(dibromonitromethylisoquinoline, 35619-73-9; 4-(dibromonitromethyl)cinnoline, 35619-74-0; 2-(dichloronitromethyl)pyridine, 35619-75-1; 1-chloro-1-(4-pyridyl)nitroethane, 35619-76-2; 4-(bromonitromethyl)-2-methylpyridine, 35619-77-3.

Acknowledgments.—Financial support of this work by the Office of Naval Research is gratefully acknowledged. We would like to thank Dr. John B. Grützner for helpful discussions of the nmr data during the preparation of the manuscript.

The Free-Radical Addition of *tert*-Butyl Hypochlorite to Some Bridged Polycyclic Olefins

PETER K. FREEMAN* AND R. S. RAGHAVAN

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

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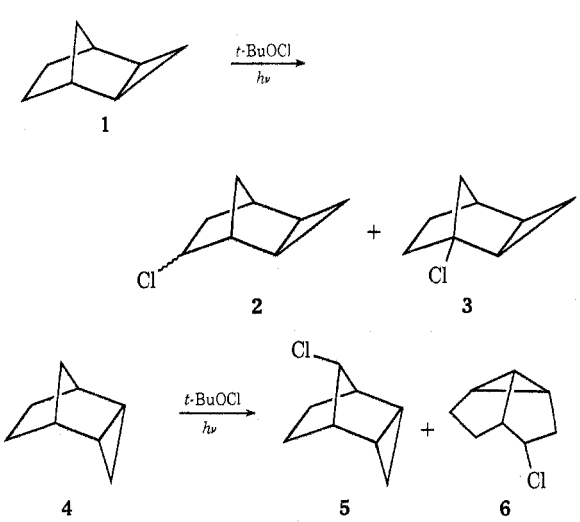
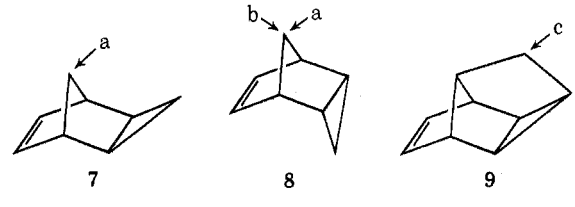
Irradiation of *tert*-butyl hypochlorite and *endo*-tricyclo[3.2.1.$0^{2,4}$]oct-6-ene in carbon tetrachloride at 40° produces a 59% yield of *exo*-6-*tert*-butoxy-*endo*-7-chloro-*endo*-tricyclo[3.2.1.$0^{2,4}$]octane and *exo*-6-*tert*-butoxy-*exo*-7-chloro-*endo*-tricyclo[3.2.1.$0^{2,4}$]octane in a ratio of 43:57, while similar treatment of *tert*-butyl hypochlorite and *exo*-tricyclo[3.2.1.$0^{2,4}$]oct-6-ene results in a 56% yield of trans adduct, *exo*-6-*tert*-butoxy-*endo*-7-chloro-*exo*-tricyclo[3.2.1.$0^{2,4}$]octane, and cis adduct, *exo*-6-*tert*-butoxy-*exo*-7-chloro-*exo*-tricyclo[3.2.1.$0^{2,4}$]octane, in a ratio of 78:22. Similar photolytic treatment of *tert*-butyl hypochlorite and deltacyclene generates *exo*-8-*tert*-butoxy-*endo*-9-chlorodeltacyclane and *exo*-8-*tert*-butoxy-*exo*-9-chlorodeltacyclane in a ratio of 85:15 in an overall yield of 37%. The stereochemistry of the chain transfer step of the intermediate *tert*-butoxycycloalkyl radicals and the lack of cyclopropylethyl radical rearrangement are rationalized as a result of predominant 1,2 addition taking place by way of classical *tert*-butoxycycloalkyl intermediates.

Recently we have reported that radical chlorination of *exo*-tricyclo[3.2.1.$0^{2,4}$]octane with *tert*-butyl hypochlorite results in abstraction of hydrogen from C-6 and C-1 to generate *exo*- and *endo*-6-chloro-*exo*-tricyclo[3.2.1.$0^{2,4}$]octane (**2**) and 1-chloro-*exo*-tricyclo[3.2.1.$0^{2,4}$]octane (**3**), while, in contrast, radical chlorination of *endo*-tricyclooctane **4** results in 93% or greater



abstraction of hydrogen at C-8, leading to *anti*-8-chlorotricyclooctane **5** and *endo*-2-chlorotricyclo[3.3.0.$0^{4,6}$]octane (**6**).[1]

Since several unique aspects of *tert*-butoxy abstraction in these tricyclooctane ring systems have been at least partially revealed, it appeared to be of some interest to pursue a complementary line of research to gain additional insight into the nature of related radical intermediates. Tobler and coworkers[2] have shown that the radical reaction of *tert*-butyl hypochlorite with norbornene results in both addition and substitution, addition predominating. Therefore, we chose to investigate the analogous reaction of *tert*-butyl hypochlorite with *exo*-tricyclo[3.2.1.$0^{2,4}$]oct-6-ene (**7**), *endo*-tricyclo[3.2.1.$0^{2,4}$]oct-6-ene (**8**), and deltacyclene (**9**). Abstraction reactions are of interest in each case, since there is the potential for anchimeric assistance to abstraction of the bishomocyclopropenyl (abstraction at a in **7** and **8**) and trishomocyclopropenyl type (abstraction at b in **8**), while abstraction at c in **9** could produce an interesting degenerate 5-deltacyclenyl radical. Addition of *tert*-butoxy to the double bond of **7** or **9** would generate a radical intermediate analogous to the major intermediate in the abstraction reaction of **1**, while addition to *endo*-tricyclooctene **8** would yield a radical we have been unable to characterize in the radical chlorination of **4**, due to the predominance of C-8 abstraction.



Results

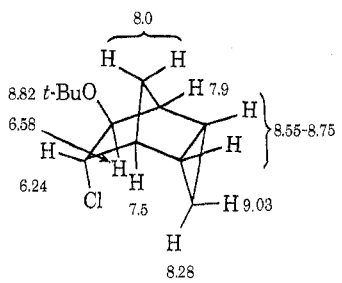
When *endo*-tricyclooctene **8** was irradiated with *tert*-butyl hypochlorite using a 2:1 molar ratio of olefin to *tert*-butyl hypochlorite in carbon tetrachloride solution at 40°, the products on vpc analysis were found to consist of two components in a ratio of 43:57 in the order of increasing retention times, in an overall yield of 59%. The retention times of the two components were much longer than expected for monochlorides, suggesting the possibility that free-radical adducts had been formed. Since the monochloride region in the chromatogram was conspicuously free of peaks, hydrogen abstraction did not compete with addition.

(1) P. K. Freeman, R. S. Raghavan, and G. L. Fenwick, *J. Amer. Chem. Soc.*, **94**, 5101 (1972).

(2) E. Tobler, D. E. Battin, and D. J. Foster, *J. Org. Chem.*, **29**, 2834 (1964).

The ir spectrum of the 43% component shows weak bands at 3096 and 3040 cm^{-1} (cyclopropane methylene), while the nmr spectrum (100 MHz, CCl_4) exhibits resonance signals at τ 6.24 (doublet of a triplet, J = 3.4, 0.7 Hz, HCCl), 6.58 (broad, poorly resolved multiplet, $W_{1/2}$ = 5 Hz, HCO-*t*-Bu), 7.5 (envelope, 1 H), 7.9 (envelope, 1 H), 8.0 (broad singlet, 2 H), 8.28 (a pair of overlapping triplets, J = 7, 3 Hz, 1 H), 8.55–8.75 (multiplet, 2 H), 8.82 (singlet, 9 H), and 9.03 (multiplet, 1 H). The spectrum is consistent with the structure of the trans adduct, *exo*-6-*tert*-butoxy-*endo*-7-chloro-*endo*-tricyclo[3.2.1.$0^{2,4}$]octane (**10**).

The ir spectrum of the 57% component exhibits peaks characteristic of cyclopropane methylene at 3080 and 3032 cm^{-1}, while in the nmr spectrum (100 MHz, CCl_4) signals at τ 6.36 (doublet of a doublet, J = 5.6, 1.7 Hz, HCCl), 6.68 (doublet of a doublet, J = 5.6, 1.7 Hz, HCO-*t*-Bu), 7.68 (envelope, 1 H), 7.73 (A component of an AB pattern, J = 9.5 Hz, 1 H), 7.92 (envelope, 1 H), 8.15 (multiplet of the B doublet of the AB pattern, J = 9.5 Hz, 1 H), 8.60–8.80 (multiplet, 2 H), 8.82 (singlet, 9 H), and 9.0–9.35 (complex multiplet, 2 H) are observed. The spectrum is consistent with the structure of the cis adduct, *exo*-6-*tert*-butoxy-*exo*-7-chloro-*endo*-tricyclo[3.2.1.$0^{2,4}$]-octane (**11**).



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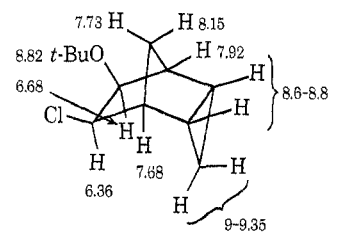

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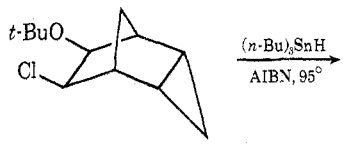
A convenient verification of these structural assignments was possible through tri-*n*-butyltin hydride reduction[3] of the two adducts. Radical reduction of both of the adducts followed by vpc analysis showed that the same exclusive product, *exo*-6-*tert*-butoxy-*endo*-tricyclo[3.2.1.$0^{2,4}$]octane (**12**), resulted from both in yields of 75% from the trans adduct and 97% from the cis adduct. The ir spectrum of the product from both the adducts showed absorptions at 3064 and 3016 cm^{-1} while the nmr spectrum (100 MHz, CCl_4) exhibited signals at τ 6.74 (doublet of a doublet, J = 6.4, 3.0 Hz, HCO-*t*-Bu), 7.8 (unresolved multiplet, 1 H, the bridgehead proton β to *tert*-butoxy), 8.0 (unresolved multiplet, 1 H, the other bridgehead proton), 8.2 (broad singlet, 2 H, the C-8 protons), 8.6–8.85 (complex multiplets, 4 H, the protons on C-7, C-2, and C-4), 8.9 (singlet, 9 H, the *tert*-butoxy protons),

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



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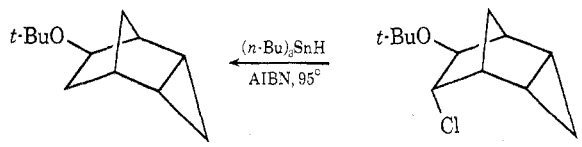
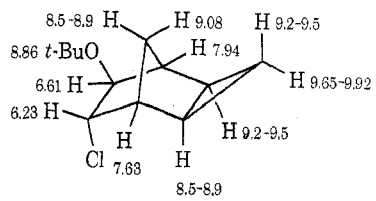


12 **10**

and 9.1–9.45 (complex multiplets, 2 H, the C-3 protons). The spectrum showed a striking similarity to that of *exo*-6-hydroxy-*endo*-tricyclo[3.2.1.$0^{2,4}$]octane.

The irradiation of a solution of *exo*-tricyclooctene **7** and *tert*-butylhypochlorite in carbon tetrachloride at 40° resulted in the formation of two adducts in 56% yield in the ratio 78:22 in the order of increasing retention times. These two components were identified as the trans and the cis adducts on the basis of their spectral data. The ir spectrum of the trans adduct showed bands attributable to a cyclopropane ring (3088 and 3032 cm^{-1}), while the nmr spectrum (100 MHz, CCl_4) exhibited resonance signals at τ 6.23 (doublet of a doublet, J = 2.9, 2.0 Hz, HCCl), 6.61 (triplet, J = 2.0 Hz, HCO-*t*-Bu), 7.63 (unresolved multiplet, 1 H, the bridgehead proton β to chlorine), 7.94 (singlet, 1 H, the bridgehead proton β to *tert*-butoxy), 8.5–8.9 (multiplets with a large singlet at 8.86, 11 H, the anti C-8 proton, the C-2 proton, and O-*t*-Bu), 9.08 (a poorly resolved multiplet of a doublet of an AB pattern, J = 12 Hz, the syn C-8 proton), 9.2–9.5 (multiplets, the C-4 and the syn C-3 protons), and 9.65–9.92 (a quartet, J = 7 Hz, the anti C-3 proton) (structure **13**). The ir



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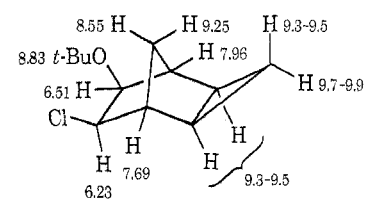
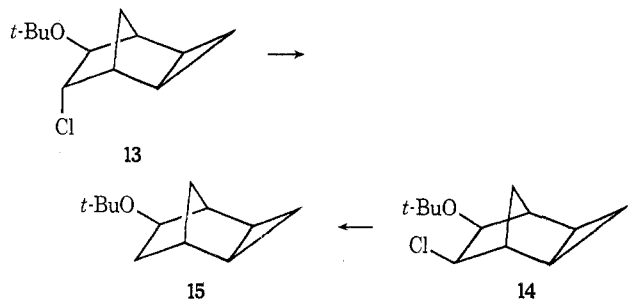


14

spectrum of the cis adduct showed characteristic bands at 3092 and 3032 cm^{-1} (cyclopropane methylene stretching), while the nmr spectrum (100 MHz, CCl_4) showed resonance signals at τ 6.23 (doublet of a doublet, J = 6.0, 2.3 Hz, HCCl), 6.51 (doublet of a doublet, J = 6, 1.9 Hz, HCO-*t*-Bu), 7.69 (singlet, 1 H, the bridgehead proton β to chlorine), 7.96 (singlet, 1 H, the bridgehead proton β to *tert*-butoxy), 8.55 (a doublet of an AB pattern, J = 11 Hz, the anti C-8 proton), 8.83 (a large singlet, 9 H, the *tert*-butoxy protons), 9.25 (an unresolved multiplet of a doublet of an AB pattern, J = 11 Hz, the syn C-8 proton), 9.3–9.5

(multiplet, 3 H, the C-2, C-4, and the syn C-3 protons), and 9.7–9.9 (multiplet, the anti C-3 proton) (structure **14**). In addition vpc analysis indicated that no monochlorides were formed (<1%).

Both the trans and the cis adducts on reduction with tri-*n*-butyltin hydride at 95° (AIBN initiation) gave exclusively *exo*-6-*tert*-butoxy-*exo*-tricyclo[3.2.1.0^{2,4}]octane (**15**). The ir spectrum of the tricyclic *tert*-butyl



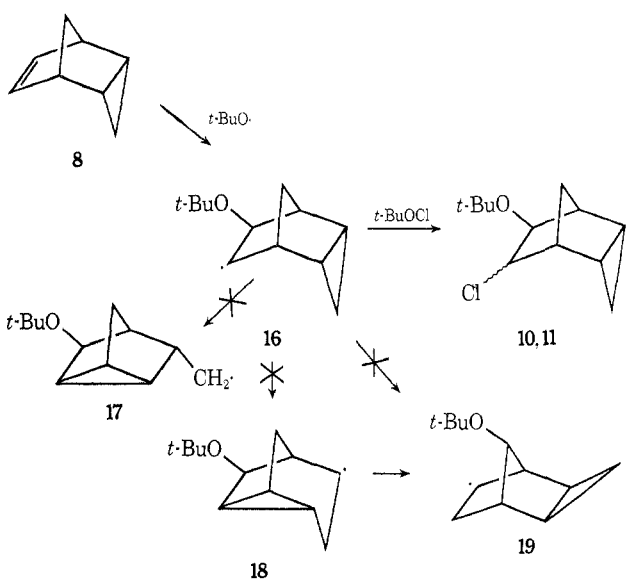
ether shows bands at 3092 and 3016 cm^{-1}, while the nmr spectrum (100 MHz, CCl_4) exhibits resonance signals at τ 6.54 (doublet of a doublet of a doublet, J = 7.0, 3, 1 Hz, HCO-*t*-Bu), 7.87 (poorly resolved multiplet, 1 H, the C-1 proton), 7.95 (singlet, 1 H, the bridgehead proton β to *tert*-butoxy), 8.35 (a doublet of an AB pattern split additionally by 2 H, J = 12.5, 7.0, 2.2 Hz, the endo C-7 proton), 8.75 (a doublet of an AB pattern split into a pair of triplets, J = 12.5, 3 Hz, the exo C-7 proton), 8.86 (singlet, 9 H, O-*t*-Bu), 8.96 (doublet of an AB pattern, J = 12 Hz, the anti C-8 proton), 9.28 (a doublet of an AB pattern, J = 12 Hz, with additional splitting by *ca.* 1 Hz, the syn C-8 proton), 9.35–9.6 (multiplet, 3 H, the C-2 and C-4 protons and the syn C-3 proton), and 9.85–10.09 (multiplet, 1 H, the anti C-3 proton). The spectrum shows a remarkable resemblance to that of *exo*-6-hydroxy-*exo*-tricyclo[3.2.1.0^{2,4}]octane.

A similar picture emerged from the irradiation of a solution of deltacyclene (**9**) with *tert*-butyl hypochlorite under conditions identical with those employed for the exo and endo tricyclooctene. The product fraction was found by vpc analysis to consist of two components, the trans and the cis adducts in the ratio 85:15, in a yield of 37%. No significant amounts of monochlorides (>2% could have been detected) were observable. The ir spectrum of the trans adduct shows the presence of a cyclopropane ring (a weak band at 3056 cm^{-1}) and a nortricyclene ring (a strong band at 800 cm^{-1}), while the nmr spectrum (100 MHz, CCl_4) exhibits signals at τ 6.07 (doublet of a doublet, J = 4.0, 2.0 Hz, HCCl), 6.24 (poorly resolved doublet, J = 2 Hz, HCO-*t*-Bu), 7.8 (unresolved multiplet, the bridgehead proton β to chlorine), 7.88 (unresolved multiplet, the bridgehead proton β to *tert*-butoxy), 8.15 (unresolved triplet, the C-6 proton), 8.42 (singlet, 2 H, the C-5 protons), 8.74 (singlet, 2 H, the C-2 and C-3 protons), 8.82 (singlet, 9 H, *tert*-butoxy protons), 9–9.15 (a multiplet, the C-4 proton), consistent with **22** (endo Cl). The cis adduct was contaminated to the extent of 32% by an unidentified, inseparable material. The ir spectrum shows bands at 3056 (cyclopropane) and 800 cm^{-1} (nortricyclene ring), and the nmr spectrum (100 MHz, CCl_4) exhibits signals at τ 5.9 (doublet, J = 6 Hz) and 6.15 (doublet, J = 6 Hz).

Both the adducts on reduction with tri-*n*-butyltin hydride at 95° gave the same product, *exo*-8-*tert*-butoxydeltacyclane (**22**, Cl = H). The cis adduct, in addition to this ether, gave 32% of an unidentified product, probably due to its contaminant. The ir spectrum of **22** (Cl = H) shows the presence of a cyclopropane ring (3056 cm^{-1}) and a nortricyclene skeleton (798 cm^{-1}), while the nmr spectrum (100 MHz, CCl_4) contains resonance signals at τ 6.2 (doublet with additional poorly resolved splitting, J = 6.6 Hz, HCO-*t*-Bu), 8.0–8.25 (a series of poorly resolved multiplets, 4 H, the bridgehead C-1 and C-7 protons, the endo proton on C-9, and the C-6 proton), 8.46 (sharp singlet with poorly resolved adjacent multiplet, 3 H, the C-5 and exo C-9 protons), 8.85 (a large singlet with a poorly resolved multiplet buried under it, 10 H, O-*t*-Bu and the C-4 proton), and 9.25 (multiplet, 2 H, the C-2, C-3 cyclopropyl protons). The spectrum shows marked similarity to that of *exo*-8-hydroxydeltacyclane.

Discussion

In each case, irradiation of solutions of *tert*-butyl hypochlorite and polycyclic alkene in carbon tetrachloride result exclusively in 1,2 addition of the elements of *tert*-butyl hypochlorite. It seems reasonably certain, therefore, that the addition proceeds by a radical process, analogous to that suggested by Tobler for the addition of *tert*-butyl hypochlorite to norbornene,[2] since extensive rearrangement has been observed upon generation of the 6-*endo*-tricyclo[3.2.1.0^{2,4}]octyl,[4] 6-*exo*-tricyclo[3.2.1.0^{2,4}]octyl,[4,5] and 8-deltacyclyl[6] carbonium ions.[7] Since, as noted above, it was not possible to characterize the 6-*endo*-tricyclo[3.2.1.0^{2,4}]octyl radical in our investigation of abstraction reactions of **4**, the radical **16** generated by *tert*-



(4) G. D. Sargent, M. J. Harrison, and G. Khoury, *J. Amer. Chem. Soc.*, **91**, 4937 (1969); K. B. Wiberg and G. R. Wenzinger, *J. Org. Chem.*, **30**, 2278 (1965).

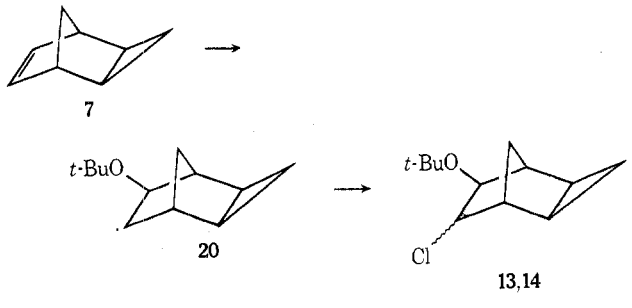
(5) J. A. Berson, R. G. Bergman, G. M. Clarke, and D. Wege, *J. Amer. Chem. Soc.*, **90**, 3236 (1968); R. R. Sauers, J. A. Beisler, and H. Feilich, *J. Org. Chem.*, **32**, 569 (1967); A. K. Colter and R. C. Musso, *ibid.*, **30**, 2462 (1965); R. R. Sauers and J. A. Beisler, *Tetrahedron Lett.*, 2181 (1964).

(6) P. K. Freeman, D. M. Balls, and J. N. Blazevich, *J. Amer. Chem. Soc.*, **92**, 2051 (1970).

(7) The evidence for a radical process is qualitative only and rests principally on the lack of skeletal rearrangements and lack of stereospecificity found in the addition processes. No quantum yields were determined.

butoxy addition is of considerable interest. The observation of a cyclopropylethyl radical rearrangement in the chlorination of *endo*-tricyclooctane **4** suggests, *a priori*, that one might expect interaction and/or rearrangement involving either the C-2–C-3 or C-2–C-4 cyclopropane bonds. Rearrangement using the C-2–C-3 bond would produce the nortricyclylmethyl radical **17**, while rearrangement *via* fission of the C-2–C-4 bond would result in the tricyclo[3.2.1.$0^{2,7}$]octyl radical **18** and/or the 6-*exo*-tricyclo[3.2.1.0]octyl radical **19** (equivalent to a Wagner–Meerwein rearrangement). Since the chlorides related to these radicals are clearly not formed, as evidenced by the nmr spectra of the addition products, the results are explained by chlorine atom transfer to the radical center at C-6 to produce cis,exo (**11**) and trans (**10**) adducts in a ratio of 57:43. A comparison with the 3-*tert*-butoxy-2-norbornyl radical, which undergoes chain transfer to generate a 1:4 ratio of cis and trans addition products,[2] suggests that the addition of the endo-fused cyclopropane ring provides steric shielding for endo approach, which balances the steric shielding of the exo *tert*-butoxy group. The fact that no monochlorides were formed demonstrates that hydrogen abstraction, even with trishomocyclopropenyl assistance, cannot compete with radical addition to a strained double bond.

Radical addition of *tert*-butyl hypochlorite to *exo*-tricyclooctene **7** proceeds *via* *tert*-butoxytricyclooctyl radical **20** with chlorine atom transfer to C-6, yielding



cis,exo (**14**) and trans (**13**) addition products in a ratio of 22:78. Rearrangements involving the C-2–C-3 and C-2–C-4 cyclopropane bonds can be ruled out by consideration of the spectral data of the addition products. The ratio of exo to endo attack of *tert*-butyl hypochlorite on *exo*-tricyclooctyl radical **20** is quite similar to that of the 3-*tert*-butoxy-2-norbornyl radical, as expected.

Radical addition of *tert*-butyl hypochlorite to deltacyclene (**9**) was considered in order to obtain additional evidence which would provide either reinforcement for, or an interesting contrast to, the data on addition to *exo*- and *endo*-tricyclooctene. In the case of addition to deltacyclene, a cyclopropylethyl radical rearrangement involving the C-3–C-4 cyclopropane bond is more likely than in addition to **7**, since it involves a rearrangement of a secondary radical to a secondary radical, in contrast to the secondary to primary process anticipated for **20**. Such a process would be analogous to that observed in the case of the 8-deltacyclyl carbonium ion[6] and would generate the 5-*tert*-butoxy-8-deltacyclyl radical (**23**). Reduction of the monochloride(s) **25** formed from **23** with tri-*n*-butyltin hydride would have produced 5-*tert*-butoxydeltacyclane (**25**, Cl = H). That this route was not utilized, at least to an extent of 95% or greater (the uncertainty being due to the unknown contaminant present to an extent of 5%), was established by nmr spectral comparison of product *tert*-butyl ether with an authentic sample of 5-*tert*-butoxydeltacyclane.[8]

A cyclopropylethyl rearrangement involving the C-2–C-3 bond would result in radical **24**, with chain transfer producing chlorides **26**. Since the *tert*-butyl hypochlorite adducts labeled as trans and cis above exhibit splitting in the nmr for hydrogen α to chlorine (trans adduct, doublet of a doublet, J = 4.0, 2.0 Hz; cis adduct, doublet, J = 6 Hz), it is clear that neither is the expected major rearranged epimer (**26**, exo Cl), for **26** (exo Cl) should exhibit an unsplit HCCl in the nmr.[9] The hydrogen α to chlorine in the endo epimer **26** (endo Cl) would be expected to be split (HCCl in **26**, endo Cl, O-*t*-Bu = 0 appears as a doublet of a doublet, J = 8, 2 Hz),[9] so that **26** (endo Cl) might be considered as a structural possibility. This appears highly unlikely, however, since we have demonstrated above that an endo fused cyclopropane ring provides steric shielding of the endo face of radical **16**, and thus the ratio of exo to endo chain transfer for radical **24** should be enhanced (>7:1)[10] over that expected for norbornyl and one would not expect to observe **26** (endo Cl) if **26** (exo Cl) is not observed. Moreover, tri-*n*-butyltin hydride reduction of both major *tert*-butyl hypochlorite adducts to the same *tert*-butyl ether strongly suggests that the adducts are epimers. Thus, addition proceeds *via* **21** to exo,endo epimers **22**.

In summary, we find that the irradiation of *tert*-butyl hypochlorite in the presence of *endo*-tricyclooctene **8**, *exo*-tricyclooctene **7**, and deltacyclene (**9**) results in radical addition of *tert*-butoxy, which produces a classical radical, which, in turn, undergoes chain transfer to form *tert*-butyl hypochlorite adduct, a step which appears to be simply controlled by steric factors. There is no evidence for participation of the cyclopropane bonds in cyclopropylethyl rearrangements, and the radical addition to the strained alkene double bond, in each case, is rapid enough to mask all hydrogen abstraction reactions, anchimerically assisted or not.

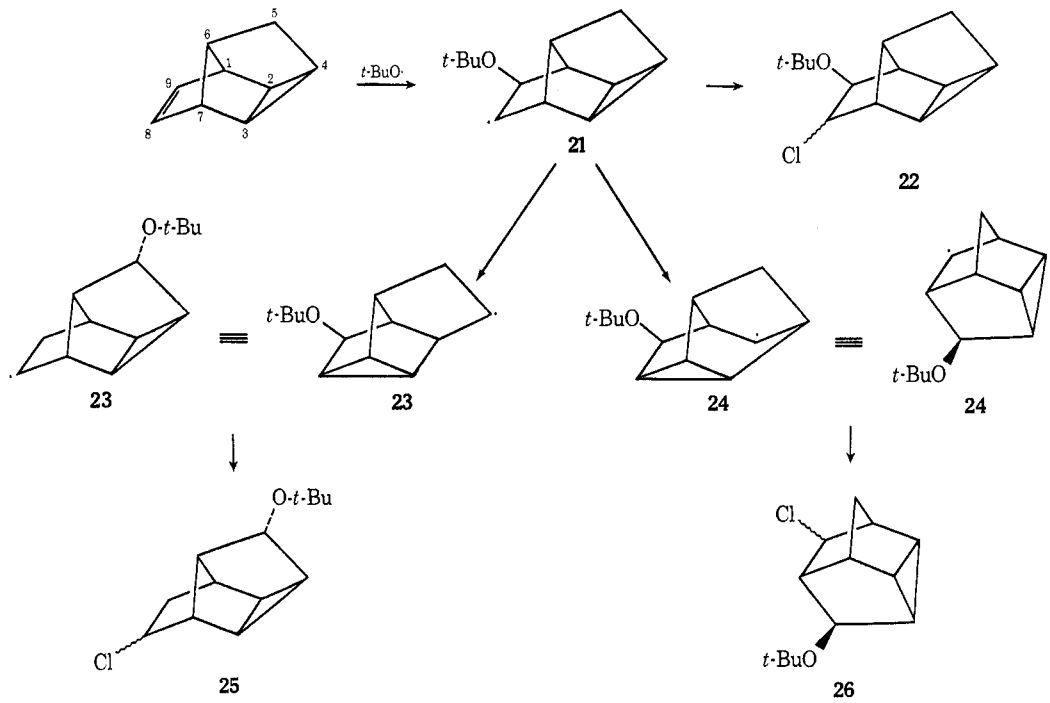
Experimental Section

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. Mass spectra were measured using an Atlas CH7 mass spectrometer. Elemental analyses were performed by Alfred Bernhardt, Mikroanalytisches Laboratorium, West Germany, or Dornis U. Kolbe, 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. The following columns were employed: (1) 18 ft × 0.25 in. alu-

(8) We express our appreciation to Professor P. v. R. Schleyer for providing us with nmr spectral data for 5-*tert*-butoxydeltacyclane.

(9) Related derivatives, **26** (exo Cl, *t*-BuO = =O), **26** (Cl = exo OAc, *t*-BuO = =O), and **26** (Cl = exo OAc, *t*-BuO = H) show a singlet for the corresponding proton α to Cl in the first case and α to OAc in the latter two cases; in contrast the epimeric hydrogen appears as a doublet of a doublet: B. K. Stevenson and D. H. Jones, unpublished observations.

(10) P. D. Bartlett, G. N. Fickes, F. C. Haupt, and R. Helgeson, *Accounts Chem. Res.*, **3**, 177 (1970).



minimum column containing 15% QF-1 on Anakrom 70-80 ABS; (2) 28 ft × 0.25 in. aluminum column containing 9% FFAP on Anakrom 70-80 ABS.

Reaction of *exo*-Tricyclo[3.2.1.0^{2,4}]oct-6-ene with *tert*-Butyl Hypochlorite.—The title olefin (1.40 g, 13.2 mmol) was dissolved in 4 ml of carbon tetrachloride in a flask provided with a reflux condenser, a drying tube, and a magnetic stirrer. The flask was covered with aluminum foil to avoid exposure to light. After addition of *tert*-butyl hypochlorite (0.71 g, 6.5 mmol), the foil was removed and the flask was placed in a 40 ± 2° bath and irradiated for 20 min with a 300-W Sylvania light bulb from a distance of 1 in. After partial removal of volatile components at reduced pressure (20 mm), the mixture (1.37 g) was analyzed by vpc (column 1, 140°, 40 ml/min). The product mixture contained two components in the ratio of 78:22 (in the order of increasing retention times) in a yield of 56%.

The 78% component was identified as *exo*-6-*tert*-butoxy-*endo*-7-chloro-*exo*-tricyclo[3.2.1.0^{2,4}]octane (trans adduct) on the basis of its spectral data: ir (neat) 3088 and 3032 (w, cyclopropane C–H stretching), 1190 (s), 1116 (s), 1064 (s), 1030 (s) (C–O stretching region), 806 (s) and 755 cm^{-1} (m) (C–Cl stretching region); nmr (100 MHz, CCl_4) τ 6.22 (poorly resolved doublet of doublet, J = 2.9, 2.0 Hz, HCCl), 6.61 (triplet, J = 2.0 Hz, HCO-*t*-Bu), 7.63 (unresolved multiplet, bridgehead proton β to chlorine), 7.94 (singlet, the bridgehead proton β to *tert*-butoxy), 8.5–8.9 (multiplets with a large singlet at 8.86, 11 H, the anti C-8 proton, the *tert*-butoxy protons, and the C-4 proton), 9.08 (a poorly resolved multiplet of a doublet of an AB pattern, J = 12 Hz, the syn C-8 proton), 9.2–9.5 (multiplets, the C-2 proton and the syn C-4 proton), and 9.65–9.92 (a quartet, J = 7 Hz, the anti C-3 proton).

Anal. Calcd for $C_{12}H_{19}OCl$: C, 67.13; H, 8.92. Found: C, 67.29; H, 9.07.

The 22% component was identified as *exo*-6-*tert*-butoxy-*exo*-7-chloro-*exo*-tricyclo[3.2.1.0^{2,4}]octane (cis adduct) on the basis of its spectral data: ir (neat) 3092 (w) and 3032 (s), both assignable to cyclopropane C–H stretching, 1195 (s), 1110 (s), 1090 (s), 1080 (s), 1030 (s) (C–O stretching, region), 745 (s), 712 cm^{-1} (s) (C–Cl stretching region); nmr (100 MHz, CCl_4), τ 6.23 (doublet of a doublet, J = 6.0, 2.3 Hz, HCCl), 6.51 (doublet of a doublet, J = 6, 1.9 Hz, 1 H, HCO-*t*-Bu), 7.69 (singlet, 1 H, the bridgehead proton β to chlorine), 7.96 (singlet, 1 H, the bridgehead proton β to *tert*-butoxy), 8.55 (a doublet of an AB pattern, J = 11 Hz, the anti C-8 proton), 8.83 (a large singlet, 9 H, the *tert*-butoxy protons), 9.25 (an unresolved multiplet of a doublet of an AB pattern, J = 11 Hz, the syn C-8 proton), 9.3–9.5 (multiplet, 3 H, the C-2, C-4, and syn C-3 protons), and 9.7–9.9 (multiplet, the anti C-3 proton).

Anal. Calcd for $C_{12}H_{19}OCl$: C, 67.13; H, 8.92. Found: C, 67.05; H, 8.72.

Reduction of the Trans Adduct, *exo*-6-*tert*-Butoxy-*endo*-7-chloro-*exo*-tricyclo[3.2.1.0^{2,4}]octane, with Tri-*n*-butyltin Hydride.—A sample of the trans adduct (0.12 g, 0.56 mmol) was combined with tri-*n*-butyltin hydride (0.17 g, 0.58 mmol) and a crystal of AIBN in a small tube, and the tube was sealed and placed in a 95° bath. After 12 hr the tube was cooled and opened and the contents were analyzed by vpc (column 2, 155°, 40 ml/min). There was only one product, estimated to be formed in a yield of *ca.* 90%. The product was identified as *exo*-6-*tert*-butoxy-*exo*-tricyclo[3.2.1.0^{2,4}]octane on the basis of its spectral data and the similarity of its nmr spectrum to that of *exo*-6-hydroxy-*exo*-tricyclo[3.2.1.0^{2,4}]octane: ir (neat) 3092 (w), 3016 (m) (cyclopropane C–H stretching), 1195 (s), 1185 (s), 1155 (s), 1088 (s), 1060 (s), 1025 cm^{-1} (s) (C–O stretching region); nmr (100 MHz, CCl_4) τ 6.54 (doublet of a doublet of a doublet, J = 7.0, 3, 1 Hz, HCO-*t*-Bu), 7.87 (poorly resolved multiplet, the bridgehead proton β to *tert*-butoxy), 7.95 (singlet, 1 H, the other bridgehead proton), 8.35 (a doublet of an AB pattern split additionally by 2 H, J = 12.5, 7.0, 2.2 Hz, the endo C-7 proton), 8.75 (a doublet of an AB pattern split into a pair of triplets, J = 12.5, 3 Hz, the exo C-7 proton), 8.86 (singlet, 9 H, the *tert*-butoxy protons), 8.96 (a doublet of an AB pattern, J = 12 Hz, the anti C-8 proton), 9.28 (a doublet of an AB pattern, J = 12 Hz, with additional splitting by 3 H, J = 1 Hz, the syn C-8 proton), 9.35–9.6 (multiplet, the C-2, C-4, and syn C-3 protons), and 9.85–10.09 (multiplet, 1 H, the anti C-3 protons).

Anal. Calcd for $C_{12}H_{20}O$: C, 79.91; H, 11.19. Found: C, 79.93; H, 11.15.

Reduction of the Cis Adduct, *exo*-6-*tert*-Butoxy-*exo*-7-chloro-*exo*-tricyclo[3.2.1.0^{2,4}]octane, with Tri-*n*-butyltin Hydride.—The cis adduct (0.044 g, 0.21 mmol) was reduced with tri-*n*-butyltin hydride (0.0575 g, 0.198 mmol) with AIBN initiation under conditions identical with those employed for the trans adduct. Vpc analysis (column 2, 155°, 40 ml/min) showed only one product, in a yield of *ca.* 64%, which had retention time and ir spectrum identical with those of the product obtained from the trans adduct.

Reaction of *endo*-Tricyclo[3.2.1.0^{2,4}]oct-6-ene with *tert*-Butyl Hypochlorite.—The endo olefin (3.13 g, 29.5 mmol) in 6 ml of carbon tetrachloride was irradiated with *tert*-butyl hypochlorite (1.57 g, 14.5 mmol) for 20 min at 40 ± 2° with a 300-W Sylvania light bulb as in the case of the exo olefin. After partial removal of solvent at reduced pressure, the mixture was analyzed by vpc (column 1, 140°, 40 ml/min). Two adducts were observed in the ratio 43:57 in the order of increasing retention times, formed in a yield of 59%. There was no peak in the monochloride region.

The 43% component was identified as *exo*-6-*tert*-butoxy-*endo*-7-chloro-*endo*-tricyclo[3.2.1.0^{2,4}]octane (trans adduct) on the basis of its spectral data: ir (neat) 3096 (w), 3040 (w) (cyclo-

propane C–H stretching), 1190 (s), 1125 (s), 1096 (s), 1065 (s), 1040 (s) (C–O stretching region), 783 (m), 770 (m), 748 (m) and 736 cm^{-1} (m); nmr (100 MHz, CCl_4) τ 6.24 (doublet of a triplet, J = 3.4, 0.7 Hz, HCCl), 6.58 (broad, poorly resolved multiplet, $W_{1/2}$ = 5 Hz, HCO-*t*-Bu), 7.5 (envelope, 1 H, the bridgehead proton β to chlorine), 7.9 (envelope, 1 H, the bridgehead proton β to *tert*-butoxy), 8.0 (a broad singlet, 2 H, the C-8 protons), 8.28 (a pair of overlapping triplets, J = 7, 3 Hz, the syn C-3 proton), 8.55–8.75 (multiplet, the C-2 and C-4 protons), 8.82 (singlet, 9 H, the *tert*-butoxy protons), and 9.03 (multiplet, the anti C-3 proton).

Anal. Calcd for $C_{12}H_{19}OCl$: C, 67.13; H, 8.92. Found: C, 67.10; 8.89.

The 57% component was identified as *exo*-6-*tert*-butoxy-*exo*-7-chloro-*endo*-tricyclo[3.2.1.$0^{2,4}$]octane on a consideration of its spectral data: ir (neat) 3080 (shoulder), 3032 (shoulder) (cyclopropane C–H stretching), 1190 (s), 1114 (s), 1104 (s), 1042 (s) (C–O stretching region), 780 (s), 770 (s), 757 (m), 750 (s), 718 cm^{-1} (s) (C–Cl stretching region); nmr (100 MHz, CCl_4) τ 6.36 (doublet of a doublet, J = 5.6, 1.7 Hz, HCCl), 6.68 (doublet of a doublet, J = 5.6, 1.7 Hz, HCO-*t*-Bu), 7.68 (envelope, the bridgehead proton β to chlorine), 7.73 (a component of an AB pattern, J = 9.5 Hz, the anti C-8 proton), 7.92 (envelope, 1 H, the bridgehead proton β to *tert*-butoxy), 8.15 (multiplet of the B doublet of the AB pattern, J = 9.5 Hz, the syn C-8 proton), 8.60–8.80 (multiplet, the C-2 and C-4 protons), 8.82 (singlet, 9 H, the *tert*-butoxy protons), and 9.0–9.35 (complex multiplet, the C-3 protons).

Anal. Calcd for $C_{12}H_{19}OCl$: C, 67.13; H, 8.92. Found: C, 67.11; H, 8.90.

Reduction of the Trans Adduct, *exo*-6-*tert*-Butoxy-*endo*-7-chloro-*endo*-tricyclo[3.2.1.$0^{2,4}$]octane, with Tri-*n*-butyltin Hydride.—The trans adduct (0.081 g, 0.38 mmol) was treated with tri-*n*-butyltin hydride (0.114 g, 0.392 mmol) and cyclohexane (60 μl) in a small tube. Approximately 5 μl was removed for later analysis. A crystal of AIBN was added and the tube was sealed and placed in a 95° bath for 12 hr. Vpc analysis (column 2, 155°, 40 ml/min) showed only one product, formed in a yield of 75% (*vs.* cyclohexane internal standard). The product was identified as *exo*-6-*tert*-butoxy-*endo*-tricyclo-[3.2.1.$0^{2,4}$]octane on the basis of its spectral data and on the basis of the similarity of its nmr spectrum to that of *exo*-6-hydroxy-*endo*-tricyclo[3.2.1.$0^{2,4}$]octene: ir (neat) 3064 (w), 3016 (shoulder) (cyclopropane C–H stretching), 1194 (s), 1086 (s), and 1030 cm^{-1} (s) (C–O stretching region); nmr (100 MHz, CCl_4) τ 6.74 (doublet of doublets, J = 6.4, 3.0 Hz, finer splitting of each of the lines to about 0.5 Hz was also observable, HCO-*t*-Bu), 7.8 (unresolved multiplet, bridgehead proton β to *tert*-butoxy), 8.0 (unresolved multiplet, 1 H, the other bridgehead proton), 8.2 (broad singlet, 2 H, the C-8 protons), 8.6–8.85 (complex multiplets, 4 H, protons on C-7, C-2, and C-4), 8.9 (singlet, 9 H, *tert*-butoxy protons), 9.1–9.45 (complex multiplets, 2 H, protons on C-3).

Anal. Calcd for $C_{12}H_{20}O$: C, 79.91; H, 11.19. Found: C, 79.80; H, 11.00.

Reduction of the Cis Adduct, *exo*-6-*tert*-Butoxy-*exo*-7-chloro-*endo*-tricyclo[3.2.1.$0^{2,4}$]octane, with Tri-*n*-butyltin Hydride.—A sample of the cis adduct (0.15 g, 0.71 mmol) was reduced with tri-*n*-butyltin hydride (0.21 g, 0.73 mmol), cyclohexane (130 μl), and a crystal of AIBN under conditions identical with those used for the trans isomer. Vpc analysis (column 2, 155°, 40 ml/min) showed only one product in a yield of *ca.* 97% (*vs.* cyclohexane internal standard). The sole product was identical with the one obtained from the trans adduct as observed by comparison of vpc retention times and ir spectra.

Reaction of Deltacyclene with *tert*-Butyl Hypochlorite.—The reaction of deltacyclene[11] (4.00 g, 34 mmol) in carbon tetrachloride (11 ml) with *tert*-butyl hypochlorite (1.84 g, 17 mmol) was performed exactly as above for the other olefins. Vpc analysis of the products (column 1, 155°, 45 ml/min), after partial removal of solvent at reduced pressure (20 mm), showed four peaks in the ratio 12.5:4.5:66:17 in the order of increasing retention times. The 12.5% component showed a multiplicity of signals, including aromatic proton signals, in the nmr and possibly arose from indene, a contaminant in deltacyclene. The 4.5% component on further vpc analysis was found to be a mixture of four components none of which showed the correct molecular weight for the monochloride or the *tert*-butyl hypochlorite addition product on mass spectra analysis.

The 66 and 17% components were identified as the trans and cis adducts on the basis of their spectral data and on the basis of their reduction to *exo*-8-*tert*-butoxydeltacyclane. The trans adduct (66% component) had the following spectral characteristics: ir (neat) 3056 (w) (cyclopropane C–H stretching), 1185 (s), 1152 (m), 1060 (s), 1021 (s) (C–O stretching region), 800 (s) (nortricyclene), 790 (s), 775 (m), 733 cm^{-1} (m) (C–Cl stretching region); nmr (100 MHz, CCl_4) τ 6.07 (doublet of a doublet, J = 4.0, 2.0 Hz, HCCl), 6.24 (poorly resolved doublet, J = 2 Hz, HCO-*t*-Bu), 7.8 (unresolved multiplet, bridgehead proton β to chlorine), 7.88 (unresolved multiplet, bridgehead proton β to *tert*-butoxy), 8.15 (unresolved triplet, C-6 proton), 8.42 (singlet, 2 H, C-5 protons, 8.74 (singlet, 2 H, C-2 and C-3 protons), 8.82 (singlet, 9 H, *tert*-butoxy protons), 9–9.15 (multiplet, the C-4 proton).

Anal. Calcd for $C_{13}H_{19}OCl$: C, 68.85; H, 8.45. Found: C, 68.58; H, 8.23.

The cis adduct (17% component) was contaminated to the extent of about 32% by an unidentified material: ir (neat) 3056 (w) (cyclopropane C–H stretching), 1185 (m), 1086 (s) (C–O stretching region), 800 (s) (nortricyclene ring), 765 (w), 715 cm^{-1} (w) (C–Cl stretching region); nmr (100 Mz, CCl_4) τ 5.9 (doublet, J = 6.0 Hz) and 6.15 (doublet, J = 6 Hz).

Anal. Calcd for $C_{13}H_{19}OCl$: C, 68.85; H, 8.45. Found: C, 68.50; H, 8.23.

Reduction of the Trans Adduct, *exo*-8-*tert*-Butoxy-*endo*-9-chlorodeltacyclane, with Tri-*n*-butyltin Hydride.—A sample of the trans adduct (0.1780 g, 0.786 mmol) was treated with tri-*n*-butyltin hydride (0.25 g, 0.85 mmol) and cyclohexane (100 μl) in a small tube. Approximately 4 μl was removed for later analysis. A crystal of AIBN was added and the tube was sealed and placed in a 95° bath for 10 hr. After cooling to room temperature, the tube was opened and the contents were analyzed by vpc (column 2, 155°, 40 ml/min). There was only one product (*ca.* 81% yield *vs.* cyclohexane internal standard) which was identified as *exo*-8-*tert*-butoxydeltacyclane on the basis of its spectral data and the similarity of its nmr spectrum to that of *exo*-8-hydroxydeltacyclane: ir (neat) 3056 (w) (cyclopropane C–H stretching), 1190 (s), 1178 (s), 1136 (m), 1070 (s), 1040 cm^{-1} (s) (all C–O stretching region); nmr (100 MHz, CCl_4) τ 6.2 (poorly resolved multiplet of a doublet, J = 6.6 Hz, HCO-*t*-Bu), 8–8.25 (a series of poorly resolved multiplets, 4 H, bridgehead protons on C-1 and C-7, endo proton on C-9 and the proton on C-6), 8.46 (singlet with adjacent multiplet, 3 H, C-5 and exo C-9 protons), 8.85 (large singlet with a poorly resolved multiplet buried under it, 10 H, *tert*-butoxy and the C-4 protons), and 9.25 (multiplet, 2 H, the C-2 and C-3 cyclopropyl protons).

Anal. Calcd for $C_{13}H_{20}O$: C, 81.17; H, 10.49. Found: C, 81.30; H, 10.62.

Reduction of the Cis-Adduct, *exo*-8-*tert*-Butoxy-*exo*-9-chlorodeltacyclane, with Tri-*n*-butyltin Hydride.—The cis adduct (0.0490 g, 0.22 mmol) was reduced with tri-*n*-butyltin hydride (0.0680 g, 0.23 mmol), cyclohexane (*ca.* 40 μl), and a crystal of AIBN at 95° for 10 hr. Vpc analysis (column 2, 155°, 40 ml/min) showed two products in the ratio of 68:32 in a yield of *ca.* 67%. The 68% component was identical (retention time and ir) with the sole product obtained on reduction of the trans adduct. The 32% component could not be isolated in sufficient quantities to enable its characterization.

Registry No.—**7**, 3635-95-8; **8**, 3635-94-7; **9**, 7785-10-6; **10**, 36005-00-2; **11**, 36005-01-3; **12**, 36005-02-4; **13**, 36005-03-5; **14**, 36005-04-6; **15**, 36005-05-7; **22** (endo Cl), 36005-06-8; **22** (exo Cl), 36005-07-9; **22** (Cl = H), 36005-08-0; *tert*-butyl hypochlorite, 507-40-4.

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