. The same mixture of semidiones was also formed from 1-methylbicyclo[3.2.0]hept-2-en-6,7-acyloin, indicating that the rearrangement is reversible.

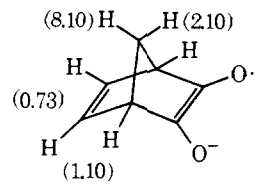
An interest in evaluating the magnitude of through-space delocalization of the π-electron systems in norbornadiene derivatives led us to investigate the synthesis of **1a**. Our initial attempt at the synthesis of **1** was thwarted by the apparent rearrangement of **1** to **2**.[2] We have subsequently shown that **1** can be detected by the treatment of the *endo-tert*-butyldimethylsiloxynorborn-5-en-2-one and other difficultly hydrolyzed derivatives of 3-hydroxynorborn-5-en-2-one with base and DMSO or by electrolysis of the diketone in the esr cavity.[3] The esr spectra of **1** indicated that perhaps 15% of the unpaired electron is transferred by delocalization to the vinyl bridge, a result in agreement with the photoelectron spectrum of norbornadiene[4] or norbornenone.[5] We now present evidence concerning the mechanism and the scope of the rearrangement of **1** to **2** which is formally a 1,3-sigmatropic rearrangement.



1a, R_1–R_4 = H
b, R_1 = CH_3
c, R_2 = CH_3
d, R_3 = *t*-butyl
e, R_4 = *t*-butoxy

1,3~ 1,3~

2B **2A**



(8.10) (2.10) (0.73) (1.10)

1a
(a^H in G)

Synthesis of Semidione Precursors. Norbornadienes **3a–c** were converted to the *exo*-3-benzoyloxynorbornen-2-ones **4a–e** by reaction with benzoyl nitrite followed by hydrolysis, Scheme I. An additional series of bicyclo[2.2.1]heptene