

TABLE I

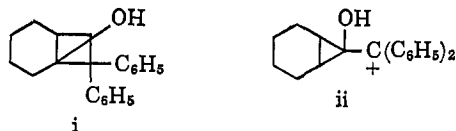
Sample No.	Compound and its origin	Deuterium analysis (atom % excess D) ^a	k_{1a}/k_{1b} ^b
1	I, original adduct	4.67, 4.69, 4.73, 4.70	
2	I, 1 after 19-hr. base wash ^c	2.23	1.11
3	IIb ^d	2.01, 2.03	1.11
4	I, original adduct	4.63, 4.64, 4.65	
5	I, 4 after 18-hr. base wash	2.24, 2.24	
6	I, 5 after 14.5-hr. base wash	2.21, 2.15, 2.16, 2.17	1.14
7	IIb ^d	2.02	1.09
8	I, original adduct	4.71, 4.70, 4.72	
9	I, 8 after 3-hr. acid wash ^e	2.55, 2.56	
10	I, 9 after 3-hr. acid wash	2.30	
11	I, 10 after 3-hr. acid wash	2.23, 2.24	
12	I, 11 after 6-hr. acid wash	2.15	
13	I, 12 after 6-hr. acid wash	2.16, 2.17	1.18
Average isotope effect			1.13 ± 0.03

^a Analyses by the falling drop method were performed by Josef Nemeth, Urbana, Illinois. ^b The ratio of the two products Ia and Ib. The probable error in this ratio is ±0.03. ^c A solution of I (0.07 M) and NaOCH₃ (0.2 M) was refluxed in CH₃OH. ^d From saponification of the IIa isolated in the preparation of the preceding sample of I. ^e I was heated at 80° in a large excess of a mixture of 10 parts of glacial acetic acid and 1 part of a solution of 10% HCl (1 volume of concentrated HCl and 3 volumes of water).

The observed excess of Ia indicates that, at the transition state determining the formation of the product, bond formation is not symmetrical (*i.e.*, the bonds are not equally formed). The magnitude of the isotope effect (1.13 ± 0.03) is similar to the maximum secondary α -deuterium effect observed in numerous solvolytic,⁹ thermal cleavage¹⁰ and addition¹¹ reactions, in which the isotope effect has been attributed to mass-sensitive changes in vibrational frequencies¹² or steric crowding¹³ accompanying rehybridization of the carbon bearing hydrogen. If the bond *a* in I were formed first, deuterium would be expected to accumulate on the carbon atom adjacent to the carbonyl. The observation of this effect indicates that the transition state is asymmetrical in this sense. The opposite should be expected if the inductive effect of deuterium or the β -isotope effect were dominant.^{14,15}

The technique described in this communication is applicable only to cycloaddition reactions between one

(5) Heating I and a 3:1 mixture of acetic acid and 10% HCl on a steam bath removed not only the deuterium atoms on the carbon adjacent to the carbonyl, but some of the remaining deuteriums as well, which might indicate that homoionization to (i) occurs,⁵ but more probably represents a cyclo-butyl-cyclopropylcarbonyl rearrangement⁷ to (ii) and its reversal.



- (6) A. Nickon and J. L. Lambert, *J. Am. Chem. Soc.*, **84**, 4604 (1962).
 (7) M. S. Silver, M. C. Caserio, H. E. Rice and J. D. Roberts, *ibid.*, **83**, 3671 (1961), and earlier papers.
 (8) The reaction was not appreciably reversible. Simultaneously with one of the addition reactions, adduct I (sample 4) was heated with a 16 M excess of cyclohexene, after which it contained 4.56 atom % of excess D.
 (9) A. Streitwieser, Jr., "Solvolytic Displacement Reactions," McGraw-Hill Book Co., Inc., New York, N. Y., 1962; see also R. Stewart, A. L. Gatzke, M. Mocek and K. Yates, *Chem. Ind. (London)*, 331 (1959).
 (10) S. Seltzer, *J. Am. Chem. Soc.*, **85**, 14 (1963); **83**, 2625 (1961).
 (11) (a) S. Seltzer, *ibid.*, **83**, 1861 (1961); (b) D. B. Denney and N. Tun-
 kel, *Chem. Ind. (London)*, 1383 (1959); (c) M. Feld, A. P. Stefani and M. Szwarc, *J. Am. Chem. Soc.*, **84**, 4451 (1962); (d) M. Takahashi and R. J. Cvetanovic, *Can. J. Chem.*, **40**, 1037 (1962); (e) G. A. Olah, S. J. Kuhn and S. H. Flood, *J. Am. Chem. Soc.*, **84**, 1688 (1962); (f) D. E. van Sickle, *Tetrahedron Letters*, 687 (1961); (g) S. Seltzer, *ibid.*, 457 (1962).
 (12) A. Streitwieser, Jr., R. H. Jagow, R. C. Fahey and S. Suzuki, *J. Am. Chem. Soc.*, **80**, 2326 (1958).
 (13) L. S. Bartell, *ibid.*, **83**, 3567 (1961).
 (14) Reviewed by R. E. Weston, Jr., *Ann. Rev. Nucl. Sci.*, **11**, 439 (1961).
 (15) The β -isotope effect might have affected analysis methods 1 and 2 if the ring cleavage were fast compared to enolization, and a lower apparent effect in analysis 1 and a higher one in analysis 2 probably would have resulted [cf. J. M. Jones and M. L. Bender, *J. Am. Chem. Soc.*, **82**, 6322 (1960); M. L. Bender and M. S. Feng, *ibid.*, **82**, 6318 (1960)]. This was not observed.

reactant, symmetrical except in the isotopic substituent, and another so unsymmetrical that if it were to add asymmetrically, it would do so in only one sense.¹⁶⁻¹⁸

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(16) That bond *a* forms first in diphenylketene cycloadditions follows from the isomer specificity observed in its additions to cyclohexadiene, cyclopentadiene, styrene, etc.,¹⁷ as well as from the probable bond dissociation energies¹⁸ of atoms attached to the carbonyl and to the benzhydryl carbon adjacent to the carbonyl.

- (17) Reference 2 and references in ref. 1b.
 (18) C. Walling, "Free Radicals in Solution," John Wiley and Sons, Inc., New York, N. Y., 1957, p. 50.
 (19) NSF Fellow, 1960-1961; NSF Coöperative Fellow, 1962-1963.

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Unusual Nuclear Magnetic Resonance Dilution Shift for Acetic Acid in Acetic Anhydride¹

Sir:

N.m.r. studies of carboxylic acids in electron-donating solvents have revealed a marked concentration-dependence of the chemical shift of the acidic hydrogen.^{2,3} This "dilution shift" is believed to result from a rapid equilibrium between dimeric acid molecules and a monomeric species, probably hydrogen-bonded to a solvent molecule. A difficulty with this interpretation is that the data appear to imply that at moderate concentrations (10 to 20 mole %) considerably more than half of the solute is dimerized. This conflicts with the earlier view⁴ that in such solvents "carboxylic acids associate with the solvent molecules rather than with their own species. Thus they give normal molecular weights in ethers, esters, and ketones." Another alarming symptom is the poor quantitative agreement between two independently determined curves of chemical shift *vs.* concentration for acetic acid (AcOH) in acetone.^{2,3}

If AcOH is dissolved in acetone contaminated with water, rapid proton exchange between water and acid should occur and the observed hydroxyl chemical shift should be the weighted average of the true value for the

- (1) Supported by research grant NSF G-17421 from the National Science Foundation.
 (2) C. M. Huggins, G. C. Pimentel and J. N. Shoolery, *J. Phys. Chem.*, **60**, 1311 (1956).
 (3) L. W. Reeves, *Trans. Faraday Soc.*, **55**, 1684 (1959).
 (4) G. Allen and E. F. Caldin, *Quart. Rev. (London)*, **7**, 278 (1953).

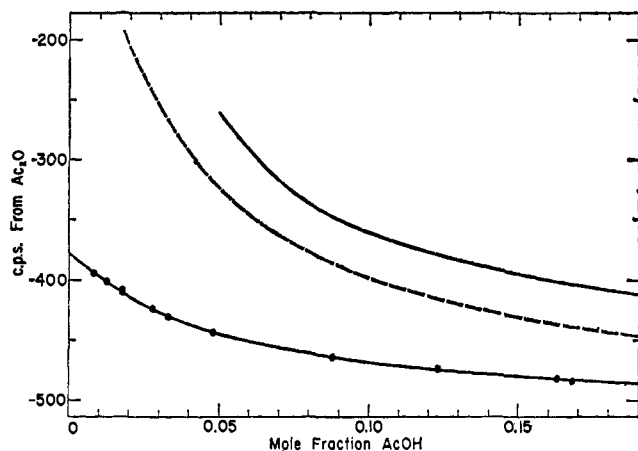
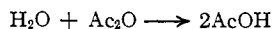


Fig. 1.—Chemical shift (in c.p.s. from Ac_2O at 56.4 M.c.p.s.) of the hydroxyl proton as a function of AcOH concentration: lower curve, results of this study for AcOH in Ac_2O ; middle curve, calculated shifts for AcOH in "hypothetical wet solvent" (see text); upper curve, results of ref. 3 for AcOH in acetone.

acid and that for water. Although each of these varies with concentration, it is safe to say that the proton resonance for water in dilute solution⁵ is several parts per million upfield from the averaged hydroxyl resonances of the acid species present. A very large spurious "dilution shift" for the acid will result even if the solvent contains as little as 0.2 weight % water. Quite elaborate procedures are often necessary to prepare solvents free of such traces of water. However, in ref. 2 "analytical or reagent grade" solvents were used, and it has been reported⁶ that Baker C.P. acetone, for example, contained 0.39 weight % water. Then perhaps the discrepancy between the results of ref. 2 and 3 is due to a difference in dryness of the solvents used. Moreover, there is some likelihood that neither study was made with solvent sufficiently anhydrous to reveal the true AcOH dilution shift from which reliable conclusions about the dimerization equilibrium might be drawn.

In order to determine the dilution shift in rigorously anhydrous samples we examined n.m.r. spectra of solutions of AcOH in acetic anhydride (Ac_2O). Our purified Ac_2O contained 0.8 ± 0.1 mole % of AcOH, found by comparing the intensity of the methyl n.m.r. peak of the AcOH with that of the C^{13} side band from Ac_2O . A series of samples was prepared volumetrically by adding known amounts of water to Ac_2O . The reaction



could be followed by studying the n.m.r. spectrum as a function of time. A sharp, time-independent hydroxyl signal was not obtained until hydrolysis was complete and all water, from whatever source, had been decomposed.

Figure 1 shows a plot of the hydroxyl chemical shift against the total AcOH concentration. The Varian high-resolution spectrometer was operated at 56.4 Mc.p.s. The zero of the chemical shift scale is the Ac_2O resonance, which is 2.28 p.p.m. downfield from tetramethylsilane. The sample temperature was $30 \pm 2^\circ$. The dashed curve was calculated for a hypothetical situation where the true dilution shift coincides with our measured curve but the "observed" value is shifted because the solvent is wet. For this calculation the chemical shift for dissolved water was taken as -2.3 p.p.m. from tetramethylsilane⁷ and the mole fraction of water

(5) J. R. Holmes, D. Kivelson and W. C. Drinkard, *J. Am. Chem. Soc.*, **84**, 4677 (1962).

(6) W. M. D. Bryant, J. Mitchell, Jr., and D. M. Smith, *ibid.*, **62**, 3504 (1940).

(7) This is approximately where we found the water peak for dilute solutions of water in acetone.

as 0.01 times the mole fraction of solvent. In a real situation this might represent 0.2 to 0.4 weight % water, depending on the molecular weight of the solvent. The uppermost curve in the figure represents the data of Reeves³ for AcOH in acetone.

These results for AcOH- Ac_2O solutions are quite different from any previously reported for a carboxylic acid in a donor solvent. For the first time the dilution shift can be extrapolated to zero concentration yielding an average shift of -9.04 ± 0.06 p.p.m. from tetramethylsilane for the solute species (presumably free AcOH in equilibrium with an AcOH· Ac_2O complex) at infinite dilution at 30° . This value represents an upper bound for the hydroxyl chemical shift of AcOH· Ac_2O , in sharp contrast to the shift near -3 p.p.m. estimated² for the AcOH·acetone complex. Since in either case the acid proton is strongly hydrogen bonded, a value near -9 p.p.m. seems more in accord with other observations on hydroxy-bonded species.

The difference between our dilution curve and that^{2,3} for AcOH-acetone, together with the similarity between the latter and our "hypothetical wet solvent curve," may indicate that indeed the solvents used in the earlier work were not adequately dried.⁸

(8) Note added June 3, 1963: Preliminary results of experiments with carefully dried acetone as solvent confirm this and indicate that the hydroxyl signal from AcOH·acetone is at approximately -10.4 p.p.m.

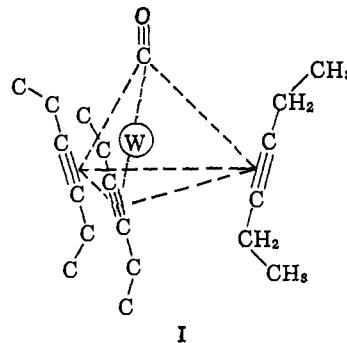
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A Novel Acetylenic Complex of Tungsten(0) Carbonyl Sir:

We wish to report a new acetylenic complex of tungsten that appears to have a very unusual structural and electronic arrangement. On refluxing 3.59 g. of $(\text{CH}_3\text{CN})_3\text{W}(\text{CO})_3$ ¹ for 2 hr. in 35 ml. of 3-hexyne, 2 equivalents of CO are evolved. After filtration and evaporation of excess hexyne, the crude product (3.1 g.) is precipitated from benzene by addition of ethanol. Sublimation under high vacuum at 70° gives pure pale yellow $(\text{CH}_3\text{CH}_2\text{C}\equiv\text{CCH}_2\text{CH}_3)_3\text{WCO}$ (I); m.p. $55\text{--}56^\circ$. *Anal.* Calcd: C, 49.79; H, 6.60; W, 40.12; mol. wt., 458. Found: C, 50.44; H, 7.13; W, 40.02; mol. wt., 464. In order to account for the physical and chemical properties of I we are led to propose the structure



where the four ligands are arranged around the tungsten in a tetrahedral-like fashion.

In the assignment of such a structure of unusually low coordination number around the central metal atom, the analysis is most crucial. The absence of nitrogen in the molecule precludes the presence of undisplaced acetonitrile. The presence of a single carbonyl group was established by oxidation with I_2 in refluxing methanol. Exactly one equivalent of CO was evolved. In-

(1) D. P. Tate, J. M. Augl and W. R. Knipple, *Inorg. Chem.*, **1**, 422 (1962).