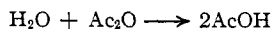


Fig. 1.—Chemical shift (in c.p.s. from Ac_2O at 56.4 M.c.p.s.) of the hydroxyl proton as a function of AcOH concentration: lower curve, results of this study for AcOH in Ac_2O ; middle curve, calculated shifts for AcOH in "hypothetical wet solvent" (see text); upper curve, results of ref. 3 for AcOH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

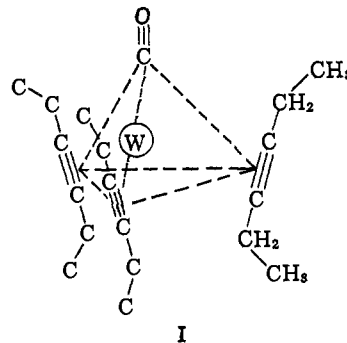
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RECEIVED APRIL 1, 1963

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. $55-56^\circ$. *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-

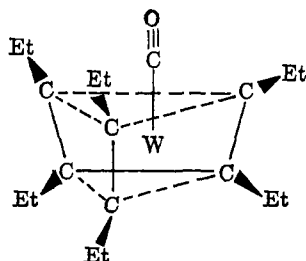
(1) D. P. Tate, J. M. Augl and W. R. Knipple, *Inorg. Chem.*, **1**, 422 (1962).

frared inspection of the oxidation residues showed no bands in the region of metal or organic carbonyl absorptions. Pyrolysis of I gave 3-hexyne with no evidence for hexaethylbenzene or other cyclic compounds that might be anticipated.²

The infrared spectrum is consistent with structure I. A single strong band at 2036 cm^{-1} is characteristic of a terminal metal carbonyl³ and a band at 1702 cm^{-1} suggests an acetylene doubly π -bonded to a metal atom.⁴

The n.m.r. spectrum strongly supports the proposed structure. Whereas 3-hexyne has the typical A_2B_3 spectrum for ethyl groups consisting of a quartet and a triplet (2.30 and 1.24 p.p.m. from TMS, respectively), I has *two* equal quartets and *two* equal triplets [3.54 and 3.07 (quartets) and 1.34 and 1.09 (triplets) p.p.m. from TMS]. Since the quartets and triplets are of equal intensity, it suggests that all three acetylenic molecules are equivalent but that in each of the ligands one of the two ethyl groups is in a different environment from the other. The chemical shift of the CH_3 and CH_2 groups in the vicinity of the CO would not be expected to be the same as the ones extending in the opposite direction. Since in each case the CH_3 groups are further from the CO it is reasonable to expect less of a difference in the two types of CH_3 groups than in the two types of CH_2 groups, in excellent agreement with observation. In addition, some long-range spin coupling through the triple bond is seen in the spectrum of the hexyne, but not in the spectrum of the complex. This is further evidence that the triple bond is perturbed. The location of the multiplets is not consistent with the formation of a benzene type ring.

The effective atomic number for tungsten requires that a total of 10 electrons be donated by the acetylenic ligands. This could be accomplished if two of the three ligands served in the unusual capacity of four-electron donors, similar to that observed in the complexes $(\text{R}_3\text{P})_2\text{Pt}(\text{acetylene})_4$ or $\text{ReCl}(\text{acetylene})_2$,⁵ (which are also complexes of the heaviest metals in their respective sub-groups). Since the sharp proton magnetic resonance spectrum precludes paramagnetism and indicates all acetylenes are equivalent, the function of two-electron bonding and four-electron bonding must somehow be resonated throughout the entire hydrocarbon system. In this respect, this system might resemble that in cyclooctatetraeneiron tricarbonyl,⁶ which shows equivalence of all hydrogens in solution, even though association of iron with the entire olefinic system would lead to a superfluity of electrons donated to the metal. In a single crystal, however, it was shown that the iron is associated with only one of the two diene systems in the ligand.⁷ In view of the electron delocalization, (or at the very least a rapid tautomerism, in solution) a better representation of the bonding in I might be



(2) For a recent review of this subject see B. L. Shaw, *Advan. Inorg. Chem. Radiochem.*, **4**, (1962).

(3) R. K. Shelton, *J. Am. Chem. Soc.*, **73**, 1615 (1951).

(4) J. Chatt, G. A. Rowe and A. A. Williams, *Proc. Chem. Soc.*, 208 (1957).

(5) R. Colton, R. Levitus and G. Wilkinson, *Nature*, **186**, 233 (1960).

(6) T. A. Manuel and F. G. A. Stone, *Proc. Chem. Soc.*, 90 (1959).

(7) B. Dickens and W. N. Lipscomb, *J. Am. Chem. Soc.*, **83**, 4862 (1961).

Acknowledgment.—We are indebted to Miss Bonnie Ross for infrared interpretation, Dr. William Ritchey for n.m.r. interpretation and to Mrs. Jeanette G. Grasselli and Dr. Herbert Kaesz (Dept. of Chemistry, U.C.L.A.) for helpful discussions.

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The Cyclohept(a)acenaphthylene Cation: Synthesis of a Pentaphenyl Derivative¹

Sir:

The recent preparation of heptaphenylcycloheptatriene² by a Diels–Alder reaction of triphenylcyclopropene and tetraphenylcyclopentadienone suggests a general method for the synthesis of other difficultly accessible polyarylcycloheptatrienes,³ which in turn may be readily converted to the corresponding polyaryltropylium ions.⁴ A particularly attractive aryltropylium ion for synthesis and study, the cyclohept(a)acenaphthylene cation (I) is of interest because of similarity to the non-alternant hydrocarbon, fluoranthene, and unique ring fusion that allows extensive charge delocalization. The synthetic challenge of the cyclohept(a)acenaphthylene ring system is immense, apparently, as no derivatives have been reported prior to this work. We now wish to report the first entry into this ring system with the preparation of 7,8,9,10,11-pentaphenylcyclohept(a)acenaphthylene bromide (VI) and several interesting covalent derivatives.

The reaction of acceyclone (IIa)⁵ and triphenylcyclopropene (IIIa) in refluxing xylene solution for 4–7 hr. yielded 70–75% of a crystalline orange solid, m.p. 304–306° (*Anal.* Calcd. for $\text{C}_{47}\text{H}_{32}$: C, 94.59; H, 5.41; mol. wt., 597. Found: C, 94.40; H, 5.56; mol. wt., 605) and 15–20% of a mixture of two unidentified crystalline ketones. Acetonitrile solutions of the hydrocarbon showed absorption maxima at 402 (log ϵ 4.11), 339 (4.18), 303 (4.38) and 248 (4.64) $\text{m}\mu$. The analytical and spectral data, including infrared, are consistent with the 9H-cyclohept(a)acenaphthylene structure IVa; however, the lack of model compounds in this series does not permit ruling out isomeric structures on these data alone. Accordingly the carboxylic acid IVb, m.p. 326–329° (*Anal.* Calcd. for $\text{C}_{42}\text{H}_{28}\text{O}_2$: C, 89.33; H, 5.00. Found: C, 89.52; H, 5.14), $\lambda_{\text{max}}^{\text{MeCN}}$ 397 (3.94), 339 (3.98), 297 (4.26) and 244 (4.60) $\text{m}\mu$, was synthesized from acceyclone and diphenylcyclopropenecarboxylic acid (IIIb) in the above manner. The close similarity of the ultraviolet spectra of IVa and IVb suggests nearly identical chromophoric systems in support of the proposed structures.

Considering further the problem of possible isomerization under refluxing xylene conditions, the reaction of acceyclone with triphenylcyclopropene was run in refluxing benzene and in benzene–chloroform solution at room temperature.⁶ The hydrocarbon product from

(1) (a) This research was supported in part by the National Science Foundation, Grant No. GP-254, for which grateful acknowledgment is made; (b) Polyarylcycloheptatrienes. Part IV; (c) a preliminary report of portions of this work was presented at the 14th Annual Southeastern Regional Meeting of the American Chemical Society, Gatlinburg, Tennessee, November, 1962.

(2) M. A. Battiste, *Chem. Ind. (London)*, 550 (1961).

(3) Although alkylcyclopentadienones are generally unstable, with certain modifications it seems reasonable that this method may be extended to the preparation of alkylcycloheptatrienes.

(4) Cf. M. A. Battiste, *J. Am. Chem. Soc.*, **83**, 4101 (1961).

(5) W. Dilthey, I. ter Horst and W. Schommer, *J. prakt. Chem.*, **143**, 189 (1935).

(6) Due to the limited solubility of acceyclone in cold organic solvents this reaction is extremely sluggish, taking 5–6 weeks to yield appreciable adduction products. In this interval considerable decarbonylation of the adduct V occurs despite the mild conditions of reaction and work-up.