phenyl-4-*p*-methoxyphenylcyclohex-2-en-1-one plus 30.16 g (0.251 mole, 0.251 *M*) of acetophenone in anhydrous benzene was photolyzed for 11.0 min through the filter solution previously described.[17]

Next, a control photolysis was carried out in which 500 mg (1.80 mmoles) of 4-phenyl-4-*p*-methoxyphenylcyclohex-2-en-1-one in 1 l. of anhydrous distilled benzene was photolyzed for 11.0 min using the filter solution previously described,[17] but with no acetophenone present. Both the control and the sensitized runs were purged with nitrogen 1 hr prior to photolysis.

Before and after these photolyses, the light output of the lamp (Hanovia medium pressure mercury lamp, 450 w) was determined by ferrioxalate actinometry as previously described. These actinometry runs indicated that the light output of the lamp had not changed during the course of the experiment. Ultraviolet spectra of the reaction solution taken before and after the sensitized run were virtually identical. Additionally, the ultraviolet of the filter solution before and after the experiment showed that it had not changed appreciably during the course of photolysis.

The control and sensitized runs were freed of benzene by concentration *in vacuo*. In addition, the acetophenone was removed from the sensitized run at 35–40° (0.05 mm) with stirring. Each run was then chromatographed on a 2.5 × 95 cm silica gel column, slurry packed with 5% ether–hexane; 250-ml fractions were taken in each case. After elution with 250 ml of 5% ether–hexane, 1 l. of 10% ether–hexane, 1 l. of 15% ether–hexane, and 1 l. of 20% ether–hexane, the crude photolysate from the control run (521 mg) afforded 490 mg of a mixture of 4-phenyl-4-*p*-methoxyphenylcyclohex-2-en-1-one and *trans*-5-phenyl-6-*p*-methoxyphenylbicyclo[3.1.0]-hexan-2-one upon elution with 3 l. of 22.5% ether–hexane. The composition of this mixture was determined directly by infrared and nmr analysis as previously described, and gave the results shown in Table XII. No *cis*-5-phenyl-6-*p*-methoxyphenylbicyclo-[3.1.0]hexan-2-one was isolated or indicated.

Table XII. Over-all Results of Sensitized Photolyses of 4-Phenyl-4-*p*-methoxyphenylcyclohex-2-en-1-one for Varying Times[a]

Type of photolysis	Photolysis time, min	%					
		Recovered enone		17a			
		Infrared	Nmr	Infrared	Nmr	**17b**	**17c**
Sensitized	4.0	. . .	91.8	. . .	7.7	None[b]	0.5
Control	11.0	89.6	85.5	9.4	13.5	None[b]	1
Sensitized	11.0	66	64.9	32.0	33.1	None[b]	2

[a] **17a** is *trans*-5-phenyl-6-*p*-methoxyphenyl bicyclic ketone, **17b** is *cis*-5-phenyl-6-*p*-methoxyphenyl bicyclic ketone, and **17c** is *trans*-5-*p*-methoxyphenyl-6-phenyl bicyclic ketone. [b] <0.2%.

The column containing the crude material (591 mg) from the sensitized photolysis was eluted with 500 ml of 5% ether–hexane, 750 ml of 10% ether–hexane, 750 ml of 15% ether–hexane, and 1 l. of 20% ether–hexane; 479 mg of a mixture of starting 4-phenyl-4-*p*-methoxyphenylcyclohex-2-en-1-one and *trans*-5-phenyl-6-*p*-methoxyphenylbicyclo[3.1.0]hexan-2-one was obtained by elution with 3 l. of 22.5% ether–hexane. This mixture was analyzed by infrared and nmr; the results are shown in Table XII. Again, no *cis*-5-phenyl-6-*p*-methoxyphenylbicyclo[3.1.0]hexan-2-one could be detected.

A second sensitized photolysis was carried out exactly as above, but for 4.0 min. The results of this run are summarized in Table XII.

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A Reinterpretation of the Nuclear Magnetic Resonance Spectrum of Cyclobutene

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Abstract: A reinvestigation of the nmr spectrum of cyclobutene has led to a revised set of coupling constants which is consistent both with the ^{13}C proton satellite spectra of cyclobutene and with the spectra of partially deuterated cyclobutene isomers. The present treatment differs from that reported previously by inclusion of long-range ^{13}C–C–H and ^{13}C–C–C–H couplings which in effect make the two methylene groups and the two vinyl hydrogens nonequivalent.

The nmr spectrum of cyclobutene consists of two rather sharp lines without obvious indication of spin–spin coupling.[2–4] Several explanations have been put forth for the intriguing simplicity of this spectrum.[3,5,6] Most recently, Borčić and Roberts[6] have examined the ^{13}C satellites in the proton resonance spectra of cyclobutene and cyclobutene-1,2-d_2. These exhibit coupling patterns of considerable complexity. A complete set of proton–proton coupling constants was derived by matching observed and calculated ^{13}C satellite spectra. It now appears, on the basis of results presented below, that an oversimplification in the calculations resulted in a substantial error in the derived values for J_{13} $(=J_{25})$ and J_{15} $(=J_{23})$. In addition, higher quality satellite spectra have now been obtained, which require slightly revised values for some of the other coupling constants. In the discussion to follow, the numbering (I) of Borčić and Roberts[6] is retained.

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(2) J. D. Roberts, "Nuclear Magnetic Resonance, Applications to Organic Chemistry," McGraw-Hill Book Co., Inc., New York, N. Y., 1959, pp 54, 103.

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(4) W. G. Dauben and R. L. Cargill, *Tetrahedron*, **12**, 186 (1961).

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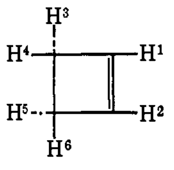
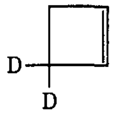
(6) S. Borčić and J. D. Roberts, *J. Am. Chem. Soc.*, **87**, 1056 (1965).

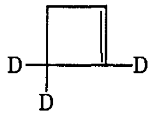


I

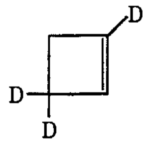
Samples of cyclobutene-3,3-d_2 (II) and an equimolar mixture of cyclobutene-2,3,3-d_3 (III) and cyclobutene-1,3,3-d_3 (IV) were obtained in connection with other work.[7] Deuterium-decoupled proton resonance spectra were consistent with the deuterium distribution indicated, but required assignments of coupling constants which were different from those reported earlier.[6]



II



III

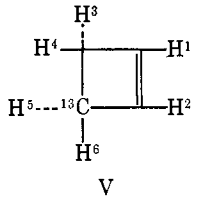


IV

The methylene resonance of cyclobutene-3,3-d_2 (Figure 1a) is a triplet with an apparent coupling constant of 0.32 cps. Such a spectrum is consistent with $J_{13} = J_{15} = 0.32$ cps, or with a "deceptively simple" spectrum[8] where coupling between the two vinyl hydrogens is substantially stronger than that with the methylene hydrogens. In the latter case, $^{1}/_{2}|J_{13} + J_{15}|$ would be 0.32 cps.

The methylene spectrum of the mixture of trideuterated cyclobutenes III and IV (Figure 1b) supports the second alternative in showing four lines consistent with a coupling constant of 1.00 cps in one isomer, and 0.35 cps in the other. If these coupling constants are of opposite sign, then $^{1}/_{2}|J_{13} + J_{15}| = 0.33$ cps. The vinyl resonance of the same mixture (Figure 1c) appears to be two overlapping triplets, with coupling constants of about 0.35 and 1.0 cps. One triplet is shifted by about 0.6 cps with respect to the other, presumably due to an isotopic effect of the deuterium.[9] In the earlier study,[6] the values derived for J_{13} and J_{15} were -0.80 and 1.55 cps.

If the values of J_{13} and J_{15} obtained from the deuteriocyclobutenes are used to calculate the ^{13}C satellite spectra of cyclobutene itself with the other parameters of Borčić and Roberts,[6] the result bears very little resemblance to the observed spectrum (Figure 2, which as shown here has a far more favorable signal-to-noise ratio than the spectrum reported earlier[6]). The discrepancy lies in neglect of the long-range ^{13}C–H couplings. The difficulties can be illustrated by consideration of the high-field methylene ^{13}C satellite of cyclobutene. This resonance represents a portion of the spectrum of cyclobutene-3-^{13}C (V) when the ^{13}C nucleus is in a particular spin state. It is convenient to reduce the total number of spins included in the calculation by representing the coupling of hydrogens with ^{13}C by a chemical shift. Thus, since the methylene ^{13}C–H coupling constant is 140 cps, H^5 and H^6 are represented as shifted 70 cps upfield from H^3 and H^4, which are assumed to be located approximately at the normal methylene resonance position of cyclobutane. In the earlier calculations, this one-bond coupling constant was the only ^{13}C–H coupling introduced into the calculation. Such a simplification is suitable either if $J_{^{13}C-H^1}$ and $J_{^{13}C-H^2}$ are quite small, or if they are large and nearly identical. However, if these two coupling constants are different, H^1 and H^2 have effectively different chemical shifts, and the resulting removal of what amounts to a chemical-shift degeneracy produces a significant change in the calculated spectrum. Spectra bearing general resemblance to the observed ^{13}C satellites were found to be obtained with the new values of J_{13} and J_{15}, using an artificially introduced chemical shift between H^1 and H^2 of 4–10 cps for the methylene satellites, and 6–11 cps between H^3 and H^5 for the vinyl satellites.



V

Table I lists the spectral parameters which give the best fit to the experimental spectra (see also Figure 2). The tabulated values involve refinements of coupling constants other than the ones whose correction is specifically involved in the present study. The proton–proton coupling constants are considered to be accurate to ±0.05 cps, with the exception of J_{34}, whose value has only very minor influence on the appearance of the spectra. The remote ^{13}C–H couplings appear to be accurate within about 1–2 cps, with those involving the methylene satellites being the more accurate.

Table I. Nmr Parameters of Cyclobutene (cps)[a]

1,2 protons	δ 6.03 ppm;	$J_{^{13}C-H} = 170$
3,4,5,6 protons	δ 2.57 ppm;	$J_{^{13}C-H} = 140$
$J_{12} = +2.85^{b}$		$J_{34} = J_{56} = -12.00$
$J_{13} = J_{14} = J_{25} = J_{26} = +1.00^{b}$		$J_{35} = J_{46} = +4.65^{c}$
$J_{15} = J_{16} = J_{23} = J_{24} = -0.35^{b}$		$J_{36} = J_{45} = +1.75^{c}$
$J_{^{13}C-C-C-H^1} - J_{^{13}C-C-H^2} = +4.0^{d}$		
$J_{^{13}C-C-C-H^5} - J_{^{13}C-C-H^3} = +7.0^{e}$		

[a] For the numbering convention, see I. [b] See text for discussion of the assignment of values and signs. [c] The *cis* couplings were taken as being larger than the *trans* couplings in accord with the usual expectations for systems of this kind. [d] From calculation of methylene satellite, with H^5 and H^6 bonded to ^{13}C. [e] From calculation of vinyl satellite, with H^1 bonded to ^{13}C.

In Table I, we show $J_{13} = +1.00$ cps and J_{15} $(=J_{23}) = -0.35$ cps. The calculations do not uniquely determine this pair of values, but rather fix a relationship between several parameters. Any one of four operations produces the same alternate calculated methylene satellite: (1) exchanging J_{13} and J_{15}; (2) reversing the signs of both J_{13} and J_{15}; (3) exchanging the chemical shifts of H^1 and H^2; (4) exchanging the chemical shifts of H^3 and H^5. Any two operations in succession return the original spectrum. All of these operations amount in effect to exchanging the numbering of atoms in the molecule, or to changing the relationship

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(7) Cyclobutene-3,3-d_2 was obtained by heating the Grignard reagent from 4-bromo-1-chloro-1-butene-4,4-d_2. The trideuterated cyclobutene mixture was similarly obtained from the Grignard reagent from 4-bromo-1-chloro-1-butene-2,4,4-d_3. The mechanism of this reaction and conclusive spectroscopic evidence for the deuterium distribution postulated for the product will be discussed in a later publication.

(8) R. J. Abraham and H. J. Bernstein, *Can. J. Chem.*, 39, 216 (1961).

(9) J. R. Holmes, D. Kivelson, and W. C. Drinkard, *J. Chem. Phys.*, 37, 150 (1962); H. S. Gutowsky, *ibid.*, 31, 1683 (1959), and references therein.

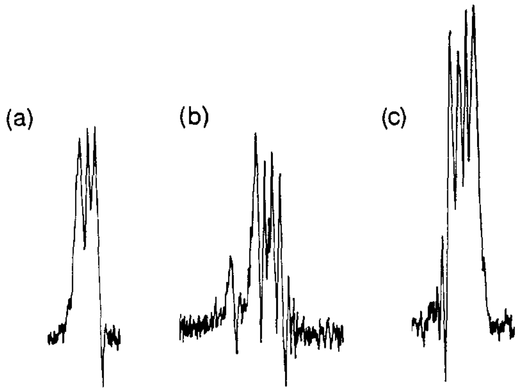

Figure 1. Proton magnetic resonance spectra of neat samples of deuterated cyclobutenes at 60 Mc/sec run with deuterium decoupling: a, methylene hydrogens of cyclobutene-3,3-d_2; b, methylene hydrogens of a cyclobutene mixture of -2,3,3-d_2 and -1,3,3-d_2; c, vinyl hydrogens of the same mixture as in b.

between the sign of $J_{15} - J_{25}$ and the sign of $J_{^{13}C-H^1} - J_{^{13}C-H^2}$. The fourth of these variables may be chosen arbitrarily for the high-field methylene satellite by taking H^5 and H^6 as bonded to ^{13}C. The third variable amounts to a choice of the sign of $J_{^{13}C-C-C-H^1} - J_{^{13}C-C-H^2}$. This is taken as positive since the prediction has been made that two-bond $J_{^{13}C-C-H}$ should be negative and three-bond $J_{^{13}C-C-C-H}$ should be positive.[10,11] It is then required that either $J_{13} = +1.00$ cps, $J_{23} = -0.35$ cps, or $J_{13} = +0.35$ cps, $J_{23} = -1.00$ cps. Either assignment is in accord with the signs and magnitudes of allylvinyl coupling constants for other cycloalkenes,[12] but the former is preferred because in the vinyl spectra of the trideuteriocyclobutenes (Figure 1b), the triplet with the smaller coupling is shifted by the deuterium isotope effect to higher field. This latter fact suggests that the isomer yielding the narrower triplet is actually IV on the basis that isotopic substitution with deuterium produces upfield shifts on nearby protons.[9,13]

The sign of J_{12} produces a noticeable effect on the symmetry of the two triplets in the calculated vinyl satellite spectrum (see Figure 2). The observed spectrum appears to be more in line with J_{12} as $+2.85$ cps, which also seems to be consistent with similar coupling constants in other cyclic olefins.[12,14]

The long-range ^{13}C couplings, which are responsible for the difference of the calculated spectra from those previously reported, are of interest. A number of reports place both three- and four-bond couplings in a number of systems in the general range of 3–10 cps.[10,11,15] It might be noted that in the present case there are two bond routes for the four-bond couplings. Given opposite signs, it is then quite reasonable that differences between $J_{^{13}C-C-H}$ and $J_{^{13}C-C-C-H}$ should have magnitudes of 4 and 7 cps, which are required to fit the experimental spectra. Since the present study cannot provide individual values for these coupling constants, the artificial chemical shifts used in the calculations were chosen for convenience to correspond to equal and opposite vales for these constants.

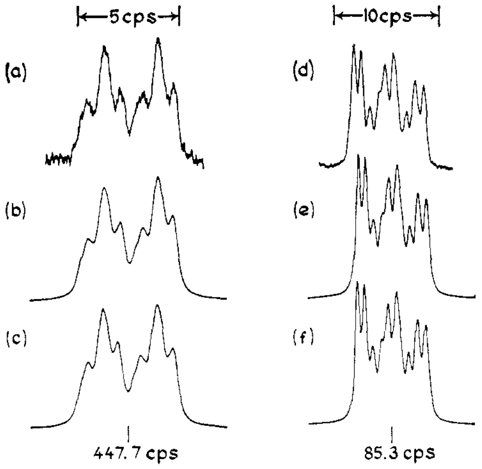

Figure 2. Magnetic resonance spectra of vinyl and methylene ^{13}C satellites of neat cyclobutene at 60.0 Mc/sec: a, downfield vinyl ^{13}C satellite spectrum (30 scans); b, calculated spectrum downfield vinyl satellite with parameters of Table I; c, same as b except that J_{12} is -2.85 cps; d, upfield methylene ^{13}C satellite spectrum (150 scans); e, calculated spectrum for upfield methylene satellite with parameters of Table I; f, same as e except that J_{12} is -2.85 cps.

One further feature of the present spectra is of interest. In the deuterium-decoupled spectrum of cyclobutene-3,3-d_2 (Figure 1a), the methylene triplet differs from a first-order distribution of intensities. A calculation shows that the observed spectrum can be reproduced if it is assume that the two methylene deuterium atoms produce a shift of the nearest vinyl hydrogen by about 0.7 cps. The difference between the centers of the vinyl triplets of III and IV is similarly about 0.6 cps. By contrast, there appears to be little or no isotope effect (of vinyl deuterium) between the methylene resonances of the same pair of isomers.

Experimental Section

Spectra of cyclobutene ^{13}C satellites were run on a neat sample at ambient temperature at 60 Mc/sec on a Varian A-56/60 spectrometer equipped with a Mnemotron 1024 CAT digital computer. Spectra of deuterated cyclobutenes were taken in dilute carbon tetrachloride solution on a Varian A-60 spectrometer equipped with a NMR Specialties HD heteronuclear decoupler.

Calculations of theoretical spectra were performed on an IBM 7090 computer equipped with an X–Y plotter, and on a Control Data 1604 computer[16] using a plotting program NVELOPE written by Dr. W. B. Schwabacher.[17] Spectra were calculated by a trial-and-error method using the program of Wiberg and Nist[18] and LAOCOON II (first part).[19]

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(10) See G. J. Karabatsos, J. D. Graham, and F. M. Vane, *J. Am. Chem. Soc.*, **84**, 37 (1962), footnote 13 referring to unpublished work by P. T. Narasimhan.

(11) The direction of this difference appears consistent with relatively scattered experimental evidence: the spectrum of methylacetylene (H. Dreeskamp, E. Sackmann, and G. Stegmeier, *Ber. Bunsenges. Physik. Chem.*, 67, 860 (1963)), spectra of ethylmetal derivatives (P. T. Narasimhan and M. T. Rogers, *J. Chem. Phys.*, **34**, 1049 (1961)), the spectrum of ethyl ether (R. Freeman and W. A. Anderson, *ibid.*, **42**, 1199 (1965)).

(12) G. V. Smith and H. Kriloff, *J. Am. Chem. Soc.*, **85**, 2016 (1963).

(13) A somewhat poorer fit to both methylene and vinyl satellites may be obtained with a set of "reversed" parameters having $J_{13} = -0.9$ cps and $J_{15} = +0.3$ cps, and with about a 3 cps greater difference between the long-range ^{13}C–H couplings. These spectra differ by 0.1–0.2 cps in some of the peak spacings and in some relative intensities, but the fit to the experimental spectra is still passable.

(14) P. Laszlo and P. von R. Schleyer, *J. Am. Chem. Soc.*, **85**, 2017 (1963); O. L. Chapman, *ibid.*, **85**, 2014 (1963).

(15) G. J. Karabatsos and C. E. Orzech, Jr., *ibid.*, **86**, 3574 (1964); **87**, 560 (1965); J. G. Karabatsos, J. D. Graham, and F. Vane, *ibid.*, **83**, 2778 (1961).

(16) We acknowledge the contribution of a portion of the computer time used by the University of Minnesota Numerical Analysis Center.

(17) We acknowledge assistance of Dr. Schwabacher in this and several other aspects of this problem.

(18) K. B. Wiberg and B. J. Nist, "Interpretation of Nmr Spectra," W. A. Benjamin, Inc., New York, N. Y., 1962.

(19) S. Castellano and A. A. Bothner-By, *J. Chem. Phys.*, **41**, 3863 (1964).