

Reaction of 3-ethoxy- Δ^2 -cholestene (XVI) and 3-ethoxy- Δ^2 -androstene-17 β -ol acetate (XVII) with acetic anhydride and boron trifluoride etherate under the same reaction conditions yielded 58% of XIV and 53% of XV, respectively.

Acknowledgment.—The author is grateful to Professors Franz Sondheimer and Y. Mazur for their interest and encouragement.

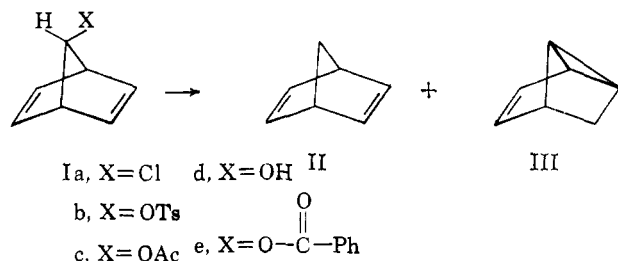
DANIEL SIEFF RESEARCH INSTITUTE RAYMOND D. YOUSSEFYEH
THE WEIZMANN INSTITUTE OF SCIENCE
REHOVOTH, ISRAEL

RECEIVED SEPTEMBER 6, 1963

A Solvent-Sensitive Rearrangement of 7-Substituted Norbornadienes to Cycloheptatriene Using Complex Hydrides

Sir:

Recently 7-substituted norbornadienes (I) have been found to react with hydrides to afford norbornadiene (II) and the tricyclic hydrocarbon III.^{1,2} These reductions have been postulated to proceed *via* a hydride

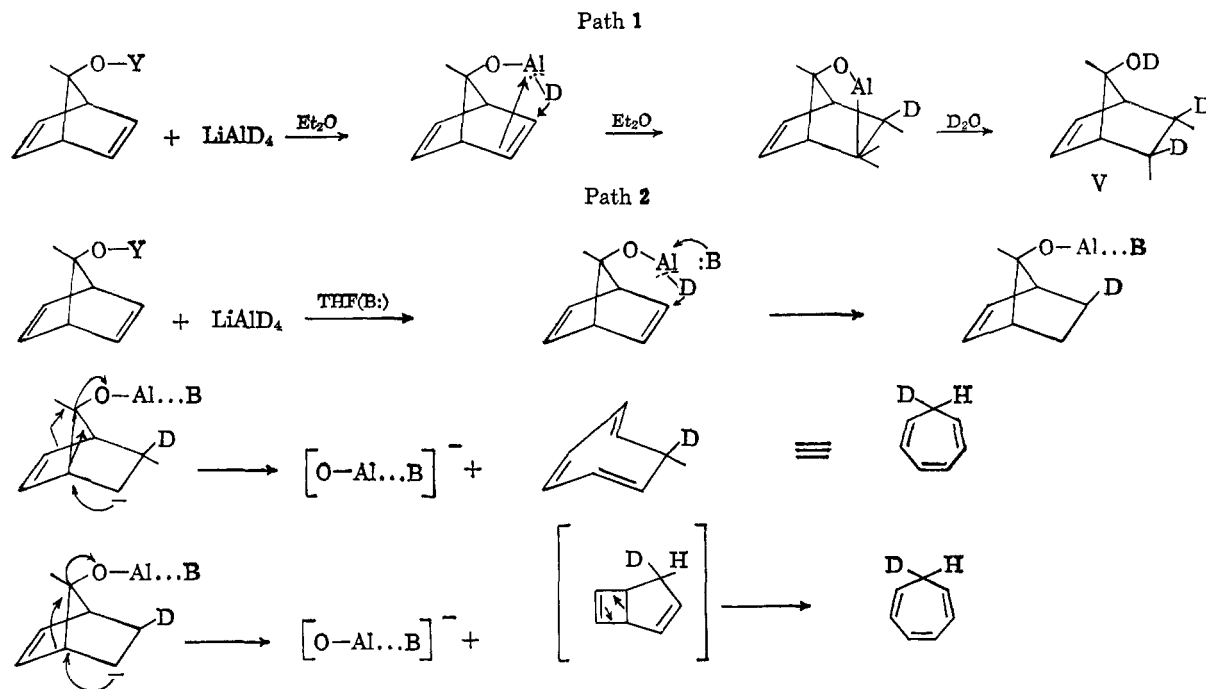


displacement at the bridge carbon and/or *via* hydride abstraction by an intermediate with carbonium ion character.^{1,3} We here describe observations which

for 6–16 hr. affords high (80–90%) yields of cycloheptatriene (IV). In a small-scale preparative experiment cycloheptatriene was isolated from Ie in 63.4% yield. Positive identification of a sample isolated by v.p.c. was made by comparison of its infrared and n.m.r. spectra and its retention time on v.p.c. with those of an authentic sample. The concordance of yield data from quantitative ultraviolet measurements on the crude reaction mixture and those from quantitative v.p.c. measurements provides assurance that IV is a primary product of reaction rather than an artifact of work-up procedures. The stability of III under the reaction conditions demonstrates it is not a precursor of IV. This same rearrangement occurs with other hydrides (e.g., NaBH₄, LiBH₄) in THF and/or diglyme at 60° using Ic or Id, although IV is formed in much lower yields (25–50% by quantitative ultraviolet and v.p.c.).⁴ When the reduction was performed with lithium aluminum deuteride 1.00 atoms of deuterium was incorporated into cycloheptatriene, all of which was in the methylene group.

The course of reaction described above stands in sharp contrast to results of reduction in diethyl ether as solvent. With Ic or Id a stereospecific carbon–carbon double bond reduction occurs to afford anti-7-norbornenol (V) in high yield⁵ with approximately 5.5% IV formed.

All observations described above are consistent with the reaction proceeding according to 1 in diethyl ether and 2 in THF. Path 1 is fully consistent with deuterium labeling experiments⁶ as is path 2. The difference between the two paths we ascribe solely to the coordinating ability of the solvent. If the latter interpretation is correct we would predict that the course of reduction should be a function of the Lewis base properties of the solvent or



demonstrate the incursion of still another process in hydride reactions with 7-substituted norbornadienes which can, perhaps, be best described as a solvent-sensitive anionic carbon skeletal rearrangement.

Treatment of the 7-acetate, alcohol, or benzoate (Ic–e) with excess lithium aluminum hydride (LAH) in tetrahydrofuran (THF) solution at or below 40°

of any other constituents present in the reduction system. We also hope to distinguish between the two modes of decomposition indicated in path 2.

(1) P. R. Story, *J. Am. Chem. Soc.*, **83**, 3347 (1961).

(2) H. C. Brown and H. M. Bell, *ibid.*, **85**, 2324 (1963).

(3) S. Winstein, A. H. Lewin, and K. C. Pande, *ibid.*, **85**, 2324 (1963).

(4) Cycloheptatriene also accompanies norbornadiene and the tricyclic hydrocarbon III in reductions of 7-chloronorbornadiene (Ia) with various complex hydrides. These latter results will be elaborated upon in the full paper describing results of reductions of 7-substituted norbornadienes.

(5) P. R. Story, *J. Org. Chem.*, **26**, 287 (1961).

(6) B. Franzus and E. I. Snyder, unpublished results; see also footnote 8 of reference 1.

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 AlCl_3) 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.

CENTRAL BASIC RESEARCH LABORATORIES BORIS FRANZUS
ESSO RESEARCH AND ENGINEERING COMPANY EUGENE I. SNYDER
LINDEN, NEW JERSEY

RECEIVED SEPTEMBER 30, 1963

Solvent Effects on the C^{13} 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.^{2,4,8,9,11} 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.

C^{13} 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 $\text{NaO}_2\text{C}^{13}\text{CH}_3$ in the center sphere, using the side-band technique.

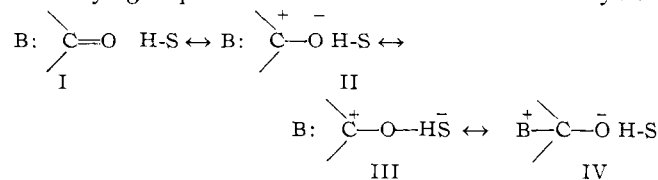
The observed shifts referred to that of pure acetone are presented in Table I. These shifts are the average result of at least five field scans in both increasing and decreasing senses and can be considered accurate to about ± 0.5 p.p.m. They cover a total range of about 40 p.p.m. with the largest positive 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
 C^{13} CHEMICAL SHIFTS OF $\text{CH}_3\text{C}^{13}\text{OCH}_3$ IN 1:6 MOLE FRACTION SOLUTIONS IN SEVERAL SOLVENTS

Solvent	Chemical shift, p.p.m. with respect to $\text{CH}_3\text{C}^{13}\text{OCH}_3$	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 $1.5 \times 10^{-40}\%$,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).