ticipated oxidative-coupling reactions of the catechol and quinone materials which might form as a result of the rearrangement of **2**.
(5) The synthesis of a compound like **2** was also attempted unsuccessfully by autoxidation of *p-tert*-butylphenyl isopropyl ether,[6] prepared by the procedures of White, *et al.*[7] Although only a limited number of autoxidation conditions were tried, no compound like **2** could be isolated.
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(17) CAUTION: High strength hydrogen peroxide forms highly explosive mixtures with many organic compounds. Adequate safety precautions were always taken when handling and using this material.
(18) Active oxygen content determined according to the following procedure (see Mair, *et al.*,[19] for further discussion). An accurately weighed sample of hydroperoxide in 50 ml of isopropyl alcohol, 10 ml of glacial acetic acid, and 1 ml of saturated KI solution was heated on a steam bath for 15 min, cooled, and titrated with standard aqueous $Na_2S_2O_3$.
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On Cyclopropyl Radical Intermediates in the *exo*-Tricyclo[3.2.1.$0^{2,4}$]octane System

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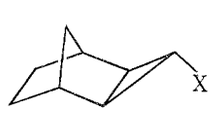
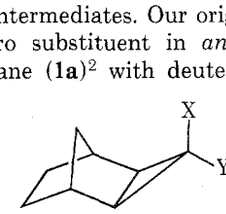
Prompted by the recent reports of Hatem and Waegell on the stereoselectivities of 1-halocyclopropyl radicals generated by halogen abstraction from *gem*-dihalocyclopropanes,[1] we report on the unique behavior of *exo*-tricyclo[3.2.1.$0^{2,4}$]octan-3-yl radical intermediates. Our original interest in replacing the chloro substituent in *anti*-3-chloro-*exo*-tricyclo[3.2.1.$0^{2,4}$]octane (**1a**)[2] with deuterium



1a, X = Cl
b, X = Br



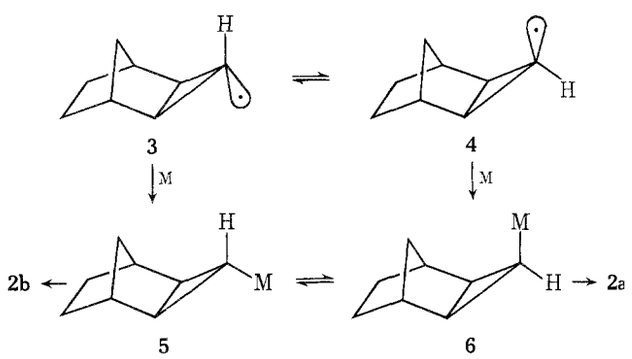
2a, X = D; Y = H
b, X = H; Y = D

was stimulated by the need for development of a method for syn and anti C-3 deuterium placement on this ring system in connection with a different mechanistic study; however, initial experiments revealed that the chemistry of replacement of chloro by deuterio by treatment of **1a** with alkali metals in deuterated solvents is of considerable intrinsic interest, allowing one to view the steric interaction in *anti*- and *syn*-tricyclooctyl radicals **3** and **4**. Treatment of *anti*-3-chlorotricyclooctane (**1a**) with sodium in *tert*-butyl alcohol-*O*-*d*–tetrahydrofuran generated tricyclooctane **2** with a syn C-3 deuterio:anti C-3 deuterio ratio (**2a:2b**) of 2.11 ± 0.05. Similar results were obtained when **1a** was allowed to react with potassium or lithium in *tert*-butyl alcohol-*O*-*d*–THF or with lithium in diethyl ether followed by deuterolysis (Table I). Since it is plausible that alkyl halides react with alkali metals in one-electron processes,[3] and since it is established that cyclopropyllithium derivatives[4] maintain configuration under moderate reaction conditions, it seems reasonable to suggest that the stereochemistry of replacement of chloro by deuterio is determined according to the sequence of steps outlined in Scheme I.

Table I
Reduction of Halotricyclooctanes 1a and 1b

Run	Halide	Reagent and Conditions	2a:2b
1	**1a**	Na/*t*-BuOD–THF, reflux	2.11 ± 0.05
2	**1a**	K/*t*-BuOD–THF, reflux	1.25
3	**1a**	Li/*t*-BuOD–THF, reflux	1.70
4	**1a**	(1) Li, Et_2O, 0°, (2) D_2O	2.1 ± 0.3
5	**1b**	(1) *n*-BuLi, Et_2O, 0° (2) D_2O	≤0.06
6	**1a**	(1) LiNaph, THF, −78°, (2) D_2O	≥100:1
7	**1a**	(1) LiNaph, THF, −78°, (2) 0°, (3) D_2O	≥30:1

Scheme I



This scheme explains the stereoselectivity in terms of (a) the preequilibrium of radicals created in the initial one electron transfer step, (b) the rate of trapping of the initially formed radical **3**, and (c) equilibration of the organometallics **5** and **6**. Reinforcement for the view that the *anti*-cyclopropyllithium substrate, once formed, is configurationally stable, was obtained by treatment of bromotricyclooctane **1b** with *n*-butyllithium, followed by deuterolysis, which afforded entirely *anti*-3-deuterio-*exo*-tricyclo[3.2.1.$0^{2,4}$]octane with no detectable quantity of syn-3-deuterio substrate (Table I). The generation of a cyclopropyllithium substrate with retention of configuration would be anticipated by analogy to similar reactions.[4b-d]

At this point an attractive, alternative approach to the generation of cyclopropyl radicals **3** and **4** and then cyclopropyllithium reagents under conditions which would prevent epimerization of the organolithium reagents was the treatment of chlorotricyclooctane with lithium naphthalenide[5] at a low temperature. The treatment of **1a** with lithium naphthalenide in THF at −78°, followed by neutralization with D_2O, generates syn-3-deuterio **2a** and anti-3-deuterio **2b** in a ratio of >100:1 (Table I). Since this high ratio of syn-3-deuterio to anti-3-deuterio could be the result of anti radical **3** coupling more rapidly with lithium naphthalenide than syn radical **4**, due to steric hindrance to approach of naphthalene radical anion, coupling products were searched for very carefully and none (<0.1%) detected. The results of lithium naphthalenide treatment not only provide insight into the chemistry of tricyclooctyl rad-

icals **3** and **4**, but allow a check to be made on the stability of the syn lithium reagent **6** under conditions similar to those of the reaction of **1a** with lithium–Et_2O (run 4). Run 6 was repeated and the reaction mixture allowed to warm up to 0°; neutralization with D_2O generated a ratio of **2a:2b** which was determined to be >30:1 establishing the stability of the syn lithium reagent. On the basis of these experiments, it seems reasonably certain, therefore, that the stereoselectivity in the reactions of alkali metals and lithium naphthalenide with **1a** is governed primarily by a radical preequilibrium such as that of Scheme I, the initially formed anti radical **3** being less stable than the syn radical **4** due to the greater severity of syn C_8-H–syn C_3-H nonbonding interactions relative to those of the syn C_8-H and the half-filled orbital at C-3. In the reactions of **1a** with lithium (run 4), the greater amount of anti-3-deuterio substrate relative to that observed in the reaction of **1a** with lithium naphthalenide is due to more efficient trapping of the initially formed radical on the surface of the metal, while in the reactions of **1a** with sodium and potassium the greater amount of anti-3-deuterio product is due, perhaps, to both an efficient trapping of initially formed radical and equilibration of **5** and **6**.[6]

Experimental Section

Analytical. Nuclear magnetic resonance spectra were obtained on a Varian Associates HA-100 spectrometer equipped with a digital time averaging accessory. Gas chromatography columns used include a 0.25 in. × 6 ft 5% CW20M on 60–40 Chromosorb PAW and a 0.25 in. × 10 ft 10% XF-1150 on 60–40 Chromosorb PAW. Halides **1a**[2] and **1b**[2] were purified by preparative glpc before use.

Work-up, in all cases, consisted of dilution of the reaction mixture with water followed by extraction with pentane. Pentane extracts were dried over Na_2SO_4 and most of the pentane was distilled off the product through a Vigreux column followed by preparative glpc of the residue.

Deuteration patterns of C-3 deuterated *exo*-tricyclooctane **2** were obtained by integration of the nmr signals of the syn C-3-H (δ 0.28, $J_{3,3}$ = 6, $J_{2,3}$ = 3 Hz) and anti C-3-H (δ −0.11, $J_{2,3}$ = 7.4 Hz), referenced to the C-1 and C-5 protons (δ 2.23). The syn and anti C-3 protons are cleanly separated from all other signals. The identity of the C-3 syn and anti proton signals was firmly established by a $Eu(fod)_3$ shift reagent study on the epoxide prepared from a partly C-3 deuterated sample of *exo*-tricyclo[3.2.1.$0^{2,4}$]oct-6-ene and comparison with the nmr spectrum of the *exo*-tricyclooctane **2** obtained by hydrogenation of the same starting sample of *exo*-tricyclo[3.2.1.$0^{2,4}$]oct-6-ene.

Alkali Metal–*t*-BuOD–THF Reduction of *anti*-3-Chloro-*exo*-tricyclo[3.2.1.$0^{2,4}$]octane (1a). To a refluxing solution of **1a** (50 mg, 0.35 mmol) in a mixture of 1 ml of *t*-BuOD (98% d_1) and 2 ml of anhydrous THF was added 5 mmol of the alkali metal. Heating at reflux was continued until aliquots indicated the absence of **1a**. Reaction time, yield, and syn to anti deuterio ratio were for Na, 1.5 hr, 70%, 2.11; for K, 30 min, 50%, 1.25; and for Li, 1 hr, 16%, and 1.70. Deuterium incorporations were above 95% as determined from nmr integrations.

Reaction of 1a with Lithium in Ether. A suspension of Li was prepared 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 **1a** and after 1 min at room temperature the flask was cooled to 0°. After 5 min the reaction was 75% complete and after 15 min all chloride was absent. D_2O (0.5 ml) was then added and followed by the work-up described above; 40% yield, syn/anti = 2.1 ± 0.3, 87% deuterium incorporation.

Reaction of 1b with *n*-BuLi. To 1 ml of 1 *M* *n*-BuLi (Ventron) and 3 ml of anhydrous ether was added 55 mg of **1b**. After 10 min at 0°, reaction was complete. D_2O (1 ml) was added after 45 min and work-up as above gave 20 mg (85% yield) of hydrocarbon; >95% deuterium incorporation; syn/anti ≤0.061:1.

Reaction of 1a with Lithium Naphthalenide. A solution of lithium naphthalenide was prepared from 0.1 g of Li and 2 g of naphthalene in 20 ml of anhydrous THF. After 1 hr at room temperature the deep green solution was cooled to −78° and 50 mg of **1a** in 3 ml of THF was slowly added *via* a dropping funnel. After stirring for 10 min, 1 ml of D_2O in THF was added dropwise. Glpc collection gave 10 mg of hydrocarbon **2** with >96% deuterium incorporation. The ratio of the anti C_3-H pmr integration to syn C_3-H integration was 28:1 with the splitting pattern of the residual syn C_3-H indicating that at least 75% of this signal originated from the undeuterated species. The syn to anti deuteration ratio corrected for the presence of undeuterated hydrocarbon is, therefore, at least 100:1.

Stability Study of 6. Chloride **1a** (50 mg) was allowed to react with lithium naphthalenide as above except the reaction mixture was allowed to warm from −78 to 0° over a period of 6 hr before being quenched with D_2O. The deuterium incorporation was only 82% and the syn to anti deuterium incorporation ratio could thus not be determined directly from the integration of the pmr signals. A consideration of the relative intensities of the splitting of the syn C_3-H pmr signal indicates that at least 92% of the signal is due to the undeuterated compound. The correct syn:anti deuterium ratio is >30:1.

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Registry No.—**1a**, 6518-27-0; **1b**, 15598-75-1; **2a**, 52882-74-3; **2b**, 52882-75-4.

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Trimethylsilylketene. Acylation and Olefination Reactions

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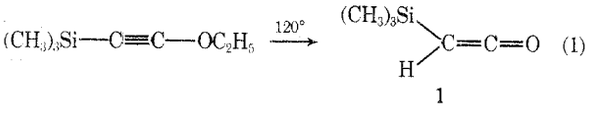
Trimethylsilylketene (TMS-ketene), **1**, a remarkably stable yet reactive ketene has been prepared by the pyrolysis of trimethylsilylethoxyacetylene[1,2] (eq 1). We wish to rec-

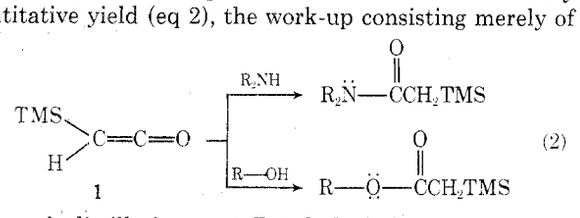


(1)

1

ord its use as a potent acylating agent for hindered amines and tertiary alcohols[3] and for the preparation of trimethylsilyl-substituted allenes and acetylenes.

TMS-ketene reacts almost instantly in carbon tetrachloride with hindered amines such as diisopropyl- and isopropylcyclohexylamine to produce the amide in essentially quantitative yield (eq 2), the work-up consisting merely of



(2)

1

short-path distillation. *tert*-Butyl alcohol also reacts with TMS-ketene in CCl_4, but the reaction is quite slow, requiring 48 hr for 80% completion. We have found however, that $BF_3 \cdot O(C_2H_5)_2$ strongly catalyzes the reaction. Addition of