cinnamic acid and 2.2 g (15%) of diphenethyl ketone. The latter compound was compared with a sample prepared by dry distillation of barium hydrocinnamate at 340–350°. Both absorbed at $\bar{\nu}_{max}^{KBr}$ (C=O) 1700 cm^{-1}; nmr ($CDCl_3$) τ 2.83 (br s, 10 H), 7.19, 73.7, 7.58 [J = 5, 7, and 5 cps (sextet 4 H)].

The red **2,4-dinitrophenylhydrazone** melted at 115°[31] (from ethanol).

Reaction of Benzoic Anhydride with 1 in Aromatic Hydrocarbons as Solvents.—To a stirred solution of 0.41 g of 1 in 10 ml of *o*-xylene at 140°, there was added 0.1 g of benzoic anhydride. A yellow precipitate started to separate immediately. After heating for 30 min at 140°, the mixture was filtered, while still hot. On cooling of the filtrate to 0°, a second complex precipitated. It was found to be pure chlorocarbonylbis(triphenylphosphine)rhodium (6): mp 203–205°, $\bar{\nu}_{max}^{Nujol}$ 1965 cm^{-1}.

Anal. Calcd for $C_{37}H_{30}ClOP_2Rh$: C, 64.3; H, 4.3; Cl, 5.1. Found: C, 64.0; H, 4.4; Cl, 5.4.[10b]

The first *insoluble* precipitate was heated either with benzene or better with methylene chloride to remove the still adhering compound 6 and dried at room temperature at 0.5 mm. Thus was obtained 0.104 g of yellow crystals, mp 232–233°, of **chloro(phenyl)bis(triphenylphosphine)rhodium(II)** (**5**, Ar = C_6H_5).

Anal. Calcd for $C_{42}H_{35}ClP_2Rh$: C, 68.2; H, 4.7; Cl, 4.8. Found: C, 68.0, 68.2; H, 4.9, 4.3; Cl, 4.8, 4.7.

The complex does not show any carbonyl absorption in the infrared spectrum and is too insoluble for nmr measurements. The esr spectrum, in which strong lines between g = 2.85 and 9.85 are observed, indicated the paramagnetic character of the compound.

(31) H. A. Weidlich and M. M. Delius, *Ber.*, **74**, 1195 (1941).

p-Toluic anhydride gave in the analogous experiment only chlorocarbonylbis(triphenylphosphine)rhodium (6); the same was the case for benzoic anhydride and 1 in boiling mesitylene, whilst in boiling benzene or toluene benzoic anhydride did not react with the rhodium complex 1 at all.

When a mixture of 0.59 g of *p*-chlorobenzoic anhydride, 0.185 g of 1, and 2 ml of toluene was refluxed for 1 hr, the orange-yellow crystals that separated proved to be a mixture of a rhodium–aroyl complex and 6, having strong absorption bands at 1685 and 1965 cm^{-1} (relative intensities of 1.4:1). When the experiment was repeated in 3 ml of *o*-xylene, the mixture showed the same absorption peaks, but the ratio of intensities was 1:2.5. Heating either of the two mixtures in boiling mesitylene for 30 min caused the aroyl carbonyl peak at 1685 cm^{-1} to disappear.

Registry No.—1, 14694-95-2; **5** (Ar = C_6H_5), 21537-43-9; 6, 13938-94-8; benzoic anhydride, 93-97-0; *o*-toluic anhydride, 607-86-3; *m*-toluic anhyride, 21436-44-2; *p*-toluic anhydride, 13222-85-0; *p*-chlorobenzoic anhydride, 790-41-0; *p*-deuteriobenzoic anhydride, 21494-28-0; 1,5-dimethylfluorenone, 21436-47-5; 2,6-dimethylfluorenone, 21436-48-6; 2,6-dideuteriofluorenone, 21436-49-7; *p*-deuteriobenzoic acid, 4551-62-6.

Acknowledgment.—The authors wish to thank Professor Ernst D. Bergmann for his advice.

The Synthesis, Spectral Properties, and Chemical Ring Opening of Tricyclo[3.3.0.0^{2,8}]octan-3-one, a Rigid Model for Unsymmetrical Cyclopropyl Ketone Participation

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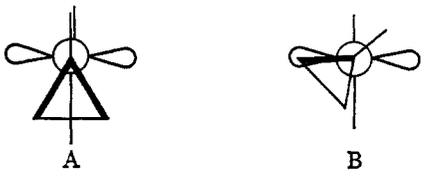
Stereomodels reveal that the skeletal framework of tricyclo[3.3.0.0^{2,8}]octan-3-one (4) constitutes a rigid model for cyclopropyl ketone participation in an unsymmetrical conformation. Ketone 4 and three specifically deuterated derivatives (C_2-*d*, C_4-d_2, and C_8-*d*) were synthesized. These compounds were used, in conjunction with spin decoupling experiments, to interpret the nmr spectrum of ketone 4. Unambiguous chemical shift assignments for the C_1, C_2, C_4, C_5, and C_8 protons were made. The major fragmentation pathway of this tricyclic ketone in the mass spectrum involves the loss of ketene to give a base peak at *m/e* 80. Reductive cleavage of ketone 4 with lithium in liquid ammonia yielded as products 95% *cis*-bicyclo[3.3.0]octan-3-one (12) and 5% bicyclo[3.2.1]-octan-3-one (13). Treatment of ketone 4 with hydrogen bromide in methylene chloride gave, after reductive removal of the bromine atom, a mixture of 80% 12 and 20% 13. Interpretation of these results in terms of ground-state cyclopropyl ketone delocalization in an unsymmetrical conformation is discussed. The stereoselectivity of the dissolving metal cleavage is consistent with the known stereoelectronic requirements for reductive elimination of α-substituted ketones. The product mixture from the acid-catalyzed opening appears to reflect (in part) thermodynamic control. It is concluded that an evaluation of product composition data from either of these general chemical probes is not a valid method to assess ground-state cyclopropyl ketone delocalization.

It has been firmly established that freely rotating systems containing a cyclopropane ring adjacent to an electron-deficient center (carbonyl group[4] or carbonium ion[5]) adopt the symmetrical, bisected conformation A in preference to the unsymmetrical geometry B. Collectively, these data have been advanced in support of the theoretical prediction[6] that maximum delocalization should occur in the bisected conformation A. A more rigorous test of this hypothesis, however, requires a



A B

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(2) Partial financial support from the University of Texas Research Institute is gratefully acknowledged.

(3) Predoctoral Fellow of the National Institutes of Health, 1966–1968.

(4) L. S. Bartell and J. P. Guillory, *J. Chem. Phys.*, **43**, 647, 654 (1965); L. S. Bartell, J. P. Guillory, and A. P. Parks, *J. Phys. Chem.*, **69**, 3043 (1965).

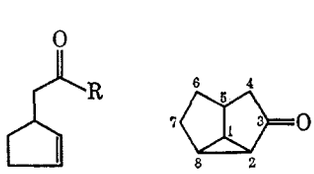
(5) N. C. Deno, H. G. Richey, Jr., J. S. Liu, D. N. Lincoln, and J. O. Turner, *J. Amer. Chem. Soc.*, **87**, 4533 (1965); C. U. Pittman, Jr., and G. A. Olah, *ibid.*, **87**, 5123 (1965); T. Sharpe and J. C. Martin, *ibid.*, **88**, 1815 (1966); H. C. Brown and J. D. Cleveland, *ibid.*, **88**, 2051 (1966); P. von R. Schleyer and G. W. VanDine, *ibid.*, **88**, 2321 (1966); H. G. Richey, Jr., and J. M. Richey, *ibid.*, **88**, 4971 (1966).

(6) R. Hoffman, *Tetrahedron Lett.*, 3819 (1965), and references cited therein; K. Shimizu, H. Kato, and T. Yonezawa, *Nippon Kagaku Zasshi*, **88**, 1050 (1967); *Chem. Abstr.*, **68**, 77601 (1968).

comparison of the delocalization possible in A with the delocalization possible in B. Clearly, conformationally mobile molecules are not suitable for such a study. In contrast, however, an examination of cyclopropyl participation in geometrically defined, rigid systems provides a way to individually evaluate both conformations (A and B).

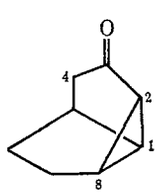
The criteria for a model of cyclopropyl ketone delocalization held in the conformationally less favorable geometry B are fulfilled by the rigid, tricyclo[3.3.0.0^{2,8}]-octan-3-one (**4**) molecule. Stereomodels of **4** show that the π bond of the carbonyl group forms a dihedral angle of approximately 25° with the C_2–C_8 σ-cyclopropane bond. Thus, this bond is geometrically disposed for preferential overlap with the adjacent electron-deficient center. In addition to the synthesis and spectral properties of tricyclo[3.3.0.0^{2,8}]octan-3-one (**4**), the course of both the acid-catalyzed and the reductive ring-opening reactions of **4** are described. As discussed in detail below, it is concluded that an evaluation of product composition data from either of these general chemical probes[7] is not a valid method to assess ground-state cyclopropyl ketone delocalization. The use of proton and carbon-13 nuclear magnetic resonance to examine cyclopropyl ketone participation in rigid systems will be communicated separately.

Synthesis and Spectral Properties.—The well-documented synthetic route to cyclopropyl ketones utilizing an intramolecular diazo ketone addition to a carbon–carbon double bond[8] seemed admirably suited for the preparation of tricyclo[3.3.0.0^{2,8}]octan-3-one (**4**). Conversion of 2-cyclopenten-1-acetic acid[9] (**1**) into its acid chloride (**2**), followed by treatment with ethereal diazomethane, furnished the diazo ketone **3a**. Decomposition of the latter with cupric sulfate in refluxing cyclohexane yielded the desired tricyclo[3.3.0.0^{2,8}]-octan-3-one (**4**).



1, R = OH
2, R = Cl
3a, R = CHN_2
3b, R = CDN_2

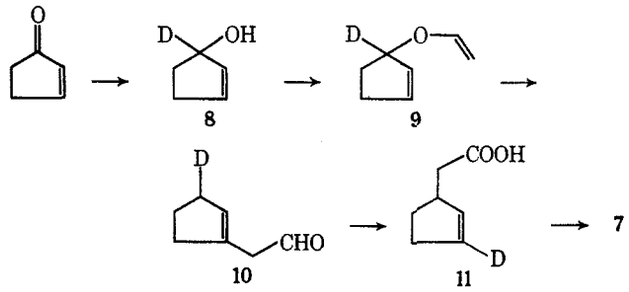
4



4
5, C_2-*d*
6, C_4-d_2
7, C_8-*d*

In order to interpret the nmr spectrum of **4** (*vide infra*), three specifically deuterated derivatives were prepared. Substitution of deuteriodiazomethane into the sequence described above gave, after decomposition of the deuteriodiazo ketone **3b**, the C_2-*d* ketone **5**. The C_4-d_2 ketone **6** was prepared smoothly by base-catalyzed deuterium exchange of the parent material **4**. Finally, specifically deuterated C_8-*d* ketone **7** was synthesized. As outlined[10] in Scheme I, the deuterium atom was introduced by lithium aluminum deuteride reduction of

SCHEME I



8 **9** **10** **11**

2-cyclopentenone to give the deuterated allylic alcohol **8**. Thermal rearrangement of the allyl vinyl ether **9**, prepared from **8** by mercuric acetate catalyzed exchange[11] with ethyl vinyl ether, yielded 2-cyclopenten-1-acetaldehyde-3-*d* (**10**). Silver oxide oxidation of aldehyde **10** then gave corresponding deuterated acid **11**. With the position of the deuterium atom in acid **11** firmly established by virtue of the synthetic sequence, this material was converted into the C_8-*d* ketone **7** using the procedure previously described.

The 100-MHz nmr spectrum of the parent ketone **4** is shown in Figure 1a. The low-field portion reveals three distinct one-proton signals, while the remaining seven protons of **4** appear in two broad multiplets of four and three protons each. Since all ten protons of **4** are nonequivalent, the detailed analysis of this spectrum was facilitated by examination of the spectra for the deuterated ketones **5**, **6**, and **7**.

The C_4-d_2 ketone **6** spectrum showed complete disappearance of the one-proton pair of doublets centered at 2.38 ppm (J = 9, 17 Hz). The high-field doublet marked in Figure 1a (1.56 ppm, J = 17 Hz) was also absent and integration revealed the loss of one proton from this high-field region. In addition, the broad one-proton signal at 2.9 ppm was sharpened considerably in the C_4-d_2 spectrum. Consequently, this resonance must be coupled strongly to the C_4 methylene group. The remainder of the spectrum was unchanged. Molecular models suggest that only one of the two C_4 methylene protons should be coupled with the C_5 proton, *i.e.*, $J_{5\text{-}endo\ 4} \approx 0$ (dihedral angle *ca.* 90°) and $J_{5\text{-}exo\ 4} > 0$ (dihedral angle *ca.* 30°).[12] Thus, the high-field doublet at 1.56 ppm is assigned to the C_4-*endo* proton, the low-field pair of doublets at 2.38 ppm to the C_4-*exo* proton, and the broad multiplet at 2.9 ppm to the tertiary C_5 proton.

The approximate position of the C_2 cyclopropyl proton was ascertained from the nmr spectrum of the C_2-*d* ketone **5**. The intensity of the "triplet" at 1.85 ppm in Figure 1 was reduced considerably in the spectrum of the partially deuterated **5** (71% d_1; see Experimental Section). As shown below, however, this *apparent* triplet results from overlap of two resonances and does not correspond to the exact chemical shift for the C_2 proton. In addition, the signal at 2.65 ppm appeared as a complex multiplet in the C_2-*d* ketone **5** spectrum. This observed coupling, the complex appearance of which undoubtedly reflects the partially deuterated nature of **5**, requires that the 2.65-ppm resonance be assigned to either the C_1 or the C_8 cyclopropyl proton.

(7) *Cf.* H. O. House and C. J. Blankley, *J. Org. Chem.*, **33**, 47 (1968), and references cited therein; A. J. Bellamy and G. H. Whitham, *Tetrahedron*, **24**, 247 (1968); W. G. Dauben and E. J. Deviny, *J. Org. Chem.*, **31**, 3794 (1966).

(8) W. von E. Doering, E. T. Fossel, and R. L. Kaye, *Tetrahedron*, **21**, 25 (1965).

(9) J. T. Fitzpatrick and E. Marcus, U. S. Patent 3,014,960; *Chem. Abstr.*, **56**, P8590*d*. Commercially available from Aldrich Chemical Co.

(10) *Cf.* R. K. Hill and A. G. Edwards, *Tetrahedron Lett.*, 3239 (1964).

(11) W. H. Watanabe and L. E. Conlon, *J. Amer. Chem. Soc.*, **79**, 2828 (1957).

(12) M. Karplus, *J. Chem. Phys.*, **30**, 11 (1959).

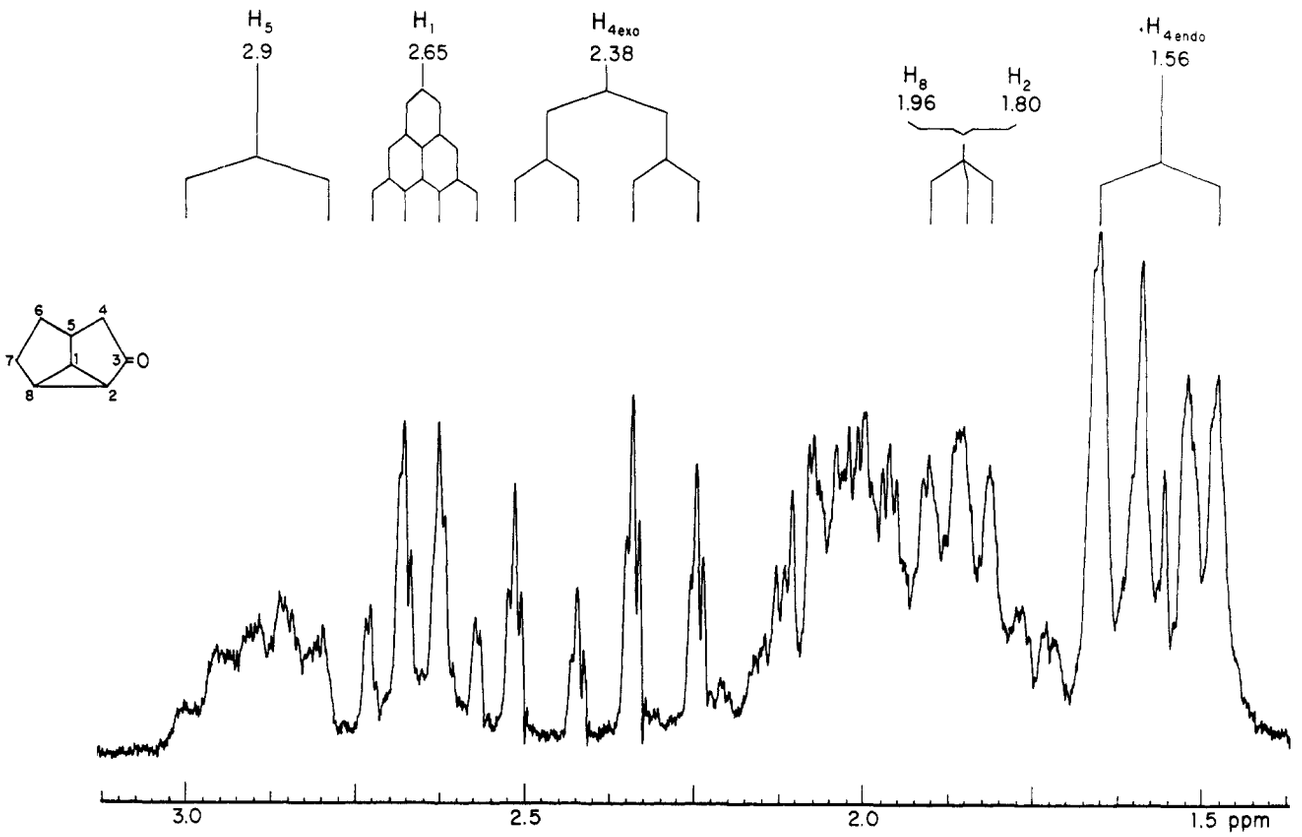


Figure 1a.—100-MHz nmr spectrum of tricyclo[3.3.0.0^{2,8}]octan-3-one (**4**).

The problems associated with making an unambiguous distinction between these two positions were resolved by the nmr spectrum of the C_8-*d* ketone **7**. This spectrum is presented in Figure 1b. A comparison of the two spectra in Figure 1 reveals that the one-proton signal at 2.65 ppm (a fortuitous quartet due to coupling with three different protons) has collapsed to a superimposed doublet of doublets which appears as a triplet; the *apparent* triplet at 1.85 ppm now appears as a doublet at 1.80 ppm; and integration shows that one proton has disappeared from the 2.0-ppm region. These data, coupled with the observations from the C_2-*d* ketone spectrum, allow the unique assignment of the 2.65-ppm resonance to the C_1 proton and the 1.80-ppm signal to the C_2 proton. The loss of a proton from the 2.0-ppm region and the appearance of a one-proton doublet at 1.80 ppm in the C_8-*d* spectrum indicates that the third (C_8) cyclopropyl proton resonance is close to that for the C_2 proton and results in the apparent triplet seen at 1.85 ppm in Figure 1a.

An approximate chemical shift for this C_8 cyclopropyl proton was obtained from spin decoupling experiments on the parent ketone **4**. Irradiation at 1.88 ppm resulted in collapse of the "quartet" at 2.65 ppm into a *doublet*, indicating decoupling of both remaining cyclopropyl protons. Assuming this frequency is *ca.* halfway between the C_2 and C_8 proton resonances, this gives an approximate chemical shift of 1.96 ppm for the C_8 proton. Finally, extensive spin decoupling experiments on both **4** and **7** were in complete accord with all the assignments made above. No attempt was made to assign the two sets of methylene resonances (two protons each, *ca.* 1.6 and 2.0 ppm) to the C_6 and C_7 protons or to evaluate the small, long-range couplings present.

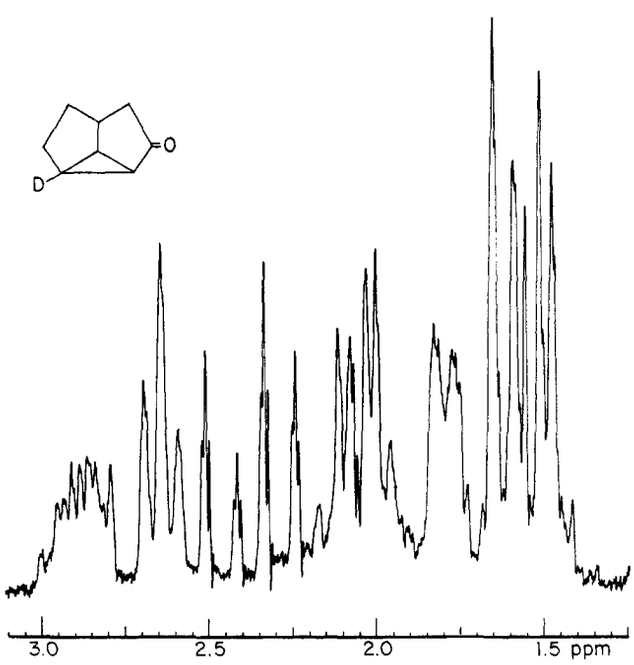


Figure 1b.—100-MHz nmr spectrum of tricyclo[3.3.0.0^{2,8}]octan-3-one-8-*d* (**7**).

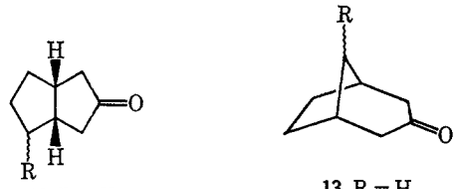
The major fragments observed in the mass spectrum of tricyclo[3.3.0.0^{2,8}]octan-3-one (**4**) are given in Table I. The base peak, *m/e* 80, apparently results from loss of ketene from the parent ion. A metastable peak at *m/e* 52.5, corresponding to the fragmentation 122 → 80, is present. The mass spectra of the deuterated derivatives of **4** confirm the direct loss of the C_3 and C_4 carbon atoms. The C_4-d_2 ketone **6** showed a base peak at *m/e* 80, while both the C_2-*d* derivative **5** and the C_8-*d* ketone

TABLE I
MASS SPECTRUM OF TRICYCLO[3.3.0.0^{2,8}]OCTAN-3-ONE (4)

m/e (rel intensity)		
123 (1.5)	81 (11)	68 (5)
122 (15)	80 (100)	66 (6)
121 (2)	79 (40)	53 (10)
94 (5)	78 (5)	51 (4)
91 (4)	77 (10)	41 (6)

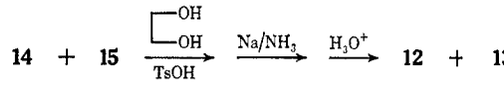
7 had base peaks at *m/e* 81. Loss of a hydrogen atom from the *m/e* 80 fragment to yield the only other significant fragment at *m/e* 79 for **4** (and **6** and at *m/e* 80 for **5** and **7**) is supported by a strong metastable peak at *m/e* 78.2.

Ring Cleavage.—In theory, ring cleavage of the tricyclic ketone **4** can yield two different bicyclic skeletons. For example, reductive opening (dissolving metal) of the C_2–C_8 bond yields *cis*-bicyclo[3.3.0]octan-3-one (**12**), while rupture of the C_1–C_2 bond gives bicyclo[3.2.1]octan-3-one (**13**). The initial bond cleavage in both cases furnishes a secondary center. In an analogous fashion, hydrobromic acid treatment of **4** gives the corresponding bromo ketones **14** and **15**. In practice, the initial acid-cleavage products were converted into ketones **12** and **13**, as shown below. Thus, the actual course of both of these ring-opening reactions was monitored by vpc analysis of ketones **12** and **13**.



12, R = H
14, R = Br

13, R = H
15, R = Br



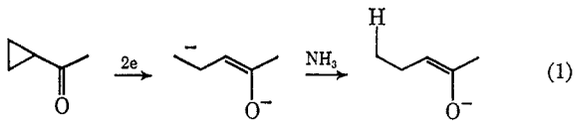
The reductive opening of ketone **4** was carried out using a limited amount of lithium in liquid ammonia. Under conditions resulting in approximately 50–65% reaction, the formation of alcoholic products was essentially avoided. Analysis of the resulting mixture of bicyclic ketones showed 95% *cis*-bicyclo[3.3.0]octan-3-one (**12**) and 5% bicyclo[3.2.1]octan-3-one (**13**).

Ketone **4** was treated with excess hydrogen bromide in methylene chloride solution (−10°, 2 hr). After removal of the bromine atom (as shown above), the product mixture contained 80% ketone **12** and 20% ketone **13**.

Both of these reactions yield predominantly the product expected from selective cleavage of the cyclopropane σ bond best oriented for overlap with the adjacent p orbital (*i.e.*, the bond darkened in B). In agreement with similar studies, the reductive opening[7] is more stereoselective than the acid-catalyzed opening.[13] Although this apparent stereoselectivity has been rationalized previously[7,13] on the basis of preferential overlap of one cyclopropane σ bond, as shown in B, a consideration of the individual mechanisms involved does not support this hypothesis.

(13) *Cf.* J. R. Williams and H. Ziffer, *Chem. Commun.*, 194 (1967); B. A. Shoulders, W. W. Kwie, W. Klyne, and P. D. Gardner, *Tetrahedron*, **21**, 2973 (1965).

The net stoichiometry of the dissolving metal opening of a cyclopropyl ketone requires a two-electron addition to yield an enolate ion and a carbanion (see eq 1). The

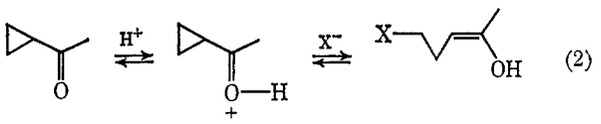


(1)

actual ring opening may occur at either the anion-radical or the dianion stage; but, in either case, the reaction is effectively *irreversible*, since the carbanion formed will be protonated by ammonia. A kinetically controlled bond rupture therefore determines the product composition.

It is well known that cyclohexanone derivatives containing α substituents such as halo, amino, acyloxy or hydroxy undergo reductive α elimination to yield the corresponding cyclohexanone enolate ion. These reactions show distinct stereoelectronic requirements. An axial substituent is eliminated in preference to an equatorial one. This conformational preference is due to the energetically favorable possibility of continuous overlap in the developing π framework of the enolate ion when the leaving group is axial.[14] The reductive opening of a cyclopropyl ketone can be viewed as simply an intramolecular example of such an α-elimination process. The same stereoelectronic requirements for continuous overlap in the developing enolate ion, therefore, should apply. Consideration of these leads to the stereoselective formation of the same product as predicted from B. For example, rupture of the C_2-C_8 σ bond in **4** results in maximum overlap during enolate formation. Thus, the stereoselective reductive opening of rigid cyclopropyl ketones is consistent with the general geometric requirements for elimination of an α substituent.[15] The presence of any preferential ground state participation analogous to that shown in B is not required.

A reasonable mechanism for the acid-catalyzed opening of a cyclopropyl ketone involves initial protonation of the carbonyl group followed by nucleophilic ring opening (stepwise *or* concerted) to yield a halo enol (see eq 2). In principle, the ring-opening step is



(2)

reversible. Consequently, the final product composition could reflect *both* kinetic and thermodynamic control. Although no specific equilibria data are available, the formation (in part) of the more stable product would account for the decreased stereoselectivity generally exhibited by these acid-catalyzed openings.[7,13,15] The formation of bromo ketones **14** (*ca.* 80%) and **15** (*ca.* 20%) from ketone **4** is in qualitative agreement with this hypothesis.

In conclusion, it has been shown that ground-state delocalization plays little or no role in determining the product compositions from either of these ring-opening reactions. Thus, the use of these chemical probes does

(14) H. O. House, "Modern Synthetic Reactions," W. A. Benjamin, Inc., New York, N. Y., 1965, pp 56–57.

(15) Other nonconjugative factors may be important in determining the course of these ring openings; see, for example, A. Nickon and N. H. Werstiuk, *J. Amer. Chem. Soc.*, **89**, 3914, 3915, 3917 (1967).

not constitute a valid method to evaluate ground-state cyclopropyl ketone delocalization.

Experimental Section

Nmr spectra were obtained on a Varian Associates Model A-60 or HA-100 spectrometer; infrared spectra were measured on a Perkin-Elmer Model 237 or 257 grating infrared spectrometer; mass spectra were obtained on an AEI MS-9 double-focusing instrument. Vpc analysis was performed on a Model 600-C Aerograph HiFi instrument with a flame detector and nitrogen carrier gas, or on an Aerograph A-90-P3 instrument. Optimum separation of ring-cleavage products was obtained using a 15% QF-1 column (20 ft × 1/8 in., 100–120 mesh Chromosorb W). The order of elution was ketone **13**, followed closely by ketone **12**, and finally ketone **4**. Microanalyses were performed by Spang Microanalytical Laboratory, Ann Arbor, Mich.

Tricyclo[3.3.0.0^{2,8}]octan-3-one (4) was prepared from 2-cyclopentene-1-acetic acid[9] (**1**) by the general method of Doering.[8] **1** gave 2-Cyclopentene-1-acetyl chloride (**2**), bp 82–83° (30 mm), ir (CCl_4) 1805 cm^{-1} (thionyl chloride method, 86%), and **3a**, not purified, ir (film) 2100 cm^{-1}. A solution of **3a** [from 6.0 g (0.042 mol) of acid chloride] in cyclohexane (40 ml) was added over a 4-hr period to a stirred, refluxing suspension of cupric sulfate (16 g) in cyclohexane (400 ml). After an additional 3 hr of heating, the mixture was cooled, filtered, and concentrated to furnish an orange oil. Distillation yielded impure **4**, bp 76–82° (6.8 mm). This yellow liquid was chromatographed on silica gel (64 g) in benzene to give a homogeneous material (tlc). Distillation furnished pure **4**; bp 76–77° (6.5 mm), yield 2.7 g (53% from acid chloride); mol wt (mass spectrum) 122; ir (CCl_4) 1723 cm^{-1}; nmr, Figure 1a. The semicarbazone derivative had mp 211–212°; the 2,4-dinitrophenylhydrazone had mp 163–165°.

Anal. Calcd for $C_8H_{10}O$: C, 78.65; H, 8.25. Found: C, 78.34; H, 8.23.

Tricyclo[3.3.0.0^{2,8}]octan-3-one-4-d_2 (6).—A solution of ketone **4** (600 mg, 4.9 mmol) and sodium methoxide (*ca.* 50 mg) in methanol-O-*d* (9 ml) was heated at reflux for 54 hr. The crude product obtained by ether extraction was resubmitted to the above procedure (19-hr reflux). Work-up and preparative vpc (4% QF-1, 130°) yielded the C_4-d_2 ketone **6**; yield 184 mg (31%); mass spectrum indicated 95% d_2, 5% d_1; ir (CCl_4) 2950, 2100, and 1723 cm^{-1}; nmr, see text.

Tricyclo[3.3.0.0^{2,8}]octan-3-one-8-*d* (7).—The sequence[10] is outlined in Scheme I.

2-Cyclopenten-1-ol-1-*d* (8).—A solution of freshly distilled 2-cyclopentenone[16] (5.00 g, 61 mmol) in ether (15 ml) was added over a 6-min period to a cold (ice bath), stirred suspension of lithium aluminum deuteride (0.80 g, 19 mmol) in ether (150 ml). After stirring for an additional 30 min at 0°, the excess hydride was carefully decomposed with water, the organic phase was decanted, and the residue was extracted with hot ether. The combined organic phases were dried ($MgSO_4$) and distilled to yield **8**; bp 65–69° (31 mm); yield 4.2 g (80%); ir (CCl_4) 3300, 2950, and 2150 cm^{-1}; nmr, no signal for allylic proton adjacent to OH.

2-Cyclopenten-1-yl-1-*d* vinyl ether (9) was prepared from alcohol **8** by mercuric acetate catalyzed[11] exchange with ethyl vinyl ether; bp 62–63° (31 mm); yield 2.7 g (59%, corrected for recovered alcohol); ir, no OH; nmr δ 6.2 (m, 1) and 4.0 (m, 2) (both O—CH=CH_2).

2-Cyclopentene-1-acetaldehyde-3-*d* (10) was prepared by pyrolysis of vinyl ether **9** (vertical tube, 320°, N_2 carrier gas); bp 72–79° (56 mm); yield 1.6 g (76%, corrected for recovered ether; ir (CCl_4) 1730 cm^{-1}.

2-Cyclopentene-1-acetic acid-3-*d* (11) was prepared by silver oxide oxidation[17] of aldehyde **10**; bp 79–80° (1.1 mm); yield 1.1 g (60%); ir (CCl_4) 1705 cm^{-1}; nmr δ 5.64 (m, 1, vinyl H).

C_8-*d* Ketone 7.—Acid **11** was converted to **7** as described above for **4**; bp 77–78° (6.8 mm); yield 400 mg (41% from acid); mass spectrum, 93% d_1; ir (CCl_4) 1723 cm^{-1}; nmr, Figure 1b.

(16) K. Alder and F. H. Flock, *Chem. Ber.*, **89**, 1732 (1956).

(17) V. Migrdichian, "Organic Synthesis," Vol. I, Reinhold Publishing Co., Inc., New York, N. Y., 1957, p 258.

Tricyclo[3.3.0.0^{2,8}]octan-3-one-2-*d* (5) was prepared from 2-cyclopenten-1-acetic acid (**1**) using the procedure previously described, except that diazomethane-d_2[18] was employed. Preparative vpc (10% FFAP, 180°) gave ketone **5**; mass spectrum indicated 71% d_1 and 29% d_0; ir (CCl_4) 1723 cm^{-1}; nmr, see text.

***cis*-Bicyclo[3.3.0]octan-3-one (12)** was prepared from ethyl 2-cyclopentanone-1-ylacetate (see below) by the method of Linstead and Meade[19] in an over-all yield of 10%. Pure **12** had bp 104–105° (4 mm); ir (CCl_4) 1740 cm^{-1}; nmr (CCl_4) δ 2.60 (m, 2, C_1 H and C_5 H) and 1.3–2.4 (m, 10); the 2,4-dinitrophenylhydrazone derivative had mp 112–113° (lit.[20] mp 115°); the semicarbazone had mp 188–189° (lit.[19] mp 187–188°).

Ethyl 2-cyclopentanone-1-ylacetate was prepared from ethyl-(and methyl-) 2-cyclopentanone-1-ylcarboxylate by the method of Dev[9,20] in an overall yield of 51%. In one small-scale run, the desired keto ester was prepared from cyclopentanone and ethyl chloroacetate by the enamine procedure[21] in an over-all yield of 16%. Pure product had bp 89–92° (3 mm); ir (CCl_4) 1740 cm^{-1}; nmr (CCl_4) δ 1.2, 4.1 (ethyl ester), and 1.6–3.0 (m, 9); the 2,4-dinitrophenylhydrazone derivative had mp 107–108°.

Bicyclo[3.2.1]octan-3-one (13) was prepared by the method of Moore[22] and purified by silica gel chromatography or *via* its semicarbazone.[23] Pure **13** (very volatile) had ir (CCl_4) 1715 cm^{-1}; nmr (CCl_4) δ 2.50 (m, 2, C_1 and C_5 H), 1.77 (m, 6, C_6, C_7, and C_8 H); the 2,4-dinitrophenylhydrazone derivative had mp 163–164° (lit.[22] mp 165–166°); the semicarbazone had mp 188–189°.

Lithium in Liquid Ammonia Reduction of Ketone 4.—A solution of ketone **4** (244 mg, 2.0 mmol) in ether (1 ml) was added over a 3-min period to a stirred solution of lithium (30 mg, 5.0 mmol) in liquid ammonia (50 ml). The reaction mixture turned white immediately. After stirring for 30 min, ammonium chloride (500 mg) was added and the ammonia was evaporated. The resulting residue was dissolved in a mixture of water (25 ml) and ether (25 ml). The aqueous phase was saturated with sodium chloride and extracted with ether. The combined ether phases were dried ($MgSO_4$) and carefully concentrated. Vpc analysis of this ether solution showed 65% reaction; the products were 95% ketone **12** and 5% ketone **13**.

Hydrogen Bromide Treatment of Ketone 4.—Excess, anhydrous hydrogen bromide gas was bubbled into a stirred solution of ketone **4** (488 mg, 4.0 mmol) in methylene chloride (30 ml) at −10°. This mixture was stirred at −10° for 2 hr, then poured onto ice (100 g) and extracted with ether. The ether extracts were washed with dilute sodium hydroxide solution, dried ($MgSO_4$), and evaporated. Distillation yielded a mixture of bromo ketones **14** and **15**, bp 115–118° (7 mm), yield 600 mg (61%). Treatment with ethylene glycol in benzene in the presence of a catalytic amount of *p*-toluenesulfonic acid yielded the corresponding bromo ketals, bp 70–72° (0.05 mm), yield 469 mg (64%). Removal of the bromine atom was effected by treatment with sodium (115 mg) in liquid ammonia (50 ml) and ether (10 ml). The crude ketal mixture was hydrolyzed with hydrochloric acid–water (40 ml, 1:1 mixture) and extracted into ether. After drying ($MgSO_4$), the ether was carefully concentrated. Vpc analysis of this solution showed 80% ketone **12** and 20% ketone **13**.

Registry No.—**4**, 20826-85-1; **4** (semicarbazone), 20826-86-2; **4** (2,4-dinitrophenylhydrazone), 20826-87-3; **5**, 20826-88-4; **6**, 20826-89-5; **7**, 20826-90-8; **8**, 20826-91-9; **9**, 20858-74-6; **10**, 20826-92-0; **11**, 20826-93-1; **12**, 19915-11-8; ethyl 2-cyclopentanon-1-ylacetate, 20826-94-2.

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(20) S. Dev, *J. Indian Chem. Soc.*, **30**, 815 (1953).

(21) *Cf.* G. Stork, A. Brizzolara, H. Landesman, J. Szmuszkovicz, and R. Terrell, *J. Amer. Chem. Soc.*, **85**, 220 (1963).

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(23) *Cf.* W. Kraus, *Chem. Ber.*, **97**, 2719 (1964).