Hydrolysis of Trimethylmethoxysilane. Trimethylsilanol.—A mixture of 10 g. of trimethylmethoxysilane and 40 ml. of water was refluxed for two hours using acid-washed equipment as indicated above. After cooling, the organic layer was extracted with 50 ml. of ether and the resulting ether solution was dried over sodium sulfate and distilled. There was obtained the trimethylsilanol–hexamethyldisiloxane azeotrope as the sole product, b.p. 89–90°, $n^{20}\text{D}$ 1.3790 (reported b.p. 90°, $n^{20}\text{D}$ 1.3800).[7] This azeotrope contains 33 to 35% silanol. Several hydrolyses of trimethylmethoxysilane were carried out with water in quartz equipment, but in each case the same azeotrope was obtained. The use of a solvent such as dioxane or methanol to dissolve the methoxysilane prior to hydrolysis did not stop the condensation to hexamethyldisiloxane.

Hydrolysis of Methyltrimethoxysilane.—A mixture of 10 g. of methyltrimethoxysilane and 40 ml. of distilled water was refluxed using acid-washed equipment. The upper layer of alkoxysilane slowly went into solution. After 15 minutes of refluxing, the aqueous solution became cloudy and slowly an oil precipitated. A total of 20 minutes was needed to dissolve the upper organic layer but during the last 5 minutes approximately 1 cc. of heavy oil had settled to the bottom of the flask. The mixture was cooled and filtered to remove most of the oil. Although the filtrate was kept cold to minimize condensation, nevertheless, more oil slowly precipitated. The water-insoluble oil was soluble in methanol and insoluble in toluene. On heating the oil lost water to give a clear hard and brittle solid which was extremely thermally stable. The aqueous solution precipitated a gel either upon acidification with hydrochloric acid or basification with sodium hydroxide. The aqueous solution was evaporated *in vacuo* to leave a clear gel which was partially water soluble and completely methanol soluble. The evaporation of several drops of the methanol solution on a glass plate in an oven at 150° gave a brittle, crazed, clear residue. No crystalline solid was isolated from the water solution of the hydrolysis products which possibly included the monomeric trimethylsilanetriol but certainly included lower polymers therefrom. Several hydrolyses of methyltrimethoxysilane using quartz equipment failed to yield the monomeric trimethylsilanetriol.

Hydrolysis of Phenyltrimethoxysilane.—A mixture of 5 g. of phenyltrimethoxysilane and 50 ml. of distilled water was refluxed for about 0.5 hour in a quartz r.b. flask using a quartz water-cooled condenser. Most of the alkoxysilane dissolved and a milky solution was obtained. The solution was cooled immediately and filtered, but the filtrate, which at first was clear, slowly precipitated a viscous oil. This oil was both benzene and alcohol soluble. A benzene solution of the oil continually precipitated some solid indicating that further condensation was taking place. The benzene solution was evaporated to dryness to leave a sticky solid which was soluble in benzene and methanol. On heating this solid lost more water and gave a shiny, white, brittle, mica-like solid (a monophenylpolysiloxane, phenyl-T-polymer). On standing in air, the oil slowly dehydrated and became less soluble. On heating the oil, water was driven out and the same phenyl-T-polymer was obtained. This solid was insoluble in water, methanol or benzene, and was extremely thermally stable.

The aqueous solution obtained from the hydrolysis of phenyltrimethoxysilane was rapidly evaporated to dryness under vacuum. In this case a solid residue was obtained which was insoluble in water indicating that condensation occurred during the evaporation. However, this residue was soluble in benzene and in methanol. On heating the solid turned to a liquid with considerable loss in water and finally the brittle phenyl-T-polymer was obtained.

SCHENECTADY, N. Y.

[CONTRIBUTION FROM THE NOYES CHEMICAL LABORATORY, UNIVERSITY OF ILLINOIS]

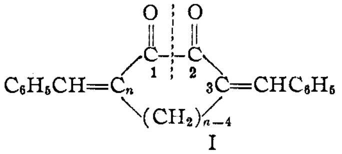
The Ultraviolet Absorption Spectra of Dibenzylidene-1,2-cycloalkanediones

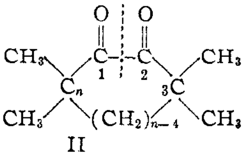
BY NELSON J. LEONARD AND GENE C. ROBINSON[1]

RECEIVED DECEMBER 15, 1952

A number of 3,*n*-dibenzylidene-1,2-cycloalkanediones (*n* = ring size = 7, 9, 10, 11) have been made and their ultraviolet absorption spectra have been determined, along with that of the open-chain analog, cinnamil. Although the cyclic system with varying ring size permits variation in the angle between the planes of the carbonyl groups, the absorption spectra of the cyclic molecules studied were found to be strikingly similar.

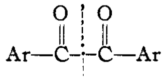
The present investigation represents a continuation of studies in this Laboratory[2-4] on the 1,2-dicarbonyl chromophore and constitutes the spectral examination of a series of 3,*n*-dibenzylidene-1,2-cycloalkanediones (I, *n* = size of ring). This particular system I was selected for synthesis and absorption spectrum determination because it provided the possibility of varying the angle between the planes of the carbonyl groups by varying the ring size, and thus of following the effect of such variation on the ultraviolet absorbing unit which consists effectively of coupled cinnamoyl groups.


I


II

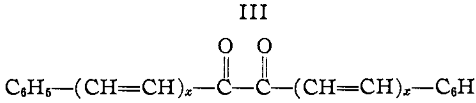
(a, *n* = 6; b, *n* = 7; c, *n* = 8; d, *n* = 9; e, *n* = 10; f, *n* = 11)

It has been shown previously, in a study of the 3,3,*n*,*n*-tetramethyl-1,2-cycloalkanediones II,[4] that the wave length of the dicarbonyl ultraviolet absorption maximum varies in a regular way with the angle between the planes of the carbonyl groups: the band moves toward shorter wave lengths as the intercarbonyl angle increases from 0° (*cis* coplanarity) to about 90° (insulation) and shifts back again toward longer wave lengths as the angle increases beyond 90°. It has also been shown, in studies of substituted benzils III, that the main contribution to the ultraviolet absorption results from the benzoyl groupings which constitute the halves of the molecule, wherein the phenyl and carbonyl groups are coplanar.[2] With increasing hindrance



$$\text{Ar}\text{—}\overset{\overset{\text{O}}{\|}}{\text{C}}\text{—}\overset{\overset{\text{O}}{\|}}{\text{C}}\text{—Ar}$$

III



$$C_6H_5\text{—}(CH{=}CH)_x\text{—}\overset{\overset{\text{O}}{\|}}{\text{C}}\text{—}\overset{\overset{\text{O}}{\|}}{\text{C}}\text{—}(CH{=}CH)_x\text{—}C_6H_5$$

IV

(a, *x* = 1; b, *x* = 2; c, *x* = 3; d, *x* = 4)

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[1] Monsanto Chemical Company Fellow, 1951–1952.

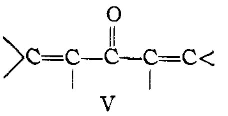
[2] N. J. Leonard, R. T. Rapala, H. L. Herzog and E. R. Blout, THIS JOURNAL, **71**, 2997 (1949).

[3] N. J. Leonard and E. R. Blout, *ibid.*, **72**, 484 (1950).

[4] N. J. Leonard and P. M. Mader, *ibid.*, **72**, 5388 (1950).

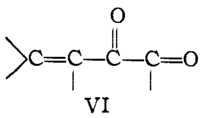
at the ortho carbons of benzil, there is decreasing tendency to coplanarity of the phenyl and carbonyl groups, and increasing tendency to coplanarity of the two carbonyl groups. The attendant spectral changes include a decrease in intensity of the phenyl–carbonyl absorption maximum and a shift to longer wave length of the dicarbonyl absorption band.[3] The type I presently under investigation represents an extended system, $C_6H_5CH{=}\underset{|}{C}{-}CO{-}CO{-}\underset{|}{C}{=}CHC_6H_5$, in which coplanarity relationships will be important in determining the position of the main absorption bands. The acyclic analog, cinnamil (IVa),[5] should exist largely in the completely *trans* coplanar configuration and has therefore been included in our study as a representative of one of the limiting arrangements of the cinnamoyl groups.

The 3,*n*-dibenzylidene-1,2-cycloalkanediones Ib,d,e,f were prepared by condensation of benzaldehyde with the appropriate 1,2-cycloalkanedione in ethanol solution in the presence of piperidine. The optimum temperature and time for the condensation had to be determined in each case. The reaction between benzaldehyde and 1,2-cyclohexanedione gave an anomalous product (see Experimental section) rather than the desired 3,6-dibenzylidene-1,2-cyclohexanedione (Ia), and compound Ic was not obtainable because of the lack of availability of pure 1,2-cycloöctanedione. For those 3,*n*-dibenzylidene-1,2-cycloalkanediones (Ib,d,e,f) synthesized, the ultraviolet absorption spectra are strikingly similar (Fig. 1). Shifts in the position and intensity of the main absorption are not large. The shortest wave length band, at 232–234 mμ, lies in the region ascribed to α,β- or β,β-disubstituted α,β-unsaturated ketones, namely, 232 ± 5 mμ (corrected to hexane as the solvent).[6] Thus, the excited structures which give rise to the absorption in this region are probably closely related to those which contribute to the absorption of a compound such as mesityl oxide (λ_{max} 229.5 mμ, log ε 4.1 in hexane).[7] The absorption at 260–266 mμ which first makes its appearance as an inflection point for the ten-membered ring compound Ie is a real maximum for the eleven-membered ring compound If and for cinnamil (IVa). This maximum appears to be due more to a decrease in the intensity of the absorption band at 301–306 mμ than to an increase in the intensity of the absorption at 260–266 mμ. Nevertheless, absorption in this region may be due to an excited state similar to that encountered in phorone (V) (λ_{max} 259 mμ, log ε 4.37 in hexane),[7] whereby the second carbonyl partially fulfills the function of the second olefinic linkage in phorone. For similar excitation to be probable, the second carbonyl should be capable of achieving coplanarity with the α,β-unsaturated carbonyl grouping. From a consideration of the Fisher–Taylor–Hirschfelder models, the inter-carbonyl angle in 3,9-dibenzylidene-1,2-cyclononanedione (Id) (no inflection point) can vary from 0 to 180°, but lies at 130° to allow most complete conjugation throughout the molecule with maximum separation of the carbonyl oxygens. By contrast, the inter-carbonyl angle in 3,10-dibenzylidene-1,2-cyclodecanedione (Ie) (inflection point at 266 mμ), which can vary between 0 and 180°, lies near 180° (*trans*) to allow most complete conjugation throughout this molecule. For 3,11-dibenzylidene-1,2-cyclohendecanedione (If) (maximum at 266 mμ), there are many favorable configurations for angles between 90 and 180°, and for cinnamil (IVa), the most favored inter-carbonyl angle is 180° (*trans*).



$$>C{=}\underset{|}{C}{-}\overset{\overset{O}{\|}}{C}{-}\underset{|}{C}{=}C<$$

V



$$>C{=}\underset{|}{C}{-}\overset{\overset{O}{\|}}{C}{-}\underset{|}{C}{=}O$$

VI

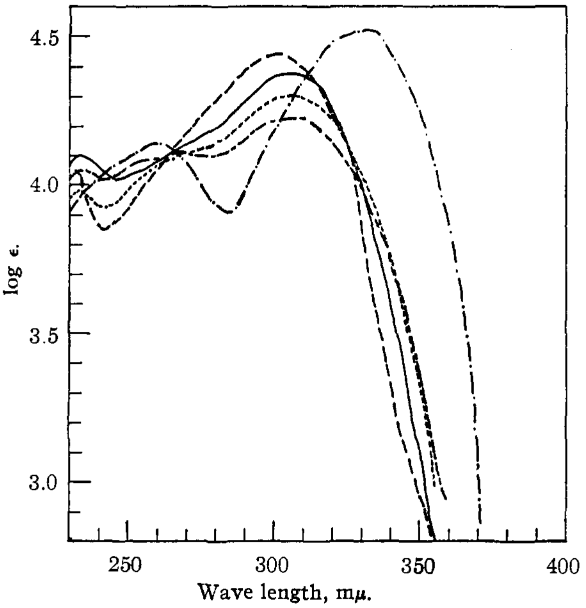


Fig. 1.—Ultraviolet absorption spectra: —, 3,7-dibenzylidene-1,2-cycloheptanedione; — — —, 3,9-dibenzylidene-1,2-cyclononanedione; - - - - - - -, 3,10-dibenzylidene-1,2-cyclodecanedione; —- - ——, 3,11-dibenzylidene-1,2-cyclohendecanedione; —·—·—, cinnamil (in cyclohexane).

Interpretation of the long wave length absorption maxima at 301–306 mμ for the cyclic compounds Ib,d,e,f is facilitated by comparison with the absorption of several model compounds. In the cyclic system, when the carbonyl group and the adjacent carbon–carbon double bond are coplanar, they have the *cis* configuration, as do the same groups in 2-benzylidenecyclohexanone. The maxima at 301–306 mμ (cyclohexane) are somewhat displaced from the maxima for 2-benzylidenecyclohexanone, 290 mμ (ethanol), but are in the range of intensity twice that observed for the latter (log 2ε 4.35),[8] so that some similarity between the absorbing unit in 2-benzylidenecyclohexanone and two such units in I is suggested. However, the fact that the excitation responsible for the absorption of I at

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(5) The spectra of the higher vinylogs in this series (IVb,c,d) have been determined by P. Karrer and Ch. Cochand (*Helv. Chim. Acta*, **28**, 1181 (1945)), who showed that the spectra were very different from those of the corresponding diphenylpolyenes possessing the same number of carbons. The "conjugate" influence of the dicarbonyl group was thereby found to be much less than that of an olefinic linkage in the chain.

(6) R. B. Woodward, THIS JOURNAL, **63**, 1123 (1941).

(7) G. Scheibe, G. Rössler and F. Backenköhler, *Ber.*, **58**, 536 (1925).

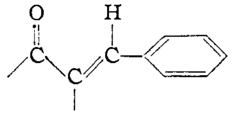
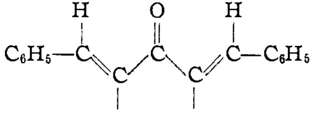
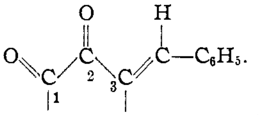
(8) H. S. French and L. Wiley, THIS JOURNAL, **71**, 3702 (1949).

TABLE I

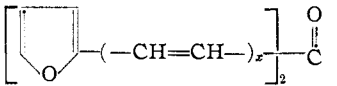
ULTRAVIOLET AND INFRARED ABSORPTION MAXIMA

Compound	Ultraviolet						Infrared frequency, cm.$^{-1}$	
	λ, mμ	log ε	λ, mμ	log ε	λ, mμ	log ε	Conj. C=O	Conj. C=C
3,7-Dibenzylidene-1,2-cycloheptanedione	306	4.38			233	4.10	1685	1602
3,9-Dibenzylidene-1,2-cyclononanedione	301	4.44			232	4.04	1666, 1671	1590
3,10-Dibenzylidene-1,2-cyclodecanedione	305	4.30	266[a]	4.10	233	3.98	1663	1602
3,11-Dibenzylidene-1,2-cyclohendecanedione	306	4.23	266	4.12	234	4.05	1669, 1677	1609
Cinnamil[9]	330	4.52	260	4.16	?		1667	1607
2,6-Dibenzylidenecyclohexanone[8]	319[b]	4.51			232	4.28	1663	1610
2,7-Dibenzylidenecycloheptanone[10]	290	4.50			226	4.23	1672	1612, 1623

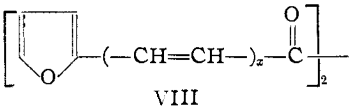
[a] Inflection point. [b] The λ_{max} 330, log ε 4.40 in ethanol.[8]

301–306 mμ is related to a more extended conjugated system than  alone is evidenced by a comparison with the long wave length ultraviolet absorption maxima of 2,6-dibenzylidenecyclohexanone (319 mμ) and 2,7-dibenzylidenecycloheptanone (290 mμ) (see Table I). In 2,6-dibenzylidenecyclohexanone, the chromophoric system,  $C_6H_5-\overset{H}{C}=\underset{|}{C}-\overset{O}{\overset{\|}{C}}-\underset{|}{C}=\overset{H}{C}-C_6H_5$ can be almost completely coplanar, according to Fisher–Taylor–Hirschfelder models, whereas the same system is prevented from attaining complete coplanarity in 2,7-dibenzylidenecycloheptanone. The absorption maxima at 301–306 mμ for the 3,*n*-dibenzylidene-1,2-cycloalkanediones would thus appear to result from excitations in the related chromophoric system,  $O=\underset{|1}{C}-\overset{O}{\overset{\|}{C}}_2-\underset{|}{C}^3=\overset{H}{C}-C_6H_5$.

The bathochromic shift of 16 mμ caused by the introduction of a second carbonyl group into the seven-membered ring (compare 2,7-dibenzylidenecycloheptanone and 3,7-dibenzylidene-1,2-cycloheptanedione in Table I) is in the range of that observed by Karrer, Cochand and Neuss[11] in a comparison of the spectra of the mono- and diketones of types VII and VIII (9,10 mμ). The bathochromic shift caused by the introduction of a second carbonyl into dibenzylidene-acetone (λ_{max} 330 mμ, log ε 4.54 in ethanol),[12] giving cinnamil (IVa) (λ_{max} 330 mμ, log ε 4.52 in cyclohexane) depends upon the correction to be applied in going from ethanol to hydrocarbon solvent and is probably in the range of 11–14 mμ.[13,14] The foregoing interpretation of the 3-benzylidene-1,2-diketone system as an extended chromophore compared with the cinnamoyl system is consistent with the consideration of Szmant and Basso[13] that chalcone is an extended chromophoric system as compared with benzylideneacetone.



VII



VIII

Experimental[15]

Absorption Spectra.—The infrared absorption spectra were determined in Nujol mull (Perkin-Elmer Infrared Spectrometer, Model 12B) and the ultraviolet absorption spectra (Cary Recording Spectrophotometer, Model 11) were determined in cyclohexane.

Dibenzylidenediketones.—**3,7-Dibenzylidene-1,2-cycloheptanedione** has been described previously.[16] **3,9-Dibenzylidene-1,2-cyclononanedione** was prepared similarly from 1,2-cyclononanedione[17] by condensation with benzaldehyde in ethanol in the presence of piperidine. The reflux time was 3 hours at steam-bath temperature. The product was obtained as fine yellow needles from ethanol, m.p. 109.5–110.5°, yield 17%.

Anal. Calcd. for $C_{23}H_{22}O_2$: C, 83.60; H, 6.71. Found: C, 83.69; H, 6.72.

3,10-Dibenzylidene-1,2-cyclodecanedione was obtained by allowing a solution of sebacil[17] (3 millimoles), benzaldehyde (12 millimoles), piperidine (3 drops) and ethanol (3 ml.) to stand at 30° for 2 days.[5] The product crystallized from ether as yellow needles, m.p. 139–140°, yield 71%.

Anal. Calcd. for $C_{24}H_{24}O_2$: C, 83.69; H, 7.02. Found: C, 83.92; H, 7.02.

2-Hydroxycyclohendecanone, obtained by the acyloin condensation[17] of diethyl hendecanedioate,[18] was oxidized to 1,2-cyclohendecanedione with chromium trioxide in acetic acid. The crude dione was converted to the dibenzylidene derivative by allowing a mixture with the usual reagents to stand at 30° for two weeks. The crude 3,11-dibenzylidene-1,2-cyclohendecanedione, which was obtained in 51% yield, was partially separated into two isomeric forms by fractional crystallization: yellow needles from ethanol, m.p. 129–136°; yellow prisms from ethyl acetate, m.p. *ca.* 150°.

Anal. Calcd. for $C_{25}H_{26}O_2$: C, 83.76; H, 7.31. Found: (m.p. 129–136°): C, 84.07; H, 7.03; (m.p. *ca.* 150°): C, 83.91; H, 7.47.

Reaction of Benzaldehyde with 1,2-Cyclohexanedione.—A solution of 1 g. (9 millimoles) of 1,2-cyclohexanedione, 2.3 g. (21 millimoles) of benzaldehyde and 4 drops of piperidine

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[9] N. A. Sarensen, E. Samuelsen and Fr. Oxaal, *Acta Chem. Scand.*, **1**, 458 (1947).

[10] R. Cornubert, R. Joly and A. Strébel, *Bull. soc. chim. France*, [5] **5**, 1501 (1938).

[11] P. Karrer, Ch. Cochand and N. Neuss, *Helv. Chim. Acta*, **29**, 1836 (1946); see also P. Karrer and N. Neuss, *ibid.*, **28**, 1185 (1945).

[12] E. A. Braude, *Ann. Rep. Chem. Soc.*, **42**, 105 (1945); compare D. Rădulescu, *Ber.*, **64**, 2243 (1931).

[13] H. H. Szmant and A. J. Basso, THIS JOURNAL, **74**, 4397 (1952).

[14] L. P. Kuhn, R. E. Lutz and C. R. Bauer, *ibid.*, **72**, 5058 (1950).

[15] All melting points are corrected. We are indebted to Miss Emily Davis, Mrs. Katherine Pih, Mrs. Esther Fett and Mr. Joseph Nemeth for microanalyses, and to Miss Helen Miklas, Miss Ella Richards and Mrs. Barbara Burnett for determination of the absorption spectra. We wish to thank Mr. James W. Berry for technical assistance.

[16] N. J. Leonard and G. C. Robinson, THIS JOURNAL, **75**, 2143 (1953).

[17] V. Prelog, L. Frenkiel, M. Kobelt and P. Barman, *Helv. Chim. Acta*, **30**, 1741 (1947).

[18] W. P. Hall and E. E. Reid, THIS JOURNAL, **65**, 1468 (1943).

in 2 ml. of 2-propanol deposited 0.67 g. of colorless solid after standing at 25° for 2 days. The supernatant deposited a further 0.35 g. of solid following the addition of 3 drops of piperidine and long standing. The solid crystallized from acetic acid as very fine colorless needles, m.p. 204–205°.

Anal. Calcd. for $C_{19}H_{22}O_5$: C, 69.07; H, 6.71; mol. wt., 330. Found: C, 68.92; H, 6.89; mol. wt. (Rast procedure in tribromophenol), 370 ± 50.

The structure of this product was not established, but it appears, according to analysis and molecular weight, to be constituted from two molecules of 1,2-cyclohexanedione and one of benzaldehyde. The infrared absorption spectrum, determined on a Nujol mull, exhibited maxima at 1654 (conjugated C=O), 1629 (conjugated C=C), and at 3470, 3369 and 3327 cm.$^{-1}$ (all O–H). The product was insoluble in most organic solvents, appeared to add bromine reversibly, and was rapidly oxidized by potassium permanganate in acetone. Attempts to dehydrate the compound by iodine treatment were unsuccessful. We prefer not to suggest a structure for this substance at the present time of writing since several formulations are still possible with the information on hand.

4,4-Dimethyl-1,2-cyclohexanedionedioxime.—This compound was obtained from 4,4-dimethylcyclohexanone[19] by selenium dioxide oxidation followed by oximation,[20] colorless microcrystals from water, m.p. 162–170°.

Anal. Calcd. for $C_8H_{14}N_2O_2$: C, 56.45; H, 8.29; N, 16.46. Found: C, 56.50; H, 8.62; N, 16.29.

1,2-Cycloöctadecanedione-bis-2,4-dinitrophenylhydrazone.—Treatment of 2-hydroxycycloöctadecanone[21] with 2,4-dinitrophenylhydrazine in the usual manner formed the osazone, orange needles from methyl ethyl ketone, m.p. 231–232°.

Anal. Calcd. for $C_{30}H_{40}N_8O_8$: C, 56.24; H, 6.29; N, 17.49. Found: C, 56.50; H, 6.36; N, 17.52.

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[19] R. F. Miller and R. Adams, This Journal, **58**, 787 (1936).

[20] C. C. Hack, C. V. Banks and H. Diehl, *Org. Syntheses*, **32**, 35 (1952).

[21] M. Stoll and J. Hulstkamp, *Helv. Chim. Acta*, **30**, 1815 (1947).

URBANA, ILLINOIS

[CONTRIBUTION FROM THE U. S. DEPARTMENT OF THE INTERIOR, BUREAU OF MINES, SYNTHETIC FUELS RESEARCH BRANCH]

The Chemistry of Metal Carbonyls. II. Preparation and Properties of Cobalt Hydrocarbonyl[1]

BY HEINZ W. STERNBERG, IRVING WENDER, ROBERT A. FRIEDEL AND MILTON ORCHIN

RECEIVED DECEMBER 6, 1952

A rapid and simple method is described for preparing cobalt hydrocarbonyl from dicobalt octacarbonyl. Kinetic data indicate that the decomposition of cobalt hydrocarbonyl is a second-order reaction, and that k is approximately 3×10^{-3} (mole/liter)$^{-1}$ second^{-1}. In aqueous solution cobalt hydrocarbonyl is stable, completely dissociated, and sparingly soluble. Infrared spectra of cobalt hydrocarbonyl, cobalt deuterocarbonyl and dicobalt octacarbonyl are presented. No –OH band could be detected in the infrared spectrum of cobalt hydrocarbonyl at the concentrations studied.

Although cobalt hydrocarbonyl was first isolated[2] in 1936, comparatively little is known concerning its properties. The development in this Laboratory of a convenient method of preparation provided an opportunity to study some of the properties of this unusual compound.

Preparation of Cobalt Hydrocarbonyl.—Dicobalt octacarbonyl, on treatment with pyridine,[1] disproportionates according to equation (1)

$$12C_5H_5N + 3[Co(CO)_4]_2 \longrightarrow 2[Co(C_5H_5N)_6]^{++}[Co(CO)_4]_2^{-} + 8CO \quad (1)$$

It has now been found that dropwise addition to excess dilute sulfuric acid of the pyridine solution containing the salt produces the free hydrocarbonyl, which can be swept out of the reaction mixture in a current of carbon monoxide. Condensation after passage through a phosphorus pentoxide drying tube gives pure hydrocarbonyl in a yield of 95%.[3]

Stability of Cobalt Hydrocarbonyl.—Although cobalt hydrocarbonyl decomposes[5] rapidly as a liquid above its melting point (−26°) according to equation (2a)

$$2HCo(CO)_4 \longrightarrow H_2 + [Co(CO)_4]_2 \quad (2a)$$

$$2[Co(CO)_4]_2 \rightleftarrows [Co(CO)_3]_4 + 4CO \quad (2b)$$

it is fairly stable in the gas phase. Hieber[5] studied the decomposition in a closed vessel and emphasized that the last traces of cobalt hydrocarbonyl decomposed very slowly. Also it has been previously reported and amply verified that cobalt hydrocarbonyl can be carried through an absorption train in a current of carbon monoxide[4] without noticeable decomposition. These facts implied and previous workers have assumed[6] that the presence of hydrogen and/or carbon monoxide somehow stabilized the hydrocarbonyl. While carbon monoxide stabilizes dicobalt octacarbonyl (equation 2b) it can effect a stabilization of the hydrocarbonyl only if equation (2a) is reversible. If indeed this were the case, it would be necessary for the reverse reaction of equation (2a) to occur at a finite rate. Experimental data bearing on this point were secured as follows: To a gas mixture containing equimolar (volume) quantities of hydrogen, deuterium and carbon monoxide at room temperature was added 1 volume per cent. of gaseous cobalt hydrocarbonyl. If equation (2a) were reversed under these conditions, the formation of some deuterocarbonyl would be expected according to equation (3)

$$D_2 + [Co(CO)_4]_2 \longrightarrow 2DCo(CO)_4 \quad (3)$$

The decomposition of the deuterocarbonyl on collision with the hydrocarbonyl should provide HD according to equation (4)

$$HCo(CO)_4 + DCo(CO)_4 \longrightarrow HD + [Co(CO)_4]_2 \quad (4)$$

The gas mixture was allowed to stand four days at

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[1] I. Wender, H. W. Sternberg and M. Orchin, This Journal, **74**, 1216 (1952); paper I in this series.

[2] G. W. Coleman and A. A. Blanchard, *ibid.*, **58**, 2160 (1936).

[3] If dicobalt octacarbonyl is available this method of preparation of cobalt hydrocarbonyl is to be preferred to previous methods.[4,5]

[4] A. A. Blanchard and P. Gilmont, This Journal, **62**, 1192 (1940).

[5] W. Hieber and H. Schulten, *Z. anorg. allgem. Chem.*, **232**, 29 (1937).

[6] P. Gilmont and A. A. Blanchard, "Inorganic Syntheses," Vol. II, McGraw-Hill Book Co., Inc., New York, N. Y., 1946, p. 242.