bons are formed[8,25]; second, in the absence of excess sodium metal, half of the original hydrocarbon is recovered unchanged, while in the presence of excess sodium the original hydrocarbon is completely converted to the dihydro derivative.[25a,c] The first fact led previous investigators to the conclusion that disodium addition products, rather than negative free radicals, were formed in the reaction of sodium metal with aromatic hydrocarbons. The second set of observations remained unexplained.

A mechanism for the reactions of aromatic hydrocarbon free radicals with substances such as carbon dioxide or water, which is consistent with the observations described above, is shown in formulas I–VI. The conversion of I to III involves an activated state, two of whose possible resonance structures are represented by II. Conversion of II to III is simply a reaction between a Lewis base and acid. It is assumed that I → III is a relatively slow reaction because both I and carbon dioxide require activation. The interchange of an electron between III and $(C_{10}H_8)^-$ to give IV is assumed to be very rapid.[26] The final step (IV → V and VI) is assumed to be slow compared to III → IV, but rapid compared to I → III. This is not an unreasonable assumption, since the conversion of IV to V and VI involves only the activation of the carbon dioxide. It is apparent from the given reaction scheme that in the absence of excess metallic sodium, for each mole of I converted to V and VI one mole of naphthalene is reformed in the step III → IV.

(25) (a) W. E. Bachmann, *J. Org. Chem.*, **1**, 347 (1936); (b) A. Jeanes and R. Adams, THIS JOURNAL, **59**, 2608 (1937); (c) J. F. Walker and N. D. Scott, *ibid.*, **60**, 951 (1938).

(26) R. L. Ward and S. I. Weissman, *ibid.*, **76**, 3612 (1954).

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[CONTRIBUTION OF BRANCH OF COAL-TO-OIL RESEARCH, BUREAU OF MINES, AND THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF PITTSBURGH (CONTRIBUTION NO. 959)]

Acetylenic Dicobalt Hexacarbonyls. Organometallic Compounds Derived from Alkynes and Dicobalt Octacarbonyl[1,2]

BY HAROLD GREENFIELD,[3] HEINZ W. STERNBERG,[3] ROBERT A. FRIEDEL,[3] JOHN H. WOTIZ,[4] RAYMOND MARKBY[3] AND IRVING WENDER[3]

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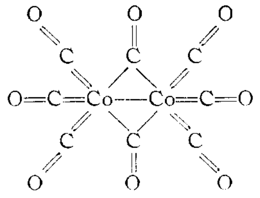
It has been found that acetylene and substituted acetylenes, RC≡CR′, readily displace the two bridge carbonyl groups in dicobalt octacarbonyl, $Co_2(CO)_8$, to yield a new type of organometallic compound, $RC_2R'Co_2(CO)_6$. The structure and properties of these "acetylenic dicobalt hexacarbonyls" are discussed.

Recent investigations[5,6] have shown that dicobalt octacarbonyl (I), like iron enneacarbonyl,[7] contains two types of carbonyl groups, *i.e.*, bridge and terminal carbonyl groups.



I

It has now been found that the two bridge carbonyl groups in I can be replaced by alkynes. The reaction, which proceeds smoothly and quantitatively at room temperature, can be represented by equation 1

$$RC{\equiv}CR' + Co_2(CO)_8 \longrightarrow \underset{\text{II}}{RC_2R'Co_2(CO)_6} + 2\overline{CO} \quad (1)$$

The reaction is general and occurs with all types of alkynes (see Table I). If the alkyne contains two triple bonds, each triple bond reacts with a mole of dicobalt octacarbonyl. This is the case even with conjugated diacetylenes, where a steric effect might have been expected.

The acetylenic dicobalt hexacarbonyls are generally deeply colored. In the ultraviolet region diphenylacetylene dicobalt hexacarbonyl has a broad band near 2800 Å. with a molar extinction coefficient, ϵ, of about 21,000. An interesting property of the acetylenic dicobalt hexacarbonyls is their weak intermolecular forces of attraction. This is indicated by their high volatility, high solubility in organic solvents and the ease with which they can be eluted from a column of activated alumina. For example, acetylene dicobalt hexacarbonyl, with a molecular weight of 312, distils at 64 to 66° at 3.5 to 4 mm. pressure. Diphenylacetylene dicobalt hexacarbonyl, with a molecular weight of 464, sublimes at 90° at 1 mm. pressure, and can be eluted from a column of activated alumina with a small volume of an aliphatic hydrocarbon solvent; 1,7-octadiyne tetracobalt dodecacarbonyl, with a molecular weight of 678, is soluble in pentane at room temperature.

Magnetic susceptibility measurements on diphenylacetylene dicobalt hexacarbonyl indicate that this compound is diamagnetic.

The Infrared Spectra of Acetylenic Dicobalt Hexacarbonyls.—The infrared spectrum of dicobalt octacarbonyl (I) contains a group of three bands at 4.83, 4.89 and 4.94 μ and a single band at

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(1) For a preliminary communication, see H. W. Sternberg, H. Greenfield, R. A. Friedel, J. Wotiz, R. Markby and I. Wender, THIS JOURNAL, **76**, 1457 (1954).

(2) This paper is based, in part, on the Ph.D. Thesis of Harold Greenfield, University of Pittsburgh.

(3) Branch of Coal-to-Oil Research, Bureau of Mines, Bruceton, Pa.

(4) Department of Chemistry, University of Pittsburgh.

(5) J. W. Cable, R. S. Nyholm and R. K. Sheline, THIS JOURNAL, **76**, 3373 (1954).

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

(7) R. K. Sheline, *ibid.*, **73**, 1615 (1951).

TABLE I

ACETYLENIC DICOBALT HEXACARBONYLS

Acetylenic dicobalt hexacarbonyl	Formula	Description	M.p., °C.	Analyses, % Calcd. C	Calcd. H	Calcd. Co	Found C	Found H	Found Co
Acetylene dicobalt hexacarbonyl	$C_8H_2O_6Co_2$	Dk. red oil, b.p. 64–66° (3.5–4 mm.)	13.0–13.6	30.80	0.65		30.76	0.62	
2-Butyne dicobalt hexacarbonyl	$C_{10}H_6O_6Co_2$	Dk. red oil	....	35.32	1.78		35.38	1.84	
1,7-Octadiyne tetracobalt dodecacarbonyl	$C_{20}H_{10}O_{12}Co_4$[a]	Red crystals	85.0–85.4[c]	35.43	1.49	34.77	35.62	1.64	34.78
Phenylacetylene dicobalt hexacarbonyl	$C_{14}H_6O_6Co_2$	Dk. red oil	....	43.33	1.56		42.92	1.61	
Diphenylacetylene dicobalt hexacarbonyl	$C_{20}H_{10}O_6Co_2$[b]	Dk. purple cryst., subl. at 90° (1 mm.)	109.5–110.0[d]	51.75	2.17	25.40	51.61	2.22	25.6
Cyclodecyne dicobalt hexacarbonyl	$C_{16}H_{16}O_6Co_2$	Dk. red oil	....	45.52	3.82		45.94	4.04	
Isopropenylacetylene dicobalt hexacarbonyl	$C_{11}H_6O_6Co_2$	Dk. reddish-brown cryst.	31.8–32.8	37.53	1.72		37.47	1.84	
Propargyl alcohol dicobalt hexacarbonyl	$C_9H_4O_7Co_2$	Orange-red needles	52.2–52.6[e]	31.60	1.18	34.49	31.65	1.26	34.33
2-Butyne-1,4-diol dicobalt hexacarbonyl	$C_{10}H_6O_8Co_2$	Orange-red needles	*ca.* 135 dec.[f]	32.28	1.63	31.69	32.24	1.67	31.67
2,7-Dimethylocta-3,5-diyne-2,7-diol tetracobalt dodecacarbonyl	$C_{22}H_{14}O_{14}Co_4$	Dk. greenish-black cryst.	Dec. without[e] melting	35.80	1.91		36.59	2.08	
Propylpropiolic acid dicobalt hexacarbonyl	$C_{12}H_{18}O_8Co_2$	Dk. reddish-brown cryst.	83–85 dec.[e]	36.21	2.03		36.26	2.09	
Pentylpropiolic acid dicobalt hexacarbonyl	$C_{14}H_{12}O_8Co_2$	Dk. red oil	....	39.46	2.84		40.15	3.08	
Phenylpropiolic acid dicobalt hexacarbonyl	$C_{15}H_6O_8Co_2$	Dk. purple-brown cryst.	*ca.* 120 dec.[g]	41.69	1.40		41.81	1.50	

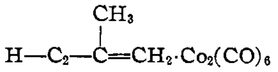
[a] Molecular weight: calcd., 678; found, 669 ± 15 (ebullioscopic in benzene). [b] Molecular weight: calcd., 464; found, 463 ± 5 (cryoscopic in cyclohexane). [c] Recrystallized from ethanol. [d] Recrystallized from methanol. [e] Recrystallized from petroleum ether (b.p. 60–68°). [f] Recrystallized from ethanol–water. [g] Recrystallized from pentane.

5.38 μ. The three bands at 4.83, 4.89 and 4.94 μ were assigned to the terminal carbonyl groups in I; the single band at 5.38 μ was assigned to the bridge carbonyl groups in I.[5,6]

The spectrum of each of the acetylenic dicobalt hexacarbonyls contains a characteristic group of three sharp bands at approximately 4.78, 4.88 and 4.94 μ. The position of these bands is very similar to the position of the three bands at 4.83, 4.89 and 4.94 μ in I, attributable to the terminal carbonyl groups in I. It is very significant that the band at 5.38 μ in I, attributable to its bridge carbonyl groups, is absent in the spectra of the acetylenic dicobalt hexacarbonyls. This is interpreted as meaning that the two moles of carbon monoxide that are displaced from I on treatment with an alkyne are both bridge carbonyl groups.

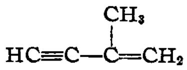
The bands characteristic of the carbon–carbon triple bond are absent in the spectra of the acetylenic dicobalt hexacarbonyls. The spectra of those acetylenic dicobalt hexacarbonyls which were derived from terminal acetylenes contain a band at about 3.23 μ, characteristic of an olefinic or an aromatic C–H stretching frequency. There is a concurrent disappearance of the acetylenic C–H stretching band in the 3.1 μ region. It therefore appears that there is no carbon–carbon triple bond in acetylenic dicobalt hexacarbonyls.

The spectrum of isopropenylacetylene dicobalt hexacarbonyl has a band at 6.16 μ, attributable to



$$H—C_2—\overset{\displaystyle CH_3}{\overset{|}{C}}{=}CH_2\cdot Co_2(CO)_6$$

a conjugated terminal ethylenic bond. The position of the conjugated terminal ethylenic band in isopropenylacetylene is at 6.18 μ.



$$HC{\equiv}C—\overset{\displaystyle CH_3}{\overset{|}{C}}{=}CH_2$$

The spectrum of phenylpropiolic acid dicobalt hexacarbonyl, $C_6H_5–C_2–COOH\cdot Co_2(CO)_6$, has a band at 6.00 μ, and the spectra of both propyl- and pentylpropiolic acid dicobalt hexacarbonyl, $R–C_2–COOH\cdot Co_2(CO)_6$ (R = propyl, pentyl), have bands at 5.98 μ. These absorptions are characteristic of a conjugated carboxy group. For comparison, the carboxy group absorption bands are at about 5.80 μ for saturated carboxylic acids, at about 5.90 μ for conjugated olefinic acids such as crotonic acid, at 5.94 μ for benzoic acid, at 5.92 μ for pentylpropiolic acid, and at 5.94 μ for phenylpropiolic acid. The conjugated nature of the acetylenic dicobalt hexacarbonyls is also indicated by the absorption in the visible and near ultraviolet regions.

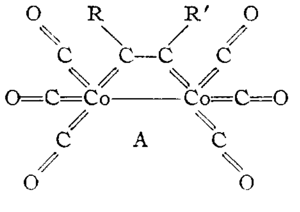
In the spectrum of propargyl alcohol dicobalt hexacarbonyl, $H–C_2–CH_2OH\cdot Co_2(CO)_6$, in carbon tetrachloride solution, the associated hydroxyl group absorption band becomes weaker with dilution while the band due to the non-associated group becomes stronger. This indicates that the hydrogen-bonding is intermolecular.

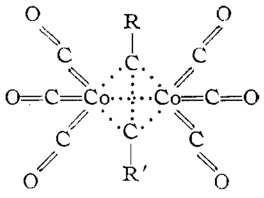
Copies of the spectra discussed in this paper can be procured from the authors.

Discussion of the Structure of Acetylenic Dicobalt Hexacarbonyls.—The stoichiometry of the reaction of alkynes with dicobalt octacarbonyl (I), and the ultimate analyses and infrared spectra of the resulting products, acetylenic dicobalt hexacarbonyls (II), indicate that the two bridge carbonyl groups in I have been replaced by the alkyne. Although it is not possible at present to establish the position of the C–C bond with respect to the Co–Co bond, it is readily seen that only the following three basic arrangements need be considered:

The C–C axis is parallel to the Co–Co axis (structure A); the C–C axis is perpendicular to the Co–Co axis and either in the same plane (structure B) or in a different plane (structure C).

Of these structures only B has a center of symmetry, provided it is derived from acetylene or a symmetrically substituted alkyne, and provided the carbonyl groups are symmetrically arranged.


A


B

From analogy with dicobalt octacarbonyl,[5,6] it may be assumed that the carbonyl groups are so arranged as to give a center of symmetry. It should be possible, therefore, to distinguish between structure B, on the one hand, and A and C, on the other hand, by determining the dipole moment. Determination of the dipole moment of diphenylacetylene dicobalt hexacarbonyl (II, $R = R' = C_6H_5$) gave the value of 2.0 to 2.1 *D*. Unless we are dealing here with an extremely large anomalous atomic polarization,[8] this result would seem to eliminate B as a possible structure.

It should be emphasized that each of the acetylenic dicobalt hexacarbonyls contains the same number (three) of observed infrared absorption bands in the terminal carbonyl group region. This is unexpected on the basis of symmetry considerations. Structure B in which $R = R'$ has C_{2h} symmetry, for which group theory predicts three infrared-active terminal carbonyl stretching frequencies; structures A and C, having lower symmetry, should give rise to a greater number of infrared-active terminal carbonyl stretching frequencies. Furthermore, in the case in which $R \neq R'$, each of the proposed structures, A, B and C, should give rise to more than three infrared-active terminal carbonyl stretching frequencies.

It seems unlikely that the predicted additional frequencies should all be unobservable. Perhaps the explanation for these results lies in the nature of the bonding between the acetylenic carbon and the cobalt atoms in II. It is tempting to speculate upon a possible similarity between this bonding and the bonding in aromatic molecular complexes of the electron donor–acceptor type.[9] The information relative to the infrared spectra of these complexes is very meager.[9] Unpublished work in this Laboratory indicates that the infrared spectra of such complexes show little if any difference from the summation of the spectra of the components when all the spectra are determined in the same physical state.

It appears that investigations of the geometry of II by means of X-ray and/or electron diffraction would be most likely to supply the information necessary to make a choice between the postulated structures.

It is interesting to note that the structure of an acetylenic dicobalt hexacarbonyl may be somewhat analogous to intermediates in heterogeneous catalysis involving the adsorption of a molecule on dual surface sites. Such intermediates have been proposed, for example, for the adsorption of ethylene[10] and the adsorption of methylene radicals[10] on a solid surface, and in a mechanism for the Fischer–Tropsch reaction.[11]

The Stability of Acetylenic Dicobalt Hexacarbonyls.—The results of experiments on the stability of diphenylacetylene dicobalt hexacarbonyl indicate that oxidation is an important factor in the decomposition of acetylenic dicobalt hexacarbonyls at room temperature. Benzil was a major product of such a decomposition of diphenylacetylene dicobalt hexacarbonyl.

The thermal decomposition of diphenylacetylene dicobalt hexacarbonyl at 101° did not yield diphenylacetylene.

Experimental

All melting points are corrected.

Macroanalyses were obtained at the U. S. Bureau of Mines at Bruceton, Pa., and are reported to two decimal places. Microanalyses were obtained from the Galbraith Microanalytical Laboratories, Knoxville, Tenn., and are reported to one decimal place. Infrared absorption spectra were obtained from a Perkin–Elmer recording spectrophotometer, model 21.

2-Butyne, isopropenylacetylene and 2,7-dimethylocta-3,5-diyne-2,7-diol were gifts of the Air Reduction Chemical Co. Propargyl alcohol was a gift of the General Aniline and Film Corp. Cyclodecyne[12] was a gift of Dr. Alfred T. Blomquist of Cornell University.

Acetylene was purchased from Linde Air Products Co. Phenylacetylene was purchased from Farchan Research Laboratories. Diphenylacetylene was purchased from Metro Industries and from Organic Specialties, Inc.

1,7-Octadiyne,[13] 2-butyne-1,4-diol,[14] propylpropiolic acid,[15] pentylpropiolic acid,[15] phenylpropiolic acid[16] and dicobalt octacarbonyl[17] were prepared by methods described in the literature.

The Stoichiometry of the Reaction of Alkynes with Dicobalt Octacarbonyl (I).—Since the reaction of an alkyne with I is accompanied by an evolution of gas, an attempt was made to determine the stoichiometry of the reaction by following it gasometrically. The reaction was studied in an apparatus consisting of a reaction flask connected to a gas buret. Two sets of experiments were carried out, one using an excess of the alkyne and the other using an excess of I. Both reagents were dissolved in toluene and mixed under an atmosphere of carbon monoxide or synthesis gas (a mixture of hydrogen and carbon monoxide). The reaction mixture was then stirred by means of a magnetic stirrer, and the amount of gas evolved was measured.

When the alkyne was in excess, two moles of carbon monoxide were evolved per mole of I. When I was in excess, two moles of carbon monoxide were evolved per mole of the alkyne. Therefore, the reaction of one mole of the alkyne with one mole of I results in the evolution of two moles of carbon monoxide, as illustrated by equation 1.

The Preparation and Properties of Acetylenic Dicobalt Hexacarbonyls.—In a typical preparation, the alkyne and I were allowed to react at room temperature for at least one hour in an inert, low-boiling solvent such as pentane, low-boiling petroleum ether or diethyl ether, in a flask fitted with a mercury valve to permit the escape of the evolved carbon monoxide. Stoichiometric amounts or an excess of either the alkyne or I were used, depending upon the subsequent purification procedure. The reaction mixture then was usually filtered to remove insoluble impurities, and the filtrate was taken to dryness in a stream of nitrogen. The

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[8] I. E. Coop and L. E. Sutton, *J. Chem. Soc.*, 1269 (1938).

[9] L. J. Andrews, *Chem. Revs.*, **54**, 713 (1954).

[10] K. J. Laidler, Chapter 5 in "Catalysis," Vol. I, edited by P. H. Emmett, Reinhold Publishing Corp., New York, N. Y., 1954.

[11] H. H. Storch, N. Golumbic and R. B. Anderson, "The Fischer–Tropsch and Related Syntheses," John Wiley and Sons, Inc., New York, N. Y., 1951, p. 592.

[12] A. T. Blomquist, R. E. Burge, Jr., and A. C. Sucsy, THIS JOURNAL, **74**, 3636 (1952).

[13] R. Lespieau and R. Deluchat, *Compt. rend.*, **183**, 889 (1926).

[14] G. F. Hennion and F. P. Kupiecki, *J. Org. Chem.*, **18**, 1601 (1953).

[15] A. O. Zoss and G. F. Hennion, THIS JOURNAL, **63**, 1151 (1941).

[16] T. W. Abbott, "Organic Syn.," Coll. Vol. 2, John Wiley and Sons, Inc., New York, N. Y., 1943, p. 515.

[17] I. Wender, H. Greenfield and M. Orchin, THIS JOURNAL, **73**, 2656 (1951).

acetylenic dicobalt hexacarbonyl residue was then purified by recrystallization, distillation or sublimation, or by dissolving it in a suitable solvent, filtering to remove insoluble impurities and evaporating the solvent in a stream of nitrogen. In most cases, the purpose of the preparation was to obtain pure material, and no attempt was made to determine yields or to obtain maximum yields.

A description of the compounds prepared and the analytical data are given in Table I.

A preparation of diphenylacetylene dicobalt hexacarbonyl is described in detail below:

To a solution of 29.6 g. (8.65×10^{-2} mole) of I in 150-ml. of petroleum ether (b.p. 35–55°) in an erlenmeyer flask was added 14.8 g. (8.31×10^{-2} mole) of diphenylacetylene. A mercury valve was placed on the flask to permit evolved carbon monoxide to escape. The reaction mixture was allowed to stand overnight. The solvent was removed at room temperature in a stream of nitrogen, and the solid residue was recrystallized from one liter of methanol. Filtration gave 29.0 g. (75.2% yield) of dark, purple crystals of diphenylacetylene dicobalt hexacarbonyl, m.p. 108.4–110.0°. The mother liquors were concentrated and cooled. Filtration gave 2.5 g. (6.5% yield) of diphenylacetylene dicobalt hexacarbonyl, m.p. 108.4–109.8°. Both solid fractions were combined and, after a second recrystallization from methanol, yielded 23.5 g. (61% yield), m.p. 109.2–109.7°.

The Dipole Moment of Diphenylacetylene Dicobalt Hexacarbonyl.—Dielectric constant and density measurements for solutions of diphenylacetylene dicobalt hexacarbonyl in benzene at 30° gave a value of 204 ± 2% for the total molar polarization of the solute. The data are given in Table II.

TABLE II

MOLAR POLARIZATION DATA FOR DIPHENYLACETYLENE DICOBALT HEXACARBONYL IN BENZENE SOLUTION AT 30°

Solution	Mole fraction solute	Density	Dielectric constant	Molar polarization, P
Pure solvent	0	0.86823	2.2627	..
1	0.0026122	.87236	2.2802	209
2	.0040660	.87484	2.2902	209
3	.0052331	.87751	2.2964	199
4	.0062175	.87976	2.3054	203

Average P = 204 ± 4 (±2%)

The molecular refraction for the D-sodium line was calculated from bond refractivities, using structures A and B. Denbigh's[18] values of 1.25, 2.73 and 1.69 were used for the (C–C), (C–C) benzene and (C–H) bond moments, respectively. Using literature values for the refractive indices[19] and densities[20] of iron pentacarbonyl and nickel carbonyl, their molecular refractions were calculated to be 40.8 and 35.1, respectively. This gave a value of 8.2 for the total (Fe=C=O) bond moment and a value of 8.8 for the total (Ni=C=O) bond moment, and an estimated value of 8.4 for the (Co=C=O) bond moment. Taking into account the value of 4.98 for the induced polarization of carbon monoxide[21] the (Co–C) bond moment was estimated to be between 3 and 5, with a probable value of 3.4, and the (Co=C) bond moment was estimated to be between 4 and 6, with a probable value of 5. The (Co–Co) bond moment was estimated to be between 2 and 11, with a probable value of 7. The calculated value for the molecular refraction was 117 for structure A and 125 for structure B.

The orientation polarization was calculated from the experimental value for the molar polarization and the calculated values for the molecular refraction. Values of 87 and 79 were obtained, depending upon whether structure A or B was used to calculate the molecular refraction. These values of 87 and 79 correspond to dipole moment values of 2.1 and 2.0 *D*, respectively. It is conservatively estimated that the maximum error introduced by the calculation of the molecular refraction is 0.3 *D*.

The Stability of Acetylenic Dicobalt Hexacarbonyls.—Qualitative observations had indicated that many of the acetylenic dicobalt hexacarbonyls decomposed on exposure to air. When freshly prepared, the solid propargyl alcohol dicobalt hexacarbonyl and the solid 2-butyne-1,4-diol dicobalt hexacarbonyl were readily soluble in organic solvents such as ethanol and diethyl ether. After a few days these solid compounds had formed material which was insoluble in organic solvents. This indicated that some chemical change had occurred on standing. Acetylene dicobalt hexacarbonyl and 2-butyne dicobalt hexacarbonyl, both liquids, formed solid material after exposure to the air for a few hours. The infrared spectra of the acetylenic dicobalt hexacarbonyls that had been prepared from acetylenic carboxylic acids showed considerable change in cyclohexane or carbon disulfide solution over a period of a few hours or less. For example, after a solution of phenylpropiolic acid dicobalt hexacarbonyl in carbon tetrachloride had stood for one-half hour, its infrared spectrum no longer showed the presence of a carboxylic acid group, and the absorption in the terminal carbonyl group region was of very low intensity. At the same time, new bands had appeared in the regions characteristic of the carboxyl anion.

In order to determine the importance of oxygen in these decompositions, solutions of 0.020 g. of diphenylacetylene dicobalt hexacarbonyl in 5-ml. of cyclohexane (purified by distillation and subsequent chromatography on activated carbon) were allowed to stand at room temperature in glass vials under one of the following gases: (1) oxygen, (2) air, (3) nitrogen (containing 0.2% oxygen), and (4) synthesis gas (0.25 H_2:1CO). A second set of four similar samples was kept in the dark. The samples were then examined for signs of decomposition. The criterion for decomposition was taken to be the visible formation of an insoluble, solid sediment. After a period of 24 hours, there had been some decomposition in the solutions under air and oxygen, but no visible decomposition had occurred in the solutions under nitrogen and synthesis gas. There was no apparent difference between the samples that had been kept in the dark and those which had been exposed to light. After a period of about three months, the samples under oxygen were almost completely decomposed, as shown by the large amount of brown solid and the change in the color of the solution from the dark red to pale yellow. There had been considerable decomposition of the samples under air, slight decomposition of the samples under nitrogen, and no visible decomposition of the samples under synthesis gas. Again, there was no apparent difference between the samples that had been kept in the dark and those that had been exposed to light.

In a second series of experiments, solutions of 0.100 g. (2.15×10^{-4} mole) of diphenylacetylene dicobalt hexacarbonyl in 50-ml. of cyclohexane were allowed to stand in stoppered flasks at room temperature for one month. Infrared spectroscopic analysis indicated that about 75% of the diphenylacetylene dicobalt hexacarbonyl had been decomposed, and that benzil had been formed in about 28% yield. The identification of the benzil was confirmed by the formation of a benzilmono-2,4-dinitrophenylhydrazone which did not depress the melting point of an authentic sample.

The preparation of an authentic sample of the benzil 2,4-dinitrophenylhydrazone according to the procedure of Shriner and Fuson[22] gave rise to two isomeric mono-2,4-dinitrophenylhydrazones which were separated by fractional recrystallization from ethanol. The less soluble isomer, (A), melted at 192.0–192.8° after two recrystallizations from ethyl acetate–ethanol. The literature values for the melting point of benzil 2,4-dinitrophenylhydrazone are 185[23] and 189°.[24] The more soluble isomer, (B), melted at 161.8–162.8° after two recrystallizations from ethanol–water followed by two recrystallizations from ethanol.

Anal. Calcd. for $C_{20}H_{14}N_4O_5$: C, 61.55; H, 3.61. Found: (A) C, 61.5; H, 3.6; (B) C, 61.5; H, 3.8.

In order to determine its thermal stability, a solution of

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[18] K. G. Denbigh, *Trans. Faraday Soc.*, **36**, 936 (1940).

[19] Landolt-Börnstein" Physikalisch-Chemische Tabellen," 5th ed., J. Springer, Berlin, 1923.

[20] "International Critical Tables," Vol. III, McGraw-Hill Book Co., Inc., New York, N. Y., 1928.

[21] H. E. Watson, G. G. Rao and K. L. Ramaswamy, *Proc. Roy. Soc. (London)*, **A143**, 558 (1934).

[22] R. L. Shriner and R. C. Fuson, "The Systematic Identification of Organic Compounds," 3rd ed., John Wiley and Sons, Inc., New York, N. Y., 1948.

[23] C. F. H. Allen, THIS JOURNAL, **52**, 2955 (1930).

[24] N. R. Campbell, *Analyst*, **61**, 391 (1936).

1.000 g. (2.15×10^{-3} mole) of diphenylacetylene dicobalt hexacarbonyl in 20 ml. of methylcyclohexane (b.p. 101°) was refluxed for 31 hours under an atmosphere of nitrogen. Infrared and ultraviolet spectroscopic analyses indicated that 86% of the diphenylacetylene dicobalt hexacarbonyl had been decomposed and that no diphenylacetylene had been formed.

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Molecular Rearrangements. VI. The Dehydration of *cis*- and of *trans*-2-Phenylcyclohexanol[1]

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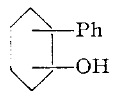
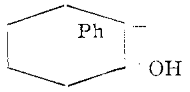
The dehyration of *cis*-2-phenylcyclohexanol-2-C^{14} (Ia) with phosphoric acid has been shown to produce 88% 1-phenylcyclohexene (III) and 2% 3-phenylcyclohexene (IV), in qualitative agreement with the results of Price and Karabinos (ref. 3). When *trans*-2-phenylcyclohexanol-2-C^{14} (IIa) was subjected to the same dehydrating conditions there was produced 21% of 1-phenylcyclohexene (III) but only 9% of 3-phenylcyclohexene (IV). These results are in disagreement with those of previous investigators (ref. 3). In addition to III and IV, the *trans*-alcohol IIa was shown to yield 4-phenylcyclohexene (V), 6%; 1-benzylcyclopentene (VI), 32%, and benzalcyclopentane (VII), approximately 20%. Phenyl migration was shown to occur during the formation of 1-phenylcyclohexene-1,2-C_1^{14} (IIIab) from the *trans*-alcohol IIa. The same mixture of olefins as was produced from the dehydration of the *trans*-alcohol IIa was obtained when labeled 3-phenylcyclohexene (IV) was subjected to the dehydration conditions. These results are discussed, in terms of a mechanism which is consistent with the foregoing observations.

Introduction and Preliminary Results

The dehydrations, with phosphoric acid, of *cis*- and of *trans*-2-phenylcyclohexanol (I and II, respectively) were reported in 1940 by Price and Karabinos.[3] The results of this study were interpreted as evidence for the *trans* elimination of the elements of water in such dehydrations, since the *cis*-alcohol was reported to yield chiefly 1-phenylcyclohexene (III) whereas the *trans*-alcohol was said to yield predominantly 3-phenylcyclohexene (IV).


I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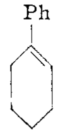
III


IV

It was suggested[3] that the small amount of isomeric olefin formed in each dehydration was the result either of (a) isomerization of the alcohols I $\rightleftarrows$ II before dehydration, or (b) competitive *cis* elimination of the elements of water from each carbinol.

The Chugaev reactions of the methyl xanthates, and the thermal decompositions of the acetates of I and II were next studied by Alexander and Mudrak,[4] who showed that in each of these reactions *cis* elimination occurred, for the results were the reverse of those reported for the phosphoric acid-catalyzed dehydrations of I and II. Thus, both the acetate and the methyl xanthate of the *cis*-alcohol I yielded primarily 3-phenylcyclohexene (IV), whereas the corresponding *trans* compound yielded principally 1-phenylcyclohexene (III).

The difficulties of determining the yields and identities of liquid, isomeric olefins are indicated by Alexander and Mudrak,[4] who measured the refractive indices of the redistilled products from each reaction for this purpose. These authors point out that the yields calculated by Price and Karabinos[3] are based upon an incorrect refractive index for 3-phenylcyclohexene, but state that the general conclusions[3] concerning the acid-catalyzed dehydrations of I and II remain valid.[5]

By the use of the carbon-14 dilution technique,[6] a method not available to Price and Karabinos[3] at the time of their experiments, it should be possible, by employing carbon-14 labeled reactants, to gain accurate information concerning the yields of olefins III and IV upon dehydration of *cis*-2-phenylcyclohexanol (Ia) and *trans*-2-phenylcyclohexanol (IIa). It should be possible also to determine whether the small amount of 1-phenylcyclohexene (IIIab) obtained upon dehydration of alcohol IIa is the consequence of *cis* elimination of the elements of water, or of participation of the phenyl group during removal of the hydroxyl ion. This latter possibility has been speculated upon by Cram.[5] Thus, in the dehydration of *trans*-2-

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[3] C. C. Price and J. V. Karabinos, THIS JOURNAL, **62**, 1159 (1940).

[4] E. R. Alexander and A. Mudrak, *ibid.*, **72**, 1810 (1950).

[5] See, however, D. J. Cram, *ibid.*, **74**, 2137 (1952), footnote 2.

[6] R. H. Mayor and C. J. Collins, *ibid.*, **73**, 471 (1951).