The Base-Catalyzed Hydrogen–Deuterium Exchange of Nonenolizable Bicyclic Ketones

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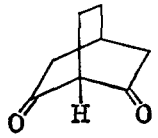
Abstract: The hydrogen–deuterium exchange of nortricyclanone, 7-ketonorbornane, and some related compounds has been investigated. Considerable hydrogen–deuterium exchange was observed utilizing potassium *t*-butoxide in *t*-butyl alcohol-O-*d* solution at elevated temperatures. Approximately 36% of the hydrogen in nortricyclanone was exchanged, with exchange being limited to the four bridgehead positions. These results are discussed in relation to (a) the purely inductive effect of the carbonyl function, (b) carbanion stabilization by an electron-deficient cyclopropane ring, and (c) the occurrence of homoenolization in bicyclic ketones.

The area of carbanion chemistry has rapidly expanded during the last decade.[2] Many of the investigations carried out over this period were devoted to establishing the relative stability of various carbanions and to determining the features of a molecule which contributed to anion stability. The contribution of the carbonyl function to carbanion stability has normally been thought to result from delocalization of the electron pair onto the more electronegative oxygen. Bartlett and Woods have shown that when such delocalization cannot occur, such as to the bridgehead in **1**, there is a drastic reduction in the acidity of **1** as compared



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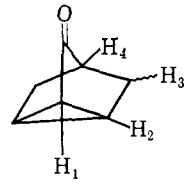
to an open-chain analog.[3] While delocalization of charge to the more electronegative atom is undoubtedly the major factor in the stabilization of carbanions adjacent to carbonyl functions, there is some question as to what extent the carbonyl function can stabilize an adjacent carbanion in other ways.

It has been stated that "About the only common substituents that stabilize carbanions by a pure inductive effect are the quaternary ammonium and fluoride groups."[4] Obviously, a carbonyl group would also be expected to provide inductive stabilization for an adjacent negative charge. Although orbital overlap has been recognized as the principal factor in acidifying α hydrogens, the experimental conditions which are required to effect abstraction of α hydrogens in the absence of any orbital overlap factor have not been determined. We wish to present evidence which indicates that a carbonyl group, through inductive effect alone, can acidify α hydrogens sufficiently to permit proton abstraction by potassium *t*-butoxide at temperatures in the vicinity of 200°.

In order to determine the degree of stabilization which a carbonyl group can provide purely by inductive effect, it is necessary that the carbonyl function be incorporated into a system in which enolization cannot occur. This can best be accomplished by incorporating the carbonyl function into a strained bicyclic or tricyclic structure. We have chosen nortricyclanone (**2**) as our



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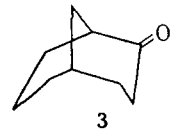

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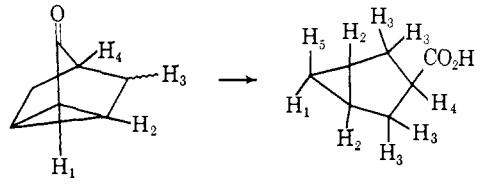
model system. In this system the geometrical requirements necessary to accommodate a double bond at the bridgehead cannot be met (Bredt's rule).[5] In larger ring systems such as **3**, it has been concluded that sufficient orbital overlap occurs in the enolate ion to confer substantial acidity on the bridgehead hydrogen.[6]

Results

When nortricyclanone was treated with approximately a 2 molar excess of potassium *t*-butoxide in *t*-butyl alcohol-O-*d* for 24 hr at *ca.* 200°, deuterium exchange resulted to the extent of 36%. Deuterium exchange occurred only at the bridgehead position (H_4) and at the cyclopropyl positions (H_1 and H_2). No detectable deuterium exchange occurred at H_3. The position of the incorporated deuterium was determined by the cleavage of nortricyclanone (**2**) to *cis*-bicyclo[3.1.0]-hexane-3-carboxylic acid (**4**),[7] followed by nuclear magnetic resonance (nmr) analysis of this partially deuterated acid. It had been shown previously[7] that

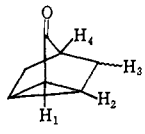
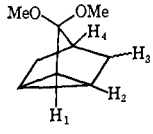
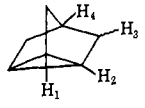
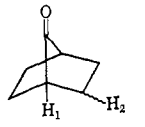


2 **4**

this cleavage in dimethyl sulfoxide–potassium *t*-butoxide proceeds with stereospecific placement of hydro-

(1) Sinclair Oil Corp. Foundation Fellow, 1964–1965.
(2) For a recent review of carbanion chemistry see D. J. Cram, "Fundamentals of Carbanion Chemistry," Academic Press Inc., New York, N. Y., 1965.
(3) P. D. Bartlett and G. F. Woods, *J. Am. Chem. Soc.*, **62**, 2933 (1940).
(4) See ref 2, p 55.
(5) J. Bredt, *Ann.*, **437**, 1 (1924); *cf.* F. S. Fawcett, *Chem. Rev.*, **47**, 219 (1950).
(6) J. P. Schaefer and J. C. Lark, *J. Org. Chem.*, **30**, 1337 (1965).
(7) P. G. Gassman and F. V. Zalar, *Tetrahedron Letters*, **No. 40**, 3031 (1964); **No. 44**, 3251 (1964).

Table I

Compound	Time, hr	Temp, °C	% D incorporation per hydrogen[a] H_1	H_2	H_3	H_4	Total % D incorporated Calcd[b]	Found[c]
 2	22	195–200	73	70	0	68	35.1	35.7
	29	195–200	83	73	0	76	38.1	38.8
 7	48	215–220	60	40.4	0	0	17.6	18.1
 5	48	215–220	10	10	0	0	3	3.2
	64	260–265	22	22	0	0	6.6	...
 6	22	195–200	...	...	...	...	...	2.1
	48	195–200	25	0	...	...	4.1	4.6

[a] The values reported are limited by the accuracy of integration by nmr. [b] Deuterium incorporation determined by nmr analysis. [c] Deuterium analysis performed by J. Nemeth, Urbana, Ill.

gen (or deuterium) at H_5. A stereospecific cleavage could also be carried out in diethyl ether–potassium *t*-butoxide solution.[8] The well-defined nmr spectrum of **4** provided a convenient source of data about the position of deuterium in **2**. By considering the proton (H_5), which was stereospecifically placed in **4** during cleavage, as unity and measuring the integrated areas of the remaining protons relative to H_5, the per cent deuterium incorporation could be determined. The results of this determination are listed in Table I. Since the per cent deuterium incorporation at each position could be measured from the nmr, the total deuterium content of the molecule was readily available. As shown in Table I, the total deuterium content measured for a number of compounds by nmr was in excellent agreement with the deuterium content as measured by the classical falling-drop method of deuterium analysis.

In order to evaluate the effect of the carbonyl function, it was necessary to look at some model compounds. The obvious models were nortricyclane (**5**) and 7-ketonorbornane (**6**). In addition, 7,7-dimethoxynortricyclane (**7**) was exchanged. As shown in Table I, compounds **5** and **7** required considerably more vigorous reaction conditions for exchange. While **6** gave deuterium exchange under the same conditions as nortricyclanone, the amount of deuterium exchange was less. The reasons for this behavior will be discussed later.

Nortricyclane (**5**) was analyzed for deuterium incorporation directly by nmr. The dimethyl ketal **7** was hydrolyzed to **2** followed by cleavage to **4** prior to nmr analysis for deuterium content. 7-Ketonorbornane was reduced *via* Wolff–Kishner reduction to norbornane (**8**) and the extent of H–D exchange was determined from the nmr of the resultant deuterated norbornane.[9]

(8) A detailed account of the mechanism and experimental parameters of the cleavage of nonenolizable ketones will be presented in a forthcoming publication from this laboratory.

Discussion

Of the four compounds investigated, the H–D exchange of nortricyclanone occurred under the mildest conditions and to the greatest extent. The various factors influencing this behavior merit evaluation.

It has been recognized for some time that the greater the s character in a carbon–hydrogen bond the more acidic the hydrogen and the more stable the anion resulting from abstraction of that hydrogen.[10] The early work of Shatenshtein[11] on the relative rates of hydrogen–deuterium exchange of some cyclopropanes in deuterated ammonia–potassium amide showed that cyclopropyl hydrogens are much more acidic than normal acyclic hydrogens. This enhanced acidity gives ample evidence that the increased s character of the carbon–hydrogen bonds of cyclopropanes ($sp^{2.28}$–s σ bond)[10,12] correlates with the ease of removal of hydrogens from strained rings. The incorporation of a cyclopropyl ring into a highly strained tricyclic framework results in even greater acidity of the hydrogens on the strained ring as demonstrated by the ease of formation and alkylation of the carbanions **9**[13] and **10**.[14]

(9) It has been shown that no deuterium exchange occurs at C-6 in the Wolff–Kishner reaction of bicyclo[2.2.1]heptan-2-one: A. Nickon, J. H. Hammons, J. L. Lambert, and R. O. Williams, *J. Am. Chem. Soc.*, **85**, 3713 (1963). We feel that it is unlikely that deuterium loss would occur at C-1 or C-4 in the formation of **8**.

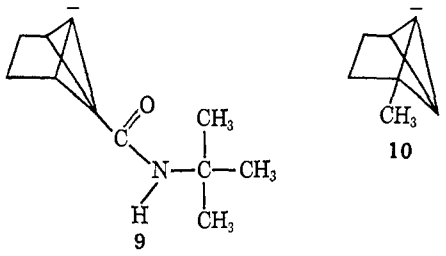
(10) L. L. Ingraham in "Steric Effects in Organic Chemistry," M. S. Newman, Ed., John Wiley and Sons, Inc., New York, N. Y., 1956, p 518; C. A. Coulson and W. E. Moffitt, *J. Chem. Phys.*, **15**, 151 (1947); A. D. Walsh, *Trans. Faraday Soc.*, **45**, 179 (1949).

(11) A. I. Shatenshtein, *Advan. Phys. Org. Chem.*, **1**, 176 (1963).

(12) C. S. Foote, *Tetrahedron Letters*, No. **9**, 579 (1963).

(13) J. Meinwald, C. Swithenbank, and A. Lewis, *J. Am. Chem. Soc.*, **85**, 1880 (1963).

(14) G. L. Closs and R. B. Larrabee, *Tetrahedron Letters*, No. **4**, 287 (1965).



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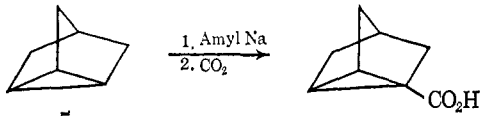
In addition, Finnegan and McNees[15] have shown that the reaction of nortricyclane (**5**) with amylsodium for 6 months at room temperature followed by carbonation yielded 18% of the acid **11**. Thus the fact that nortricyclane underwent H–D exchange of the cyclopropyl hydrogens with potassium *t*-butoxide in *t*-butyl alcohol-O-*d* at 220° was not surprising. It should be stressed at this point that no evidence was obtained for removal of any other hydrogens from the nortricyclane by either Finnegan or us.



5 11

Evidence for an inductive effect in the nortricyclyl system was obtained from the H–D exchange of the dimethyl ketal of nortricyclanone. In this case, the hybridization at the functionalized carbon is very similar to that of nortricyclane. Yet two significant changes can be noted. First, all of the cyclopropyl hydrogens showed increased acidity over the nortricyclane case. Second, proton H_1 which is adjacent to the ketal function was more acidic than H_2 which was one carbon removed. These changes can be rationalized by assuming that the inductive effect of the two methoxyl groups increased the s character of the carbon–hydrogen bond of the carbon adjacent to the ketal carbon. However, this does not offer an obvious explanation for the increased acidity of H_2 in comparison to nortricyclane. When the unique nature of the cyclopropane ring is considered, it is realized that the carbon–carbon bonds have increased p character. As a result, the cyclopropane ring is very efficient at transmitting inductive effects and in acting as an "electron sink."[16] Due to the ease with which inductive effects are delocalized throughout the cyclopropyl ring, the inductive effect of the two methoxyl groups was only slightly decreased when H_1 was compared to H_2 in **7**.

Since the methoxyl functions showed a significant influence on the H–D exchange of the cyclopropyl-type hydrogens, the carbonyl function of nortricyclanone would be expected to show an even greater effect because the inductive effect of a carbonyl ($CH_3C(O)$, $\sigma^* = +1.65$)[17] is considerably greater than the inductive effect of two methoxyl groups (CH_3OCH_2, $\sigma^* = +0.64 \times 2 = +1.28$).[17] The incorporation of a carbonyl function into the tricyclic molecule will also incorporate additional strain into the nortricyclyl system. From Table I it can be seen that the cyclopropyl hydrogens of nortricyclanone are far more acidic than the cyclopropyl hydrogens of either the ketal **7** or of the hydrocarbon **5**. Again the proton of the cyclopropyl ring on the carbon α to the carbonyl group was more acidic than the protons on the cyclopropyl carbons β to the ketone function. The relative acidities of H_1 and H_2 coupled with the greatly increased acidities of all the cyclopropyl hydrogens is consistent with a significant inductive effect of the carbonyl function.

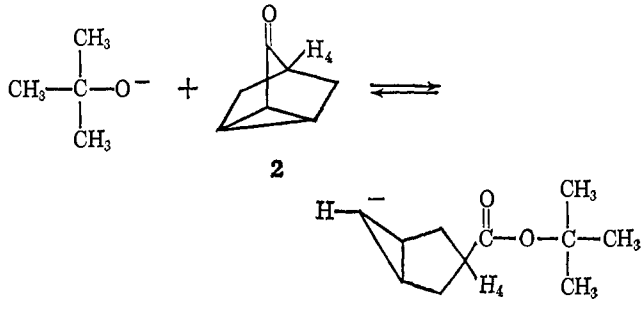
Perhaps the most surprising feature of the H–D exchange of nortricyclanone was the dramatic increase in the acidity of H_4 as compared to **5** and **7**. In fact, the acidity of H_4 was equal to the acidity of the cyclopropyl hydrogen H_2. If this increased acidity were due to the strain incorporated into the tricyclic system, it would be anticipated that exchange would also occur to a detectable extent at H_3 since methylene hydrogens in a strained system have been shown to be more acidic than methine hydrogens in the same system.[11] Thus, the major factor involved in the increased acidity of H_4 appears to be the inductive effect of the carbonyl group.[18] The absence of detectable exchange of H_4 in

(15) R. A. Finnegan and R. S. McNees, *J. Org. Chem.*, 29, 3234 (1964).

(16) For a discussion of this point, see P. G. Gassman and F. V. Zalar, *ibid.*, 31, 166 (1966).

(17) J. Hine, "Physical Organic Chemistry," 2nd ed, McGraw-Hill Book Co., Inc., New York, N. Y., 1962, p 97.

(18) (a) A by-product of the H–D exchange of nortricyclanone was *trans*-bicyclo[3.1.0]hexane-3-carboxylic acid. This raises the question of whether deuterium incorporation at H_4 of nortricyclanone might be due to the cleavage of **2** by *t*-butoxide to yield a, followed by enolization of a, deuterium incorporation at H_4, and recyclization to yield **2**.



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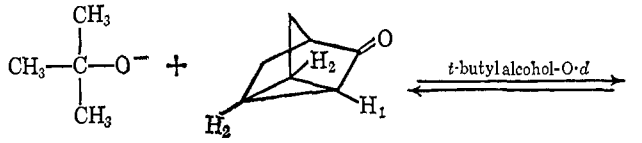
a

This possibility seems unlikely because the anion would have to maintain its existence in a *t*-butyl alcohol solution, while the *t*-butyl ester a underwent enolization and conversion back to the keto form of the ester. In addition, it has been shown in this laboratory that the *t*-butyl ester of *cis*-bicyclo[3.1.0]hexane-3-carboxylic acid is isomerized to the *trans* ester on enolization: J. T. Lumb, unpublished results. (b) An alternate mechanism for deuterium incorporation which we considered and which has been discussed by a referee is the possibility of reversible Michael addition of *t*-butoxide to nortricyclanone to yield b. Compound b



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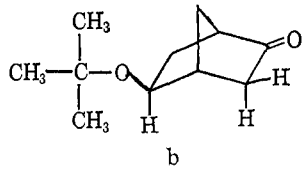
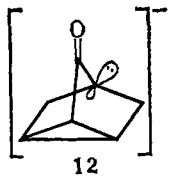


b

could undergo deuterium exchange of the three hydrogens shown. The *exo* proton next to the carbonyl would be expected to undergo exchange most rapidly. As a result, such a mechanism would call for overwhelming exchange of H_1 in comparison to H_2. This is not in agreement with the observed results. In addition, the facts that *t*-butoxide is a poor nucleophile and that no trace of b was found in the reaction mixture make this mechanism seem unlikely. It should be pointed out that alternate mechanisms such as discussed above could alter the quantitative aspects of our data. This reservation should be kept in mind in relation to the ensuing discussion.

the ketal, **7**, indicated that the inductive effect of the carbonyl might not be the only factor involved in the increased acidity of H_4.

The possibility exists that removal of H_4 might yield an anion, **12**, in which the negative charge at the bridge-



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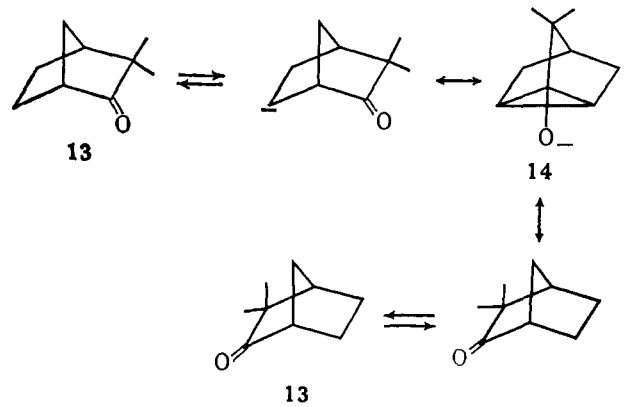
head position is stabilized by the presence of a cyclopropyl ring which is held in close proximity to the negatively charged carbon. The interaction of the cyclopropyl ring with H_4 has been noted in nmr studies of nortricyclanone.[19] When the position of H_4 in nortricyclane (τ 8.09)[20] was compared to the position of H_4 in nortricyclanone (τ *ca.* 8.2),[19] an upfield shift of *ca.* 6 cps was observed. In contrast to the upfield shift observed in going from nortricyclane to nortricyclanone, a downfield shift of *ca.* 16 cps was noted in comparing the same bridgehead proton of norbornane (τ 7.78)[9] with that of norcamphor (τ 7.51).[19] Since the downfield shift is the expected result of placing a carbonyl group next to the position under consideration, both the upfield shift and the actual position of H_4 of nortricyclanone seem anomalous. The position of H_4 in the nmr spectrum of nortricyclanone has been explained by Sauers and Sonnet[19] on the assumption that H_4 feels the induced field of the cyclopropyl ring. Such effects of cyclopropyl ring current have been generally accepted and discussed in detail.[21] Although the position of H_4 of nortricyclanone in comparison to the corresponding proton in norcamphor has been rationalized, the relative position of H_4 in **2** and **5** still poses a problem. We feel that the occurrence of the nmr signal for H_4 at higher field in **2** than in **5** may be due to an increase of the cyclopropyl ring current due to the adjacent carbonyl function. This would result in H_4 being exposed to a greater induced field in **2** than in **5**. This effect would have to be large enough to cancel the normal downfield shift (as observed in going from norbornane to norcamphor) and to add *ca.* 6-cps upfield shift in going from **5** to **2**.

In view of the unusually pronounced interaction of the cyclopropyl ring of **2** with H_4 as demonstrated by nmr, the probability that the acidity of H_4 is in part due to stabilization of the resulting anion by the cyclopropyl ring seems good.

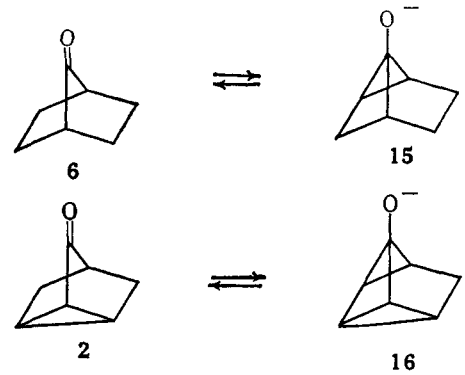
A second example of increased acidity due to the inductive effect of a carbonyl function was noted when 7-ketonorbornane (**6**) was heated to *ca.* 200° in a solution of potassium *t*-butoxide in *t*-butyl alcohol-O-*d*. As noted in Table I, the bridgehead hydrogens of **6** underwent H–D exchange but at a somewhat slower rate than H_4 of **2**. Whether the faster rate of exchange of H_4 of **2** was due to the increased strain of **2** or whether it was due to stabilization of the resulting anion by the cyclopropyl ring has not been established. We feel that the exchange of hydrogen observed in the reactions of **2** and **6** with strong base clearly demonstrates that a carbonyl group can provide considerable stabilization for an adjacent carbanion by a purely inductive effect.

One interesting facet of our exchange reactions was the complete absence of any evidence for homoenolization.[22–26] As elegantly shown by Nickon and coworkers[9,22] camphenilone (**13**) undergoes conversion to the anion **14** in the presence of strong base. This con-



13 **14** **13**

version resulted in the racemization of optically active camphenilone and, when the reaction was carried out in deuterated solvent, in deuterium incorporation. An analogous type of homoenolization might be expected with 7-ketonorbornane and with nortricyclanone to yield the anions **15** and **16**, respectively. If such reac-



6 **15** **2** **16**

tions took place, deuterium incorporation would be expected to occur at H_2 in **6** and H_3 in **2**. An alternate possibility is that **15** and **16** could undergo bond cleavage in a different direction to give other low molecular weight bicyclic ketones. Since neither of these possibilities were substantiated experimentally, it appears that **2** and **6** do not undergo homoenolization. This lack of homoenolization is probably due to the failure of **2** and **6** to meet the geometrical requirements necessary for a spatial stabilization of the incipient anion by the carbonyl group.

Experimental Section

Nuclear magnetic resonance spectra were obtained on a 60-Mc Varian Model A-60 spectrometer. Vapor phase chromatographic work was performed with an Aerograph Autoprep Model A-700.

Hydrogen–Deuterium Exchange of Nortricyclanone (2). Nortricyclanone was prepared according to the procedure of Meinwald,

(19) R. R. Sauers and P. E. Sonnet, *Chem. Ind.* (London), 786 (1963).
(20) R. Srinivasan, *J. Am. Chem. Soc.*, **83**, 4923 (1961).
(21) K. B. Wiberg and B. J. Nist, *ibid.*, **83**, 1226 (1961); K. L. Williamson, C. A. Lanford, and C. R. Nicholson, *ibid.*, **86**, 762 (1964).
(22) A. Nickon and J. L. Lambert, *ibid.*, **84**, 4604 (1962).
(23) R. Howe and S. Winstein, *ibid.*, **87**, 915 (1965).
(24) T. Fukunaga, *ibid.*, **87**, 916 (1965).
(25) A. Nickon, H. Kwasnik, T. Swartz, R. O. Williams, and J. B. DiGiorgio, *ibid.*, **87**, 1615 (1965).
(26) D. J. Cram, "Fundamentals of Carbanion Chemistry," Academic Press Inc., New York, N. Y., 1965, p 65.

et al.[27] In a drybox under constant nitrogen pressure a solution of 9 g of potassium *t*-butoxide (0.08 moles) in 73 ml of dry *t*-butyl alcohol-O-*d* (*ca.* 1 *M*) was prepared in a Pyrex test tube with 4 g (0.037 mole) of nortricyclanone. The tube was sealed and placed in a steel bomb with a small amount of *t*-butyl alcohol outside the sealed tube to offset a pressure differential encountered during heating. The bomb was sealed and heated in an oil bath at 195–200° for 29 hr. After slowly cooling to room temperature, the tube was opened and the dark brown contents was poured into about 200 ml of water. The aqueous solution was extracted with three 50-ml portions of ether, and the ether extracts were combined, dried over anhydrous magnesium sulfate, filtered and distilled through a short column packed with glass helices. The residue was distilled *in vacuo* to give 145 mg (3.8% recovery) of deuterated nortricyclanone, bp 78° (25 mm), and 1.9 g of a viscous liquid, bp 120–121° (0.07 mm). Acidification of the basic aqueous solution with concentrated hydrochloric acid followed by extraction with ether gave 1.5 g (0.011 mole) of *trans*-bicyclo[3.1.0]hexane-3-carboxylic acid, mp 58–59° after two recrystallizations from pentane.

Nmr Analysis of Deuterated Nortricyclanone. A solution of 1.2 g (0.01 mole) of potassium *t*-butoxide, 0.056 ml of water (0.003 mole, butoxide:water ratio 10:3), and 10 ml of dry ether (distilled from lithium aluminum hydride) was prepared in a 100-ml, side-arm, round-bottom flask. The deuterated nortricyclanone from above was slowly added by syringe and the suspension magnetically stirred at room temperature for 25 min. The mixture was quenched with about 50 ml of ice–water, acidified with concentrated hydrochloric acid, and extracted with three 50-ml portions of ether. The extracts were combined, dried, and filtered. Distillation of the residue gave 125 mg (71%) of *cis*-bicyclo[3.1.0]-hexane-3-carboxylic acid, bp 69–70° (0.25 mm), contaminated with 8% of the *trans* epimer. The acid was dissolved in aqueous bicarbonate, reacidified with concentrated hydrochloric acid, extracted, and redistilled to remove trace impurities.

The nmr spectrum of the nondeuterated acid **4** displayed the following characteristics: a multiplet at τ 10.00 (H_5) and 9.60 (H_1), a broad peak at 8.79 (H_2), an intense band at 7.99 (H_3), and a complex multiplet centered at 7.14 (H_4). The relative areas of these protons were in the ratio 1:1:2:4:1 ($H_1:H_5:H_2:H_3:H_4$). The relative areas of these protons in the acid from the cleavage described above, considering H_5 as unity, were 0.18:1:0.55:4.1:0.24. *Deuterium Anal.* Calcd for C_7H_8O from nmr analysis (3.05 atoms of D): 38.1 atom % excess D. Found: 38.8 atom % excess D.

Hydrogen–Deuterium Exchange of 7,7-Dimethoxynortricyclane (7). The dimethyl ketal, **7**, bp 65–67° (10 mm), was prepared from nortricyclanone in 83% yield using commercial trimethyl orthoformate and *p*-toluenesulfonic acid as catalyst. A solution of 5 g (0.044 mole) of potassium *t*-butoxide, 40 ml of *t*-butyl alcohol-O-*d*, and 2.0 g (0.013 mole) of ketal **7** was sealed in a Pyrex tube and heated to 215–220° for 48 hr in a steel bomb as described for nortricyclanone. After suitable cooling, the tube was opened and the contents were quenched with about 50 ml of water, extracted with three 50-ml portions of pentane, dried, and filtered, and the residue was distilled *in vacuo* to give 1.35 g (67.5% recovery) of deuterated **7**. The ketal was hydrolyzed to **2** in 78% yield with 5% aqueous sulfuric acid. The resultant deuterated nortricyclanone was cleaved to **4** and the extent of deuterium incorporation determined as described above. The relative areas of protons H_1, H_5, H_2, H_3, and H_4 were found to be in the ratio 0.405:1:1.19:4.3:0.94. *Deuterium Anal.* Calcd for C_7H_8O from nmr analysis (1.41 atoms of D): 17.6 atom % excess D. Found: 18.1 atom % excess D.

Hydrogen–Deuterium Exchange of 7-Ketonorbornane (6). Ketone **6** was obtained from the hydrogenation of 7-ketonorbornene,[28] mp 78–79°. A solution of 9 g (0.08 mole) of potassium *t*-butoxide in 70 ml of *t*-butyl alcohol-O-*d* and 3.3 g (0.03 mole) of 7-ketonorbornane was sealed in a tube and heated to 195–200° for 48 hr as described above. The solution was then quenched with about 100 ml of water, extracted with three 50-ml portions of pentane, dried, and filtered, and the majority of the pentane and residual *t*-butyl alcohol was distilled through a 1-ft Vigreux column. The residue was added to a 50-ml, three-neck, round-bottom flask along with 500 mg of powdered potassium hydroxide, 4 ml of anhydrous hydrazine, and 20 ml of ethylene glycol.[29] The solution was stirred and slowly heated to 190° while a slow stream of dry nitrogen flushed the vapors into a trap immersed in Dry Ice–isopropyl alcohol. After 6 hr the contents of the trap was extracted with about 30 ml of pentane. The pentane extract was successively washed with 10-ml portions of water, dried, filtered, and concentrated to about 2 ml. The residue was preparatively vapor phase chromatographed on a 6 ft × 0.25 in., 15% didecyl phthalate on Chromosorb P column at 60° yielding about 150 mg of norbornane, mp 85–86°. The area due to the bridgehead hydrogens in the nmr (τ 7.78) of this hydrocarbon, in comparison to the remaining hydrogens, was in the ratio of 1.50:10. The Wolff–Kishner reduction of a deuterated norcamphor has been reported to proceed without loss of deuterium.[9] Therefore, it is likely that the conversion of **6** to norbornane also proceeds without deuterium loss. *Deuterium Anal.* Calcd for C_7H_{12} from nmr analysis (0.5 atom of D): 4.1 atom % excess D. Found: 4.6 atom % excess D.

The basic aqueous solution was acidified with concentrated hydrochloric acid and extracted with ether, and the ethereal solution was dried and filtered. The residue was distilled *in vacuo* to give 1.25 g of a carboxylic acid, bp 85° (0.27 mm), mp *ca.* 30°, infrared spectrum identical with that of cyclohexanecarboxylic acid.

Hydrogen–Deuterium Exchange of Nortricyclane (5). The Wolff–Kishner reduction of the hydrazone of **2**, employing the same conditions as described above for the reduction of **6**, proved adequate for the small-scale preparation of the extremely volatile hydrocarbon **5**. A solution of 600 mg (0.0053 mole) of potassium *t*-butoxide in 6 ml of *t*-butyl alcohol-O-*d* and 200 mg (0.0021 mole) of nortricyclane was sealed in a Pyrex tube and heated to 260–265° from 64 hr as described above. The tube was cooled and the contents was slowly distilled through a small Vigreux column into a receiver immersed in a Dry Ice–isopropyl alcohol bath. About 3.5 ml of volatile material was collected. The nortricyclane was isolated from this collected liquid by preparative vpc at 80° on a 6 ft × 0.25 in. 15% didecyl phthalate on Chromosorb P column to give nortricyclane, mp 57–58°.

The nmr peak heights of cyclopropyl, H_3, and H_4 protons in **5** were in the ratio of 2.34:6:1 which calculated for 22% deuterium incorporation per cyclopropyl hydrogen.

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