possessed purities of 94 and 91.5%, respectively. The latter peroxide contained less than 2% of benzoic acid by potentiometric titration. More vigorous conditions[28] (sodium iodide in refluxing, acidified isopropyl alcohol) were necessary in the case of the *t*-butyl peresters, perbenzoic acid, and lauroyl peroxide. *t*-Butylperoxyisopropyl carbonate, 87.5% pure by this method, was shown to contain 8% of di-*t*-butyl peroxide by iodometry and glpc. Benzoyl peroxide was analyzed with aqueous sodium iodide-carbon tetrachloride–acetic acid–ferric chloride hexahydrate.[59]

C. For Product Yields. 1. Aryl Esters.—Tolylcyclohexyl carbonates (mesitylisopropyl carbonate marker) and aryl benzoates (phenyl benzoate marker) were determined on glpc column 3 at 195°. The tolylisopropyl carbonates were analyzed as described earlier.[20]

2. Nonoxygenated Aromatic Products.—Glpc column 1 (195°) was the choice for most nonoxygenated material with trichlorobenzene as internal standard. Exceptions were benzene and chlorobenzene from the benzoyl peroxide decompositions, which were determined on glpc column 2 (mesitylene marker) at 135°. The phenylated products from the same runs were analyzed on the column described for the benzoate esters.

3. Low-Boiling Materials.—Glpc column 8 provided most of the data for the low-boiling materials (either methyl ethyl ketone or benzene as internal standard). Cyclohexanol and cyclohexanone were detected on glpc column 5 with *o*-xylene as marker.

4. Benzoic Acid.—Potentiometric titration was carried out on reaction aliquots to determine the amount of benzoic acid. Cupric ion was shown not to interfere at the concentrations employed in this study. Duplicate analyses indicated excellent precision in all cases.

5. Carbon Dioxide.—This gas was determined by a known procedure (method A).[30]

D. For Isomer Distributions.—The combination glpc–ir technique described elsewhere[20] was employed to obtain the isomeric composition of the tolylcyclohexyl carbonates and tolyl benzoates. Direct glpc analysis provided the orientation of the anisyl benzoates and the tolylisopropyl carbonates.

Registry No.—Toluene, 108-88-3; cupric chloride, 7447-39-4; I (X = Y = $C_6H_{11}OCO$), 1561-49-5; I (X = C_6H_5CO; Y = *i*-PrOCO), 16136-81-5; I (X = *t*-Bu; Y = *i*-PrOCO), 2372-21-6; benzoyl peroxide, 94-36-0.

Acknowledgment.—We are grateful to the National Science Foundation for support of this work.

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[59] L. S. Silbert and D. Swern, *J. Amer. Chem. Soc.*, **81**, 2364 (1959).

Cyclobutane Compounds. V.[1] Long-Range Spin Coupling in the Cyclobutyl System

Peter E. Butler and K. Griesbaum

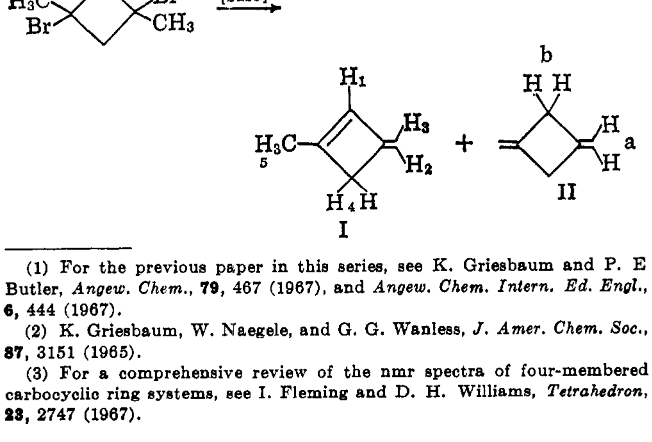
Esso Research and Engineering Company, Linden, New Jersey 07036

Received October 30, 1967

The 100-Mc nuclear magnetic resonance spectrum of 1-methyl-3-methylenecyclobutene (I) and 1,3-dimethylenecyclobutane (II) were examined. These (spectra) are novel examples of eight-spin first-order systems containing five sets of mutually coupled, nonequivalent protons. Several novel ^4J and ^6J long-range spin couplings are identified using double and triple irradiation techniques.

In connection with our interest in the chemistry and spectral characterization of four-membered carbocyclic ring systems,[2] we wish to report several novel examples of four- and six-bond (^4J, ^6J) long-range spin coupling in the cyclobutene (I) and cyclobutane (II) systems.[3] The nuclear magnetic resonance (nmr) spectra of these compounds are novel examples of eight-spin first-order systems containing five sets of nonequivalent protons in which all of the protons in each molecule are mutually coupled.

Base-catalyzed dehydrobromination of 1,3-dibromo-1,3-dimethyl-cyclobutane produces, in approximately 50% over-all yield,[4] a mixture of the isomeric olefins 1-methyl-3-methylenecyclobutene (I) and 1,3-dimethylenecyclobutane (II). The structures of these materials were established by an analysis of their characteristic nmr spectra (Figure 1) and by comparison of their physical constants with literature values.[5,6] Compound II has been previously reported to be the product of pyrolysis of (3-methylenecyclobutylcarbinyl)dimethylamino oxide[5] and a minor component in the dimerization of allene.[6] The conjugated diene (I) was previously prepared by treatment of (3-methylenecyclobutylcarbinyl)trimethylammonium hydroxide with silver oxide.[5]



The nmr spectrum of I has multiplets at 5.99 (H_1), 4.49 (H_2), 4.28 (H_3), 2.76 (H_4), and 1.86 ppm (H_5) in a ratio of 1:1:1:2:3, respectively. On expansion under conditions of high resolution (Figure 2), these multiplets may be fully resolved.[7] A clearly first-order spectrum is observed for the eight-spin system (which may be analyzed using the usual rules) even though all of the

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[1] For the previous paper in this series, see K. Griesbaum and P. E Butler, *Angew. Chem.*, **79**, 467 (1967), and *Angew. Chem. Intern. Ed. Engl.*, **6**, 444 (1967).

[2] K. Griesbaum, W. Naegele, and G. G. Wanless, *J. Amer. Chem. Soc.*, **87**, 3151 (1965).

[3] For a comprehensive review of the nmr spectra of four-membered carbocyclic ring systems, see I. Fleming and D. H. Williams, *Tetrahedron*, **23**, 2747 (1967).

[4] The synthetic details of the dehydrobromination step and the reactions of these olefins will be described elsewhere.

[5] F. F. Caserio, Jr., S. H. Parker, R. Piccolini, and J. D. Roberts, *J. Amer. Chem. Soc.*, **80**, 5507 (1958).

[6] B. Weinstein and A. H. Fenselau, *J. Chem. Soc., Sect. C*, 368 (1967); Y. M. Slobodin and A. P. Khitrov, *Zh. Obshch. Khim.*, **33**, 153, 2822 (1963); **34**, 1727 (1964).

[7] Previous workers examined the nmr spectra of I and II under conditions of low resolution. Roberts, *et al.*, reported[5] the 40-Mc spectrum of I showing two groups of five component lines for the terminal olefin and allylic methylene protons, however, Weinstein, *et al.*,[6] reported a 60-Mc spectrum showing multiplets at 4.8 and 3.31 ppm for the same protons. The 40-Mc spectrum of II reported by Roberts was taken on a neat sample and showed broad absorptions with chemical shifts similar to those we report. No fine structure was observed.

TABLE I

DOUBLE AND TRIPLE IRRADIATION DATA[a]

Compd	Proton	Single irradiation	Double irradiation					Triple irradiation				
I	H_1	t of dq	←	nc	tq	dq	td	tq	dq	dt	d	←
	H_2	q of t	nc	←	nc	q	t	←	←	←	s	q
	H_3	sep	h	nc	←	qu	q	←	qu	dt	d	q
	H_4	d of d qu	dqu	d of dq	dqu	←	ddd	dq	←	dd	←	←
	H_5	t of td	tt	d of td	d of td	td	←	td[b]	dd	←	←	t
II	H_a	qu	←	s								
	H_b	qu	s	←								

[a] In the double and triple irradiation experiments the arrow(s) indicate the proton(s) being irradiated. The effect of these multiple irradiation experiments is noted in the same vertical column: nc = no change, s = singlet, d = doublet, t = triplet, q = quartet, qu = quintet, h = hextet, sep = septet. [b] Due to line broadening this signal appears as a quartet with line separations of 1.42 cps (*ca.* $(J_{1,5} + J_{4,5})/2$).

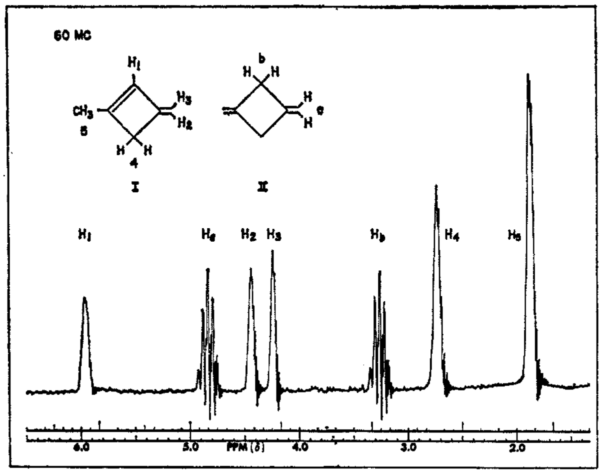

Figure 1.

five nonequivalent sets of protons within the system mutually interact ($J_{1,2} = 0$, $J_{1,3} = 0.77$, $J_{1,4} = 0.50$, $J_{1,5} = 1.55$, $J_{2,3} = 0$, $J_{2,4} = 1.28$, $J_{2,5} = 0.60$, $J_{3,4} = 0.83$, $J_{3,5} = 0.65$, and $J_{4,5} = 1.31$ cps). This unusual phenomenon is the result of the small magnitude of spin couplings involved. Even though the chemical shifts between the interacting groups are small in several instances, in no case is the chemical shift difference/coupling constant ratio $[(\delta_x - \delta_y)/J_{xy}]$ for any combination of sets less than 40.5:1 at 60 Mcps.

All of the coupling constants and multiplicities were assigned as the result of exhaustive frequency-sweep, multiple-irradiation studies.[8,9] Each set of protons was irradiated in turn and the rest of the spectrum was observed. Five triple irradiation studies were also performed in which several combinations of sets were irradiated in pairs. All of these multiple irradiation data are summarized in Table I.

An example of the use of these techniques is illustrated in the detection of long-range (^6J) coupling over six bonds between the olefinic methyl group (H_5) and both of the nonequivalent terminal olefin protons (H_2, H_3) in I. The signal for the methyl protons appears as a triplet of a triple doublet due to spin coupling with the terminal olefin protons ($J_{2,5} = 0.60$, $J_{3,5} = 0.65$), the ring methylene protons ($J_{4,5} = 1.31$), and the vinylic olefin proton ($J_{1,5} = 1.55$ cps). Double irradiation at either H_2 or H_3 removes the *ca.* 0.6-cps coupling with these protons and collapses the methyl signal to a doublet of a triple doublet (Figure 3). Likewise triple irradiation of H_1 and H_4 simultaneously leaves only the 6-bond coupling ($J_{2,5}$ and $J_{3,5}$) resulting in a triplet for the methyl signal and quartets for H_2 and H_3. Triple irradiation of H_2 and H_3 yields a triple doublet (which appears as a quartet with line separations equal to $(J_{1,5} + J_{4,5})/2$ for the methyl group which reflects the original coupling constants (Figure 3).

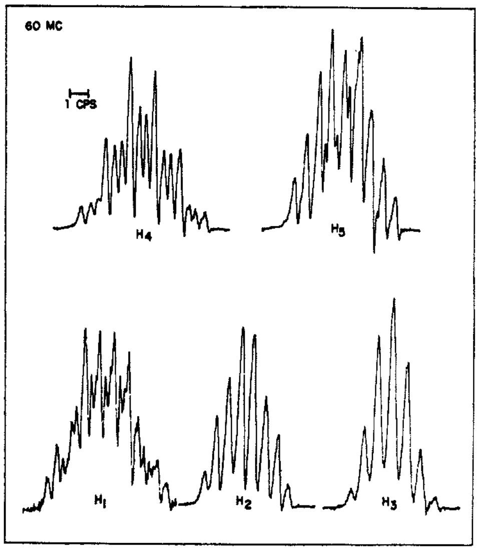

Figure 2.

Conversely, the signal for H_2 is a quartet of triplets due to coupling with both the ring methylene ($J_{2,4} = 1.28$) and methyl ($J_{2,5} = 0.60$ cps) protons. The signal for H_3 is a septet due to nearly equivalent coupling with the olefinic ($J_{1,3} = 0.77$), the ring methylene ($J_{3,4} = 0.83$ cps), and the methyl protons. In this system, geminal coupling ($J_{2,3}$) and allylic coupling ($J_{1,2}$) are very close to zero (the full widths at half height of peaks within these groups are no wider than peaks in other groups having no residual coupling). Double irradiation of the methyl group signal (H_5) again removes the 6-bond coupling and collapses H_2 to a triplet and H_3 to a quartet (Figure 4) while irradiation at H_4 collapses H_2 to a quartet and H_3 to a quintet. Triple irradiation of both H_4 and H_5 greatly simplifies the spectrum. Protons H_1 and H_3 are doublets due to mutual coupling ($J_{1,3} = 0.77$ cps) whereas H_2 is a sharp singlet due to the absence of re-

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(8) Double and triple irradiation experiments were performed at 100 Mc on the JEOLCO 4H-100 spectrometer. In the nmtr experiments, a Kakusui-Dempa RC signal generator (Model ORC-27) was used. Routine 60-Mc spectra were obtained on dilute CCl_4 solutions on the Varian A-60A spectrometer.

(9) L. M. Jackman "Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry," Pergamon Press, Inc., New York, N. Y., 1959.

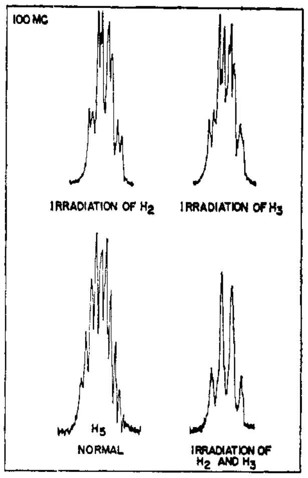


Figure 3.

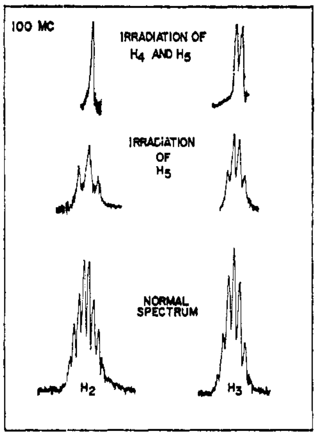


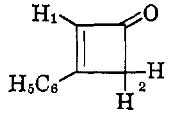
Figure 4.

sidual coupling (Figure 4). In a similar manner the remaining long-range couplings in the system were isolated by multiple irradiation experiments (see Table I).

The assignment of H_2 and H_3 is based on the known values of the allylic couplings, in which the cisoid are usually greater than the transoid,[10–13] although this assignment must be tentative in view of the known exceptions to this rule[14] and the effect of strain on coupling constants in the cyclobutane system.[15]

Our assignment of H_2 and H_3 is in line with that predicted from a study of the Dreiding model of I. The upfield olefinic proton is assigned to H_3 on the basis of a diamagnetic shift experienced by this proton (relative to H_2) due to the anisotropy of the eclipsed carbon–hydrogen bond (whereas the dihedral angle between the plane of the double bond and H_1 is zero, H_2 is staggered between the protons, H_4).

It is apparent from the spectral symmetry exhibited by I (the ring methylene protons, H_4, are equivalent and couple equally with the other four sets of protons) that the ring system is planar or rapidly equilibrating. This is probably the result of the rigidity introduced by the *exo* and *endo* double bonds. A similar situation exists



in cyclobutenone III in which the ring methylene protons are also equivalent.[16] The reported cross-ring coupling ($J_{1,2}$) of 0.44 cps is in good agreement with our $J_{1,4} = 0.50$ cps.

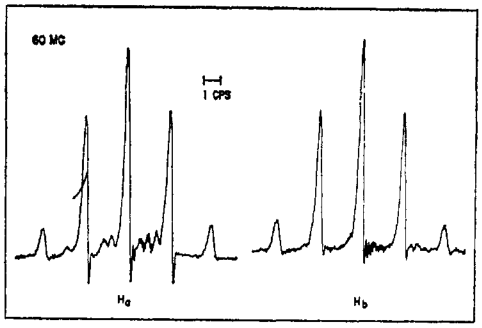


Figure 5.

A consequence of the planarity of the ring is that it allows considerable overlap of the π orbitals of the double bonds. This conjugated character is shown by the low-field shift of the vinylic proton (H_1) and by the much more rapid addition of thiols to I relative to II.[4]

In contrast to these findings, recent nmr studies on cyclobutane itself in a nematic solvent indicate that the molecule is rapidly flipping between two equivalent geometries.[3] Variable-temperature nmr studies indicate that unsymmetrically substituted cyclobutanes are also conformationally mobile.[17]

In regard to II the allylic methylene and terminal olefin groups on expansion (Figure 5) appear as symmetrical (1:4:5:4:1) quintets at 3.27 and 4.86 ppm and are coupled together with ${}^4J_{av} = 2.55$ cps. The magnitude of this coupling between the exocyclic olefin protons and the allylic methylene protons is somewhat larger than the range of 0.5 – 2.0 cps given by Jackman[9] for acyclic systems. Each of the quintets could be collapsed to a very sharp singlet on frequency sweep irradiation at the chemical shift of the other group.[8]

Registry No.—I, 15082-13-0; II, 2045-78-5.

Acknowledgment.—The authors would like to thank Professor L. M. Jackman for his helpful discussion of the manuscript and the Japanese Electron Optics Laboratory (JEOLCO) for making available their 4H-100 nuclear magnetic resonance system. We are particularly indebted to Mr. I. Ogawa for his excellent technical assistance with the multiple irradiation experiments.

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