

It must be mentioned that the role of aluminum halides in this and previously reported reductions¹⁻³ may be an important, although yet unknown variable, for we have observed in other LAH reductions of 7-substituted norbornadienes that both the extent and course of reaction are sensitive to the amount of trivalent aluminum (as AlCl₃) present in the reaction medium.

Results of the extension of this type of rearrangement to other systems and further mechanistic studies on the rearrangement will be reported in the complete paper.

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Solvent Effects on the C¹³ Chemical Shift of the Carbonyl Group of Acetone

Sir:

A considerable volume of carbon-13 chemical shift data on a wide variety of compounds has been accumulated during the past few years,¹⁻¹³ but almost no information is yet available concerning solvent effects on these parameters. Some investigators have mentioned the uncertainties involved in the interpretation of results without the knowledge of solvent effects,^{2,4-11} and a few have run limited control experiments to demonstrate the magnitude of the solvent shifts in isolated cases where data obtained in different solvents had to be compared.^{2,4,5,8,9,11} We have undertaken an extensive study of these effects and wish to report here what is apparently the first systematic investigation of solvent effects in the carbon-13 n.m.r. spectra of any system.

C¹³ chemical shifts of the carbonyl group of acetone were obtained in natural abundance in 1:6 mole fraction solutions of acetone in a wide variety of reagent, spectro-grade, or Eastman White Label solvents. A measuring frequency of 15.1 Mc./sec. and the rapid passage dispersion mode technique described previously by Lauterbur² were employed. Shifts were measured in a concentric-sphere sample container,⁹ to eliminate bulk susceptibility effects, with respect to an external reference of saturated aqueous NaO₂C¹³CH₃ in the center sphere, using the side-band technique.

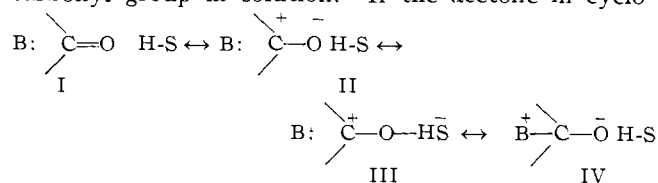
The observed shifts referred to that of pure acetone are presented in Table I. These shifts are the average result of at least five field scans in both increasing and decreasing senses and can be considered accurate to about ±0.5 p.p.m. They cover a total range of about 40 p.p.m. with the largest positive shift occurring with cyclohexane as solvent and the largest negative shift corresponding to a sulfuric acid solvent. Eleven aprotic solvents give shifts at the positive end of the scale covering a range of only 3.1 p.p.m. In contrast fifteen protic solvents,¹⁴ capable of forming hydrogen bonds with, or actually protonating, the carbonyl oxygen atom

TABLE I
C¹³ CHEMICAL SHIFTS OF CH₃C¹³OCH₃ IN 1:6 MOLE FRACTION SOLUTIONS IN SEVERAL SOLVENTS

Solvent	Chemical shift, p.p.m. with respect to CH ₃ C ¹³ OCH ₃	Dielectric constant ^a
Cyclohexane	+2.4	2.02
Diethyl ether	+2.0	4.34
Carbon tetrachloride	+1.3	2.24
Tetrahydrofuran	+0.80	8.20
Benzene	+0.80	2.28
Ethyl bromide	+0.40	9.39
Acetone	0.0	21.2
Methyl iodide	0.0	7.00
1,4-Dioxane	0.0	2.21 ^b
N,N-Dimethylacetamide	-0.4	38.9 ^c
N,N-Dimethylformamide	-0.7	37.6
<i>t</i> -Butyl alcohol	-1.6	10.9
2-Propanol	-1.9	19.0
Acetonitrile	-2.1	37.5
Chloroform	-2.3	4.81
Ethanol	-2.9	25.1
Methanol	-3.7	33.6
Acetic acid	-6.2	6.2
<i>m</i> -Cresol	-8.2	11.8 ^b
Phenol	-8.7	13.1 ^d
Water	-9.1	80.4
Formic acid	-9.1	57.9
Dichloroacetic acid	-11.9	
Trichloroacetic acid	-13.0	ca. 7 ^d
Trifluoroacetic acid	-14.1	39.5
Sulfuric acid	-37.4	110

^a Unless otherwise indicated the dielectric constants refer to 20° and were obtained from either A. A. Maryott and E. R. Smith, "Table of Dielectric Constants of Pure Liquids," National Bureau of Standards Circular No. 514, N.B.S., Washington, D. C., 1951, or from "The American Institute of Physics Handbook," McGraw-Hill Book Co., New York, N. Y., 1957, pp. 5-133. ^b Refers to 25°. ^c G. R. Leader and J. F. Garmley, *J. Am. Chem. Soc.*, **73**, 5731 (1951). ^d Estimated from data obtained at a higher temperature.

are seen to cover a range of 35.8 p.p.m. in their solvent effects. Thus it appears that the chemical shift of the carbonyl group is quite sensitive to an environment of proton donors and relatively insensitive to environment if proton donors are not present. That the observed shifts are not due to changes in the position of a rapid equilibrium with the enol form is apparent if one notes that the enol concentration in pure acetone is only 1.5 × 10⁻⁴⁰%,¹⁵ so small as to be incapable of appreciably influencing the resultant shift of an equilibrating system. Furthermore, Gero has stated that the enol concentration decreases as a simple ketone is diluted by solvents.¹⁵ Also, similar solvent effects have been observed with carbonyl compounds such as 2,2,4,4-tetramethyl-3-pentanone in which the possibility of enol formation is precluded by structure.¹⁶ It appears that the solvent shift is to be explained in terms of the effect of solvent on the relative importance of the following various structures in the valence-bond description of a carbonyl group in solution. If the acetone in cyclo-



hexane solution can be represented by I, then the shifts relative to that system must be due to increased importance of the polarized structures II, III, and IV in

(15) A. Gero, *J. Org. Chem.*, **19**, 1960 (1954).

(16) G. E. Maciel and J. J. Natterstad, unpublished results.

(1) P. C. Lauterbur, *J. Chem. Phys.*, **26**, 217 (1957).

(2) P. C. Lauterbur, *J. Am. Chem. Soc.*, **83**, 1838 (1961).

(3) R. A. Friedel and H. L. Retcofsky, *ibid.*, **85**, 1300 (1963).

(4) P. C. Lauterbur, *ibid.*, **83**, 1846 (1961).

(5) P. C. Lauterbur, *Ann. N. Y. Acad. Sci.*, **70**, 841 (1958).

(6) G. B. Savitsky, *J. Phys. Chem.*, **67**, 2430 (1963).

(7) G. B. Savitsky, *ibid.*, in press.

(8) H. Spiesecke and W. G. Schneider, *J. Chem. Phys.*, **35**, 722 (1961).

(9) H. Spiesecke and W. G. Schneider, *ibid.*, **35**, 731 (1961).

(10) P. C. Lauterbur, *ibid.*, **38**, 1415 (1963).

(11) P. C. Lauterbur, *ibid.*, **38**, 1432 (1963).

(12) C. H. Holm, *ibid.*, **26**, 707 (1957).

(13) P. C. Lauterbur, *ibid.*, **38**, 1406 (1963).

(14) Acetonitrile and chloroform do not fit into this category, but ample evidence exists to show that chloroform is a good proton donor in hydrogen-bond formation: G. J. Korinek and W. G. Schneider, *Can. J. Chem.*, **35**, 1157 (1957); C. M. Huggins and G. C. Pimentel, *J. Chem. Phys.*, **23**, 1244 (1955), and there is some evidence which indicates that acetonitrile can also function in this manner: R. S. Becker, *J. Mol. Spectry*, **3**, 1 (1959).

the other solvents. While the polar structure II should become more important with increasing dielectric constant of the solvent, the solvent effects observed in this study cannot be explained satisfactorily on this basis if one notes the marked deviations from any such trend in Table I. It seems more likely that the predominant effect is that of hydrogen bonding which can be represented by an increased importance of structure III in the valence-bond description. This interpretation is supported by the fact that intramolecular hydrogen bonding in methyl salicylate and related compounds has been shown to cause a downfield shift of about 3 to 8 p.p.m.^{5,17} However, dielectric favoring of structure II and Lewis base interaction represented by structure IV most likely contribute to these solvent shifts and are probably primarily responsible for the 3.1-p.p.m. range in solvent shift between cyclohexane and N,N-dimethylformamide. The question of the relative importance of the various solvent-solute interactions in determining the solvent effects will be discussed more completely in future publications dealing with other carbonyl compounds as well as different classes of solute substances.

(17) G. E. Maciel and G. B. Savitsky, unpublished results.

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Photoisomerization of Pyrazolenines and Formation of 7,7-Dimethylbicyclo[4.1.0]heptene- Δ -1,6¹

Sir.

Recently, we reported the preparation of some alkylpyrazolenines and their photolysis to cyclopropenes.² We now wish to communicate a photoisomerization of pyrazolenines and a remarkable solvent dependence of this reaction. In addition, we have prepared the unusually strained 7,7-dimethylbicyclo[4.1.0]heptene- Δ -1,6 (IIb) and have found it a highly labile compound.

Photolysis³ of pyrazolenine Ia in pentane at 13° gave the stable cyclopropene derivative IIa in high yield.² However, on irradiating a solution of Ia in methylene chloride at -60° no nitrogen was evolved. Under these conditions, Ia was isomerized quantitatively to a labile compound, which we believe to have the tricyclic structure IVa. The n.m.r. spectrum of the photoisomer IVa (singlets at δ , from tetramethylsilane, 1.10 and 1.38 p.p.m. and multiplets centered around 1.6 and 2.3 p.p.m., in methylene chloride at -60°, relative intensities 3:3:8:2) indicates nonequivalent methyl groups attached to saturated carbon. This, together with the occurrence of a band in the infrared at 1604

cm.⁻¹ (—C=N—), and, most significant, the spontaneous reversal of the photoisomerization upon warming to 0°, strongly support the structure assignment.

Photolysis of pyrazolenine Ib in methylene chloride at -60° yielded the photoisomer IVb (n.m.r. CH₂Cl₂, -60°, singlets at δ 1.08 and 1.35 p.p.m., unresolved multiplet between 1.6 and 2.3 p.p.m., relative intensities ~3:3:8; infrared 1608 cm.⁻¹) which on warming to 0° converted back to Ib. Irradiation in pentane at -60° led to loss of nitrogen (70% of calcd.). The isolation of 7,7-dimethylnorcarane (V) from the hydrogenated (-40°) reaction mixture⁴ is taken as evidence for the

(1) This work was supported by NSF Grants NSF-G19927 and NSF-GP-1027.

(2) G. L. Closs and W. Böll, *Angew. Chem.*, **75**, 640 (1963); *Intern. Ed.*, **2**, 399 (1963).

(3) All irradiations reported here were carried out with a Hanovia type A lamp, using Pyrex reaction vessels.

(4) For comparison V was synthesized independently by pyrolysis of the corresponding pyrazoline.

TABLE I
SOLVENT DEPENDENCE OF PRODUCT DISTRIBUTION
ON PHOTOLYSIS OF Ib

Solvent	Temp., °C.	Product distrib. ^{a,b}	
		% IIb	% IVb
n-Pentane	-60	70 ^c	30 ^c
Cyclopropane	-60	70	30
Butadiene	-57	40	60
Monoglyme	-59	25	75
Tetramethylsilane	-55	5	95
Methylene chloride	-60	0	100
Methanol	-58	0	100

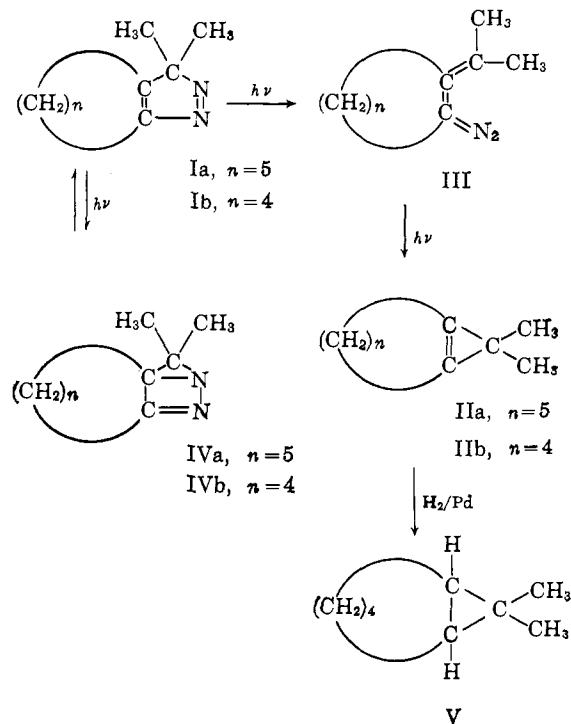
^a Determined from integrated intensities of methyl resonances in n.m.r. spectra. ^b Probable accuracy not better than $\pm 5\%$. ^c Determined from volume of nitrogen evolution.

formation of cyclopropene derivative IIb under these conditions. The n.m.r. spectrum of IIb, obtained on an irradiated solution of Ib in cyclopropane, at -60° (singlet at δ 1.21 p.p.m., multiplets centered at 1.7 and 2.3 p.p.m., relative intensities ~6:4:4), confirms the structure assignment.⁵ At temperatures above -20° IIb dimerizes rapidly to give a mixture of hydrocarbons with as yet undetermined structures.

The low stability of IIb can be attributed to the additional bond angle deformation imposed on the cyclopropene system by the tetramethylene chain. The exocyclic bond angle



ca. 150° in monocyclic cyclopropenes, will be considerably decreased in the fused ring system. The resulting diminished overlap of the orbitals forming the "bent" cyclopropene single bonds (C₁-C₇ and C₆-C₇) will be responsible for the enhanced reactivity of IIb.⁶



(5) The spectrum obtained this way was a superposition of the spectra of 30% of IVb and 70% of IIb. The spectrum given here is that obtained after subtracting the resonances of IVb.

(6) R. Breslow, J. Posner, and A. Krebs, *J. Am. Chem. Soc.*, **85**, 234 (1963), reported the failure to obtain cyclohexenocyclopropene by a modified Favorskii reaction, which has been shown to give less strained cyclopropenones in high yields. Their conclusion, that this failure might be