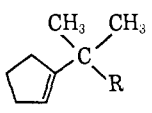
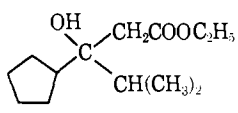
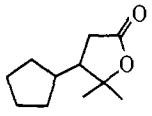
The structures of **1** and **2** were deduced from their spectroscopic properties[9] and then confirmed through oxidation with peroxytrifluoroacetic acid[10] to the related butyrolactones **9a** and **10a**, which were identical with samples prepared in the following fashion. For **9a** the long-known[11] carboxylic acid **11** was first converted through an Arndt–Eistert synthesis[12] to the homologous ester **12**.[3] Saponification of this ester and then treatment with hot dilute hydrochloric acid led to **9a**[3,9] without difficulty. For **10a**, hydroxy ester **13**[3] was prepared by a Reformatsky reaction[13] between cyclopentyl isopropyl ketone[14] and α-bromoacetic ester. Hydrolysis of **13** gave the related carboxylic acid, which underwent dehydration and cyclization in mineral acid to yield **10a**[3,9] as well as the isomeric lactone **14**.[3] These lactones were readily separated by preparative vpc.



11, R = COOH
12, R = CH_2COOCH_3



13



14

Our second route to **1** and **2** starts with lactones **9a** and **10a** and proceeds in the reverse direction. Each lactone was converted to the related ortho lactone, **9b** and **10b**, respectively, on reaction[15] with triethyloxonium fluoroborate and then ethanol containing sodium ethoxide. These ortho lactones were treated[16] directly with tosylhydrazide to furnish lactone tosylhydrazones **9c**[9,17] and **10c**.[9,17] The dry sodium salt derived from each tosylhydrazone was then pyrolyzed at 310° to give the desired cyclobutanones **1** and **2** in yields of 42[5] and 20%,[5] respectively. This transformation, which we have discussed in some detail elsewhere,[18] presumably involves rearrangement of intermediate oxycarbenes **9d** and **10d**, formed on thermal elimination of molecular nitrogen and *p*-toluenesulfinate anion from the salts. Our previous experience included decomposition of lactone tosylhydrazone salts having five-, six-, and seven-membered rings and indicated that the yield of cyclopentanone and cyclohexanone from appropriate precursors was significantly higher than yields of cyclobutanones. In this earlier work,[18] lactone tosylhydrazones were prepared indirectly through imino lactone salts, themselves available by various means from acyclic compounds. The noteworthy aspect of the present examples from the point of view of synthesis is the successful conversion of readily available lactones into derived tosylhydrazones and thence into cyclic ketones. Formally this constitutes a reversal of the Baeyer–Villiger oxidation;[10,19] if general, it should be a synthetically useful process.

We shall discuss additional examples of each of these reactions in later reports.

Acknowledgment. It is a pleasure to acknowledge partial support of this research by the National Science Foundation through Grant No. GP-17319.

(9) Characterization data are given below: **1**, ir 1775 cm^{-1} (vs); nmr (220 MHz) δ 1.14 (s, 6 H), 1.36–1.81 (m, 8 H), 2.66 (s, 2 H); **2**, 1775 cm^{-1} (vs); nmr (220 MHz) δ 0.927 (d, J = 5 Hz) and 0.955 (d, J = 5 Hz) (6 H), 1.36–2.08 (m, 10 H), 2.60 (d of d, J_1 = 17, J_2 = 8 Hz, 1 H), 2.82 (d of d, J_1 = 17, J_2 = 8 Hz, 1 H); **9a**, ir 1780 cm^{-1} (vs); nmr (220 MHz) δ 1.09 (s, 6 H), 1.55–2.04 (m, 8 H), 2.26 (s, 2 H); **10a**, ir 1780 cm^{-1} (vs); nmr (220 MHz) δ 0.945 (d, J = 7 Hz) and 0.950 (d, J = 7 Hz) (6 H), 1.55–2.03 (m, 9 H), 2.03–2.27 (m, 2 H), 2.36–2.59 (m, 1 H); **9c**, ir 3200, 1680, 1160 cm^{-1}; nmr (220 MHz) δ 0.93 (s, 6 H), 1.5–1.9 (m, 8 H), 2.40 (s) and 2.41 (s) (5 H), 7.28 (d, J = 8 Hz, 2 H), 7.38 (s, 1 H), 7.82 (d, J = 8 Hz, 2 H); mp 147.5–150.5°; **10c**, ir 3200, 1685, 1160 cm^{-1}; nmr (220 MHz) δ 0.80 (d, J = 7 Hz, 3 H), 0.92 (d, J = 7 Hz, 3 H), 1.5–2.1 (m, 10 H), 2.32 (d of d, J_1 = 17, J_2 = 5 Hz, 1 H), 2.42 (s, 3 H), 2.72 (d of d, J_1 = 17, J_2 = 4 Hz, 1 H), 7.28 (m, 3 H), 7.80 (d, J = 8 Hz, 2 H); mp 137.5–140.5°.

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

Sir:

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-norbornenyl,[2] 7-norbornenyl,[3] and cholesteryl.[4] The reactions of these radical intermediates have, in all cases to date, been most 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*-tri-

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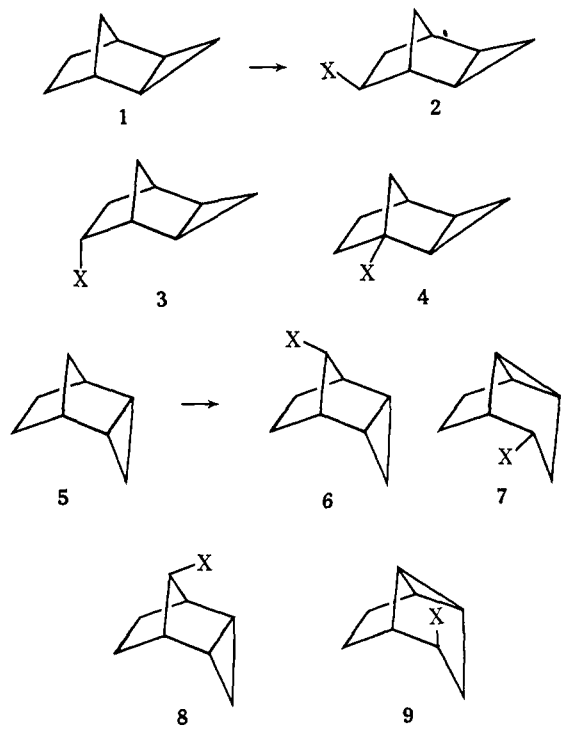
cyclo[3.2.1.0^{2,4}]oct-8-yl (10^{14})[8] substrates suggested that the most favorable ring system for a radical abstraction study would be *endo*-tricyclo[3.2.1.0^{2,4}]octane (**5**), using *exo*-tricyclo[3.2.1.0^{2,4}]octane (**1**) as a standard.

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- (**2**-Cl), *endo*-6-chloro (**3**-Cl), and 1-chloro-*exo*-tricyclo[3.2.1.0^{2,4}]octane (**4**-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 tri-*n*-butyltin hydride (AIBN initiation, 95°) combined with spectral analysis of the three major product components. The infrared and nmr spectral data of the 67% component (100-MHz nmr τ 6.25 (d split by additional 2 H, J = 6.5, 3.5, 2.0 Hz, 1 H), 7.60 (s, 1 H), 7.75 (m, 1 H), 8.03 (A of AB, split by additional two protons, J = 13, 7, 2 Hz, 1 H), 8.33 (B of AB, split by additional 2 H, J = 13, 3.5 Hz, 1 H), 8.78 (d, J = 11 Hz, 1 H), 9.11 (d, J = 11 Hz, with additional poorly resolved splitting, J = 2 Hz, 1 H), 9.22–9.62 (m, 3 H) 9.77–10.03 (m, 1 H)) were identical with those of an authentic sample of **2**-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 (d of t, 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 (q, J = 7 Hz, 1 H)) is consistent with that expected for the endo-6 isomer (**3**-Cl) and nmr and infrared comparison with a standard prepared by treatment of **2**-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 (t of d, J = 7, 3 Hz, 1 H), 9.13 (t of d, J = 7, 3 Hz, 1 H), 9.37 (overlapping pair of triplets, J = 7, 3 Hz, 1 H), 9.87 (q, J = 7 Hz, 1 H)), the correct structure must be that of bridgehead chloride **4**-Cl. As a second check on the ring skeleton, reduction of the 17% component with tri-*n*-butyltin hydride (AIBN initiation) produced tricyclooctane **1** as the sole hydrocarbon, reinforcing the structural assignment.

In the case of the *endo*-tricyclooctane ring system, irradiation of *endo*-tricyclooctane **5** 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 **6**-Cl. The rate of solvolysis in 80% aqueous acetone at 25° (k = 6.10 × 10^{-4} sec^{-1}, k(**6**-Cl)/k(*anti*-7-norbornenyl chloride) = 10^3)[10] as well as the solvolytic products (hydrolysis, **7**-OH exclusively; methanolysis in the presence of $CaCO_3$, **7**-OCH_3 exclusively) support the assignment. The 27% component exhibited identical retention time and infrared and nmr spectra with an authentic sample of rearranged *endo*-**7**-Cl.[11] The 5% component (A) was not completely characterized, but analysis of the nmr spectrum (τ 6.05 (1 H, d of t, J = 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, d of t), 8.97–9.26 (1 H)) demonstrates that it is not the syn-7 chloro epimer **8**-Cl and most likely not the exo rearranged chloride **9**-Cl (**9**-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.



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) not too dissimilar to that observed for the reaction of the 2-norbornyl radical with *tert*-butyl hypochlorite (7).[12] The normal exo:endo C-6 ratio and lack of skeletal rearrangement argue against any delocalization involving either the C-2–C-4[13] or C-2–C-3[14] cyclopropane bonds in the intermediate radical. The large fraction of hydrogen abstraction at C-1, however, is surprising in view of the lack of bridgehead abstraction which has

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been noted for norbornane[15,16] and norbornene.[17,18] The factors which are responsible for the unique role of the fused cyclopropane unit are presently under investigation.

In sharp contrast to the radical substitution pattern found for *exo*-tricyclooctane **1**, attack of *tert*-butoxy radical on *endo*-tricyclooctane **5** at C-8 occurs to an extent of 93% or greater. Since neither *anti*-8-chloride **6**-Cl nor rearranged **7**-Cl undergoes epimerization or skeletal rearrangement during the reaction conditions or vpc analysis, it seems reasonable to assume that *endo*-**7**-Cl is a primary product, and the question arises as to whether the products are generated *via* a rapid equilibrium of radicals (**10** ⇌ **11**) or a single delocalized radical **12**. The dilution experiments listed in Table I

Table I. Reaction of *tert*-Butyl Hypochlorite with **5** in CCl_4 at 40°

Run	Concn of **5**, *m*	Concn of *t*-BuOCl, *m*	Product composition, %[a] **6**-Cl	**7**-Cl	A	B
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] ±2%.

demonstrate that at high concentrations of chain transfer agent the first formed radical 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 (**10** ⇌ **11**) is favored over **12**. However, in addition, one must explain the regiospecificity for C-8 abstraction and the stereoselectivity of the radicals leading to C-8 unrearranged (anti:syn ≥ 66:2) and C-2 rearranged (endo:exo > 27:2) products (run 1). It seems clear that the high preference for C-8

10 11 12

abstraction must be due to abstraction of the anti C-8 hydrogen with the generation of a transition state in which the electronegative *tert*-butoxy radical induces some carbonium ion character on the tricyclooctyl moiety. Thus, the evidence suggests trishomocyclopropenyl anchimeric assistance to hydrogen abstraction in the transition state.[19] Once the anti C-8 hydrogen is removed, a localized pyramidal radical similar in structure to **10** might be formed. A combination of competition of chain transfer with inversion and greater steric access to the anti side ($LiAlH_4$ reduction of *endo*-tricyclo[3.2.1.$0^{2,4}$]octan-8-one gives **6**-OH–**8**-OH in a ratio of 33:67)[8] might explain the stereoselectivity. However, steric access to the C-2 position of radical **11** would be expected to be highly biased toward exo approach ($LiAlH_4$ reduction of tricyclo[3.3.0.$0^{4,6}$]-octan-2-one yields entirely *endo*-2-alcohol). Thus, intermediate **10** rearranges to a second intermediate, which, although reasonably well represented by structure **11**, might possess some degree of transannular interaction of the cyclopropane bond with the radical center, hence protecting the exo face from attack.

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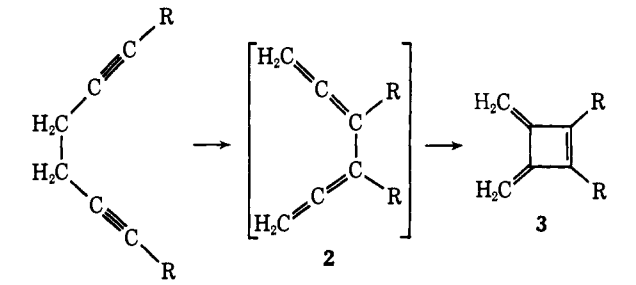
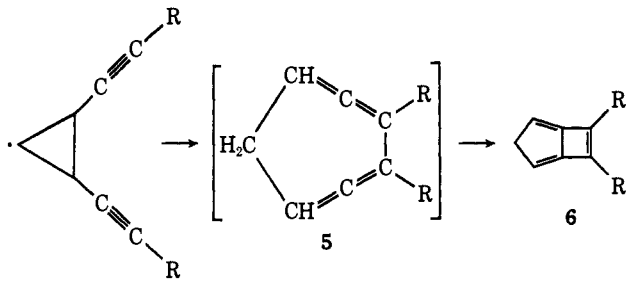
Independent Mechanisms in the Thermal Rearrangement of Mono- and Bicylic 3,4-Bismethylenecyclobutene Derivatives

Sir:

Thermolysis of 1,5-hexadiynes at moderate temperature produces 3,4-bismethylenecyclobutene derivatives.[1,2] For example, compounds **1** and **4** rearrange at 250° to trienes **3** and **6**, presumably *via* intermediate diallenes[3] **2** and **5**.



1 2 3



4 5 6

a, R = H
b, R = D

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