sodium in 120 ml of absolute ethanol. To this solution was added 7.0 g (0.029 mole) of the 2-pyranyl ether derivative of L-(+)-XVII, $[\alpha]^{21.5}D$ 61.3° (2% acetone), and the mixture was refluxed for 24 hr. After cooling, 6.27 g (0.044 mole) of methyl iodide was added and the mixture was refluxed for 30 hr. The ethanol was distilled and 100 ml of 10% H_2SO_4 solution was added. The mixture was extracted with ether and dried over anhydrous $MgSO_4$. The residue, after removal of the ether, was added to 100 ml of 10% NaOH solution; this was refluxed for 12 hr and cooled, and 100 ml of concentrated HCl solution was added. The mixture was extracted with ether and dried over anhydrous $MgSO_4$, and after removal of the ether, the residue was distilled at 0.33 mm to give 2.68 g of product (52% yield): bp 106°, $[\alpha]^{28}D$ −5.55° (neat).

Methyl D-(−)-2-Methyl-3-phenyl-4-hydroxybutyrate. To 50 ml of 10% NaOH solution was added 5.0 g (0.029 mole) of D-(−)-α-methyl-β-phenyl-γ-butyrolactone, $[\alpha]^{28}D$ −5.55° (neat), and the mixture was heated to reflux for 4 hr. The solution was carefully neutralized with 6 *N* HCl solution and *immediately* extracted with ether. The ether solution was added directly to an excess of diazomethane in ether. After 1 hr, 2 ml of formic acid was added and the solution was washed once with saturated $NaHCO_3$ solution and dried over anhydrous $MgSO_4$. The ether was removed and the residue was used directly in the following preparation.

Methyl D-(−)-2-Methyl-3-phenyl-4-tosylbutyrate [D-(−)-XXIV]. The procedure used was the same as that previously described for the preparation of XIX. A batch of crystals formed while concentrating the ether solution of the desired tosylate. These crystals were shown by nmr and carbon, hydrogen, and sulfur analyses to be methyl D-(−)-3-phenyl-4-tosylbutyrate resulting from incomplete methylation in the step involving the preparation of D-(−)-II. After recrystallization, the melting point was 91–92° and $[\alpha]^{28}D$ −1.31° (2% chloroform).

Anal. (derivative). Calcd for $C_{18}H_{20}O_5S$: C, 62.06; H, 5.79; S, 9.19. Found: C, 61.66; H, 6.02; S, 9.22.

Further concentration of the ether solution gave the desired product, D-(−)-XXIV, mp 71–73°, $[\alpha]^{28}D$ −1.96° (2% ether).

Anal. (derivative). Calcd for $C_{19}H_{22}O_5S$: C, 62.97; H, 6.12; S, 8.83. Found: C, 63.16; H, 6.19; S, 8.86.

D-(−)-1-Methyl-2-phenylcyclopropanecarboxylic Acid [D-(−)VI]. Two grams of potassium was dissolved in 50 ml of dry *t*-butyl alcohol and to this refluxing solution was added dropwise 0.73 g (0.002 mole) of D-(−)-XXIV dissolved in 50 ml of dry *t*-butyl alcohol. After complete addition the reaction mixture was refluxed for 20 hr, cooled, and acidified with 10% HCl solution. The reaction mixture was diluted with 100 ml of water and extracted with ether. The extract was dried over anhydrous $MgSO_4$ and after removal of the ether, 0.22 g of solid product was obtained (yield 68%), $[\alpha]^{28}D$ −12.9° (2% ether).

D-(−)-2-Phenylcyclopropanecarboxylic Acid [D-(−)-XXV]. This synthesis was carried out in the manner described in the previous synthesis except that methyl D-(−)-3-phenyl-4-tosylbutyrate was used as the substrate. The acid obtained was treated directly with diazomethane in ether to give the methyl ester, $[\alpha]^{26}D$ −28.6° (2% absolute ethanol).

Homoenolization and Related Phenomena. VI.[1] Stereospecificity in Alkaline and Acid Media[2,3]

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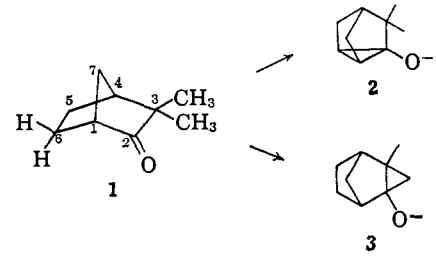
Contribution from the Department of Chemistry of The Johns Hopkins University, Baltimore, Maryland 21218. *Received March 7, 1966*

Abstract: 1-Acetoxynortricyclene has been used as a substrate to generate the related homoenolate ion and homoenol under mild conditions. In deuterated alkaline or acidic media these species homoketonized to 6-deuterionorbornan-2-one, which incorporated additional deuterium by enolization at C-3. The label was washed out from C-3 and the configuration of the C-6 deuterium was determined by Wolff–Kishner reduction of the ketone followed by infrared spectroscopic analysis of the derived deuterionorbornane. In various alkaline media the homoketonization produced an *exo* C–D bond with high stereospecificity (94.5–98%), whereas in acid medium *endo* attack was favored to at least 90–95%. The results indicate that homoenolization at C-6 in a bicyclo[2.2.1]heptan-2-one system would involve preferential abstraction of the *exo* hydrogen in base and the *endo* hydrogen in acid.

Keto–enol tautomerism in carbonyl compounds is associated with the known ability of a carbonyl group to activate α hydrogens. Recent work with camphenilone (**1**) has revealed that some activation is also extended to more distant hydrogens and that under vigorous enough conditions (*e.g.*, potassium *t*-butoxide in *t*-butyl alcohol at 185°) such hydrogens can exchange with protons in the medium by way of homoconjugated carbanions, termed homoenolate anions.[4] As many as nine deuteriums have been introduced into camphenilone and by a combination of techniques including the use of optically active ketone, nuclear magnetic resonance and infrared spectroscopy, and specifically labeled substrates it was shown that exchange occurred at C-6, at C-1, and on the methyl carbons, thereby implicating the homoenolate ions **2** and **3**. No exchange at C-7, C-5, or C-4 was detected and so these sites are not homoenolizable, or at least sufficiently less so to have escaped detection by the methods used.



(1) For Part V see A. Nickon, J. L. Lambert, and J. E. Oliver, *J. Am. Chem. Soc.*, **88**, 2787 (1966).

(2) A preliminary account of this work has been published: A. Nickon, J. H. Hammons, J. L. Lambert, and R. O. Williams, *ibid.*, **85**, 3713 (1963).

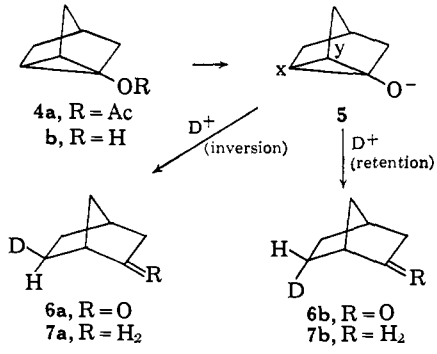
(3) This work was supported by the Petroleum Research Fund, administered by the American Chemical Society. We are grateful to the donors of this fund. The mass spectrometer was obtained with instrument grants from the Atomic Energy Commission and the National Science Foundation.

(4) (a) A. Nickon and J. L. Lambert, *J. Am. Chem. Soc.*, **84**, 4604 (1965); (b) A. Nickon and J. L. Lambert, *ibid.*, **88**, 1905 (1966).

The positional selectivity of deuterium entry supported the view that homoconjugation, and not inductive, effects primarily stabilize the homoenolate ion because the former effect should be more sensitive to geometry than the latter one. The object of the present work was to learn if any stereospecificity was associated with the loss and gain of homoenolic protons.[5] Previous work with camphenilone (**1**) established that a hydrogen is abstracted more easily from C-6 than from any other site, but no evidence was available on stereoselectivity at that center. In a bicyclo[2.2.1]heptan-2-one system the *exo* and *endo* C–H bonds differ distinctly in their geometric relationships to the carbonyl group and such a system appeared well suited for a stereochemical study.

Method

Because the high temperature employed to generate homoenolate ions could diminish any stereoselectivity we sought the stereochemical information through a study of ther everse process, homoketonization. 1-Acetoxynortricyclene (**4a**)[6] was adopted as the substrate because mild (27°) hydrolysis or alcoholysis in alkaline media generates the corresponding homoenolate ion **5**, which undergoes irreversible homoketonization to norbornan-2-one by proton capture or, in suitable medium, deuterium capture at either of the equivalent homoenolic sites, marked x and y in **5**. The deuterium in the ketone **6** will be *exo* (**6a**) if the electrophilic attack proceeds by inversion of configuration and *endo* (**6b**) if a retention mechanism prevails. Although the mild temperature of the hydrolysis of **4a** guarantees that the homoketonization is irreversible and that the stereochemical integrity of the label at C-6 will be preserved, additional deuterium is incorporated at C-3 by subsequent enolization.[7] In each case the enolizable deuterium in the ketone was washed out by repeated mild treatment with methanolic potassium hydroxide until the mass spectrum indicated that multilabeled

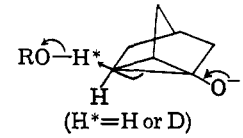


species were absent and that the percentage of monolabeled species became essentially constant (usually two or three washings were sufficient). For stereochemical assay the 6-deuterionorbornan-2-one (**6**) was then converted to the corresponding deuterated norbornane (**7**) by Wolff–Kishner reduction. Mass spectral analysis of the deuterated hydrocarbon revealed that no deuterium was lost[9] in this step and therefore that no homoenolization involving C-6 occurred under the vigorous alkaline conditions of the Wolff–Kishner method. The configurational distribution of the deuterium was then determined by appropriate infrared comparisons with the authentic *exo-d-* and *endo-d-*norbornane (and with artificial mixtures of these epimers) prepared as reported earlier.[8] In these assays minimum values for stereochemical homogeneity could be assigned with certainty, and interpolation provided a still closer estimate of the *exo-d*/*endo-d* composition.

To get stereochemical information on the cleavage of the cyclopropyl ring in acid media two methods were used. In one, the 1-acetoxynortricyclene was treated with sulfuric acid-d_2 in deuterated medium (*e.g.*, MeOD or DOAc–D_2O). In the other, the 1-acetoxynortricyclene was reduced with lithium aluminum hydride and, without purification,[10] the derived homoenol (**4b**) was transferred to an acidic deuterated medium and allowed to homoketonize. All relevant information and results are summarized in Table I.

Discussion

Alkaline Media. In alkali (runs 1–4) the homoketonizations were highly stereospecific and proceeded with inversion of configuration (>94.5%). The inversion pathway appears relatively insensitive to the nature of the alkaline media we used and is formulated in **8**, which for simplicity omits the cation, although it undoubtedly plays some role. Interestingly, these homoketonizations are among the first cases of electrophilic substitution where virtually complete inversion of configuration has been demonstrated,[11a] If only one transition state is traversed in homoketonization our results imply that the reverse process, homoenolization of norbornan-2-one at C-6, under identical conditions would involve preferential abstraction of the *exo* hydrogen. Therefore, any homoconjugation with the carbonyl group in the transition state would require orbital interaction from the back side of the *exo* HC-bond (*i.e.*, the posterior lobe of the C-6 orbital; see **9**).



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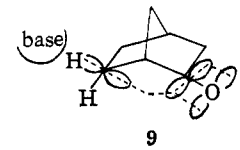

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(5) For examples of stereospecificity in keto–enol tautomerism in cyclic ketones see E. J. Corey and R. A. Sneen, *J. Am. Chem. Soc.*, **78**, 6269 (1956).

(6) H. Hart and R. A. Martin, *J. Org. Chem.* **24**, 1267 (1959); *J. Am. Chem. Soc.*, **82**, 6362 (1960).

(7) Release of enolic protons from the CH_3 of the acetate group and from C-3 in the ketone (and from dimethyl sulfoxide when it was used as solvent) lowers the deuterium content of the medium and ultimately leads to nondeuterated species (*e.g.*, 5–30%) in the final hydrocarbon. Its presence, however, was shown not to interfere significantly in the infrared assays of the *exo-d*/*endo-d* ratio by preparation of artificial mixtures containing natural abundance hydrocarbon along with the deuterium analogs (see also ref 8).

(8) A. Nickon and J. H. Hammons, *J. Am. Chem. Soc.*, **86**, 3322 (1964).

(9) Interestingly the hydrocarbon showed an apparent deuterium content slightly higher (1–4%; see Table I) than that of its ketonic precursor. Such discrepancies are not uncommon in mass spectrographic deuterium analyses, especially when the parent molecular ion (M) is accompanied by an appreciable M − 1 or M − 2 peak. (In norbornan-2-one and in norbornane the M − 1 peaks were, respectively, 12 and 22.4% of the parent peak). For a discussion of the approximations and errors in the calculation of isotopic distributions see K. Biemann, "Mass Spectrometry, Organic Chemical Applications," McGraw-Hill Book Co., Inc., New York, N. Y., 1962, pp 209–243.

(10) Excessive handling of the homoenol was avoided to minimize premature rearrangement to the ketone. In a separate experiment we converted the homoenol to a crystalline phenylurethan for characterization.

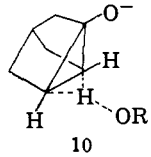
(11) (a) For discussions and literature references see D. J. Cram, "Fundamentals of Carbanion Chemistry," Academic Press Inc., New York, N. Y., 1965; (b) pp 144–153.

Table I. Stereospecificity in Homoketonizations (27 ± 3°)

Run	Solvent[b]	Reagent	Concn, vol molal at 20° Reagent	Substrate	Deuterium assay, % Ketone[a] 1-D	Ketone[a] 0-D	Hydrocarbon 1-D	Hydrocarbon 0-D	Deuterium configuration[c]
1	*t*-BuOD	*t*-BuOK	1.02	0.64	68	32	69	31	94.5–98% *exo*
2	MeOD	KOMe	0.22	1.48	90	10	93	17	94.5–98% *exo*
3	MeOD–dimethyl sulfoxide (1:1)	KOMe	0.04	0.77	86	14	88	12	94.5% *exo*
4	*t*-BuOD	$(Me)_4N^+OD^-$	1.6[d]	0.66	79	21	83	17	94.5% *exo*
5	DOAc–D_2O (1.2:1)	D_2SO_4	0.32	0.60	95	5	97	3	90–95% *endo*[e]
6	MeOD	D_2SO_4	2.6	0.53	...[f]	...	...[f]	...	90–95% *endo*
7	DOAc–D_2O (1.8:1)	D_2SO_4	0.37	0.69	...[f]	...	99	1	90–95% *endo*
8	DOAc–D_2O (1.7:1)	D_2SO_4	0.29	0.60[g]	39	61	...	...	90–95% *endo*[h]

[a] These values were obtained after the final washing; those after the penultimate washing were essentially identical. No multiply deuterated species were present. [b] In mixed solvents the ratios refer to weights. [c] A single value represents a reliable minimum as well as an estimate of the actual value. When a range is given the first number is the minimum; the second comes from interpolation of infrared spectra and is a closer estimate of the true value but does not necessarily imply a maximum limit. [d] This concentration is a maximum value and may be high by as much as 50% because the base could have retained a little D_2O from its method of preparation. [e] A slight impurity (stopcock grease?) in the norbornane allowed us to set only the minimum value. The more accurate interpolated value (95%) was obtained by spectral comparison of the ketonic precursor with that from run 7. [f] Mass spectrum not recorded. [g] The substrate was the crude homoenol **4b**. Its concentration is the maximum possible based on the assumption that the lithium aluminum hydride reduction proceeded in 100% yield. [h] Based upon infrared spectral comparison of the ketone with those from runs 5, 6, and 7. The high proportion of natural abundance ketone in run 8 probably makes our interpolated value less certain.

It is important to consider whether the observed stereospecificity is inherent to alkaline homoenolizations and homoketonizations or is uniquely associated with certain steric or electronic properties of the particular substrate being studied. For example, if stability is gained by simultaneous attraction of the proton to both of the equivalent, electron-rich carbons to give a symmetrical species such as **10**, inversion of configuration would necessarily result. This same species could be involved in the microscopically reverse process, homoenolization of norbornan-2-one. However, an intermediate (or transition state) of the same symmetry as **10** has been excluded in the alkaline homoenolization of camphenilone,[4] and we see no reason why it should be more important in the present case.



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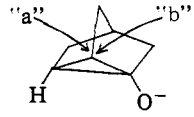

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It could be argued that involvement of the *exo* hydrogen is preferred on steric grounds, and indeed analogies can be cited to support the view that *exo* approach to a bicyclo[2.2.1]heptane system is highly favored.[12] On the other hand, steric differences between *exo* and *endo* positions are decreased when the carbons across the ring are trigonally hybridized[13] (as for example in a carbonyl group) and can be further reduced if the transition state (*e.g.*, **9**) resembles the geometry of a nortricyclene skeleton more than that of a bicyclo[2.2.1]heptyl system, a situation that probably prevails.[14] Except for the presence of the C–O unit (see **11**) the nortricyclene framework presents a symmetric environment to a reagent that delivers a proton with inversion (path a) or with retention (path b), and therefore *exo–endo* steric differences in the final product may not be developed appreciably in the transition state. Lastly, the fact that the stereospecificity is reversed in acid-catalyzed homoketonizations (runs 5–8; see below) also argues against steric hindrance as the governing factor. In studies with a different homoenol system (1-methyl-2-phenylcyclopropanol) DePuy and Breitbeil observed that protonation occurred by different stereospecific pathways in basic and acidic solution[15] and have confirmed their earlier suggestion of an inversion process in the former medium and a retention process in the latter one. Our findings, therefore, parallel those of DePuy and co-workers and lead us to conclude that the alkaline homoenolizations observed earlier[4] with camphenilone (**1**) very likely involve preferential abstraction of the 6-*exo*-hydrogen over a 6-*endo* hydrogen.[16]

The persistent high inversion in alkaline homoketonization in various media (runs 1–4) stands in contrast to findings with nonhomoconjugated carbanions by Cram and co-workers. They observed variations in the steric course that depended on solvent, base, cation, etc., and for similar alkaline media (*e.g.*, potassium *t*-butoxide in *t*-butyl alcohol) there are striking differences in behavior between their open-chain systems and our homoconjugated one.[11b] Furthermore, it is possible that different homoenols

(12) *exo* attack by the reagent occurs to the extent of 99% in the hydroboration of norbornene (H. C. Brown and G. Zweifel, *J. Am. Chem. Soc.*, **83**, 2544 (1961)) and of *ca.* 92% in the lithium aluminum hydride reduction of norbornan-2-one (P. Hirsjarvi, *Ann. Acad. Sci. Fennicae, Ser. A. II*, 81 (1957); *Chem. Abstr.*, **51**, 5004*e* (1957)). Also, virtually exclusive formation of *exo* products in solvolysis of certain norbornyl systems has been ascribed to a steric preference for *exo* approach: H. C. Brown, Special Publication No. 16, The Chemical Society, London, 1962, pp 154, 176; H. C. Brown and H. R. Deck, *J. Am. Chem. Soc.*, **87**, 5620 (1965).

(13) In bicyclo[2.2.1]heptadiene the ratio of *exo* attack to *endo* attack is *ca.* 7.3:1 in hydroboration (H. C. Brown and G. Zweifel, *ibid.*, **81**, 5832 (1959)) and *ca.* 5.7:1 in methylene transfer by the Simmons–Smith method (H. E. Simmons, E. P. Blanchard, and R. D. Smith, *ibid.*, **86**, 1347 (1964)). For recent examples involving equilibration studies see J. G. Dinwiddie, Jr., and S. P. McManus, *J. Org. Chem.*, 30, 766 (1965).

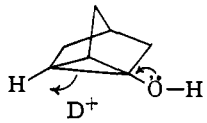
(14) The irreversible isomerization (at 27°) indicates that homoenol **4b** is thermodynamically less stable than its keto tautomer, norbornan-2-one. According to Hammond's postulate the transition-state geometry for interconversion is probably closer to the structure of the higher energy tautomer: G. S. Hammond, *J. Am. Chem. Soc.*, 77, 334 (1955).

(15) (a) C. H. DePuy and F. W. Breitbeil, *ibid.*, **85**, 2177 (1963); (b) C. H. DePuy, F. W. Breitbeil, and K. R. DeBruin, *ibid.*, **88**, 3347 (1966).

(16) The selectivity might even be greater in camphenilone if the interaction between an *endo* methyl group and the C-6 *endo* hydrogen produces steric hindrance rather than steric acceleration. We wish to emphasize that because the camphenilone studies were done at 185° the conditions are not strictly identical with those in the present study (27°) and our discussion is based on the reasonable assumption that no reversals in stereochemical pattern occur between these two temperatures.

may not respond in the same way to variation in solvent, etc., as do the bridged systems.

Acid Media. The homoketonizations under acid conditions (runs 5–8) gave predominantly *endo-d*-norbornan-2-one (**6b**) and indicated that retention of configuration is the preferred path in electrophilic (D^+) opening of the cyclopropyl ring. The high stereospecificity (*ca.* 95%) held whether the substrate was 1-acetoxynortricyclene (**4a**) or 1-hydroxynortricyclene (**4b**), and a simple mechanism for the latter case is shown in **12**.[17] With acetate **4a** it is not clear whether the ester is hydrolyzed to the homoenol **4b** prior to ring cleavage or whether D^+ attack on the cyclopropyl system occurs while the ester unit is intact to produce intermediate **13** (or its equivalent), which subsequently



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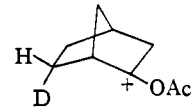

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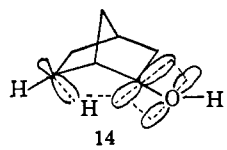
combines with solvent. If the latter pathway prevails then the stereospecificity of ring opening does not seem to depend on the nature of the oxygen function (OH or OAc) attached to the three-membered ring. How general this retention mechanism in acid medium will be for other types of cyclopropane rings must await further examples. Although acid-induced homoenolizations have not yet been demonstrated, the present results imply that an *endo*-hydrogen would be preferentially abstracted and that delocalization in the transition state would occur from the bonding C–H electrons (*i.e.*, from the anterior lobe of the C-6 orbital (**14**).



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In an attempt to study homoketonization in neutral medium, we allowed the homoenol **4b** to stand in methanol-O-*d* for 21 hr. Work-up gave ketone that was only 4% monodeuterated. Failure to incorporate more isotope indicated that homoenol **4b** survived in the neutral medium and rearranged only during the protonic work-up, which involved alkaline washings. This result has analogy in the work of DePuy and Mahoney who noted that cyclopropyl alcohol is relatively stable in the absence of acids and bases.[18]

Experimental Section[19]

1-Acetoxynortricyclene (1-Acetoxytricyclo[2.2.1.0^{2,6}]heptane). This ester was prepared from an equilibrium mixture[20] of norbornene and nortricyclene as reported.[6] We obtained 1-acetoxynortricyclene, bp 50–52° (3.5 mm) (lit[6] bp 41–42° (2 mm)), 38% yield, from nortricyclene, which was 99.8% pure by gas chromatography (at 150° on a 200-ft Golay column with SE-30 silicone gum rubber liquid phase). *Anal.* Calcd for $C_9H_{12}O_2$ (152.2): C, 71.02; H, 7.95. Found: C, 70.89; H, 7.86.

1-Hydroxynortricyclene. 1-Acetoxynortricyclene (0.5 g) was dissolved in dry ether containing an excess of lithium aluminum hydride. The mixture was stirred at room temperature for 20 hr and the excess of hydride was destroyed according to the method of Micovic and Mihailovic.[21] The ether layer was dried over anhydrous sodium sulfate and was evaporated to leave a colorless, semisolid residue that solidified at ice-bath temperature but became semisolid again at room temperature. The infrared spectrum (chloroform solution) showed strong hydroxyl absorptions at 3570 and 3400 cm^{-1}, and a carbonyl band at 1740 cm^{-1} whose intensity was approximately equal to that of the carbon–hydrogen stretching band (39% transmission). Gas chromatography indicated the presence of norbornan-2-one only, indicating that homoketonization was brought about during chromatography (140°, retention time *ca.* 7 min).

Phenyl isocyanate (0.5 g) was added to the semisolid 1-hydroxynortricyclene, and the mixture was heated on a steam bath for 10 min. When the mixture was cooled, a pale yellow solid separated which was extracted with petroleum ether (bp 66–75°) and decolorized with Darco activated carbon. Several recrystallizations from petroleum ether gave colorless needles, mp 184.5–185°.[22] The infrared spectrum (KBr disk) showed: 3279 (N–H), 3030 (cyclopropyl C–H), 1712 (carbonyl), 1546 (amide), 833, 762 cm^{-1} (1-substituted nortricyclene). *Anal.* Calcd for $C_{14}H_{15}O_2N$ (229.26): C, 73.34; H, 6.59. Found: C, 73.64; H, 6.59.

Homoketonization Run 1 and General Procedures for Removal of Enolizable Deuterium Wolff–Kishner Reduction and Infrared Assays. 1-Acetoxynortricyclene (1.50 g) was dissolved in *t*-butyl alcohol-O-*d* (12.05 g) containing potassium *t*-butoxide (1.75 g) and the solution was stirred at room temperature (*ca.* 27°) for 20 min. Deuterium oxide (0.20 g) was added, and the slightly soluble potassium deuterioxide precipitated. The mixture was stirred for another 30 min. Then water (6.12 g) was added to begin the process of removing deuterium incorporated into the normally enolizable positions in norbornan-2-one. The mixture was stirred for 2.5 hr., then poured into 100 ml of pentane. The small water layer was washed twice with fresh pentane, and the combined pentane layers were concentrated on a steam bath, dried with anhydrous sodium sulfate, and chromatographed over 11.0 g of Alcoa alumina to remove residual alcohol. 6-*d*-Norbornan-2-one was eluted with pentane and was identified by gas chromatography.

Recovered ketone was dissolved in methyl alcohol (11.0 g) containing potassium hydroxide (0.54 g) and water (5.0 g), and the homogeneous solution was stirred at room temperature, under nitrogen and in the dark for 23.5 hr. The solution was poured into 100 ml of pentane and worked-up as described before. 6-*d*-Norbornan-2-one was eluted from Alcoa alumina with pentane, and a sample was analyzed for deuterium distribution by mass spectrometry. The composition was 4% 2-D, 67% 1-D, and 29% 0-D. Another aqueous methanolic potassium hydroxide washing was performed as described above, after which the 6-*d*-norbornan-2-one gave the composition: 1% 2-D, 67% 1-D, and 32% 0-D. After a third washing the distribution of deuterated species was 0% 2-D, 68% 1-D, and 32% 0-D. Considerable material is lost as a result of these washings.

This 6-*d*-norbornan-2-one was dissolved in 8.0 ml of absolute ethyl alcohol, and 95% hydrazine (2.0 g) was added. The solution was stirred for 1 hr at room temperature, then diethylene glycol (5.0 ml, freshly distilled, bp 236–252°) was added and volatile materials (alcohol, excess of hydrazine, water) were slowly distilled off. The solution was cooled, and 5.0 ml of diethylene glycol in which 0.35 g of freshly cut sodium had been dissolved was added.

(17) DePuy and Klein (footnote 5 in ref 15a) report that acid-catalyzed rearrangement of cyclopropyl alcohols is a bimolecular reaction between the alcohol and a proton.

(18) C. H. DePuy and L. R. Mahoney, *J. Am. Chem. Soc.*, **86**, 2653 (1964).

(19) Infrared spectra were recorded on a Perkin-Elmer Model 21 spectrophotometer equipped with sodium chloride optics. Unless specified otherwise all spectra were taken in carbon disulfide solution. A Perkin-Elmer Model 226 gas chromatograph with flame detector was used for gas chromatographic analyses. Unless specified otherwise a 150-ft Golay column with polypropylene glycol liquid phase was used. For preparative gas chromatography an Aerograph Autoprep Model A-700 was used, with a 30 ft × 3/8 in. column containing 30% SE-30 silicone liquid phase on 40–60 Chrom P. Helium was the carrier gas for all chromatography. Mass spectra were taken with a Consolidated Electrodynamics Corp. mass spectrometer, Type 21–103C. For general procedures regarding mass spectrometric analyses see part IV.[1b]

Deuterated reagents were purchased from Merck and Co. Ltd. of Canada. Pentane (Fischer) was purified by stirring with concentrated sulfuric acid, by filtration through alumina, and finally by redistillation. Potassium *t*-butoxide was sublimed *in vacuo* at 250° before use.

(20) P. von R. Schleyer, *ibid.*, **80**, 1700 (1958).

(21) V. M. Micovic and M. L. Mihailovic, *J. Org. Chem.*, **18**, 1190 (1953).

(22) We are grateful to Dr. B. R. Aaronoff for the preparation and characterization of this derivative.

A stream of nitrogen (*ca.* 30 cc/min) was bubbled into the reaction solution and exited through the condenser–cold trap which was packed in Dry Ice. The reaction solution was heated, and volatile *d*-norbornane was swept from the hot solution into the condenser by the stream of nitrogen. *d*-Norbornane was collected as a white, crystalline solid (0.170 g, 18% yield from 1-acetoxynortricyclene). The mass spectrum of this *d*-norbornane indicated the isotopic distribution: 0% 2-D, 69% 1-D, and 31% 0-D.

d-Norbornane has been shown[8] to have infrared absorption bands characteristic for the *endo-d* isomer at 840 and at 790 cm^{-1} and for the *exo-d* isomer at 858 and 781 cm^{-1}. The infrared spectrum of *d*-norbornane obtained from run 1 indicated that it was almost entirely *exo-d*-norbornane. An artificial mixture was prepared containing norbornane (0.077265 g, 28% of total mixture), *exo-d*-norbornane (0.189622 g, 68% of total mixture, 94.5% of total *d*-norbornane), and *endo-d*-norbornane (0.011176 g, 4% of total mixture, 5.5% of total *d*-norbornane).[23] The infrared spectrum of this artificial mixture revealed that the 4% of *endo-d*-norbornane could be readily detected; and comparison with the spectrum of the norbornane–*d*-norbornane mixture obtained from homoketonization run 1 established that this *d*-norbornane was better than 94.5% (probably as high as 98%) *exo-d*-norbornane.

Run 2. 1-Acetoxynortricyclene (1.02 g) was added to methyl alcohol-O-*d* (3.84 g) in which potassium (0.039 g) had been dissolved. The solution was stirred at room temperature. After 1 hr a small aliquot was taken, added to water, and extracted with pentane. The pentane layer was dried with anhydrous sodium sulfate and concentrated. Gas chromatography of the residue indicated the complete absence of 1-acetoxynortricyclene and the presence of norbornan-2-one. The mixture was stirred for an additional 80 min, then water (6.0 g) was added and the work-up sequence described for run 1 was effected. *d*-Norbornan-2-one (90% 1-D, 10% 0-D) was reduced as described before to give *d*-norbornane (0.148 g, 23% from 1-acetoxynortricyclene) as a white, crystalline solid, whose infrared spectrum had bands characteristic of *exo-d*-norbornane. No absorption due to the *endo-d* isomer was observed, but a weak band due to norbornane at 817 cm^{-1} was evident.

The infrared spectrum of *exo*-6-*d*-norbornan-2-one obtained from this run had bands at 772, 842, 936, and 973 cm^{-1} which were not present in the spectrum of natural abundance norbornan-2-one. Also, the strong bands at 1043 and 1065 cm^{-1} in natural abundance norbornan-2-one had largely disappeared.

Run 3. 1-Acetoxynortricyclene (0.765 g) was dissolved in a solution of potassium (0.010 g) in methyl alcohol-O-*d* (3.0 g) containing dimethyl sulfoxide (3.0 g), and the mixture was stirred at room temperature. Gas chromatography on an aliquot taken after 1 hr showed the complete absence of 1-acetoxynortricyclene. After a further 15 min aqueous potassium hydroxide was added and the solution was stirred for 4.5 hr. After the usual work-up the purified 6-*d*-norbornan-2-one had an infrared spectrum identical with that obtained from run 2. The ketone was reduced to *d*-norbornane (0.054 g, 12% from 1-acetoxynortricyclene).

Run 4. Tetramethylammonium deuterioxide was prepared by evaporation of Fisher 10% aqueous tetramethylammonium hydroxide as dry as possible at room temperature and 1 mm pressure. About 3 g of this product was dissolved in 99.8% deuterium oxide (5.0 ml) and the excess of deuterium oxide and water was removed under vacuum. The process was repeated with a further amount of deuterium oxide (5.0 ml), and the almost dry product was used in this form.

1-Acetoxynortricyclene (0.75 g) was dissolved in *t*-butyl alcohol-O-*d* (6.0 g) containing tetramethylammonium deuterioxide (1.120 g), and the mixture was stirred for 4 hr. Gas chromatography on an aliquot showed norbornan-2-one as the only component. Water was added and the reaction mixture was worked up in the usual way to give 6-*d*-norbornan-2-one, which was then reduced to *d*-norbornane.

Run 5. 1-Acetoxynortricyclene (1.02 g) was dissolved in acetic acid-O-*d* (6.1 g) and deuterium oxide (4.75 ml) was added until the 1-acetoxynortricyclene was just about to precipitate. Sulfuric acid-d_2 (0.32 g) was added, and the homogeneous solution was stirred at room temperature. After 47 hr, gas chromatography on an aliquot showed less than 2% of 1-acetoxynortricyclene remaining in the reaction mixture. The solution was extracted with pentane (once with a 30-ml and four times with 10-ml portions) and the combined extracts were washed with 20% potassium carbonate solution (10 ml). The carbonate layer was extracted with fresh pentane (twice with 5-ml portions), and all pentane extracts were combined, dried over sodium sulfate, and evaporated to low bulk through a fractionating column. α-Deuterium was washed out (three washings) as described for run 1. A mass spectrum of the 6-*d*-norbornan-2-one indicated 0% 2-D, 95% 1-D, and 5% 0-D. One more washing yielded 6-*d*-norbornan-2-one with the same isotopic distribution. The infrared spectrum had bands at 777 and 882 cm^{-1} which were absent in norbornan-2-one and *exo*-6-*d*-norbornan-2-one.

The ketone was reduced to *d*-norbornane (0.101 g, 16% yield from 1-acetoxynortricyclene), whose infrared spectrum had bands at 790 and 840 cm^{-1} characteristic of *endo-d*-norbornane.[8] Slight shoulders at 782 and 860 cm^{-1} suggested the presence of a small amount of the *exo-d* isomer. An artificial mixture was prepared containing *endo-d* norbornane (0.04298 g, 89.2% of the mixture) and *exo-d*-norbornane (0.00523 g, 10.8% of the mixture), and the infrared spectrum of this mixture was taken. The strong bands at 790 and 840 cm^{-1} were present and shoulders at 781 and 858 cm^{-1} representing the 10.8% of *exo-d* isomer were readily observable. A comparison of the spectrum with that of *d*-norbornane from run 5 revealed at least 90%, and probably as high as 95%, *endo-d*.

Run 6. 1-Acetoxynortricyclene (1.50 g) was dissolved in methyl alcohol-O-*d* (15 g) and sulfuric acid-d_2 (0.49 g) was added. The solution was stirred for 27 hr at room temperature. Water and pentane were added and the mixture was processed further as described for run 5.

Run 7. 1-Acetoxynortricyclene (1.5 g) was dissolved in acetic acid-O-*d* (9.0 g) and deuterium oxide (*ca.* 5 g) was added. Sulfuric acid-d_2 (0.53 g) was added to the homogeneous solution and stirring at room temperature was continued for 54 hr. Gas chromatography of a small aliquot indicated the presence of norbornan-2-one only. Water was added and after work-up and reduction, deuterionorbornane (0.193 g, 23% yield from 1-acetoxynortricyclene) was obtained pure by preparative gas chromatography.

Run 8. 1-Acetoxynortricyclene (1.9 g) was dissolved in 20 ml of dry ether and the solution was added slowly (15 min) to a well-stirred slurry of lithium aluminum hydride (0.570 g) in dry ether (60 ml). The mixture was stirred at room temperature for 19 hr, then chilled to 0°, and the excess of hydride was destroyed by the method of Micovic and Mihailovic.[21] Granular salts were filtered off and washed with fresh ether. The combined ether layers were washed once with *ca.* 10 ml of water and dried over anhydrous sodium sulfate, and the solution was concentrated to *ca.* 3 ml by distillation of the ether through a fractionating column. The infrared spectrum (chloroform solution) showed strong absorptions at 3570 and 3400 cm^{-1} and a weak band at 1740 cm^{-1}. This ethereal 1-hydroxynortricyclene was divided into two equal portions and was used immediately in this run and in run 9.

The freshly prepared 1-hydroxynortricyclene (*ca.* 0.69 g) was added to a solution of acetic acid-O-*d* (6.83 g) and deuterium oxide (4.0 g) containing sulfuric acid-d_2 (*ca.* 0.3 g). The solution was stirred for 19 hr at room temperature, then worked up in the usual way. Purified 6-*d*-norbornan-2-one was obtained with the isotopic distribution: 0% 2-D, 39% 1-D, and 61% 0-D. The infrared spectrum was compared with that of run 7 *endo*-6-*d*-norbornan-2-one, and indicated prevalence of the *endo-d* isomer to the extent of 90–95%.

Run 9. Freshly prepared 1-hydroxynortricyclene (*ca.* 0.69 g) was dissolved in methyl alcohol-O-*d* (7.5 g), and the solution was stirred at room temperature for 21 hr. After work-up and washing in the usual way chromatography over Woelm neutral alumina gave norbornan-2-one whose mass spectrum revealed that monodeuterated species were present to the extent of only 4%. Although the infrared spectrum of a concentrated solution gave perceptible indications of bands due to *exo*-6-*d*-norbornan-2-one the intensities were too low to draw any conclusions.

(23) Authentic samples kindly supplied by Dr. J. H. Hammons.