Fermi-resonance in cage ketones

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FERMI-RESONANCE IN CAGE KETONES

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BY
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INTRODUCTION

The chemistry of the pentacyclodecane system, \( \text{I} \), has received little attention since the facile entry into this series of cage compounds was provided by Cookson, et.al., in 1960.\(^1\) Because of its structural similarity to the hydrocarbon cubane, \( \text{I} \) can be referred to as a bis-homocubane derivative.\(^\dagger\) Access to this ring system is afforded by the intramolecular photocyclization of derivatives of the dicyclopentadiene series.\(^1-3\) Appropriately substituted derivatives of \( \text{I} \) have been used as precursor of cubane\(^4\) and synthesis of potential antiviral drugs\(^5\) and insecticides.\(^6\) In spite of these applications, no serious attempt has been made to investigate the chemistry of these strained compounds.

\[ \text{hv} \]

In order to accommodate the geometrical requirement of the cage skeleton in \( \text{I} \), considerable departure from normal tetrahedral hybridization is required. This is particularly evident when an \( \text{sp}^2 \)-hybridized carbon is placed in the methylene bridge, e.g., ketones \( \text{2-4} \). The carbonyl stretching vibration for

\(\dagger\) The term homo refers to interposition of a methylene group between two carbons of the parent system. Bis means two such groups.
compounds 2-4 occur at wavelength significantly lower than the more usual value of 5.83μ, characteristic of a nonstrained ketone. Without exception, the carbonyl stretching vibration appears as a complex absorption band. These absorption bands, which vary in complexity from one major band with several shoulders to two distinct bands with several shoulders, are accompanied by fairly intense bands in the 10-11μ region of the infrared spectrum. Absorption in this region corresponds to the carbon-hydrogen out-of-plane bending vibration. Whereas the low wavelength shift is expected on the basis of ring strain in compounds 2-4, the complexity of the absorption is not.

It is not rare to find solvent sensitive doublets or complex absorption bands in the infrared spectra of carbonyl compounds. This occurrence has been observed in a number of carbonyl compounds. Among these are cyclopentanone, 2-cyclopentenone, 2-cyclohexenone, p-benzoquinone, and assorted α,β-unsaturated-γ-lactones, in addition to polycyclic compounds mentioned above. Several strong bands are visible in the 10-11μ region of the infrared spectrum of these compounds as well. In these cases, this phenomenon has been attributed to Fermi-resonance
coupling. Fermi-resonance interaction is ascribed to the coupling of the fundamental frequency of the carbonyl group with that of an overtone (or combination band) corresponding to a different vibration.

The complex absorption in 2-cyclohexenone was assigned to Fermi-resonance interaction by Noack, et al. This solvent-sensitive doublet occurs in those derivatives where hydrogen is present at the double bond (compounds 5-8). However, when the vinyl hydrogen was replaced by a methyl group or deuterium, the complexity of the absorption in the region corresponding to that for the carbonyl stretching vibration of the infrared spectrum was removed (compounds 9-11). This transformation, in effect, results in the appearance of the C-D bending at such a frequency that an overtone does not appear at the same frequency as does the carbonyl stretching vibration.

\[ \text{Images of compounds 5 to 11} \]
It is tempting to assign the complex carbonyl absorption in the infrared spectrum of these cage ketones to Fermi-resonance. This interpretation, though attractive, should be reserved until more corroborative evidence is secured. Complex carbonyl absorption can be ascribed to other causes: 

1. An accidental near degeneracy of the carbonyl fundamental with another fundamental overtone or combination band of different symmetry, so that no resonance interaction (Fermi-resonance) occurs;
2. Intermolecular association which causes the appearance of a carbonyl absorption at a frequency which is characteristic of the interacted form shifted from that for the non-interacted form;
3. Intermolecular effects such as conformational or rotational isomerism, intermolecular hydrogen bonding, etc., which give rise to a second carbonyl frequency; and
4. Carbonyl stretching vibrations which occur as upper stage transitions, i.e., which occur in molecules which possess one or more quanta of energy in a low frequency vibrational mode in both the upper and lower states. Because of the appearance of bands around 11\mu (twice the wavelength of the carbonyl fundamental), Fermi-resonance interaction is a conceivable cause of the bifurcate bands in the infrared spectra of these ketones having the pentacyclodecane ring skeleton.

The work described in this thesis is concerned with the initial phase of an overall problem designed to assign the multiple absorption bands in the infrared spectra of some cage
ketones to Fermi-resonance.
RESULTS AND DISCUSSION

It seems reasonable to expect that the protons alpha to the carbonyl group in ketones 2-4, in spite of the fact that these are not vinyl hydrogens, should have carbon-hydrogen bond strengths comparable to that of an sp² C-H bond. Accordingly, substitution of a deuterium at the α-position should alter the frequency of absorption to where Fermi-resonance interaction, if operative, would be removed. Preparation of the tetradeuterio-derivative 12, then, afforded the ultimate synthetic objectives. The approach is formally analogous to that of Noack⁷ described earlier. The overall plan includes preparation of 12 and the dibromo-derivative 14.

Two approaches toward the synthesis of 12 are feasible. The first of these involves the preparation of the dideuterio-derivative from 4 followed by an hydrogen-deuterium exchange reaction as outlined below:

\[
\begin{align*}
\text{Br} & \xrightarrow{\Delta H} \text{OH, H}^+ \\
\text{Br} & \xrightarrow{2, \ D_2O} \text{17}
\end{align*}
\]
Clearly, base-catalyzed deuterium exchange would not be effective if performed directly on compound 4. Under mildly basic conditions, 4 is converted quantitatively into homocubane derivative 16. Preparation of 13 should proceed without incident as outlined since there is ample precedent for each reaction. Unfortunately, there is no readily available procedure for conversion of 13 to 14. On the other hand, there is no a priori reason why this last step should not be possible.

The second procedure for preparation of 14 requires a more lengthy route. This synthetic sequence utilizes the deuterated 2-cyclopentenone derivative as shown in the flow-chart following:
The above procedure has been carried out previously for the unsubstituted ketone. Extension to the deuterated analogs depends only on the success of the first step.

Because of the availability of the dibromo-diketone, the first of the two synthetic schemes was attempted. It was hoped that even without completion of the entire sequence, the pentultimate intermediate might provide significant information concerning the possibility of Fermi-resonance interaction.

The basic material in the synthesis of this disubstituted cage diketone, is 2-cyclopentenone. The procedure of Eaton and Cole, as outlined below, was used without modification.
With the desired cage ketone $4$ in hand, our attention was next focused on the reduction of the cage dibromo-diketone and preparation of its deuterio-derivative. It may be recalled that this objective could be accomplished according to the following flow-chart:

An attempt to reduce the cage dibromo-diketone directly with methylolithium would likely give rise to ring contraction with exclusion of bromine. This would result from the attack by methylolithium at the carbonyl group giving rise to p-diacetylcubane (21).
Though this is not an undesired compound, it was not the immediate objective. To prevent the possibility of such an occurrence, it was necessary to protect the carbonyl group with a base stable group. This was accomplished by converting the ketone to the bis-ethylene cage ketal, \(15\).

Treatment of the cage ketone \(4\) with ethylene glycol and \(p\)-toluenesulfonic acid in refluxing benzene for 25 hours gave the \textit{bis}-ethylene cage ketal, \(15\), in 85 per cent yield.
The nuclear magnetic resonance spectrum of the bis-ethylene cage ketal, 15, consists of three groups of complex absorptions, centered respectively at δ = 4.18 (8H, symmetrical multiplet $A_2B_2$ pattern, ketal protons), 3.31 (4H, multiplet), and 2.71 (2H, multiplet, alpha protons) ppm. The infrared spectrum showed absence of the carbonyl group.

Of the ketones and ketals in this system Cole$^{12}$ said:

It is apparent from nuclear magnetic resonance spectra of the cage compounds prepared in this series that the resonance of hydrogens on carbons alpha to a ketone or ketal group usually appears at a higher field than the absorptions of the remaining hydrogen on the cage skeleton.

The absorption appearing at δ = 2.71 ppm is due to the hydrogen alpha to the ketal functional group. It appears that some unexpected magnetic shielding exists in these compounds. Since the commencement of this study, publications by Stedman and Davis$^{13}$ have provided additional examples of unexpected magnetic shielding of the protons alpha to the functional group in cage ketones and ketals. This is an unexpected occurrence. The protons alpha to the functional group are expected to be deshielded and, therefore, further downfield than the remaining protons. Protons alpha to the functional group usually fall within the paramagnetic influence of the carbonyl group and are usually shifted further downfield than the remaining hydrogens if all the C-H bonds are saturated.$^{14}$

Treatment of the cage dibromo-diketal 15 with methyllithium was not successful. After eight hours at reflux only unchanged ketal was isolated. When the reaction mixture was refluxed for
thirty hours approximately 80 per cent conversion was achieved. However, treatment of the ketal with n-butyllithium in hexane for one hour at 0° followed by quenching with deuterium oxide afforded an almost quantitative yield of the cage dideuterio-diketal 17. The nuclear magnetic resonance spectrum of the deuterated ketal shows the $A_2B_2$ multiplet of the cage dibromo-diketal, 15, is replaced by a multiplet centered at $\delta = 3.88$ (8H, ketal protons). The remaining protons appeared at $\delta = 2.79$ (4H, multiplet) and 2.46 (2H, multiplet, alpha protons) ppm.

Hydrolysis of the cage ketal proved to be more difficult than expected. Trial attempts to hydrolyze the cage dibromo-diketal 15 with concentrated sulfuric acid at 0-5° for thirty minutes afforded neither ketone nor starting material. It appears that under these conditions the entire cage system is ruptured. Attempts to hydrolyze the same compound using 75 per cent aqueous sulfuric acid at 0-5° afforded the unchanged starting material. Apparently, the presence of the halogens on the cage renders hydrolysis of the ketal more difficult. To hydrolyze the ketal derivatives of the bird-cage substituted with ten
chlorines, Stedman and Miller\textsuperscript{15} found it necessary to use 20 per cent fuming sulfuric acid for 2½ hours at 150°. The ketal could not be hydrolyzed with concentrated sulfuric acid. However, when hydrogens were substituted for the chlorines in the bird-cage system, the ketal was hydrolyzed in 65 per cent sulfuric acid in ten minutes. Hydrolysis of dimeric 5,5-ethylendioxytetrachloro-

\[ \text{C_10} \quad \text{20\% fuming H}_2\text{SO}_4 \quad 2.5 \text{ hr., 105°} \quad \text{H} \]

aqueous

\[ \text{24} \quad \text{65\% aqueous H}_2\text{SO}_4 \quad \text{25} \]

cyclopentadiene (26)\textsuperscript{16} with excess 96 per cent sulfuric acid gave only the mono-ketone 27. However, to hydrolyze 28, 15 per cent fuming sulfuric acid or boiling concentrated nitric acid was used. This, however, afforded only the hydrate 29.

\[ \text{C_18} \quad 96 \% \text{H}_2\text{SO}_4 \quad \text{26} \quad \text{27} \]
The deuterated ketal 17 was hydrolyzed successfully in 65 per cent aqueous sulfuric acid for thirty minutes to give the diketone in 62 per cent yield.

The most obvious change in the infrared spectrum of cage dideuterio-diketone 13 is that of the shift in carbonyl absorption band. In the dibromo-ketone, 4, the major band in the infrared spectrum appeared at $\lambda_{\text{max}} = 5.56$ and $5.61\mu$. However, removal of the bromines reduced the complexity to one major band ($\lambda_{\text{max}} = 5.68\mu$). The shift to a longer wavelength of the carbonyl stretching band is expected. Halogens on the carbon atom alpha to the ketone functional group shortens the wavelength of the carbonyl stretching absorption by about $0.07\mu$. Substitution of deuterium atoms for the bromine appears to have rendered the carbonyl absorption band less complex. The definite split carbonyl absorption band in the cage dibromo-diketone may be due, in part, to dipole-dipole interaction of the bromine with that of
the carbonyl functional group. Another change in the infrared spectrum of the cage dideuterio-diketone appears in the 10-11 μ region. The bands appearing in this region are weak compared to those in the spectrum of ketone 4.

In order to determine if the split carbonyl in the cage dibromo-diketone 4 is due to dipole-dipole interaction of the bromine with that of the carbonyl functional group, it is necessary to prepare and observe the spectrum of compound 14. If the split carbonyl is due to dipole-dipole interaction of the bromine with that of the carbonyl functional group the complexity of the carbonyl group will be retained. If, however, the complexity is due to the hydrogens alpha to the carbonyl functional group, the complexity will be reduced. The multiple absorption then could be ascribed to Fermi-resonance.
EXPERIMENTAL

Infrared spectra were recorded on a Beckman IR-5A Spectrophotometer and calibrated against the 6.24\(\mu\) band of a polystyrene film. Unless otherwise indicated, methylene chloride or carbon tetrachloride was used as the solvent for the infrared spectra. Only the most prominent absorption bands in the spectrum are listed. Nuclear magnetic resonance (NMR) spectra were taken on a Varian Associates A60-A Spectrometer using carbon tetrachloride or deuteriochloroform solutions. Chemical shifts (\(\delta\)) are reported in parts per million downfield from internal tetramethylsilane. Melting points were made using a Fisher-Johns melting point apparatus and are uncorrected.

Removal of solvent in vacuo or at the flash evaporator refers to evaporation using an all glass Büchler rotary evaporator. Alcoa activated alumina was used for column chromatography.
Cyclopentyl chloride (17).— Freshly distilled cyclopentadiene (664 g, 10.06 moles) was placed in a 3-liter flask, equipped with a thermometer, mechanical stirrer, gas inlet tube, and a cold finger condenser packed with ice. The solution was stirred vigorously and kept at a temperature below 25° by external cooling with a Dry Ice-isopropyl alcohol bath. Anhydrous hydrogen chloride was bubbled into the cooled neat liquid until a deep purple color developed. A distillation head was attached to the flask, and the mixture was distilled at aspirator pressure at room temperature into a receiver surrounded with Dry Ice. The colorless cyclopentyl chloride (17) was stored in Dry Ice until used; b.p. 27°/18 mm.

2-Cyclopentenone (18).— The cyclopentyl chloride was divided into two equal portions (332 g each, 3.25 moles). To two 3-liter three-neck flasks, immersed in an isopropyl alcohol-Dry Ice bath, each portion of cyclopentyl chloride was added. The addition required 45 minutes. The reaction mixtures were stirred efficiently and kept at 0-10° by adding Dry Ice when necessary. Dilute aqueous sulfuric acid (1260 ml, 50 per cent by volume) was added slowly (630 ml to each flask) to the brownish mixture. The temperature was maintained below 10° and the mixture was vigorously stirred throughout the addition in order to prevent the formation of dicyclopentyl ether. After the addition of the acid solution (ca. 2 hours), one liter of water was added to the green reaction mixture in each flask. The mixtures in both flasks were extracted six times each with 200-ml portions
of chloroform. The combined extracts were washed five times with 250-ml portions of water, five 250-ml portions of brine, and then dried over sodium sulfate. The solvent was removed at aspirator pressure. The dark residue was distilled at aspirator pressure into a receiving flask cooled with an ice-salt bath. The fraction distilling at 40-60°/18 mm was collected. The 2-cyclopentenone was distilled a second time through a short Vigreux column. The distillation afforded 342 g (52\% per cent from cyclopentadiene) of colorless 2-cyclopentenone, 55°/18 mm (Reported: 42°/11 mm; \( \lambda_{\text{max}} \) 5.86, 6.27\( \mu \); \( \delta \) = 7.76 (1H, multiplet), 2.68 (2H, complex multiplet), and 2.20 (2H, complex multiplet) ppm.

4-Bromo-2-cyclopentenone (19).—To a slurry of 350 ml of carbon tetrachloride and 120 g (0.67 moles) of recrystallized N-bromosuccinimide (m.p. 182-183°) in a 3-neck flask, equipped with a mechanical stirrer, a reflux condenser, and a dropping funnel, 25 g (0.305 moles) of 2-cyclopentenone were added. This mixture was heated to reflux while being stirred vigorously and illuminated by a Sears sun lamp. After the initial exothermic reaction subsided an additional 25 g (0.305 moles) of 2-cyclopentenone were added. This mixture was heated to reflux while being stirred vigorously and illuminated by a Sears sun lamp. After the initial exothermic reaction subsided an additional 25 g (0.305 moles) of 2-cyclopentenone was added carefully to the reaction flask. The mixture was illuminated and refluxed for approximately 2\( \frac{1}{2} \) hours or until the reaction mixture was definitely a brownish red color. The reaction was discontinued, and the flask was allowed to cool. The succinimide was filtered, and washed with cold carbon tetrachloride. The orange-red filtrate was concentrated on the flash evaporator. (The concentrate should be purified immediately or
stored in Dry Ice because decomposition takes place rapidly.) The residue (101 g) was used without further purification, 

\[ \text{2,4-Dibromo-3a,4,7,7a-tetrahydro-4,7-methanoindene-1,8-dione.} \]

Bromination of 4-bromo-2-cyclopentenone (20).— The concentrate (crude 4-bromo-2-cyclopentenone, 101 g, 0.627 moles) was placed in a 2-liter, three-neck flask, equipped with a low temperature thermometer, a mechanical stirrer and a pressure equalizing dropping funnel. Ether (540 ml) was added, and the temperature was lowered to 0° by external cooling with a Dry Ice-isopropyl alcohol bath. While the mixture was being stirred vigorously, 101 g (0.627 moles) of bromine were added dropwise. After the addition of the bromine was complete (30 minutes), the reaction mixture was cooled to -50°. Triethylamine (130 g, 1.287 moles in 160 ml of ether) was added to the mixture. A precipitate formed almost immediately. After the addition of the triethylamine solution, the Dry Ice bath was removed, and the temperature was allowed to rise to -10°. The brownish-yellow mixture was poured into a stirred solution of 400 ml of concentrated hydrochloric acid, 400 ml of water and crushed ice. The filter cake (27 g) was washed thoroughly with water, ether and saved. The water-ether washing was separated and the aqueous layer was discarded. The organic phase was washed with 10 per cent aqueous hydrochloric acid, followed by saturated brine and dried over sodium sulfate. Concentration of the ether layer in vacuo left 12 g of dimer. This was dissolved in methylene chloride. The solution was then washed with three 50-ml portions of water,
three 50-ml portions of saturated brine and then dried over sodium sulfate. The brownish solution was filtered through a chromatography column containing activated alumina (40 g), and eluted with ca. 200 ml of methylene chloride. The solvent was removed in vacuo. A small amount of ether (3 ml) was added to the residue and the mixture was filtered to give the dimer (35 per cent yield, m.p. 154-155°C); $\lambda_{\text{max}}$ 5.51, 5.54, and 5.59$\mu$; $\delta$ = 7.76 (1H, doublet, $J = 2.9$ Hz.), 6.32 (2H, multiplet) ppm, and two complex multiplets centered about $\delta = 3.58$ (2H), and 3.21 (1H) ppm, respectively.

Preparation of the cage dibromo-diketone. Irradiation of dimer (20).-- Five grams of the dimer (20) was dissolved in 100 ml of hot methanol. The solution was cooled to room temperature and 3 ml of methanolic hydrogen chloride (prepared by bubbling anhydrous hydrogen chloride gas into methanol) was added. The solution was transferred to a Pyrex irradiation cell, and another 100 ml of methanol was added. The solution was irradiated through a Pyrex filter with a water-cooled Hanovia 450-watt mercury arc lamp. The progress of the reaction was followed by observing the disappearance of the infrared absorption bands at 5.54, 5.77, and 6.30$\mu$, characteristic of the dimer. The reaction required 2½ hours. The solvent was removed at the flash evaporator. The orange waxy product remaining was taken up in 200 ml of benzene. Water (3 ml) and 2 drops of concentrated hydrochloric acid were added and the cloudy mixture was refluxed under a Dean-Stark trap for three hours to convert the presumed
bis-hemi-ketal to the ketone by removing methanol and water. The orange solution was treated twice with Norit and, while hot, was passed through a column containing 20 g of activated alumina. The column was then flushed with hot benzene, the eluate was concentrated to a volume of approximately 50 ml, and hot hexane (10 ml) was added. Upon cooling 3 g of colorless cage ketone (60 per cent, m.p. 232-233°) was deposited; \( \lambda = 5.56 \) and 5.62\( \mu \); \( \delta = 3.63 \) (4H, multiplet) and 3.05 (2H, multiplet) ppm. The benzene-hexane filtrate was concentrated to a volume of approximately 10 ml whereupon a second crop of crystals (0.5 g) was obtained. These crystals were identical in every respect to that of the cage diketone.

Preparation of diethylene ketal of the cage dibromo-diketone (4).—The cage diketone (2.0 g, 6.3 mm), 29 ml of benzene, and 0.5 g of \( p \)-toluenesulfonic acid monohydrate were refluxed for twenty-five hours while being stirred magnetically under a Dean-Stark trap. The flask was allowed to cool, and the contents were poured into a separatory funnel. The ethylene glycol layer was separated, washed three times with 25 ml of benzene, and the washings were combined. The benzene solution was washed three times with 25 ml of ethylene glycol followed by five washings with 50 ml of water and saturated brine. The resulting colorless solution was dried over sodium sulfate. The solvent was removed at the flash evaporator, and the white crystalline solid, 2.2 g (84.5 per cent) was crystallized from ether, m.p. 185-186°; \( \delta = 4.18 \) (8H, symmetrical multiplet, \( A_2B_2 \) pattern,
ketal protons), 3.31 (4H, multiplet), 2.71 (2H, multiplet, alpha protons) ppm.

Methyllithium. — Anhydrous ether (200 ml) was placed in a dried flask, equipped with a mechanical stirrer, a pressure equalizing dropping funnel and a reflux condenser to which a gas inlet tube was attached. A positive pressure of nitrogen was maintained throughout the course of the reaction. While the solution was being stirred 5.0 g of lithium metal was introduced. The mixture was heated to reflux for sixty minutes before methyl iodide (50 g) in anhydrous ether (25 ml) was added via the dropping funnel. (The reaction is exothermic!) The mixture was refluxed an additional sixty minutes, after which it was allowed to cool to room temperature. The methyllithium was used as prepared without further purification.

Preparation of the deuterated cage ketal (17). Treatment of the cage dibromo-diketal with methyllithium. — The dibromo-diketal 15 (500 mg, 1.22 mm) dissolved in 50 ml of ether was placed in a 500 ml flask, equipped with a magnetic stirrer, pressure equalizing dropping funnel and a condenser fitted with a gas inlet tube. The flask was immersed in an ice bath. Twenty milliliters of methyllithium solution (9 per cent) was added to the reaction vessel. A constant flow of nitrogen was maintained through the system. The addition was adjusted so that the reflux was not too violent. After the addition of the methyllithium was completed, the ice bath was removed and the flask was heated to reflux for thirty hours. Deuterium oxide (10 ml) was slowly added dropwise until
the exothermic reaction subsided. The flow of nitrogen was dis-
continued and the stirring continued for another hour. The ether
layer was separated and washed three times with 50-ml portions of
water, twice with 50-ml portions of brine, and dried over sodium
sulfate. The solvent was removed in vacuo. The viscous liquid
was used without further purification; δ = 3.88 (8H, symmetrical
multiplet, ketal protons), 2.79 (4H, multiplet), and 2.46 (2H,
multiplet, alpha protons) ppm.

Preparation of the deuterated cage ketal (17). Treatment
of the cage dibromo-diketal with n-butyllithium.— The dibromo-
diketal (708 mg, 1.727 mm) dissolved in 90 ml of hexane was
placed in a 500 ml flask, equipped with a magentic stirrer, pres-
sure equalizing dropping funnel and a condenser fitted with a
gas inlet tube. The flask was immersed in an ice bath. The
system was purged with nitrogen and maintained under a positive
nitrogen atmosphere throughout the reaction. A solution of 20 ml
of n-butyllithium (K & K Laboratories, 15 per cent) was added drop-
wise over a period of ten minutes. The stirring was continued
and the temperature was maintained at 0-5°. Ten milliliters of
deuterium oxide was added after one hour. The aqueous solution
was separated and extracted with hexane. The hexane extract
was washed with water followed by saturated brine, and dried
over sodium sulfate. The solvent was removed at the flash
evaporator. The extract afforded 426 mg (95 per cent) of crude
cage dideuterio-diketal as a colorless oil; δ = 3.88 (8H, sing-
let, ketal protons), 2.79 (4H, multiplet), and 2.46 (2H,
multiplet, alpha protons) ppm. The crude diketal in hexane was passed through a chromatography column containing three grams of activated alumina. The eluate from elution gave a product whose nuclear magnetic resonance spectrum was not consistent with that expected of the pure ketal. This spectrum contained aromatic absorption. The column was eluted with anhydrous ether. The eluate afforded pure ketal. Crystallization from hexane afforded a sample of colorless crystals, m.p. 101-102°.

Hydrolysis of the cage dideuterio-diketal (17).—A 108 mg (0.435 mm) sample of the ketal was dissolved in 2 ml of 65 per cent sulfuric acid at 0-5°. After stirring for 30 minutes the solution was poured into 50 ml of ice-water. The ice-water mixture was extracted with 10-ml portions of methylene chloride. The extract was washed with water and dried over sodium sulfate. The solvent was removed at the flash evaporator. The waxy solid (44 mg, 65 per cent) was dissolved in hexane and filtered through a small column containing 1.5 g of activated alumina. The column was flushed with hot hexane. The eluate contained unhydrolyzed ketal. Flushing the column with a hexane-ether mixture (25 ml) gave the ketone with a small amount of ketal. \( \lambda_{\text{max}} = 5.68 \mu, \delta = 3.38 \) (multiplet) and 2.70 (multiplet) ppm.
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