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The Association of an Acetylene with Three Metal Atoms; A New Trinuclear Cobalt Complex

BY RAYMOND MARKBY, IRVING WENDER, R. A. FRIEDEL, F. A. COTTON AND HEINZ W. STERNBERG

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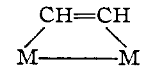
Preparation and properties of a new type of acetylenic cobalt carbonyl complex, $HCo_3(CO)_9RC\equiv CH$, are described. Evidence is presented for a structure in which the acetylene is bonded to three cobalt atoms. The cobalt atoms form a 3-membered ring with three carbonyl groups bonded to each cobalt atom. The catalytic implications of such a structure are discussed.

Introduction

It has been shown[1] that dicobalt octacarbonyl, $Co_2(CO)_8$, reacts with acetylenes to form dicobalt hexacarbonylacetylene complexes, $Co_2(CO)_6RC\equiv CR'$. As part of a study of the chemical behavior of these complexes, the reaction between the 1-pentyne complex, $Co_2(CO)_6C_3H_7C\equiv CH$, and alcoholic hydrochloric acid was investigated. Preliminary experiments indicated that two types of products were formed in approximately equal amounts. One type consisted of a mixture of saturated and unsaturated C_6-acids, the other of high molecular weight compounds containing carbonyl groups. In the course of this investigation, we isolated from the reaction products a dark red-purple crystalline compound. It was found that the elementary composition and molecular weight of this compound corresponded to that of a trinuclear complex, $HCo_3(CO)_9C_3H_7C\equiv CH$ (I). To determine the role of this complex in the formation of the reaction products, we treated I with alcoholic hydrochloric acid. Decomposition of I with acid gave only the high molecular weight products; complex I, therefore, was probably not involved in the synthesis of the C_6-acids.

A complex containing an acetylene associated with three metal atoms has never been isolated. In catalytic reactions involving unsaturated molecules, chemisorption of the substrate is generally believed[2] to be a two-point attachment to the metal surface



This postulate has ignored the possibility that neighboring metal atoms may be involved in bonding these molecules to the surface. The isolation of complex I furnished an opportunity to obtain some information regarding this question since complex I contains an unsaturated molecule associated with three metal atoms.

Preparation and Composition of $HCo_3(CO)_9HC\equiv CH$ (II).—To check the ratio $H:3Co:9CO:C_5H_8$ in I, we prepared the corresponding acetylene complex using $Co_2(CO)_6HC\equiv CH$ as a starting material. Treatment of a methanolic solution of $Co_2(CO)_6HC\equiv CH$ with aqueous sulfuric acid under reflux and extraction of the reaction mixture with petroleum ether gave the crude complex which was recrystallized from methanol. Analysis and molecular weight determination showed that the elementary composition of this complex, II, was $Co_3C_{11}H_3O_9$. The usual margin of error of ±0.1% in the determination of hydrogen (found 0.75%) does not permit one to be certain whether there are 3 hydrogens (H = 0.66%) or 4 hydrogens (H = 0.88%) in the molecule. It is possible, however, to make a choice between these two empirical formulas with the aid of magnetic susceptibility data. Complex II is diamagnetic ($123 \pm 3 \times 10^{-6}$ c.g.s.μ per mole) and must therefore contain an odd number of hydrogens. Since a formula with 1 or 5 hydrogens can be excluded on the basis of the hydrogen determination, II must contain 3 hydrogens. Complex II is soluble in organic solvents. It cannot be extracted from an ether solution with either aqueous hydrochloric acid or alkali and hence does not exhibit any acidic or basic properties.

Infrared Spectrum, Nuclear Magnetic Resonance and Dipole Moment of II.—The infrared spectrum of II taken in appropriate solvents with CaF_2 and NaCl prisms shows three C–H stretching bands at 2925, 2880 and 2840 cm.$^{-1}$ (all ±10 cm.$^{-1}$). In the carbonyl stretching region there are four well-resolved bands with the relative intensities given in parentheses: 2116(1), 2061(10), 2048(9), 2027(2) cm.$^{-1}$. From the contour of the 2061-2048 doublet, it appears possible that there may be an additional band in this region. There are weak bands at ~1425, ~1360 and ~1162 cm.$^{-1}$ and a medium band at ~1007 cm.$^{-1}$ There is also a weak doublet[3] at ~2500 cm.$^{-1}$. No other bands are found in the rock salt region. In the near infrared region there are only three definite CO stretching overtones at 4130, 4040 and 4000 cm.$^{-1}$ (all ±20 cm.$^{-1}$).

The nuclear resonance evidence clearly shows that there are two protons in equivalent positions and a third which is of a different type. Moreover, from the chemical shifts for these protons it would appear that there are no protons bound in the man-

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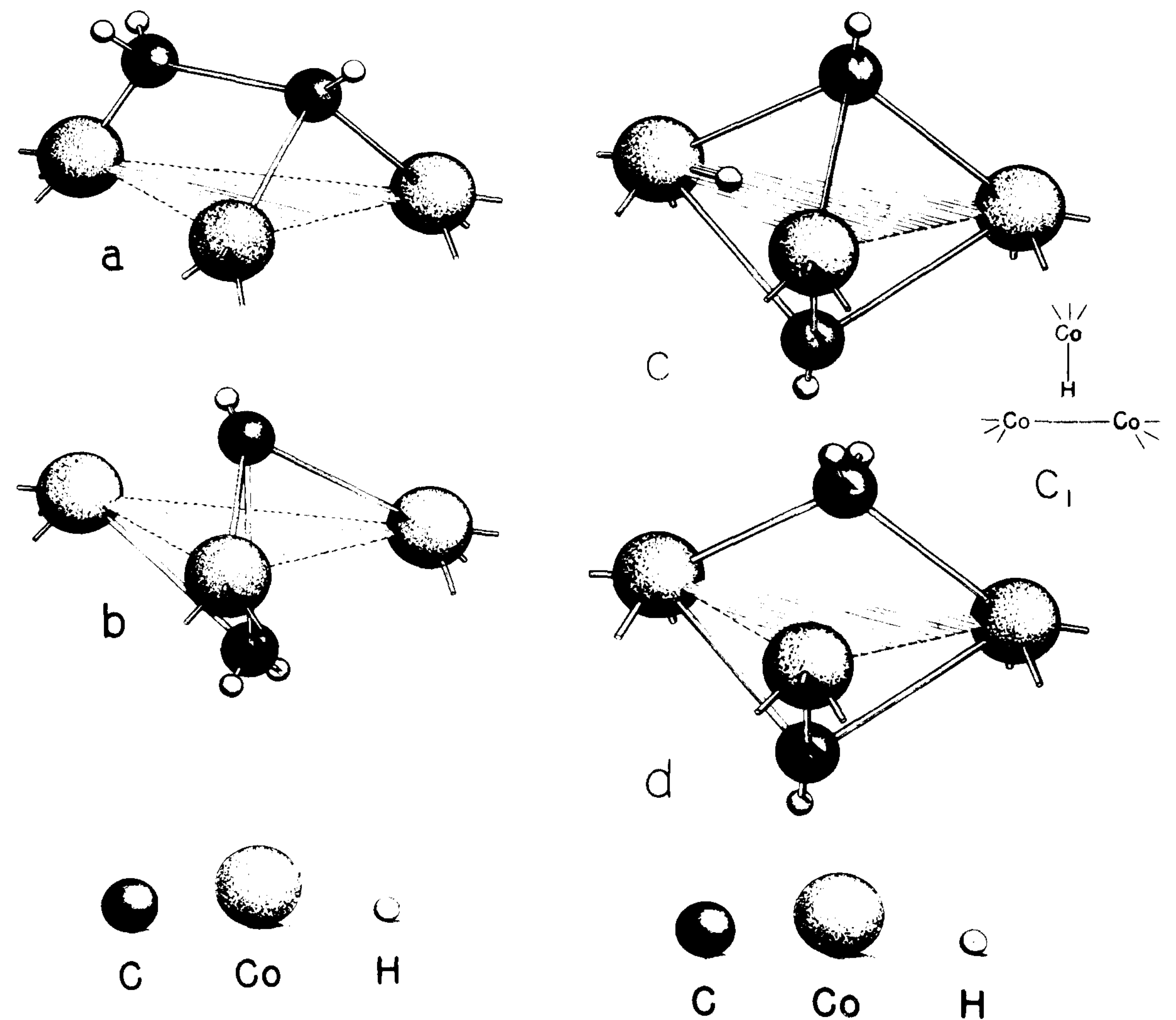
[1] H. Greenfield, H. W. Sternberg, R. A. Friedel, J. H. Wotiz, R. Markby and I. Wender, THIS JOURNAL, **78**, 120 (1956).

[2] B. M. W. Trapnell, "Chemisorption," Butterworths Sci. Pub., London, 1955.

[3] This band is also present in all dicobalt hexacarbonyl acetylene complexes, $Co_2(CO)_6RC\equiv CR'$, (unpublished work) as well as in $Co_2(CO)_8$ and $HCo(CO)_4$ (R. A. Friedel, I. Wender, S. L. Shufler and H. W. Sternberg, THIS JOURNAL, **77**, 3951 (1955)). It is probably a combination band resulting from a C–O stretch plus a Co–C stretch or C–O band. Both of the latter vibrations are known to occur in the KBr region (W. F. Edgell, C. Magee and G. Gallup, *ibid.*, **78**, 4185 (1956)).



ner characteristic of metal carbonyl hydrides, since for protons of this type a considerable amount of data on $HCo(CO)_4$,[4] $H_2Fe(CO)_4$[5] and a number of cyclopentadienylmetal hydrocarbonyls[6] indicate that they have a very characteristic chemical shift in the range −15 p.p.m. It does not at present appear possible to draw any further conclusions from the chemical shift values. Studies at M.I.T. by Mr. J. R. Leto of a number of compounds containing H–C–M groupings indicate, however, that the values observed in II are within the proper range for such protons.

On the basis of the total molar polarization and the electron polarization the dipole moment of II is less than 1.6 D. and quite possibly zero.

Discussion

The three cobalt atoms in II can be arranged either in a linear or triangular structure. A triangular arrangement of the cobalt atoms in which each cobalt is bonded to three carbonyl groups is highly probable in view of the following considerations.

The fact that no bands below 2000 cm.$^{-1}$ are present in the carbonyl stretching region leads to the conclusion that there are no ketonic bridging groups in the molecule. Any structure in which the distribution of the CO's is other than three on each cobalt atom in a locally trigonal arrangement must be eliminated since any such structure would surely have a plethora of infrared active CO stretching frequencies. Moreover, the appearance of just three bands in the 4000 cm.$^{-1}$ region supports this line of reasoning, since a $Co(CO)_3$ grouping of C_{3v} symmetry has two infrared active CO stretching frequencies of types A and E and three infrared active overtones and combinations of these, *viz.*, $A_1 + A_1$, $A_1 + E$ and $E + E$. The triangular arrangement of the cobalt atoms is also in keeping with Dahl and Rundle's[7] recent results for the structure of $Fe_3(CO)_{12}$. With regard to the position and bonding of the acetylene and the hydrogen several possibilities must be considered.

The appearance of three distinct C–H stretching frequencies all in the aliphatic range would seem, unless they are combination bands,[8] to lead to two

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(4) R. A. Friedel, I. Wender, S. L. Shufler and H. W. Sternberg, This Journal, **77**, 3951 (1955).

(5) F. A. Cotton and G. Wilkinson, *Chemistry & Industry*, 1305 (1956).

(6) T. S. Piper and G. Wilkinson, *J. Inorg. Nucl. Chem.*, **3**, 104 (1956).

(7) L. F. Dahl and R. E. Rundle, *J. Chem. Phys.*, **26**, 1751 (1957).

(8) The complex $Co_2(CO)_6C_2H_2$ has four weak bands at 3116, 2933, 2957 and 2787 cm.$^{-1}$ all of which cannot be assigned to C–H stretch (unpublished work).

conclusions. Firstly, we would conclude that no grouping of the H—C≡C type exists. Secondly, three such frequencies can be explained by the presence of three aliphatic C–H bonds in the molecule. This, together with the n.m.r. results, would imply the presence of an $H_2C<$ and an $HC<$-group. $CH_3Mn(CO)_5$, where there is almost certainly an H_3C–Mn grouping, shows absorption bands in the aliphatic C–H stretching region.[9] The four lines at 1425, 1360, 1162 and 1007 cm.$^{-1}$ cannot at present be assigned with any confidence. However, the absence of any line in the double bond region confirms the conclusion drawn from the C–H stretching region. These four lines could be assigned as –C–H deformations, and one of them could be a C–C stretching frequency.

If it is assumed that the H_2C and HC– groups are connected to give a H_2C–CH grouping, a structure of type (a) could result. This sort of structure would require the indicated Co–Co bonds in order to complete the cobalt valence shells. Such a structure is in agreement with the n.m.r. and the infrared evidence. However, it is difficult to see how a molecule with such a structure could have a near-zero dipole moment. By way of comparison, the molecules π-$C_5H_5V(CO)_4$, π-C_5H_5-$Mn(CO)_3$ and π-$C_5H_5Co(CO)_2$ have moments of 3.2, 3.3 and 2.9 D., respectively.[10] A variation of structure (a) which would improve its acceptability in respect to the dipole moment is (b). In either (a) or (b) the Co–Co distances would be of the order of 3.0-3.5 Å. While it is not to be expected that Co–Co bonds of any appreciable strength could be formed at such distances, it is conceivable that the electron pairing necessary for diamagnetism could occur. For example, $Mn_2(CO)_{10}$, which is diamagnetic, has a Mn–Mn distance[11] of 3Å.

Another possible objection to structure (a) is that one might expect to see hyperfine structure in the proton resonance spectrum since the CH and CH_2 groups are so closely joined *via* the C–C bond. From this point of view structures in which the CH and CH_2 groups are further separated might be preferred.[12]

As a quite different alternative, a structure of type (c) may be mentioned. This structure was envisioned by considering the carbon-carbon bonding in acetylene from the Lennard-Jones equivalent orbital point of view[13] as consisting of three equivalent bent bonds which could be broken and new bonds formed to the three cobalt atoms. In order to account for the equivalence of the cobalt atoms and the diamagnetism of the compound, resonance among the three equivalent canonical forms of which one is shown in (c_1) might be postulated. This structure, *ad hoc* as it is, fits many of the available data. It accounts for a zero dipole moment. If the orientation of the $Co(CO)_3$ groups is such as to give either C_{3h} or C_{3v} molecular symmetry, only 5 infrared active C–O stretching frequencies would be expected. If there is a horizontal symmetry plane, then the n.m.r. data requiring 2 equivalent protons would be satisfied. It does not, however, account readily for the presence of three aliphatic C–H stretching frequencies. Also, one might expect a proton so deeply buried in a cage of large atoms as is the remaining proton in this case to be rather highly shielded, although this need not necessarily be so.

One further structural possibility (d) suggests itself from consideration of (b) and (c). Such a structure would appear to satisfy the nuclear magnetic resonance, dipole moment and infrared data.

Nothing more definite can be said at present regarding the structure of this molecule. In fact, the entire field is at present hampered by an almost total lack of basic structural data which would perhaps reveal some of the structural principles involved in molecules of this organo-metal-carbonyl type. It is to be hoped that X-ray studies will be undertaken to fill this need.[14]

The association of an acetylene with three cobalt atoms is of fundamental interest in the field of catalysis, where interaction of an unsaturated substrate with the metal surface usually is assumed to occur by one or two site absorption. It is conceivable that the interaction of three metal atoms with the triple bonds in such molecules as N_2, CO or HC≡CH is responsible for the splitting of these bonds on the metal surface.

Experimental[15]

Reaction of $Co_2(CO)_6C_3H_7C{\equiv}CH$ with Aqueous Hydrochloric Acid in Methanol:—A mixture of 20.4 g. (59.6 millimoles) of $Co_2(CO)_8$ and 10 ml. (100 millimoles) of 1-pentyne was allowed to stand overnight and then freed of excess pentyne in a current of nitrogen at 40–50°. To the residue, $Co_2(CO)_6C_3H_7C{\equiv}CH$, was added 200 ml. of methanol and 40 ml. of concentrated hydrochloric acid; the solution was then refluxed for 5 hours. After the reaction mixture had cooled, it was diluted with water and extracted with ether. The ether was evaporated, and the residue (which contained a considerable amount of dark red crystals later identified as $HCo_3(CO)_9C_3H_7C{\equiv}CH$) refluxed with a solution of 11 g. of sodium hydroxide in 200 ml. of 90% methanol for 0.5 hour. The alkaline solution was diluted with water, acidified, and extracted with ether. The ether was removed in a current of nitrogen, the residue distilled, and the fraction boiling from 61–70° at 2–3 mm. collected. A mass spectrometric analysis of the distillate indicated the presence of a mixture of saturated and unsaturated C_6-acids. The presence of both *n*-hexanoic and 2-methylpentanoic acid in the distillate was established by comparing the mass peaks of authentic samples of these acids with those of the sample. The yield of acids was about 15% based on the amount of $Co_2(CO)_6C_3H_7C{\equiv}CH$ used. The ratio of saturated to unsaturated acids was approximately 7:3. The residue consisted of high-boiling compounds containing carbonyl groups and represented approximately 10% of the amount of 1-pentyne in the starting material, $Co_2(CO)_6C_3H_7C{\equiv}CH$.

Preparation and Properties of $HCo_3(CO)_9C_3H_7C{\equiv}CH$ (I).—The starting material, $Co_2(CO)_6C_3H_7C{\equiv}CH$, was prepared as described above from 20 g. (58.4 millimoles) of $Co_2(CO)_8$ and excess 1-pentyne. After removal of excess 1-pentyne, the reaction product $Co_2(CO)_6C_3H_7C{\equiv}CH$ was dissolved in 360 ml. of methanol. To this solution was

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[9] F. A. Cotton, unpublished observations.

[10] E. Weiss, *Z. anorg. allgem. Chem.*, **287**, 223 (1956).

[11] L. F. Dahl and R. E. Rundle, *J. Chem. Phys.*, **26**, 1750 (1957).

[12] The possibility must not be overlooked, however, that the lack of hyperfine structure may be due to the large molecular weight (456) of the complex which may preclude completely effective motional averaging to zero of dipole–dipole interactions. (Compare No. 37 of the Varian Co. "This is NMR at Work" series).

[13] G. G. Hall and J. Lennard-Jones, *Proc. Roy. Soc.* (*London*), **A205**, 357 (1951).

[14] An X-ray study of II has been undertaken by L. F. Dahl, private communication.

[15] Analyses by W. Dieter and W. Rosinski, Analytical Chemists, Central Experiment Station, Bureau of Mines, U. S. Department of the Interior, Region V, Pittsburgh, Pa.

added with stirring a solution of 13 ml. of concentrated sulfuric acid in 30 ml. of water. Sulfuric acid was used instead of hydrochloric acid since previous experiments had shown that the yield of I was higher when sulfuric acid was used. After addition of the acid, the solution was refluxed with stirring for 2.5 hours. The vigorous gas evolution which occurred at the beginning of the reaction gradually subsided. After the reaction mixture had cooled to room temperature, two volumes of water were added and the mixture extracted with low-boiling (40–50°) petroleum ether. The residue remaining after evaporation of the petroleum ether was crystallized from methanol at Dry Ice temperature. The dark purple crystals weighed, after drying *in vacuo* at 40°, 5.0 g.; this corresponded to a yield of 34%.

Anal. Calcd. for $C_{14}H_9O_9Co_3$: C, 33.76; H, 1.82; Co, 35.50; mol. wt., 498. Found: C, 34.00; H, 1.93; Co, 35.54; mol. wt. (cryoscopic in benzene), 516.

When an acetylenic dicobalt hexacarbonyl, $Co_2(CO)_6C_2H_5C{\equiv}CC_2H_5$, derived from an internal alkyne, 3-hexyne, was subjected to the above treatment, the corresponding trinuclear complex $HCo_3(CO)_9C_2H_5C{\equiv}CC_2H_5$ could not be isolated.

Complex I is soluble in all common organic solvents and is insoluble in water. It sublimes at 60° and at a pressure of 2 mm. The complex appears to be unchanged after standing in air for several hours. Complex I does not appear to possess any acidic or basic properties since it cannot be extracted from an ether solution with either aqueous acid or alkali.

Alcoholic alkali decomposes I with formation of cobalt carbonyl anion $[Co(CO)_4]^-$. A solution of 0.1 g. of I in 50 ml. of methanol was treated with a strongly alkaline sodium hydroxide solution in the absence of air. The dark red solution turned green and in a few minutes became colorless. This solution was divided into two parts, A and B. When nickel *o*-phenanthroline chloride solution was added to A, a red precipitate was obtained indicating the presence of cobalt carbonyl anion. This was confirmed by the formation of cobalt hydrocarbonyl, $HCo(CO)_4$, on acidification of B.

Decomposition of I with Aqueous Hydrochloric Acid in Ethanol.—The decomposition of I with ethanolic hydrochloric acid was carried out in the same manner as that of $Co_2(CO)_6C_3H_7C{\equiv}CH$ except that ethanol was used instead of methanol. This change in solvent was made because preliminary experiments had shown that the rate of decomposition was extremely slow in methanol. After the reaction mixture, consisting of 5.9 g. (11.8 millimoles) of I, 25 ml. of ethanol and 7 ml. of hydrochloric acid, had been refluxed for 24 hours, water was added and the reaction product extracted with ether. The residue from the ether extraction was saponified by refluxing with 0.8 g. of sodium hydroxide in 16 ml. of 90% methanol for 1 hour. The reaction mixture was extracted with ether to remove the non-acidic material and then acidified and again extracted with ether to remove the acids. The residue of the first ether extract weighed 0.48 g., corresponding to approximately 40% of the amount of 1-pentyne in the starting material and contained high molecular weight (250–300), carbonyl-containing compounds as indicated by infrared and mass spectrometric analysis. The residue of the second ether extract weighed 0.05 g., corresponding to approximately 4% of the amount of pentyne in the starting material. This material consisted of high molecular weight (C_{22}–C_{23}) acids as indicated by a mass spectrometric analysis. No trace of C_6-acids was found in these ether extracts.

Preparation and Properties of $HCo_3(CO)_9HC{\equiv}CH$ (II).—The starting material, $Co_2(CO)_6HC{\equiv}CH$, was prepared by treating $Co_2(CO)_8$ with acetylene according to $Co_2(CO)_8 + HC{\equiv}CH \rightarrow Co_2(CO)_6HC{\equiv}CH + 2CO$. The acetylene was purified by passing first through concentrated sulfuric acid and then through soda-lime.

The reaction flask was provided with an inlet tube adjusted so that the tip was near the surface of the contents of the flask and an outlet tube with a mercury valve. The flask was purged with nitrogen and charged with 38 g. (111 millimoles) of $Co_2(CO)_8$. The nitrogen then was displaced by flushing the flask with acetylene. In the presence of acetylene, the bright-orange crystals of $Co_2(CO)_8$ slowly turned dark brown and liquified with the evolution of carbon monoxide. The flask was periodically flushed with acetylene in order to maintain a high concentration of acetylene in the gas phase. The reaction, which required 8–16 hours, was complete when no more gas was evolved. The liquid reaction product was transferred to a distilling flask, distilled at 64–66°, and 3–4 mm. pressure, and the distillate collected in an ice-cooled receiver. The distillate was pure $Co_2(CO)_6HC{\equiv}CH$ and melted at 13–14°.[1] The trinuclear complex II was prepared as described above for the preparation of I, by treating a methanolic solution of $Co_2(CO)_6HC{\equiv}CH$ with aqueous sulfuric acid. The dark purple crystals of II were obtained in 49% yield. Calcd. for $C_{11}H_3O_9Co_3$: C, 28.97; H, 0.66; Co, 38.78; mol. wt., 456. Found: C, 29.10; H, 0.75; Co, 38.30; mol. wt. (cryoscopic in benzene), 416. Complex II sinters and decomposes without melting at about 185°; it sublimes at about the same temperature and pressure as I. Complex II appears to be quite stable. Several days of exposure to air did not seem to cause any changes in the appearance of the crystals. Complex II like complex I does not exhibit any acidic or basic properties and cannot be extracted from an ether solution either with aqueous acid or alkali.

Ultraviolet and Visible Absorption Spectra.—These spectra were measured on a Cary recording spectrophotometer, using ethanol solutions. The seseveral maxima, in Å., with their extinction coefficients (liters/mole-cm., $D = \log I_0/I$) were observed: 2320 (2.8×10^4), 2970sh (1.4×10^4), ~3700sh (3.7×10^3), 5000 (2.5×10^3).

No particular interpretation can be given for the ultraviolet and visible spectrum. In general, the fragmentary data available for simple metal carbonyls such as $Fe(CO)_5$ and $Ni(CO)_4$ show that they have very strong absorption in the ultraviolet as well as weaker shoulders toward the visible. Thus the spectrum of II is consistent with the presence of terminal carbonyl groups but gives no positive information on structure so far as we can see.

Proton Resonance Measurements.—The proton resonance spectrum of the compound was measured in solution at room temperature on a Varian Model 4300B high resolution n.m.r. spectrometer using a 40 megacycle fixed frequency and magnetic field of 9300 gauss. A saturated solution of the compound in carbon tetrachloride was placed in a 5-mm. tube containing also a sealed capillary of reference material, water or benzene, and was spun in the field at 400–600 r.p.m. The total sample volume was 0.5 cc.

The spectrum was recorded on a Sanborn Recorder, from which tracing the chemical shifts (relative to benzene) of the two observed resonances were measured by imposing a 200 c.p.s. side band on the reference line by means of an auxiliary audio-oscillator to so include the two resonances of the compound that a linear interpolation was possible. The oscillator was calibrated with a Hewlett-Packard Frequency Center. For the estimation of relative intensities, the carrying voltage from the probe was put across a potentiometer and traced on a Brown Recorder. The chemical shifts are accurate to ±2 c.p.s., and the intensities to ±5–20%.

The compound shows two resonances, one of intensity 79 at 33.8 c.p.s. from the resonance of the protons in benzene, and another of intensity 37 at 110.8 c.p.s. from benzene (result of averaging seven runs). This intensity ratio of 2/0.94 is close to the theoretical 2:1 for the proposed structures of the compound, and accounts for the three hydrogens. The chemical shifts calculated from the above data are

less shielded: +0.92 p.p.m. from water (intensity 2)

more shielded: −1.01 p.p.m. from water (intensity 1)

A careful search of the region of high shielding (out to −20 p.p.m.) was made but no resonance was observed. The small chemical shifts in this compound are noteworthy, but not exceptional.

Dipole Moment Measurement.—The dipole moment was measured by conventional techniques in benzene solution.[16] The data are summarized in Table I. The value of $_\infty P_2$ is 172 ± 10 cc. and the average value of $_EP$ is 144 + 5 cc.

The difference, $_\infty P_2 - {}_EP_2 = 27 \pm 15$ cc., is very small. It would lead to a permanent moment of 1.1 ± 0.3 D. However, it is much more reasonable to assume that in a molecule of this size there will be an atomic polarization amounting to at least 10–20% of $_EP$. Since 27 is ~20% of 145, one might then conclude that the permanent moment is zero. Another complication arises however. The sodium D line

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(16) See for example, R. J. W. LeFevre, "Dipole Moments," Methuen and Co., London, 1953.

TABLE I

EXPERIMENTAL DATA AND RESULTS OF DIPOLE MOMENT MEASUREMENT[a]

Soln.	N_1	N_2	ϵ_{12}	D	P_2	$_n$D	$_E$P
0	1.0000	0.0000	2.2741	0.8724	......	1.4962	..
1	0.9507	.0493	2.2967	.8843	158 ± 10	....	..
2	.8994	.1006	2.3113	.8963	162 ± 5	1.5003	143
3	.8708	.1292	2.3338	.9038	155 ± 3	1.5040	146

[a] N_1 = mole fraction benzene, N_2 = mole fraction of compound, ϵ_{12} = dielectric constant of solutions, D = density of solution, P_2 = calculated total molar polarization of compound, n_D = refractive index of solution at 27°, $_EP$ = electronic polarization of solute calculated from n_D. Solution 1 was too dilute for an accurate measurement of n_D. All measurements were made at 27 ± 1°.

(5893 Å.) is not too far removed from the absorption band at 5000 Å. with ϵ 2.5 × 10^3. It is therefore possible that, due to the dispersion of the refractive index through this absorption band, the value of n_D is higher than the true n measured well away from any absorption band. Thus 144 must be taken as an upper limit of $_EP$. One can attempt to estimate $_EP$ by consideration of the values in other carbonyl molecules. Weiss[10] reports $_EP$ values for $Fe(CO)_5$, $Co(CO)_3(NO)$ and $Fe(CO)_2(NO)_2$ of 42, 35 and 40 cc., respectively. If we then assume a contribution of ~35 cc. per $Co(CO)_3$ group and a contribution of ~10 cc. from the C_2H_2 portion of the molecule, we estimate $_EP$ for II as ~115 cc. If $_EP$ is actually this low, then, allowing ~20 cc. for $_AP$, one calculates $\mu \simeq 1.6$ D. Thus we feel it reasonable to conclude that the dipole moment is less than 1.6 D. and quite possibly zero.

Acknowledgment.—We are indebted to Mr. J. R. Leto of M. I. T. for measuring the proton resonance spectrum and to Dr. William Westphal of the Laboratory for Insulation Research, M. I. T., for help in measuring the dielectric constants.

PITTSBURGH 13, PENNA.
CAMBRIDGE 39, MASS.

[CONTRIBUTION FROM THE RESEARCH & DEVELOPMENT DEPARTMENT, PENNSALT CHEMICALS CORP.]

Reactions of Perchloryl Fluoride with Organic Compounds. II. Fluorination of Certain Active Methylene Compounds[1]

BY C. E. INMAN, R. E. OESTERLING AND E. A. TYCZKOWSKI

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Direct methods for replacement of the acidic hydrogen atoms of active methylene compounds by fluorine have not been previously reported. The reaction of perchloryl fluoride with the sodium salts of active methylene compounds constitutes a novel procedure for such fluorinations and is believed to be generally applicable. Several new fluorinated compounds have been prepared and are described.

Previous studies of perchloryl fluoride have shown it to be a surprisingly stable molecule, possessing a C_{3v} tetrahedral symmetry and essentially no electrical dipole moment.[2] In a previous paper the authors have described the heterolysis of this compound in the presence of strongly electrophilic reagents such as aluminum chloride to give the ClO_3^+ ion and bring about the novel perchlorylation reaction with aromatic hydrocarbons.[3] Perchloryl fluoride has also been shown to undergo nucleophilic attack in the presence of alkaline inorganic reagents, such as ammonia, to give fluoride ion and the ClO_3^+ ion.[4]

In the present investigation, it was found that perchloryl fluoride also reacts with strong organic bases. Moreover, in the case of the sodium salts of active methylene compounds, the reaction was found to introduce fluorine into the organic molecule. For example, when perchloryl fluoride was passed into an alcoholic solution of the sodium salt of diethyl malonate, diethyl difluoromalonate was produced. The reaction tends to replace all hydrogens of the active methylene group. Thus in the case of diethyl malonate, if an insufficiency of sodium ethylate was used to neutralize each acidic hydrogen successively, the product was diethyl difluoromalonate with unchanged diethyl malonate. When a two-to-one mole ratio was used, the reaction was essentially quantitative, and only the difluorinated product was obtained. No monofluorinated diethyl malonate was found in any case, although it was undoubtedly formed as an intermediate. The monofluoro compound, as a stronger acid than diethyl malonate, competes effectively for the available base and undergoes reaction with perchloryl fluoride a second time to form the difluoro compound before further monofluoro intermediate may be formed.

The anticipated reaction products were obtained from diethyl malonate, diethyl ethylmalonate, diethyl phenylmalonate, ethyl acetoacetate and 2,4-pentanedione. Product yields in general were high. In the case of the ethyl acetoacetate however, yields of only 30 to 40% of the fluorinated product were originally obtained, complicating the purification of the product. It was found, however, that by lowering the reaction temperature and by addition of the base in small increments to form the sodium salt, the yield could be substantially increased. By limiting the excesses of strong base present in the reaction media, this procedure is believed to avoid the possibility of cleavage of the fluorinated product at the carbonyl group. Cleavage of this type with carbonyl compounds bearing negative constituents on the α-carbon is well known.[5] This improved procedure

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[1] Presented in part before the Delaware Valley Regional Meeting of the American Chemical Society, Philadelphia, Pa., Feb. 5, 1958.

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