intensity) 302 (M$^+$, 25), 274 (11), 261 (5), 246 (2), 195 (5), 181 (8), 169 (4), 153 (3), 141 (5), 115 (5), 105 (100), 77 (98), 62 (8), 51 (5).

Anal. Calcd for $C_{21}H_{18}O_2$: C, 83.45; H, 5.96. Found: C, 83.20; H, 6.15.

Thermolysis of 2,3-Dibenzoylbicyclo[2.2.2]oct-2-ene (12). A sample of 12 (1.0 g, 2.3 mmol) was heated in a sealed tube at around 310–320 °C for 1 h. The reaction mixture, after cooling, was chromatographed over silica gel. Elution with a mixture (4:1) of petroleum ether and benzene gave 400 mg (44%) of 2-benzoyl-3-phenylbicyclo[2.2.2]oct-2-ene (**14**): mp 124 °C (after recrystallization from petroleum ether); IR (KBr) ν_{max} 3040, 2900, 1641 (C=O), 1620, and 1600 cm^{-1}; UV (methanol) λ_{max} 230 nm (ϵ 8050), 247 (12 900), 254 (11 200), 282 (4700); NMR ($CDCl_3$) δ 1.68 (8 H, m, CH_2 protons), 3.45 (2 H, m, bridgehead protons), 7.00–7.50 (10 H, m, aromatic protons); mass spectrum, *m/e* (relative intensity) 288 (M$^+$, 84), 260 (13), 232 (3), 211 (8), 183 (7), 165 (5), 155 (18), 153 (14), 151 (11), 141 (8), 128 (11), 115 (15), 105 (80), 77 (100), 51 (15).

Anal. Calcd for $C_{21}H_{20}O$: C, 87.50; H, 6.90. Found: C, 87.32; H, 6.60.

Thermolysis of 2,3-Dibenzoyl-7-oxabicyclo[2.2.1]hept-2-ene (16). A sample of 16 (1.52 g, 5 mmol) was heated at around 310 °C for 1 h in a sealed tube. Workup of the mixture by chromatography over silica gel with elution with a mixture (4:1) of petroleum ether and benzene gave 1.02 g (74%) of 3,4-dibenzoylfuran (**17**): mp 131 °C; IR (KBr) ν_{max} 3180, 2956, 1660 (C=O), 1460, and 1300 cm^{-1}; UV (ethanol) λ_{max} 252 nm (ϵ 59 900); NMR ($CDCl_3$) δ 6.84 (6 H, m, phenyl protons), 7.19–7.25 (6 H, m, phenyl protons and the olefinic protons of the furan ring); mass spectrum, *m/e* (relative intensity) 276 (M$^+$, 26), 275 (6), 248 (4), 247 (4), 231 (2), 220 (8), 219 (6), 200 (8), 199 (52), 171 (40), 143 (5), 115 (20), 105 (60), 78 (12), 77 (100), 76 (5), 65 (5), 51 (40).

Anal. Calcd for $C_{18}H_{12}O_3$: C, 78.48; H, 4.30. Found: C, 78.74; H, 4.18.

Thermolysis of 2,3-Dibenzoylbicyclo[2.2.1]hept-2-ene (19). Heating of a sample of **19** (0.6 g, 2 mmol) at around 310 °C for 1 h and workup of the mixture by chromatography over silica gel with elution with a mixture (4:1) of petroleum ether and benzene gave 160 mg (30%) of 2-*endo*-3-*exo*-dibenzoylbicyclo[2.2.1]heptane (**20**): mp 106 °C; IR (KBr) ν_{max} 3080, 2940, 2870, 1665 (C=O), 1595, 1580 cm^{-1}; UV (ethanol) λ_{max} 210 nm (ϵ 5700), 248 (24 500), 278 (4150); NMR ($CDCl_3$) δ 1.43–1.83 (6 H, m, CH_2 protons), 2.67–2.88 (2 H, m, bridgehead protons), 4.27 (1 H, d, H_3 proton, $J_{2,3}$ = 4.0 Hz), 4.58 (1 H, m, H_2 proton), 7.63–8.13 (10 H, aromatic protons); mass spectrum, *m/e* (relative intensity) 304 (M$^+$, 3), 238 (20), 200 (6), 199 (43), 184 (3), 171 (14), 157 (2), 134 (3), 133 (33), 115 (2), 106 (8), 105 (100), 91 (3), 78 (6), 77 (63), 67 (3), 66 (11), 55 (9), 51 (5).

Anal. Calcd for $C_{21}H_{20}O_2$: C, 82.88; H, 6.57. Found: C, 82.94; H, 6.47.

Hydrogenation of 2-*endo*-3-*exo*-Dibenzoylbicyclo[2.2.1]hept-5-ene (21). A solution of 1.56 g (5 mmol) of **21** in 150 mL of acetone was hydrogenated over 5% Pd on $CaCO_3$ for 1 h at room temperature and 10 psi of H_2. Removal of the catalyst by filtration and of the solvent under reduced pressure gave a product which on recrystallization from methanol gave 1.42 g (93%) of 2-*endo*-3-*exo*-dibenzoylbicyclo[2.2.1]heptane (**20**), mp and mmp 105–106 °C.

Acknowledgment. The authors thank the Office of Basic Energy Sciences of the U.S. Department of Energy, the Department of Science and Technology, Government of India, and the Indian Institute of Technology, Kanpur, for financial support of this work. We thank Mr. C. Vijaya Kumar for partial experimental assistance and Dr. E. D. Jemmis for helpful discussions.

Registry No. 11, 66933-94-6; 12, 73367-68-7; 14, 74007-31-1; 15, 66933-95-7; 16, 74007-32-2; 17, 52762-45-5; 18, 1096-50-0; 19, 56585-39-8; 20, 74035-77-1; 21, 74007-33-3; 24, 2363-83-9.

Reactions of Cyclopropyl Chlorides with Metals and Lithium Naphthalene Radical Anion and Dianion[1]

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Received April 29, 1980

The reaction of *exo*- and *endo-anti*-3-chlorotricyclo[3.2.1.0^{2,4}]oct-6-ene with magnesium in THF followed by deuterolysis gave syn/anti deuteration ratios of 2.2 and 0.42, respectively, with 85% monodeuterium incorporation. Analysis of the exo hydrocarbon involved epoxidation followed by a shift-reagent study with Eu(fod)$_3$. Reaction of the same halides with Na/*t*-BuOD gave 95% deuterium incorporation with syn/anti ratios of 1.2 and 0.37, respectively. Similarly, reaction of *anti*-3-chloro-*exo*-tricyclo[3.2.1.0^{2,4}]octane with Na, K, and Li in *t*-BuOD/THF gave 95% deuterium incorporations with syn/anti ratios of 2.11, 1.25, and 1.70. No effect of temperature or solvent composition was observed in the potassium reduction. Reaction of this halide with Li in Et_2O followed by D_2O gave 87% deuterium incorporation with a syn/anti ratio of 2.1, while reaction with lithium naphthalene in THF at −78 °C followed by addition of D_2O gave 96% deuterium incorporation with a *syn*/anti ratio >100. All of the above results are described in terms of radical equilibria and competing electron transfers. Reaction of *anti*-3-bromo-*exo*-tricyclo[3.2.1.0^{2,4}]octane with butyllithium in ether at 0 °C followed by deuterolysis gave entirely anti deuteration (anti/syn ratio >16) with 95% deuterium incorporation. Reaction of *anti*-3-chloro-*exo*-tricyclo[3.2.1.0^{2,4}]octane with lithium naphthalene dianion proceeded at −78 °C in THF with a rate constant of 5.5×10^{-2} M^{-1} min^{-1}, while under identical conditions lithium naphthalene exhibited a rate constant of 1.0 M^{-1} min^{-1}. Deuterolysis of the dianion solution gave a *syn* to *anti* deuterium incorporation ratio greater than 50.

Our original interest in the reactions of metals and alkali radical anions with cyclopropyl chlorides was sparked by the need to develop methods for replacement of a leaving group at C-3 in tricyclo[3.2.1.0^{2,4}]oct-6-ene (1) or tricyclo[3.2.1.0^{2,4}]octane (**5**) systems with deuterium in a stereospecific manner, so that either syn (**2**, **6**) or anti (**3**, **7**) 3-deuterio substrates could be prepared. During the course of our study, procedures for the desired transformations were successfully developed, and the very interesting intrinsic nature of these transformations emerged as the dominant theme of our investigation.

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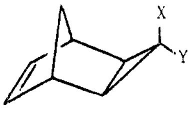
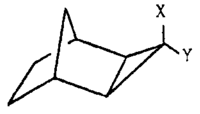
[1] Reported in part in preliminary form: P. K. Freeman, L. L. Hutchinson, and J. N. Blazevich, *J. Org. Chem.*, **39**, 3606 (1974).

0022-3263/80/1945-3191$01.00/0

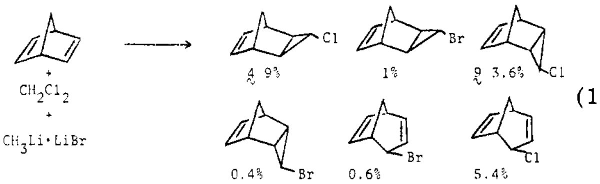


1 X,Y = H
2 X = D, Y = H
3 X = H, Y = D
4 X = H, Y = Cl



5 X,Y = H
6 X = D, Y = H
7 X = H, Y = D
8 X = H, Y = Cl

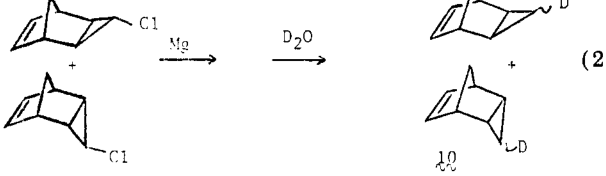
Reactions of Cyclopropyl Chlorides with Metals. The synthesis of our first key cyclopropyl chloride, *anti*-3-chlorotricyclo[3.2.1.0^{2,4}]octene (4), by addition of chlorocarbenoid to norbornadiene gave a variety of products, as anticipated,[2] in approximately 20% total yield (eq 1).



(1)

The allylic halides could be easily removed by treatment with aqueous silver nitrate, but separation of the exo and endo ring systems was much more difficult. The anti-exo and -endo cyclopropyl chlorides, 4 and 9, could not be separated by distillation or gas chromatography, but it was discovered that both the chlorides and the corresponding hydrocarbons could be separated by elution chromatography on a column of silver nitrate impregnated Silicar.

Since cyclopropyl Grignard reagents have proved to be configurationally stable under moderate reaction conditions,[3] the Grignard reaction was a reasonable starting point for the present study. It was found, however, to be repeatedly impossible to induce reaction of a purified mixture of 4 and 9 with magnesium in spite of addition of methyl iodide and dibromoethane and even slow addition of butyl bromide. All the additives underwent reaction, but no conversion of the cyclopropyl chlorides was observed. On the other hand, reaction of the crude mixture from the methyllithium–methylene chloride synthesis proceeded quite rapidly. Perhaps this was due to the presence of the bromides. Quenching the Grignard reaction mixture with D_2O followed by chromatography using silver nitrate on Silicar gave the pure deuterated hydrocarbons (eq 2). The products from the allylic halides were not investigated.



(2)

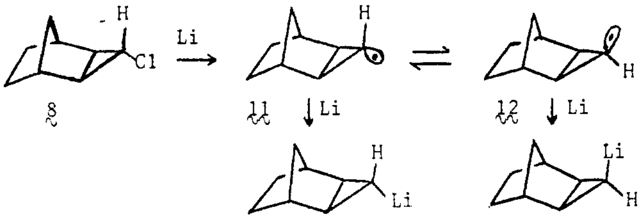
It is not possible to analyze the mixture of 1, 2, and 3 directly by NMR due to the coincidence of a number of absorptions. Epoxidation with peracetic acid followed by addition of europium shift reagent [Eu(fod)$_3$] allowed both the *syn*- and *anti-C-3* proton absorptions to be separated from the other resonances. Examination of the NMR spectrum so obtained indicated the mixture of 1, 2, and 3 was 89 ± 5% monodeuterated with an excess of syn (2) over anti (3) deuterium incorporation in a ratio of 2.2 ± 0.3 to 1. Direct examination of 10 revealed 85 ± 5% deuterium incorporation with an excess of anti over syn deuterium incorporation in a ratio of 2.4 ± 0.5 to 1. Similarly, reduction of a mixture of 4 and 9 with sodium in *tert*-butyl alcohol-*O-d*–THF followed by the same analytical procedure just described indicated the exo hydrocarbon mixture (1, 2, and 3) to be 98 ± 5% deuterated with a syn/anti (2/3) ratio of 1.16 ± 0.2, while the endo hydrocarbon (10) was 93 ± 5% deuterated with anti deuteration predominating over the syn in a 2.7 ± 0.3 to 1 ratio. It is striking that the exo and endo isomers give such different syn to anti ratios, being essentially reversed in the case of the Grignard reaction.

Table I. Stereochemistry of Reduction of Selected Cyclopropyl Halides with Metals

halide	conditions	syn-D/anti-D[a]
4	(1) Mg, THF; (2) D_2O	2.2 ± 0.3
4	Na-*t*-BuOD-THF, reflux	1.16 ± 0.2
9	(1) Mg, THF; (2) D_2O	0.42 ± 0.09
9	Na-*t*-BuOD-THF, reflux	0.37 ± 0.05
8	(1) Li, Et_2O, 0 °C; (2) D_2O	2.1 ± 0.3
8	Li-*t*-BuOD-THF, reflux	1.70 ± 0.05
8	Na-*t*-BuOD-THF, reflux	2.11 ± 0.05
8	K-*t*-BuOD-THF, reflux	1.25 ± 0.05

[a] Standard deviations from NMR integration data.

Scheme I



Our second cyclopropyl chloride substrate, *anti*-3-chlorotricyclo[3.2.1.0^{2,4}]octane (8), while preserving an essentially identical stereochemical environment at the reactive center, proved to be a much more convenient system for the development of the chemistry under consideration. Its synthesis from norbornene and methylene chloride–methyllithium, as before, although giving low yields, does not give rise to any of the troublesome endo adducts.[4] The corresponding hydrocarbon can be analyzed for syn and anti deuterium incorporation directly by 100-MHz NMR since the two protons are out in the open, with only minor overlap of the *syn*-C-3 proton and the C-2 and C-4 protons marring integration accuracy. The results of treatment of anti cyclopropyl chloride 8 with potassium, sodium, and lithium in *tert*-butyl alcohol-*O-d*–THF and with lithium in ether followed by deuterolysis are compiled in Table I along with the results just discussed. Deuterium incorporations were above 95%.

The mechanism[4,5–7] commonly put forward for reactions such as these is illustrated here by the reaction of anti cyclopropyl chloride 8 with lithium in ether (Scheme I). The classic ESR experiments of Fessenden and Schuler[8] in 1963 indicated that secondary cyclopropyl radicals have

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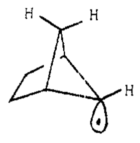
(2) R. M. Magid and S. E. Wilson, *J. Org. Chem.*, **36**, 1775 (1971).
(3) H. M. Walborsky and A. E. Young, *J. Am. Chem. Soc.*, **86**, 3288 (1964).
(4) C. W. Jefford and R. T. Medary, *Tetrahedron Lett.*, 4123 (1967).
(5) H. W. H. J. Bodewitz, C. Blomberg, and F. Bickelhaupt, *Tetrahedron Lett.*, 281 (1972).
(6) H. M. Walborsky and M. S. Arnoff, *J. Organomet. Chem.*, **51**, 55 (1973).
(7) M. J. S. Dewar and J. M. Harris, *J. Am. Chem. Soc.*, **91**, 3652 (1969).
(8) R. W. Fessenden and R. H. Schuler, *J. Chem. Phys.*, **39**, 2147 (1963).

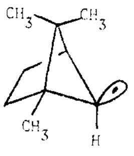
a pyramidal configuration but interconvert with a rate constant of 10^8–10^{10} s^{-1}. Thus it is apparent that only very fast reactions could trap even a fraction of the initially formed radical before equilibration. It would not seem unreasonable, however, to propose that a metal surface might be capable of donating an electron rapidly enough. After all, the radical is formed on or very near the surface and has to diffuse only a short distance (if any at all) to pick up another electron. It is apparent from the high deuterium incorporations that few radicals escape from the surface.

The syn to anti ratios observed from **4** and **8** are postulated to result from competition between inversion of the initially formed radical and its trapping by reaction on the surface to form the metal alkyl. It is thought that the syn radical **12** might be more stable than the anti radical **11** due to the compressional effect of the *syn*-C-8 and *syn*-C-3 hydrogens in the anti epimer **11**.

A similar argument has been presented by Kawamura in an ESR study of the bicyclo[2.1.1]hex-5-yl radical.[9] An analysis of the hyperfine splitting constants led to the conclusion that radicals **13** and **14** have the configurations shown.



13



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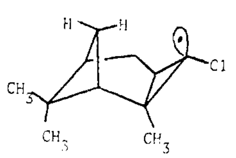

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The change in the orientation of the radical lobe with methyl substitution (**13** → **14**) was attributed to the compressional effect of the C-6 methyl group on the α-H in the radical epimeric with **14**. In a second ESR study, which included an investigation of the *exo*-tricyclo-[3.2.1.0^{2,4}]oct-3-yl radicals, Kawamura et al.[9] put forward the syn radical structure **12** for the stable epimer to rationalize the hyperfine splitting constants for this radical and some related cyclopropyl radicals. Hatem and Waegell[11] have used similar arguments to explain syn stereospecificity in the reactions of the α-halocyclopropyl radical **15**.

While cyclopropyllithium and Grignard reagents have been shown to be configurationally stable,[3,12,13] the corresponding sodium and potassium reagents are another matter. If one assumes that the metal alkyl is initially formed in the least stable syn configuration and is able to isomerize to the anti configuration at a rate competitive with reaction with *tert*-butyl alcohol-*O-d*, it would be expected that varying the alcohol concentration from high to low values might increase the proportion of the anti product. However, no change was observed upon changing the ratio of THF to alcohol from zero to 30 in the reduction with potassium. This suggests that the protonation of the potassium alkyl is faster than epimerization at all concentrations of *tert*-butyl alcohol employed. The product ratio observed must then be the result of a competition between inversion of the radical and its diffusion back to the metal surface where it is then trapped as the metal alkyl. On this basis, changing the temperature should induce a change in the product ratio. The rate of diffusion of a molecule is directly proportional to the temperature and inversely proportional to viscosity.[14] On the other hand, the rate of inversion of the radical should be exponentially related to temperature, and one might well expect that this would outweigh the effect of temperature on diffusion. Thus it was expected that markedly lowering the temperature would greatly increase the degree of retention. Since lowering the temperature of the reaction also decreases its rate, experimentally it was necessary to produce a colloidal form of potassium to increase the surface area and thus the rate of reaction. This was accomplished by evaporating metallic potassium onto a frozen surface of THF under high-vacuum conditions. It was found that when this was warmed, a black, very finely divided suspension of potassium results. This suspension was not stable at temperatures of −40 °C or above, as it conglomerated under such conditions. The experiment was performed by depositing layers of *tert*-butyl alcohol-*O-d*, THF, potassium metal vapor, THF, *tert*-butyl alcohol-*O-d*, and finally **8**. The frozen layers were then melted by being warmed to −90 °C in a slush bath and then stirred for 30 min. The mixture was then stirred at −78 °C for 1.5 h. At this temperature, a visable reaction occurred, resulting in a lightening of the color of the precipitate. Upon workup, it was found that the deuterium incorporation in the hydrocarbon was excellent at 95%, but, surprisingly enough, the syn to anti incorporation ratio was 1.28—almost exactly the same as that obtained in refluxing THF. This result seemed at first to be inconsistent with the proposed mechanism; however, it can be accommodated by theory if the experimental activation energy for radical inversion is taken to be 1.7 kcal.

The data of Carvajal and co-workers on the viscosity of THF may be manipulated to calculate the viscosity at −80 and +65 °C;[15] this then allows the calculation of the theoretical ratio of diffusion rate constants: $k_{\text{diff}}^{-80}/k_{\text{diff}}^{65} = 0.087$. By use of the Eyring equation and with the assumption that $\Delta S^\ddagger$ is zero, the ratio of rates for inversion of **11** to **12** is $k_{\text{inv}}^{-80}/k_{\text{inv}}^{65} = [193e^{-\Delta H^\ddagger/(1.98)(193)}]/[338e^{-\Delta H^\ddagger(1.98)(338)}]$. Setting $k_{\text{inv}}^{-80}/k_{\text{inv}}^{65}$ equal to 0.087 gives $\Delta H^\ddagger = 1.7$ kcal. This is a perfectly reasonable value for the heat of activation for a cyclopropyl radical. Ab initio MO–SCF calculations performed by Ellinger and co-workers[16] place the inversion barrier for the cyclopropyl radical itself at 3.8 kcal. It must be emphasized that the value of 1.7 kcal obtained above does not constitute a "value" for the inversion barrier since the mechanism is undoubtedly much more complex than that assumed. It simply demonstrates that it is not yet necessary to discard the proposed mechanism because of the lack of temperature dependence observed.

Reaction of *anti*-3-Chlorotricyclooctane 8 with Lithium Naphthalene. At this point, an attractive experimental alternative for the generation of radicals and subsequently lithium reagents under conditions which would preserve the configuration of the cyclopropyllithium

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[9] M. Matsunaga and T. Kawamura, *J. Am. Chem. Soc.*, **97**, 3519 (1975).

[10] T. Kawamura, M. Tsumura, Y. Yokomichi, and T. Yonezawa, *J. Am. Chem. Soc.*, **99**, 8251 (1977).

[11] P. J. Hatem and B. Waegell, *Tetrahedron Lett.*, 2019 (1973).

[12] H. M. Walborsky, F. J. Impastato, and A. E. Young, *J. Am. Chem. Soc.*, **86**, 3283 (1964).

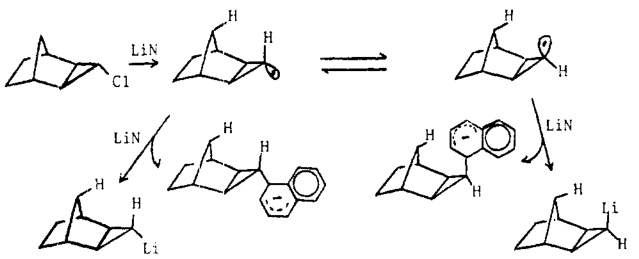
[13] H. M. Walborsky and M. S. Arnoff, *J. Organomet. Chem.*, **51**, 55 (1973).

[14] D. N. Hague, "Fast Reactions", Wiley-Interscience, New York, 1971.

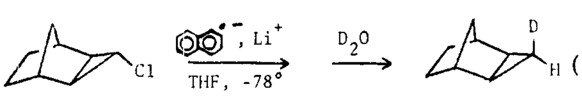
[15] C. Carvajal, K. J. Tölle, J. Smid, and M. Szwarc, *J. Am. Chem. Soc.*, **87**, 5548 (1965). These authors have reported the viscosity of THF over the temperature range of 25 to −70 °C. Although the temperatures involved in our study are outside this range, it was found by nonlinear least-squares methods that Caravajal's data can be represented very well by the equation $\eta_{\text{THF}} = 2.80 + (1.63 \times 10^3) \exp -0.02279T$, where T is the temperature in K and η is in millipoises (standard deviation 0.9%). Using this equation to extrapolate the viscosity data to −80 and +65 °C, one may calculate the ratio of $k_{\text{diff}}^{-80}/k_{\text{diff}}^{65}$.

[16] Y. Ellinger, R. Subra, B. Levy, P. Millie, and G. Berthier, *J. Chem. Phys.*, **62**, 10 (1973).

Scheme II



reagents appeared to be the alkyl halide–lithium radical anion reaction.[17] The reaction of the *anti*-3-chlorotricyclooctane **8** with lithium naphthalene in THF at −78 °C followed by deuterolysis gave surprising results: 96% deuterium incorporation and a syn/anti ratio of at least 100:1—complete inversion (eq 3). One might imagine several reasons for the extremely high stereospecificity observed. Primary, secondary, and tertiary halides give large amounts of coupling products in the reaction with sodium naphthalene.[18-21] The two radicals, anti cyclopropyl (**11**) and syn cyclopropyl (**12**), might differ markedly in their abilities to form bonds with the bulky naphthalene radical anion. Thus, the possibility existed that the high stereospecificity resulted from exclusive coupling in the case of the unhindered anti radical and exclusive electron transfer in the case of the highly hindered syn radical (Scheme II). To test this possibility, we carefully searched for the alkylated naphthalenes by gas chromatography, but none were found.[22] Another theory easily disposed of would have the *anti*-lithium reagent isomerizing to the syn reagent. This would seem highly unlikely on energetic grounds, and there is little reason to believe that the lithium reagents in question would not be stereochemically stable at −78 °C, since similar compounds are known to be stable at room temperature.[7,13] However, in order to prove the contention that the lithium reagents are stable, we performed metal–halogen exchange of **16** with butyllithium at 0 °C, followed by deuterolysis. Only the anti-deuterated material was obtained (eq 4).



(3)

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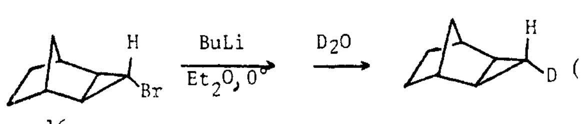
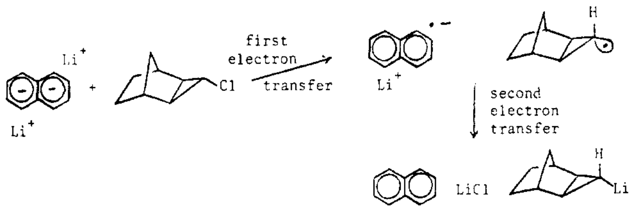


(4)

16

Testimony to the fact that cyclopropyllithium reagents are configurationally very stable was obtained from an experiment in which *anti*-3-chlorotricyclooctane **8** was treated with lithium naphthalene at −78 °C, followed by slow warming of the mixture to 0 °C over a period of 6 h and then quenching with deuterium oxide. Although the lithium reagent had apparently attacked the solvent, since it was only 82% deuterated, no isomerization had occurred in spite of the very high strain of the *syn*-lithium reagent.

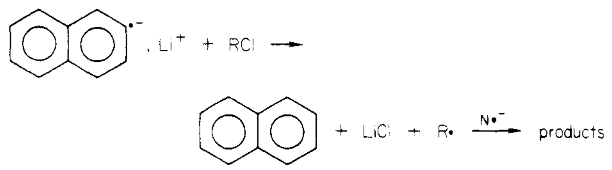
Scheme III



The theory which seems to be most likely is essentially identical with that discussed for the metal reduction of cyclopropyl chlorides **4**, **8**, and **9**. In that case, it is postulated that the radicals are formed almost in contact with the metal surface, which can then quickly donate another electron—fast enough to trap some of the first-formed radical. In the present case, the first-formed radical would have to have a diffusive encounter with another lithium naphthalene ion pair, and this can be estimated to require approximately 10^{-8} s in 0.1 M lithium naphthalene at −80 °C.[23] This rate of trapping is undoubtedly several orders of magnitude slower than that on the surface of a metal.

Since the rate at which radicals are scavenged by lithium naphthalene is likely to be very close to diffusion controlled, it is highly unlikely that any selectivity could be exhibited by the radical anion in reacting with one configuration faster than another. Even if the rate is not diffusion controlled, it would be expected that there would exist no selectivity to the steric requirements of a radical. This conclusion is based on the fact that electron transfer can occur over rather large distances.[25] Consequently, since coupling products are not observed, we are left with the conclusion that the syn cyclopropyl radical **12** is more stable than the anti cyclopropyl radical **11**.

Reaction of *anti*-3-Chlorotricyclooctane 8 with Lithium Naphthalene Dianion. The reaction of a lithium naphthalene ion pair with a halide produces an alkyl radical with an inert naphthalene molecule in juxtaposition. The radical must then diffuse to another radical anion with the proper spin state to produce the final product, requiring on the order of 10^{-8} s (eq 5).



(5)

It was reasoned that the corresponding reaction of the dianion would result, after the first electron transfer, with the radical in juxtaposition not with a "dead" naphthalene molecule but rather with a very much "alive" radical anion and in the proper spin state. The second electron, then, might be transferred within the solvent shell soon enough to capture the first-formed configuration of the radical before inversion has time to take place. In the case of anti cyclopropyl radical **11**, this would give the desired anti cyclopropyllithium reagent (Scheme III).

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(18) J. F. Garst, J. T. Barbas, and F. E. Barton, II, *J. Am. Chem. Soc.*, **90**, 7159 (1968).

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(20) J. F. Garst and F. E. Barton, II, *Tetrahedron Lett.*, 587 (1969).

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(22) 7-Chloronorcarane also undergoes reaction with lithium naphthalene with no alkylation of naphthalene (<1%).[17]

(23) This can be estimated by using the equation[13] $k_{\text{diffusion control}} = (2RT/3000\eta)(2 + r_a/r_b + r_b/r_a)$ L/(mol s) = 1.9×10^9 L/(mol s) at −80 °C in THF. The particle sizes r_a and r_b were assumed to be equal, and η was taken as 0.023 P as above. It was also assumed that only one-fourth of the encounters would be singlets and capable of reaction.[24]

(24) J. K. Kochi, Ed., "Free Radicals", Vol. I, Wiley, New York, 1973, p. 40.

(25) K. Shimada and M. Szwarc, *Chem. Phys. Lett.*, **28**, 540 (1974).

The first attempts to form the dianion by reacting naphthalene and excess lithium chips were unsuccessful. The rate at which the lithium dissolved was apparently too slow relative to the rate of attack upon THF by the dianion. A purplish black solution was prepared from a lithium dispersion, and the syn to anti ratio of deuterium incorporation from the reaction with *anti*-3-chlorotricyclooctane 8 was only 6.8. It appears likely, however, that this lower syn/anti ratio was caused by some of the halide reacting with the excess lithium metal. Finally, a pure, deep purple solution of the dianion, free from excess lithium metal, was successfully made by a high-vaccum lithium-vaporization technique. Reaction of *anti*-3-chlorotricyclooctane 8 with this solution at −78 °C followed by deuterolysis gave only the syn-deuterated hydrocarbon—thus the hope of trapping the anti radical was not realized.

Is it possible that the dianion might be so unreactive that the small amount of monoanion present might be reacting to the exclusion of the dianion? For an answer to this question, it was necessary to determine the rate of reaction of the monoanion with *anti*-chloride 8 in the same apparatus and under the same conditions as those used for the dianion experiment. The value so obtained for the second-order rate constant for the reaction between lithium naphthalene and 8 is 1.0 M^{-1} min^{-1}. From knowledge of the dianion and radical anion concentrations during the dianion experiment and the pseudo-first-order rate constant, it may be determined that the dianion is, in fact, undergoing most of the reaction. If one were to assume that only the monoanion in the dianion solution were reacting, the second-order rate constant for the monoanion must be greater than 4.5 M^{-1} min^{-1}—almost 5 times faster than the actual measured rate constant for the monoanion. With the value of 1.0 M^{-1} min^{-1} for the second-order rate constant for the monoanion, the rate constant for the reaction of lithium naphthalene dianion in THF with *anti*-3-chlorotricyclooctane 8 is then calculated to be 0.055 M^{-1} min^{-1}. This value is only $^{1}/_{18}$th of the rate constant for the monoanion. Why, then, does the dianion, which is less stable than the monoanion, react so slowly, and why did the hoped-for trapping not occur? The answers to both questions may be the same. Dianions are expected to be very tight contact ion triples in ether solvents,[26] while the lithium naphthalene radical anion consists of loose ion pairs in THF.[27-29] It has also been demonstrated in at least two types of electron-transfer reactions, electron exchange[30-32] and dissociative electron attachment to alkyl iodides, bromides, and chlorides,[33,34] that tight ion pairs react between 1 and 2 orders of magnitude slower than free ions or loose ion pairs. Thus, although the dianion is a higher energy species than the monoanion, it reacts more slowly because of the great influence of ion pairing upon the rate of reaction. Similarly, it seems reasonable to postulate that the rate of reaction of a tight ion pair with a radical might be slower than the diffusion-controlled rate of the solvent-separated ion pairs studied by Garst. If this is the case, the anti cyclopropyl radical 8, as formed in reaction with the dianion, is in juxtaposition not with a highly active loose ion pair but with, perhaps, a half-dead contact ion pair. The radical might then simply diffuse away and convert to the more stable syn configuration before picking up a second electron.

Experimental Section

General Laboratory Procedures and Conditions All temperatures are uncorrected. NMR spectra were obtained on a Varian HA-100 spectrometer (100 MHz). IR spectra were obtained on a Perkin-Elmer 621 infrared spectrophotometer. Mass spectra were obtained by using an Atlas CH7 mass spectrometer. VPC analyses were carried out with a Varian Aerograph A90-P2. Unless otherwise noted, the detector and injector temperatures were set at 230 °C. The flow rate for $^{1}/_{4}$-in. columns were generally set at 60 mL/min, with ca. 20 mL/min for $^{1}/_{8}$-in. columns. The columns used were the following: column A, 4 ft × $^{1}/_{4}$ in., 5% CW20M on 30–60-mesh Chromosorb W; column B, 10 ft × $^{1}/_{4}$ in., 10% SE30 on Anakrom 110–120-mesh AS; column C, 10 ft × $^{1}/_{4}$ in., 10% Ucon water soluble with 1% KOH on 60–40-mesh Chromosorb W; column D, 8 ft × $^{1}/_{4}$ in., 10% CW20M on 30–60-mesh Chromosorb W; column E, 20 ft × $^{1}/_{8}$ in., 8% Apiezon N on 80–100-mesh Chromosorb W AS; column F, 15 ft × $^{1}/_{4}$ in., 5% OV-17 on 60–80-mesh Chromosorb G.

Either solvents were distilled from sodium benzophenone dianion and stored over 4A molecular sieves under nitrogen. Errors are standard deviations on multiple integrations (VPC or NMR) unless otherwise noted. The term high vacuum as used in this paper means 10^{-5} torr or less.

Preparation of *exo*- and *endo*-*anti*-3-Chlorotricyclo[3.2.1.0^{2,4}]oct-6-enes. The title chloride was prepared by the procedure of Magid and Wilson.[2] To a rapidly stirred mixture of 92 g (1 mol) of norbornadiene and 43 g (0.5 mol) of methylene chloride cooled in an ice bath was added dropwise over a period of 2 h 160 mL of 1.9 M MeLi·LiBr in ether (Alfa). Workup in the normal manner was followed by distillation through a short-path distillation apparatus. Material collected between 43 and 60 °C at 4.5 torr weighed 10 g (23% yield based on MeLi). The distilled material consisted of a mixture of the two title chlorides along with the corresponding bromides (ca. 10% of the chlorides) and the cyclopropane ring-opened halides. This mixture was used in the Grignard reaction described below. The ring-opened halides could be removed by treatment with a solution of 6 g of $AgNO_3$ dissolved in 100 mL of acetone and 10 mL of water for a few minutes. The standard workup followed by quick chromatography on alumina and then short-path distillation provided a pure mixture of *exo*- and *endo*-*anti*-chlorides in a ratio of 2:1 by NMR.

The two epimers could be separated by chromatography on a 10% $AgNO_3$ on Silicar column (see below) with a loading of 1 g on a 2.5 × 22 cm column. Ether (10%) in pentane was used as the eluant, with the progress of the separation being followed by TLC (see below).

Grignard Reaction of *exo*- and *endo*-*anti*-3-Chlorotricyclo[3.2.1.0^{2,4}]oct-6-enes. To 4.8 g of Mg turnings and 50 mL of THF in a nitrogen-filled 250-mL flask was added 2 mL of CH_3I. The solution rapidly turned milky gray, and, after 5 min, 18 g of the mixture of chlorides described immediately above was added in one lot. After 5 min, the solution began frothing with sufficient vigor to bring the material close to the top of the reflux condenser. When the reaction quieted down, a clear brown solution resulted, which was heated at reflux for an additional 12 h. Addition of 5 g of D_2O was followed 2 h later with sufficient HCl to dissolve the inorganic solids. Workup with pentane followed by distillation at 60–70 °C at 100 torr resulted in 5.5 g of a crude hydrocarbon mixture (0.5 g of forerun discarded). NMR showed the presence of the expected bicyclic and exo and endo tricyclic hydrocarbons, which were then purified as described below. In spite of many attempts, it was repeatedly impossible to induce reaction in a purified chloride mixture by using the normal Grignard techniques. This includes liberal use of $C_2H_4Br_2$ and CH_3I and slow addition of butyl bromide. All of the additives reacted with the Mg, but only very little conversion of the cy-

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clopropyl chlorides could be induced. The presence of approximately 10% of bromides in the crude mixture appears to be necessary for the Grignard reaction to proceed.

A portion (3.7 g) of the above hydrocarbon mixture was chromatographed on 140 g of 10% $AgNO_3$ on Silicar by using 10% ether in pentane, with the eluate being collected in 6-in. test tubes. Tubes 11–16 contained 0.8 g of endo compound, tubes 17–19 contained 0.5 g of a mixture of endo and exo compounds, and tubes 20–30 contained 1.9 g of exo compound. The remainder was eluted with 30% ether in pentane into a single flask and consisted of a mixture of the exo compound and diene.

An NMR spectrum of the endo material indicates 85 ± 5% D incorporation and an anti/syn ratio of 2.4 ± 0.5. In the deuterated material, the syn proton absorbs δ 0.33 (t, J = 3 Hz), while the anti proton absorbs at δ 0.53 (t, J = 7 Hz). Similar direct analysis of the exo isomer was not possible due to the coincidence of a number of absorptions. The analysis was accomplished by both epoxidation and hydroboration followed by shift-reagent NMR analysis.

Epoxidation and Analysis of 3-Deuterio-*exo*-tricyclo-$[3.2.1.0^{2,4}]$oct-6-ene from the Grignard Reaction. The purified *exo*-alkene (100 μL) was treated with 200 μL of 40% CH_3CO_3H, 30 mg of $NaOAc{\cdot}2H_2O$, and 50 μL of chloroform at 0 °C for 1 h. Dilution with 200 μL of pentane and extraction with 50% NaOH (3 × 1 mL) followed by VPC collection from column A at 100 °C (injector and detector temperatures 150 °C, flow rate 220 mL/min) gave 20 mg of pure epoxide. $Eu(fod)_3$ shift analysis indicated 90 ± 10% D incorporation with a syn/anti ratio of 2.5 ± 0.5. Integration of the syn proton was excellent, but the anti proton was difficult to integrate due to trailing from the fod protons. A separate run of epoxidation and shift analysis indicated 89 ± 5% D incorporation with a syn/anti ratio of 2.2 ± 0.3.

Hydroboration and Analysis of 3-Deuterio-*exo*-tricyclo-$[3.2.1.0^{2,4}]$oct-6-ene from the Grignard Reaction. To 62 mg of GC-collected *exo*-alkene and 46 mg of $NaBH_4$ dissolved in 10 mL of anhydrous 1,2-dimethoxyethane (DME) cooled to 0 °C was added with stirring 61 mg of H_2SO_4 dissolved in 10 mL of DME. The resultant solution was allowed to stir for 30 min at 0 °C and then for 30 h at 20 °C. To this mixture was then added, cautiously at first, 5.5 mL of 3 N NaOH followed by 5.5 mL of 30% H_2O_2. The mixture was then warmed to 40–50 °C for 30 min. The usual workup followed by VPC collection gave 20 mg of alcohol. A shift study $[Eu(fod)_3]$ indicated 70 ± 10% monodeuterium incorporation with a syn/anti ratio of 2.0 ± 0.5. Integration of the syn proton was marred by overlap with the cyclopropyl bridgehead protons, and the results of this study are considered less reliable than those with the epoxide.

Reduction of *exo*- and *endo*-*anti*-3-Chlorotricyclo-$[3.2.1.0^{2,4}]$oct-6-ene with Sodium in *tert*-Butyl Alcohol-*O*-*d*. To 0.5 g (3.5 mmol) of a mixture of *exo*- and *endo*-chlorides dissolved in 1 mL of *t*-BuOD and 1 mL of THF was added 230 mg (10 mmol) of Na in small pieces. The mixture was heated at reflux for 3 h, at which time no starting chlorides were observed by VPC. The contents of the flask were extracted with pentane, and the usual workup was followed by VPC collection (column B, 115 °C) which yielded 284 mg of hydrocarbon (76% yield). This mixture was subjected to $AgNO_3$ on Silicar chromatography followed by VPC collection to yield 65 mg of the exo hydrocarbon and 13 mg of the endo material. NMR analysis of the endo isomer indicated a 93 ± 5% D incorporation, with the anti/syn ratio being 2.7 ± 0.3. The exo isomer was converted to its epoxide by reaction with 60 mg of *m*-chloroperbenzoic acid (85%, Aldrich) in 200 μL of methylene chloride at 0 °C for 2 h. Workup with 3 N sodium hydroxide and pentane was followed by VPC collection from column C, with the collector and detector temperatures at 100 °C to prevent the facile decomposition. NMR $Eu(fod)_3$ shift analysis shows 98 ± 5% D incorporation, with the syn/anti ratio being 1.16 ± 0.2 (the error is an estimate based on the degree of overlap between the anti and syn proton resonances).

Preparation of a Silver Nitrate on Silicar Chromatography Column. To 23 g of Silicar contained in a 500 mL, 24/40 flask was added a solution of 2.3 g of $AgNO_3$ dissolved in 20 mL of water and 50 mL of acetone. The flask was placed on a rotary evaporator, and the acetone and water were removed with the aid of a heat lamp. The resultant dry powder was dried further in an oven at 70 °C for 4 h. A slurry of the 10% $AgNO_3$ on Silicar powder in pentane was then added in ca. 20 portions to a chromatography column filled with pentane. The column was rotated at a constant rate of one rotation in 4 s while the side of the column was gently but rapidly tapped with the rubber handle of a screwdriver. A layer of Ottowa sand $^1/_2$ in. deep was added to the top.

Table II

metal	time, h	yield, %	syn/anti ratio
Na	1.5	70	2.11
K	0.5	50	1.25
Li	1.0	16	1.70

Table III

THF added, mL	syn-/anti-D ratio	reflux time, h	isolated yield, %
0	1.27 ± 0.13	0.5	50
2	1.25 ± 0.10	0.5	50
6	1.22 ± 0.13	1.0	57
30	1.20 ± 0.06	3.0	53

Preparation of Silver Nitrate Impregnated TLC Plates. To 15 g of $AgNO_3$ dissolved in 100 mL of water was added 30 g of TLC grade PF254 silica gel. Glass microscope slides were dipped into the resultant slurry and air-dried. Development was with 10% ether in pentane, and the endo isomers of both the hydrocarbons and chlorides described above moved faster than the corresponding exo isomers. Visualization was accomplished by spraying the plates with dilute $KMnO_4$ in acetone.

Preparation of *anti*-3-Chloro-*exo*-tricyclo$[3.2.1.0^{2,4}]$octane. The title halide was prepared from the reaction of norbornene with methylene chloride and methyllithium–lithium bromide followed by treatment with $AgNO_3$ as before and use of a slight modification of the method of Jefford and Medary.[4] Other attempts at this preparation with a variety of bases including lithium 2,2,6,6-tetramethylpiperidide failed to give better yields.

Analysis of 3-Deuterio-*exo*-tricyclo$[3.2.1.0^{2,4}]$octane. In the NMR spectrum of the deuterated hydrocarbon, the anti proton absorbs at δ 0.23 (t, J = 7.26 Hz), while the syn proton absorbs at δ 0.15 (t, J = 3 Hz). The *syn*- and *anti*-deuterio compounds have their C–D stretching frequencies too close together to permit analysis by IR spectroscopy in this region.

Alkali Metal–*tert*-Butyl Alcohol-*O*-*d* in Tetrahydrofuran Reduction of *anti*-3-Chloro-*exo*-tricyclo$[3.2.1.0^{2,4}]$octane. To a solution of the title chloride (50 mg, 0.35 mmol) in a mixture of 1 mL of *t*-BuOD (98% monodeuterated) and 2 mL of anhydrous THF, heated at reflux, was added 5 mmol of the alkali metal. Heating at reflux was continued until aliquots indicated the absence of the starting chloride. Reaction times, yields, and *syn*/*anti*-deuterium ratios are given in Table II. Deuterium incorporations were above 95% as determined by NMR.

Effect of Solvent Composition on the Reduction of *anti*-3-Chloro-*exo*-tricyclo$[3.2.1.0^{2,4}]$octane with Potassium/*t*-BuOD. To a refluxing mixture of 1.0 mL of *t*-BuOD and the indicated amount of THF was added 150 mg of potassium metal followed 30 s later by 20 μL of the title chloride. The syn/anti deuteration ratio is presented in Table III. The deuteration in all cases was above 90%. The syn to anti deuteration ratio was determined by analysis of the NMR spectrum of the GC-collected material.

Reaction of *anti*-3-Chloro-*exo*-tricyclo$[3.2.1.0^{2,4}]$octane with Lithium in Ether. A suspension of Li was prepared by leaching 200 mg of a 20% Li (1% Na, 99% Li) dispersion in paraffin with two 3-mL portions of pentane followed by the addition of 3 mL of anhydrous ether. To this mixture was added 50 mg of the title chloride, and, after 1 min at room temperature, the flask was cooled to 0 °C. After 5 min the reaction was 75% complete, and after 15 min all the chloride was absent. D_2O (0.5 mL) was then added, followed by the usual workup and VPC collection to give a 40% yield, 87% deuterium incorporation, and a syn/anti ratio of 2.1 ± 0.3.

Reaction of *anti*-3-Bromo-*exo*-tricyclo$[3.2.1.0^{2,4}]$octane with *n*-BuLi. To 1 mL of 1 M *n*-BuLi in hexane (Ventron) and 3 mL of anhydrous ether was added 55 mg of the title bromide. After 10 min at 0 °C the reaction was complete. D_2O (1 mL) was added after 45 min, and workup as above gave 20 mg (85% yield) of hydrocarbon. NMR analysis indicated greater than 95% deuterium incorporation with a syn/anti ratio of less than 0.06:1.

Low-Temperature Reaction of *anti*-3-Chloro-*exo*-tricyclo[3.2.1.0^{2,4}]octane with Potassium and *t*-BuOD. A 500-mL, three-necked flask was connected to the high-vacuum line via the center neck. Into one neck was inserted a viewing window consisting of a piece of glass cut from a microscope slide and attached to a sawed-off, 24/40 inner joint with Torr-Seal epoxy. An assembly consisting of two 1.6-mm-diameter copper wires spaced 1 cm apart projecting through a 24/40 inner joint and sealed with Torr-Seal epoxy was placed in the other neck. The flask side of each wire was tipped with an alligator clip to hold a nichrome coil. The coil was formed from eight strands of no. 30 nichrome wire wound together with an electric drill and then formed around the sharpened end of a pencil. The cone-shaped coil was 2 cm long and had 4 cm of lead wire which, when attached to the alligator clips and inserted into the side arm, suspended the coil approximately in the center of the flask. Power was applied to the coil by a Variac (voltage usually ~10 V) connected to the projecting copper wires.

The flask was dried under high vacuum combined with flaming of the exterior of the vessel. After the flask was considered dry (ca. 3 h), nitrogen was admitted and, with a strong flow, the coil assembly was pulled out until the coil was accessible but still in the neck of the flask. A 200-mg piece of potassium metal, which had been cleaned with a knife under mineral oil, was washed with toluene and immediately placed in the coil. The assembly was seated in its joint, and the flask was immediately reevaculated. After 1 h at room temperature under a high vacuum, the flask was immersed in liquid nitrogen, and 1 mL of previously degassed *t*-BuOD was deposited on the walls of the flask, followed by about 20 mL of THF. The coil was then heated at about half the voltage required to produce a red glow. The potassium deposited over a period of 30 min, with the filament being constantly monitored through the window. The very dark blue-black coating was then covered with 15 mL of THF, 1.0 mL of *t*-BuOD, and, finally, 40 μL of the title chloride. All depositions were done slowly so as to minimize local melting. The flask was warmed to −90 °C with a toluene slush bath, and the black mixture was stirred for 30 min at this temperature. The mixture was then allowed to warm to −78 °C and was stirred for an additional 1.5 h. The blue-black suspension underwent visible reaction and slowly lightened to gray after 45 min. The mixture was allowed to warm to −10 °C over a period of 2 h, at which time the mixture consisted of a milky white suspension. Careful addition of water resulted in burning particles being shot out of the neck of the flask. Workup in the usual way and NMR analysis indicated at least 95% D incorporation and a syn/anti ratio of 1.28.

Reaction of *anti*-3-Chloro-*exo*-tricyclo[3.2.1.0^{2,4}]octane with Lithium Naphthalene. A solution of lithium naphthalene was prepared by stirring 2 g (15.6 mmol) of naphthalene, 0.10 g of Li (14 mmol) in small pieces, and 20 mL of THF at room temperature for 3 h. The dark green solution was cooled to −78 °C, and 50 mg of the title chloride dissolved in 3 mL of the THF was added dropwise. After stirring for 8 min, 1 mL of D_2O in THF (3 mL) was slowly added. The usual workup was followed by a two-stage VPC collection from column B. Coupling products were searched for by analyzing the crude reaction mixture on a short (3 ft), 5% SE-30 column under conditions where hydrocarbons of a similar molecular weight came off in 5 min (Ph_3CH, 250 °C). No peaks were observed in this region, and thus the maximum extent of coupling was estimated to be 0.1%.

NMR analysis indicated greater than 96% deuterium incorporation. The ratio of *anti*-C-3 proton NMR integration to *syn*-C-3 integration was 28:1, with the splitting pattern of the residual syn proton indicating that at least 75% of this signal originated from the undeuterated species. The syn/anti deuteration ratio corrected for the presence of undeuterated hydrocarbon is, therefore, at least 100:1.

Preparation of Lithium Naphthalene Dianion Using High Vacuum Line Techniques. Two 500 mL, three-necked, round-bottom flasks, each with a glass-covered stir bar, were attached in adjacent positions on the high-vaccuum line by their center necks. The right-hand flask was used for the vaporization of Li and formation of the dianion, while the left-hand flask was used for the reaction of the dianion with the chloride to be described below. A liquid-transfer assembly was constructed out of 4-mm Pyrex tubing and two 24/40 inner joints. When in place, one end of the tubing was near the bottom of the generation flask, with the tubing passing up through one joint, passing across the space between the two flasks, and terminating just inside the reaction flask. Between the two flasks the tubing was formed into a strain-relief coil of 4 turns 4 in. in diameter and 4 in. long. The open end in the generation flask was plugged with a tuft of glass wool to filter out Li particles. The remaining neck of the generation flask was used to hold the nichrome vaporization coil described above in the low-temperature potassium experiment.

The apparatus was dried under a high vacuum for several hours with intensive flaming, especially of the coil. With argon rather than nitrogen gas, a 200-mg cube of lithium was placed in the vaporization coil as described in the previous experiment. After the apparatus had been under high vacuum for approximately 1 h, the vaporization of the lithium was commenced. Difficulty was often encountered at this point for two reasons: (a) the oxide film on the molten lithium is very tough and tenacious, requiring that the entire apparatus be vibrated vigorously to break through the film; (b) when the lithium does wet the nichrome, it lowers the resistance of that portion of the filament which becomes covered with lithium, causing a greatly increased flow of current which often burns out that portion not wet with lithium. At the same time, the walls of the flask become blackened by the vaporized lithium, making it difficult or impossible to judge the temperature of the filament. For these reasons, it is suggested that, if at all possible, tungsten be substituted for nichrome in any such apparatus.

After the lithium vaporization was complete (15 min), the apparatus was pressurized with argon, the vaporization assembly was removed, and 100 mL of THF was vacuum transferred into the formation flask. Early experiments were confounded by rapid decomposition of the dianion solution and formation of a fine precipitate which clogged the glass-wool filter plug. These problems were alleviated by the removal of the vaporization assembly before dianion formation. Apparently, the decomposition of the dianion is catalyzed by metal contamination from the filament in analogy to the well-known catalysis of the sodium and ammonia reaction by traces of iron.

A solution of 1 g of naphthalene in 10 mL of THF was formed by the usual high vacuum line techniques and transferred under an argon flow to the generation flask with a dry argon-purged syringe. The mixture was stirred at 0–10 °C until VPC analysis of aliquots quenched in water showed a naphthalene to dihydronaphthalene ratio of less than 0.01. Column D was used in this and subsequent analyses. The dianion solution was then transferred to the reaction flask through the transfer tube and glass-wool filter plug by partially evacuating the reaction flask while keeping the generation flask pressurized. The reaction flask was cooled in a thick slurry of dry ice and isopropyl alcohol during and after the transfer. The color of the dianion solution is deep purple.

Reaction of *anti*-3-Chloro-*exo*-tricyclo[3.2.1.0^{2,4}]octane with Lithium Naphthalene Dianion Produced by High Vacuum Line Techniques. After the dianion solution described immediately above had stirred for 15 min at −78 °C, an aliquot was taken and quenched in water. VPC analysis as before showed that the conversion of naphthalene to its dianion was 99.4% complete, corresponding to the solution being ca. 0.00047 M in radical anion and 0.078 M in dianion. A mixture of 40 μL (45 mg) of the title chloride and 40 μL of tridecane (C_{13}) as internal standard was then injected. Aliquots were withdrawn at intervals with a dry nitrogen filled pipette and as rapidly as possible injected into 1 mL of water in a 2-dram vial. The stopper to the reaction flask was removed only far enough to allow insertion of the pipette, and a brisk stream of Ar exiting through the neck was used to minimize introduction of air.

The aliquots were analyzed by injection of about 50 μL of the organic phase into column D with the column temperature initially at 120 °C; the temperature was increased to 150 °C after the title chloride had eluted. Due to the low concentrations involved, VPC analyses of the aliquots are shown in Table IV.

The mixture was then quenched with D_2O (2 mL), and workup in the normal fashion was followed by VPC collection of the

Table IV

aliquot	time, min	chloride/C_{13} ratio	naphthalene/C_{13} ratio
1	10	1.27	0.76
2	20	1.04	1.11
3	30	1.04	1.16
4	55	1.04	1.16
5	80	0.709	1.12
6	109	0.643	1.43
7	175	0.592	
8	199	0.386	1.73

Table V

aliquot	time, min	chloride	Nap-H_2	Nap	chloride/(Nap + Nap-H_2)
1	8	4290	44 790	67 990	0.0380
2	23	2537	64 260	83 430	0.0172
3	35	721	39 630	63 670	0.00698

deuterated hydrocarbon from column D at 100 °C. The NMR indicated at least 97% D incorporation, with the syn/anti ratio being at least 50:1.

Least-squares fitting of a plot of ln (chloride/C_{13}) vs. time gave a pseudo rate constant of $5.4 \pm 0.7 \times 10^{-3}$ min^{-1}. If the halide were reacting exclusively with the dianion, the second-order rate constant at −78 °C would be $k_{N\text{-}2} = 6.8 \pm 2.0 \times 10^{-2}$ M^{-1} min^{-1}. The data given above indicates the concentration of the radical anion as determined by the relative proportion of naphthalene to internal standard upon hydrolysis increased by a factor of 2.3 from 10 min into the reaction to 200 min. If the halide were reacting exclusively with the radical anion, the plot of ln (chloride/C_{13}) vs. time should curve downward. While the plot does not appear to be curved, the extensive scatter in the data does not allow for definite conclusions to be made. Since the concentration of the radical anion was determined to be 4.7×10^{-4} M before the addition of the halide, it is likely that the concentration is ca. 1.2×10^{-3} M at point no. 8. If one (conservatively) used this to determine the second-order rate constant, assuming reaction with the radical anion rather than with the dianion, the value of 4.5 M^{-1} min^{-1} would be obtained. This is ca. 5 times as large as the actual rate constant determined for the radical anion below. Thus it would seem that most of the halide does in fact react with the dianion.

Kinetics of the Reaction of *anti*-3-Chloro-*exo*-tricyclo[3.2.1.0^{2,4}]octane with Lithium Naphthalene. This study was carried out exactly as in the case of the dianion, except that only 50 mg of Li was used, VPC separations were done isothermally at 150 °C, and the sum of the naphthalene (Nap) and dihydronaphthalene (Nap-H_2) signals was used as the VPC internal standard. The data from this study are shown in Table V. Taking the average value for the three aliquots of 2Nap-H_2/(Nap-H_2 + Nap) to be the fraction of the naphthalene converted to the radical anion, we arrive at a concentration of 0.063 M for the radical anion. Least-squares fitting of ln [RCl/(Nap-H_2 + Nap) ratio] vs. time gives a pseudo-first-order rate constant of 6.24×10^{-2} min^{-1} and thus a second-order rate constant of 1.0 M^{-1} min^{-1}, indicating that this reaction is about 15 times faster than the dianion reaction.

Stability Study of *syn*-3-Lithio-*exo*-tricyclo[3.2.1.0^{2,4}]octane. After the above kinetic analysis was complete, the reaction mixture was allowed to warm from −78 to 0 °C over a period of 6 h, before being quenched with D_2O. The deuterium incorporation was only 82%, and the syn/anti ratio could not be determined directly from the integration of the NMR signals. As in previous cases, an analysis of the intensities of the splitting of the *syn*-C_3 hydrogen signal was required. The corrected syn/anti ratio is at least 30:1.

Registry No. **1**, 3635-95-8; **2**, 74007-34-4; **3**, 74035-80-6; **4**, 29119-63-9; **6**, 52882-74-3; **7**, 52882-75-4; **8**, 6518-27-0; **9**, 29119-61-7; **16**, 15598-75-1; lithium naphthalene dianion, 29589-67-1; naphthalene, 91-20-3; naphthalene radical anion Li, 7308-67-0; *syn*-3-lithio-*exo*-tricyclo[3.2.1.0^{2,4}]octane, 74035-81-7.

Conformational Control of Oxabicyclobutane Fragmentations

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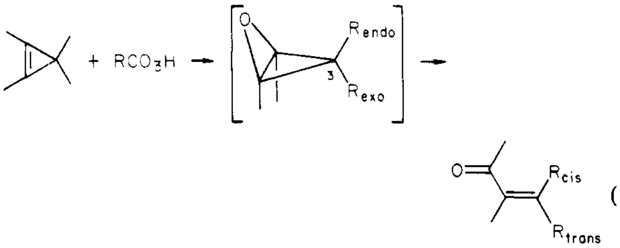
The generation and fragmentation of oxabicyclobutanes **4a–d** are described. These systems yield enones with complete loss of stereochemistry. A stepwise fragmentation is postulated for these and other oxabicyclobutane fragmentations.

Treatment of cyclopropenes with peracids is believed to give oxabicyclobutanes which are unstable and fragment to enones (eq 1). To date oxabicyclobutanes have been neither spectroscopically detected nor bimolecularly trapped. The evidence for oxabicyclobutanes is not only that enones are produced[3-7] but also that the kinetics of cyclopropene oxidation are consistent with an epoxidizing transition state.[8-12]



(1)

In spite of the inability to isolate oxabicyclobutanes in these reactions, we and others have sought to determine the stereochemistry of oxabicyclobutane fragmentations.

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[1] Taken from the Ph.D. thesis of R. A. Leckonby, who did the work on oxabicyclobutane **3b**.

[2] Taken from the Masters thesis of D. M. Stout, who did the work on oxabicyclobutane **3a**.

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