mp 166–169°; pmr spectrum (in τ values): doublet, 7.65 ($J_{PH}$ = 2.6 Hz, $CH_3$); complex multiplet, 2.78 (aromatic).

**Tri-*p*-tolyl phosphate (23)** was a commercial product (Eastman White Label) and was used without further purification; pmr spectrum (in τ values): doublet, 7.70 ($J_{PH}$ = 0.9 Hz, $CH_3$); singlet, 2.93 (aromatic).

**Dimethyl *p*-tolyl phosphate (22)** was prepared using the method of Kenner and Williams[36] and obtained as a clear, colorless liquid, bp 121–121.5° (0.9 mm) [lit.[37] bp 114° (0.5 mm), 172.2° (20 mm)]; infrared spectrum: 2994w, 2950m, 2924w, 2857w, 1613w, 1502m, 1451w, 1294s, 1280s, 1220s, 1208m(sh), 1186m, 1167w, 1068s, 1046s, 1020w, 955s, 932m(sh), and 855s cm$^{-1}$; pmr spectrum (in τ values): doublet, 7.73 ($J_{PH}$ = 0.6 Hz, $CH_3$–C); doublet, 6.30 ($CH_3$–O); broad singlet, 3.02 (aromatic).

**Acknowledgment.** This study was supported in part by the Directorate of Chemical Sciences, Air Force Office of Scientific Research, under Grant No. AF-AFOSR-470-64. Double-resonance studies were carried out with instrumentation provided by a grant (FR 00292) from the Division of Research Facilities and Resources, National Institutes of Health. We are indebted to Drs. A. A. Bothner-By and H. Dreeskamp for helpful discussions and suggestions.

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(37) H. D. Orloff, C. J. Worrel, and F. X. Markley, *J. Am. Chem. Soc.*, **80**, 727 (1958).

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# Coupling Constants in the Nuclear Magnetic Resonance Spectra of *endo*- and *exo*-Norbornene Derivatives

**F. A. L. Anet, H. H. Lee, and J. L. Sudmeier**

*Contribution No. 2044 from the Department of Chemistry, University of California, Los Angeles, California 90024.* *Received April 5, 1967*

**Abstract:** The synthesis of *endo*- and *exo*-2-carbomethoxybicyclo[2.2.1]hept-5-ene-1,4,5,6,7,7-$d_6$ is described. The proton magnetic resonance spectra, obtained with deuterium decoupling, of the *endo* and *exo* esters gave accurate chemical shifts and coupling constants for the protons in the two compounds. The claim that *endo–endo* vicinal coupling constants are much smaller than *exo–exo* coupling constants is shown to be incorrect. The relative signs of the geminal and the two vicinal coupling constants in the *exo* ester have been established by means of INDOR spectra.

There has been much interest in the factors that determine the values of vicinal coupling constants in ethanic systems.[1,2] The dependence of such coupling constants on dihedral angles is well established,[1–3] and there is also a dependence on substituents[4] and on distortions from the normal tetrahedral angle.[1,2] Rigid molecules are particularly attractive for study because the dihedral angles are fixed and are often accurately known from other evidence.[3b,4a,5–11]

In the norbornane[4a,5–7] and norbornene[10,11] systems, it has been reported that *cis*-vicinal coupling constants between pairs of *endo* protons are appreciably different from the *cis*-vicinal coupling constants between pairs of *exo* protons, even though the dihedral angle (0°) and the substituents are the same for both cases. In derivatives of norbornane, $J_{endo-endo}$ is 1 to 2 cps smaller than $J_{exo-exo}$. Even larger differences have been quoted for norbornene derivatives (Table I).

**Table I.** Vicinal Coupling Constants (cps) Reported for Norbornene Derivatives

| 2-Substituent | $J_{endo-endo}$ | $J_{exo-exo}$ | Ref |
|---|---|---|---|
| *exo*-OH | 5.6 | | 10 |
| *endo*-OH | | 8.0 | 10 |
| *exo*-CN | 4.5 | | 10 |
| *endo*-CN | | 9.1 | 10 |
| *exo*-COOMe | 4.4 | | 10 |
| *endo*-COOMe | | 8.8 | 10 |
| *exo*-Cl | 5.0 | | 11 |
| *endo*-Cl | | 8.2 | 11 |
| *exo*-Br | 8.0 | | 11 |
| *endo*-Br | | 8.2 | 11 |
| *exo*-OAc | 7.0 | | 11 |
| *endo*-OAc | | 8.2 | 11 |

The spectra of norbornene derivatives, especially of the *exo* isomers, are often complex. In such cases the use of the partial analysis, including decoupling, can lead to errors. We have therefore decided to examine the nmr spectra of some extensively and specifically deuterated norbornene derivatives, where spectral analysis can be carried out completely and unambiguously.

## Results and Discussion

**Chemical Shifts.** The nmr spectra of *endo*- and *exo*-2-carbomethoxybicyclo[2.2.1]hept-5-ene-1,4,5,6,7,7-$d_6$, with the exception of the methyl bands, are given in Figures 1 and 2. The proton ($H_2$) on $C_2$, which bears

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(1) M. Barfield and D. M. Grant, *Advan. Magnetic Resonance*, **1**, 149 (1965).

(2) A. A. Bothner-By, *ibid.*, **1**, 195 (1965).

(3) (a) M. Karplus, *J. Chem. Phys.*, 30, 11 (1959); *J. Am. Chem. Soc.*, **85**, 2870 (1963); (b) G. Conroy, *Advan. Org. Chem.*, 2, 265 (1960).

(4) (a) K. L. Williamson, *J. Am. Chem. Soc.*, **85**, 516 (1963); (b) R. J. Abraham and K. G. R. Pachler, *Mol. Phys.*, 7, 165 (1964).

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(10) J. Paasivirta, *Suomen Kemistilehti*, **38B**, 130 (1965).

(11) J. C. Davis, Jr., and T. V. Van Auken, *J. Am. Chem. Soc.*, **87**, 3900 (1965).

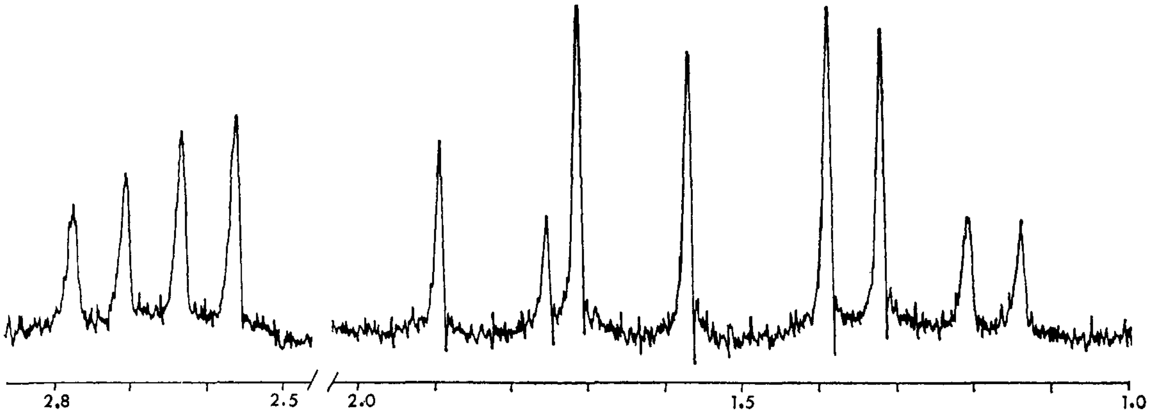


Figure 1. Proton nmr spectrum (60 Mcps) of *endo*-2-carbomethoxybicyclo[2.2.1]hept-5-ene-1,4,5,6,7,7-$d_6$. The methyl band is not shown. The scale is in ppm downfield from internal tetramethylsilane.

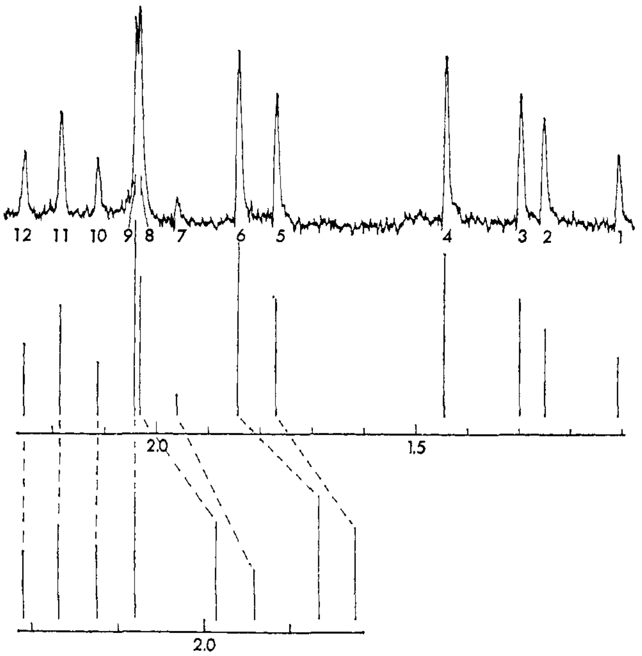


Figure 2. Top: proton nmr spectrum (60 Mcps) of *exo*-3-carbomethoxybicyclo[2.2.1]hept-5-ene-1,4,5,6,7,7-$d_6$. The methyl band is not shown. Center: calculated spectrum (60 Mcps) with parameters given in Table II. The scale is in ppm downfield from internal tetramethylsilane and refers to both the experimental and calculated spectra. Bottom: calculated spectrum (100 Mcps) with the same parameters as above. Lines 5–12 only are shown.

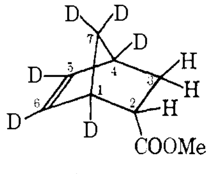
the carbomethoxy group, can be assigned to the quartet at lowest field in both the *endo* and *exo* esters. The chemical shift difference (see Table II) between $H_2$ in the two isomers is 0.72 ppm, compared to 0.53 ppm for the difference in chemical shifts between *exo* and *endo* protons in norbornene itself.

The effect of the carbomethoxy group on the protons at $C_3$ is shown in Table II. The assignments are based on chemical shifts (*endo* proton at higher field than *exo* proton) and coupling constants ($J_{vic-cis} > J_{vic-trans}$)[1–11] obtained from analyses based on the ABC system (see below).

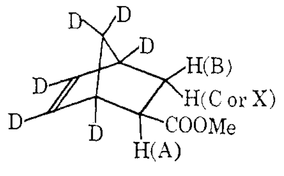
In view of the magnetic anisotropy of the carbomethoxy group and the possibilities for rotational isomerism about the $C_2$–COOMe bond, it is remarkable that the deshielding effect of the COOMe group on an adjacent *cis*-vicinal proton is the same in the two compounds. Furthermore, deshielding is only slightly greater (0.37 ppm) for the *cis*-vicinal arrangement than it is for the *trans*-vicinal arrangement (0.31 ppm). Davis and Van Auken have already commented on the similarity of these quantities, but their conclusion was based on less accurate chemical shift data (Table II), which appeared to show that the deshielding induced by a carbomethoxy group was virtually identical for *cis*- and *trans*-vicinal protons.

**Table II.** Chemical Shift and Coupling Constants (cps) of *endo*- and *exo*-2-Carbomethoxybicyclo[2.2.1]hept-5-ene-1,4,5,6,7,7-$d_6$

| | *endo* Ester | | *exo* Ester | |
|---|---|---|---|---|
| | Davis, *et al.* | This work | Davis, *et al.* | This work |
| $\delta_2$ | 2.90 | 2.863 | 2.13 | 2.143 |
| $\delta_{3n}$ | 1.30 | 1.380 | 1.28 | 1.300 |
| $\delta_{3x}$ | 1.87 | 1.848 | 1.87 | 1.898 |
| $J_{2n3n}$ | ... | ... | 4.4 | ±9.0 |
| $J_{2n3x}$ | ... | ... | 3.8 | ±4.4 |
| $J_{2x3n}$ | 3.4 | ±4.2 | ... | ... |
| $J_{2x3x}$ | 8.8 | ±9.4 | ... | ... |
| $J_{3n3x}$ | 11.8 | ∓11.8 | 12.3 | ∓11.8 |



*endo* ester



*exo* ester

**Coupling Constants in the *endo* Ester.** The ring proton of the *endo* ester gave rise to a three-spin system which was approximately of the ABX type. An iterative analysis based on the ABC system gave the parameters shown in Table II. The calculated and experimental spectral lines agreed to 0.1 cps or better. In this analysis the geminal coupling constant $J_{3n3x}$ was taken to be negative (more accurately of opposite sign to the vicinal coupling constants), but efforts were not made to prove this rigorously, as was done with the *exo* ester, to be discussed later.

**Coupling Constants in the *exo* Ester.** The spectrum of the *exo* isomer is interesting because a superficial examination is sufficient to reveal that two of the coupling constants have opposite signs. Thus, if the spectrum is considered as approximately of the ABX type, where X is the high-field proton (quartet of lines 1, 2, 3, 4), then the eight low-field lines form the AB portion. It is well known[12] that these eight lines form two distinct simple "AB" quartets. Because a simple AB quartet is symmetrical about its center for both line positions and intensities, it is easy to pick out these simple quartets[13] in the spectrum. One quartet consists of lines 5, 6, 11, and 12, and the other of lines 7, 8, 9, and 10 (Figure 2). The nature of X is only consistent with lines 5, 6, 7, and 8 belonging to one proton (say A) and the lines 9, 10, 11, and 12 belonging to B. The alternative possibility (A: lines 5, 6, 9, and 10; B: lines 7, 8, 11, and 12) gives a quartet for the X spectrum whose relative intensities are not in agreement with those found experimentally. Irrespective of this assignment, the fact that one simple AB quartet lies completely inside the two inner lines (6 and 11) of the other quartet is consistent only with $J_{AX}$ and $J_{BX}$ having opposite signs. One quartet (*e.g.*, lines 5, 6, 11, and 12) corresponds to those molecules with the same spin of X. It is clear that the effect of X with this spin on A is a shift to *high* field (lines 5 and 6 of the A quartet 5, 6, 7, and 8) while the effect of X with the same spin on B is a shift to *low* field (lines 11 and 12 of the B quartet 9, 10, 11, and 12). Thus $J_{AX}$ and $J_{BX}$ have opposite signs.

It is not unusual to find a spectrum of the ABX type in the system $-CH_2CH<$. In such cases X is invariably the CH proton. Since $J_{AX}$ and $J_{BX}$ are then both vicinal coupling constants, and therefore have the same signs, the ABX spectrum is of the "usual type," and the fact that $J_{AB}$ has an opposite sign to $J_{AX}$ is not apparent. However, the *exo* ester is highly unusual in that X is one of the $CH_2$ protons. Therefore $J_{AX}$ and $J_{BX}$ should be of opposite signs, since one coupling constant is vicinal and the other is geminal. Thus, the spectrum of the *exo* ester shows in a very simple and unambiguous way that $J_{gem}$ and $J_{vic}$ have opposite signs in the norbornene system, which was expected, but had not been previously established.

A more complete calculation of the spectrum was carried out using an iterative computer program based on the general three-spin (ABC) system. Excellent agreement was obtained for both line positions (root mean square error = 0.02 cps) and intensities of the calculated with the experimental spectrum (Figure 2). Furthermore, a spectrum of the ester obtained at 100 Mcps agreed within experimental error of one calculated on the basis of parameters obtained at 60 Mcps. The appearance of the calculated 60- and 100-Mcps spectra is shown in Figure 2. The change in appearance of the inner quartet (lines 7, 8, 9, and 10) is particularly apparent as the frequency of the spectrometer is changed. The separation of lines 8 and 9 increases manyfold as a result of a spectrometer frequency increase of only 67%. In fact, at one spectrometer frequency (below 60 Mcps) lines 8 and 9 coincide exactly, while lines 7 and 10 then have zero intensities, *i.e.*, the AB system then becomes an $A_2$ system.

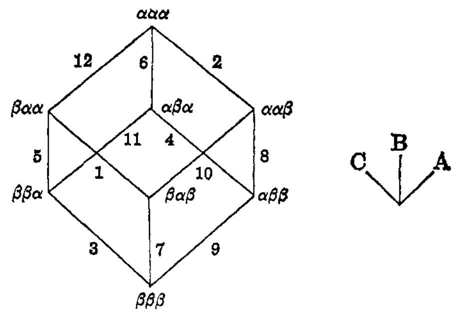


Figure 3. Energy level diagram for sign combination IV of Table III.

**INDOR Spectra of the *exo* Ester.** In order to confirm the relative signs of all the coupling constants, double-resonance experiments were undertaken. We chose to measure INDOR[14] (internuclear double resonance) spectra as these are more convenient to obtain than are weak-field double-resonance spectra[15] ("tickling" experiments). In our system the INDOR spectra arise as a result of the general nuclear Overhauser effect. For example, the intensity of a line can be monitored with a very weak radiofrequency field, while a second stronger radiofrequency field, satisfying the condition $\gamma^2 H_2^2 T_1 T_2 \approx 1$, is frequency swept over the other lines in the spectrum.

There are four possible combinations of the relative signs for the coupling constants in an ABC system, and each combination leads to a separate energy level diagram. The diagram for the sign combination IV (Table III) is shown in Figure 3 for arbitrary absolute signs.

**Table III.** Predicted Changes in the Intensity of Line 2 in INDOR Spectra of *exo* Ester for Various Signs of the Coupling Constants

| | Combinations of the signs of $J_{AB}$, $J_{AC}$, $J_{BC}$ (shown in order) | | | |
|---|---|---|---|---|
| Line satd | $\pm\pm\pm$ (I) | $\mp\pm\pm$ (II) | $\pm\mp\pm$ (III) | $\pm\pm\mp$ (IV) |
| 5 | 0 | Down | Down | 0 |
| 6 | Down | 0 | 0 | Down |
| 7 | 0 | Up | Up | 0 |
| 8 | Up | 0 | 0 | Up |
| 9 | Up | 0 | Up | 0 |
| 10 | 0 | Up | 0 | Up |
| 11 | Down | 0 | Down | 0 |
| 12 | 0 | Down | 0 | Down |

It can be seen that transitions 8 and 10 are in series (progressive) with transition 2, whereas transitions 6 and 12 are in parallel (regressive) with transition 2. Irradiation of a transition results in an increase in the intensities of transitions which are in series with it and a decrease of the intensities of the transitions which are in parallel with it.[14,15] The populations ($P$) of the spin states at thermal equilibrium decrease as the energy increases. Thus, for the energy diagram shown in Figure 3, $P_{\alpha\beta\beta} > P_{\alpha\alpha\beta} > P_{\alpha\alpha\alpha}$. Irradiation of transition

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(12) J. A. Pople, W. G. Schneider, and H. J. Bernstein, "High-Resolution Nuclear Magnetic Resonance," McGraw-Hill Book Co., Inc., New York, N. Y., 1959, p 132.

(13) The intensities of the quartets are slightly skewed because the ABX approximation is not strictly obeyed.

(14) (a) E. B. Baker, *J. Chem. Phys.*, 37, 911 (1962); **45**, 609 (1966); (b) R. Kaiser, *ibid.*, **39**, 2435 (1963); (c) V. J. Kowalewski, D. G. de Kowalewski, and E. C. Ferrá, *J. Mol. Spectry.*, 20, 203 (1966).

(15) W. A. Anderson and R. Freeman, *J. Chem. Phys.*, 37, 85 (1962). For a general review of double resonance, see R. A. Hoffmann and S. Forsén, *Progr. Nucl. Magnetic Resonance Spectry.*, **1**, 15 (1966).

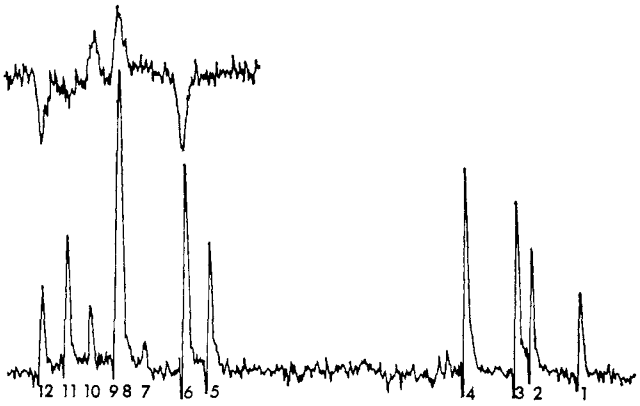

Figure 4. INDOR spectrum (top) of *exo* ester obtained by monitoring the intensity of line 2 while lines 5–12 are irradiated. The INDOR spectrum is shown superposed on a normal spectrum of the *exo* ester so as to show the correspondence between the two spectra.

2 makes $P_{\alpha\alpha\beta} = P_{\alpha\alpha\alpha}$ so that the population of $P_{\alpha\alpha\beta}$ will decrease slightly and that of $P_{\alpha\alpha\alpha}$ will increase slightly from their normal populations. Thus, the intensity of transition 8, $\alpha\beta\beta$ to $\alpha\alpha\beta$, will increase on saturation of transition 2, since the population difference ($P_{\alpha\beta\beta} - P_{\alpha\alpha\beta}$) between these two states will have increased.

Figure 4 shows the INDOR spectrum obtained when the intensity of line 2 was monitored. The intensity increases when lines 8 (or 9) and 10 are irradiated, and the intensity decreases when lines 6 and 12 are irradiated. The irradiation of other lines (5, 7, and 11) has no effect on the intensity of line 2. Because lines 8 and 9 are very close together it was not possible to distinguish the effect of irradiating these lines separately. Similar INDOR spectra were obtained by monitoring the intensities of lines 1, 3, and 4. The observed changes in intensities are summarized in Table IV.

**Table IV.** Changes in Intensities Resulting from INDOR Experiments on *exo* Ester

| Line satd | Line 1 | Line 2 | Line 3 | Line 4 |
|---|---|---|---|---|
| 5 | Down | 0 | Up | 0 |
| 6 | 0 | Down | 0 | Up |
| 7 | Up | 0 | Down | 0 |
| 8 | 0 | Up[a] | 0[a] | Down |
| 9 | 0 | 0[a] | Down[a] | Up |
| 10 | Down | Up | 0 | 0 |
| 11 | 0 | 0 | Up | Down |
| 12 | Up | Down | 0 | 0 |

[a] Because lines 8 and 9 are almost coincident, the assignments for lines 8 and 9 could be reversed.

The data in Table IV are consistent with the energy level diagram in Figure 3. In particular, the change in the intensity of line 2 is as predicted only for sign combination IV in Table III. Energy level diagrams can also be constructed for cases I, II, and III given in Table III. An examination of the transitions which are in series and in parallel with transition 2 for these cases leads to the predicted changes in intensities shown in Table III.

The INDOR spectra clearly show that $J_{AB}$ and $J_{AC}$ have the same sign which is opposite to that of $J_{BC}$. The relative signs of $J_{AB}$ and $J_{AC}$ are not apparent in the ABX analysis, and have only a slight influence in the ABC analysis. The relative signs are the ones expected from the fact that $J_{AB}$ and $J_{AC}$ are vicinal coupling constants and $J_{BC}$ is a geminal coupling constant.

As shown in Table II, the agreement between our work and that of Davis and Van Auken[11] for the coupling constants is poor. There is a striking difference between $J_{2n3n}$ in the two investigations, presumably because of the complexity of the spectra of the undeuterated compounds. The very different values of $J_{2n3n}$ found by Paasivirta[10] for *endo*-2-chloronorbornene and *endo*-2-bromonorbornene (Table I) are unexpected and it appears highly likely that the low value of $J_{2n3n}$ found for the chloro compound is in error. It is also probable that other compounds (Table I) which have been found to have apparently low values of $J_{2n3n}$ (*e.g.*, 4–5 cps) have in fact larger values.

**Isotope Effects.** The presence of an appreciable isotope effect on the coupling constants, caused by the deuterium atoms, is considered remote, especially as there is no substitution on the carbons bearing the protons. Even in extremely favorable situations, such as the comparison of $J_{C^{13}-H}$ with $J_{C^{13}-D}$, there is only a very small isotope effect (<1%) beyond the difference expected from variations in gyromagnetic ratios.[16] We estimate that any isotope effect in our work would be less than 0.1 cps, and could not explain the discrepancy in the coupling constants referred to above.

There are probably some small isotope effects on the chemical shifts found by us in I and II. Chemical shift isotope effects on the order of 0.013 ppm (0.8 cps) are common when the deuteron is attached to the same carbon as the proton.[17] Deuterons in the $\beta$ position have less effect, about 0.007 ppm (0.4 cps) upfield per deuteron.[18] Thus the chemical shifts for the undeuterated forms of I and II are probably some 0.007 ppm to lower field than in I and II. These corrections are not sufficient to bring the chemical shifts in I and II into agreement with those found by Davis, although the differences are not large, and the assignments of chemical shifts made by Davis obviously agrees with ours. Part of the difference may be the result of concentration differences in the two investigations, but mostly it is due to the difficulty of obtaining correct chemical shifts in complex spectra by the use of a first-order analysis.

## Experimental Section

**Cyclopentadiene-$d_6$.** Perdeuteriocyclopentadiene was prepared by repeated exchanges of cyclopentadiene with deuterium oxide over 20-mesh alumina at 350°. We wish to thank Professor W. von E. Doering and Dr. P. B. Shevlin for providing details of this procedure. Four exchanges gave 97% deuteration, and the yield in each exchange was 75–80%.

***endo*- and *exo*-2-Carbomethoxybicyclo[2.2.1]hept-5-ene-1,4,5,6,-7,7-$d_6$.** Reaction of acrylic acid with cyclopentadiene-$d_6$ gave a mixture of *endo* and *exo* adducts.[19] Most of the *endo* acid was removed by recrystallization from pentane and was used in another investigation. The mixture of *endo* and *exo* acids from the above

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(16) P. Diehl and T. Leipert, *Helv. Chim. Acta*, **47**, 545 (1964).

(17) J. W. Emsley, J. Feeney, and L. H. Sutcliffe, "High-Resolution Nuclear Magnetic Resonance Spectroscopy," Vol. 1, Pergamon Press Ltd., Oxford, p 99.

(18) N. Muller and P. J. Schultz, *J. Phys. Chem.*, **68**, 2026 (1964).

(19) J. D. Roberts, E. R. Trumbull, Jr., W. Bennett, and R. Armstrong, *J. Am. Chem. Soc.*, **72**, 3116 (1950).

crystallization was methylated with ethereal diazomethane at 0°. The *endo*- and *exo*-methyl esters were separated[11] by glpc through a 0.25 in. × 15 ft column of Carbowax at 160°. Retention times for the *endo* and *exo* isomers were 47 and 39 min, respectively.

Spectra were obtained on a Varian HR60 spectrometer, modified by the inclusion of an internal field-frequency control system,[20] and equipped with an NMR Specialties decoupler. The calculated spectra were obtained by means of the LAOCOON II program[21] on an IBM 7094 computer. The 100-Mcps spectrum was obtained without deuterium decoupling on a Varian HA100 spectrometer, through the kindness of Professor D. T. Sawyer, University of California, Riverside, Calif.

**Acknowledgment.** This research was supported by a research grant from the University of California.

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[20] F. A. L. Anet and A. J. R. Bourn, *J. Am. Chem. Soc.*, **89**, 760 (1967).

[21] S. Castellano and A. A. Bothner-By, *J. Chem. Phys.*, **41**, 3863 (1964). We wish to thank Dr. Bothner-By for providing us with a copy of this program.

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# Photochemical Cyclobutanol Formation of an Aryl Ketone. The Scope and Mechanism of the Reaction[1-3]

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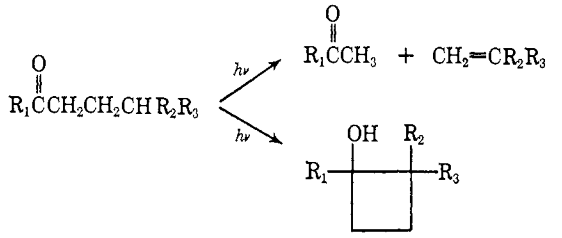
*Contribution from the Departments of Chemistry, State University of New York at Buffalo, Buffalo, New York 14214, and The Ohio State University, Columbus, Ohio 43210.* *Received February 1, 1967*

**Abstract:** The photochemistry of *trans*-1,4-diphenyl-3,4-epoxybutan-1-one (II) was investigated. The photolysis in benzene of II has been found to afford four products. The structures have been assigned as acetophenone, phenylacetic acid, dibenzoylethane, and *cis*-1,2-diphenyl-2,3-epoxy-1-cyclobutanol. Evidence is reported for the structure of the cyclobutanol epoxide. A mechanism involving intramolecular hydrogen transfer from carbon to the $p_y$ orbital of oxygen of the n–π* excited state to produce a spin-unpaired 1,4-biradical intermediate is postulated and discussed.

Studies of the photochemistry of ketones that possess a hydrogen-bearing γ carbon have shown that two major reaction pathways are available. The first involves a photoelimination reaction, commonly called the Norrish type-II cleavage,[6] to yield olefins and smaller carbonyl compounds, and the second involves the formation of cyclobutanols[7] (eq 1). Both reactions appear to be intramolecular with little or no detectable side reactions and have been visualized as arising from a common biradical intermediate.[8]



(1)

Recent studies[9-12] have verified Noyes' suggestion[13] that the Norrish type-II process proceeds by intramolecular hydrogen transfer to yield an olefin and an enol. Although the identification of the excited states responsible for the Norrish type-II process is now well established, considerable controversy exists as to the exact mechanism and nature of the excited state responsible for cyclobutanol formation. Two mechanisms have been considered to account for the photochemical formation of cyclobutanols, one a concerted mechanism and the other a stepwise process. In the original mechanism suggested by Yang,[7] a two-step reaction of hydrogen abstraction followed by ring closure was postulated. More recently, Yang has provided further proof that ketones containing γ hydrogens undergo cyclobutanol formation from their triplet states.[14] The extension of this photochemical reaction to aliphatic optically active starting materials with a single asymmetric carbon atom in a γ position to the carbonyl group has been realized in the work of Jeger[15] and Schulte-Elte and Ohloff.[16] The direct irradiation of (6*S*)-(+)-2,5-dimethyloct-7-en-3-one was found to result in cyclobutanol formation with retention of optical activity. The fact that only one of the possible stereoisomers was formed led

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[1] Support of this research by a grant from the Air Force Office of Scientific Research (Grant No. AF-AFOSR-1213-67) is acknowledged with appreciation.

[2] Photochemical Transformation of Small Ring Carbonyl Compounds. XIV. For part XIII, see A. Padwa and L. Hamilton, *J. Heterocyclic Chem.*, 4, 118 (1967).

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