The polyiodide ions mentioned here have been encountered by previous investigators in both inorganic and organic solids. Thus, for example, compounds represented by the formulas $KI_3 \cdot H_2O$, RbI_3, $KI_7 \cdot H_2O$ and $KI_9 \cdot 3C_6H_6$ have been isolated.[18] In addition, organic compounds containing the triiodide, heptaiodide or enneaiodide ion have also been mentioned in the literature. As examples of these we have the compounds $(CH_3)_4NI_3$,[19] $(C_2H_5)_4PI_3$,[20] $(C_2H_5)R_4NI_7$[19a] and $(CH_3)_4NI_9$.[19,21]

The results of a detailed study of the effect of various reaction conditions on the yields of products obtained in the reaction of cyclohexyl diphenyl phosphite with iodine may be summarized as follows: (1) The reaction is quite rapid even at 0° and is substantially complete in a few hours at this temperature. (2) The most important factors which influence the yield of cyclohexyl iodide are the solvent and the age of the phosphite ester. Yields are reduced when ether is used as a solvent or ester is used which has been allowed to stand for several weeks after its preparation. The poor yields obtained with ether as the solvent appear to be due to the separation from solution of cyclohexyl diphenyl phosphite polyiodides. (3) The order of mixing of the reactants, the use of reflux temperatures in carrying out the reaction, and the presence of as much as 50 mole per cent. anhydrous potassium carbonate in the reaction mixture are factors which have little effect on the yield of cyclohexyl iodide. Operation at elevated temperatures, however, either in the presence or absence of anhydrous potassium carbonate, does bring about destruction of diphenyl iodophosphate.

It is not understood at present why the reaction of 1,2:5,6-diisopropylidene-D-glucose 3-diphenylphosphite with iodine does not always follow the same course as the reaction of the corresponding cyclohexyl ester. A study of Fisher-Hirschfelder models indicates, however, that steric hindrance may be one factor which plays an important role in the former case. Some further evidence for this supposition is the fact that the carbohydrate phosphite rapidly decolorizes chlorine or bromine.

Acknowledgment.—This research was supported in part by the United States Atomic Energy Commission. Further, we wish to thank Mr. William L. Parr and Mr. James A. Warnhoff for the microanalyses.

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tetramethylammonium triiodide in ethylene chloride. It should be noted that in anhydrous acetonitrile there also was no detectable amount of free iodine present in equilibrium with the triiodide.

[18] For a discussion of the chemistry of polyhalides see N. V. Sidgwick, ref. 16, pp. 1190-1201.

[19] (a) A. Geuther, *Ann.*, **240**, 66 (1887); (b) R. E. Buckles, J. P. Yuk and A. I. Popov, THIS JOURNAL, **74**, 4379 (1952).

[20] S. M. Jorgensen, *J. prakt. Chem.*, [2] **3**, 334 (1871).

[21] F. D. Chattaway and G. Hoyle, *J. Chem. Soc.*, 654 (1923).

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

The Chemistry of Metal Carbonyls. III. The Reaction between Dicobalt Octacarbonyl and Dimethylamine[1]

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

RECEIVED FEBRUARY 9, 1953

Lewis bases react with dicobalt octacarbonyl under mild conditions according to the equation $12B + 3[Co(CO)_4]_2 \rightarrow 2[Co(B)_6][Co(CO)_4]_2 + 8CO$. When B is dimethylamine this homomolecular disproportionation occurs similarly, except that the carbon monoxide usually liberated appears as dimethylformamide. This transfer of carbon monoxide, which proceeds at 0° and atmospheric pressure, is probably achieved by means of an intermediate complex between the carbonyl group of the metal carbonyl and the NH-group of dimethylamine. At 220° and an initial carbon monoxide pressure of 200 atmospheres, dimethylamine and piperidine were readily carbonylated to the corresponding formamides in the presence of catalytic amounts of dicobalt octacarbonyl.

In a previous paper[2] it was shown that many apparently unrelated reactions involving the attack of a variety of reagents on dicobalt octacarbonyl could be generalized by viewing these reactions as examples of a homomolecular disproportionation induced by Lewis bases

$$3[Co(CO)_4]_2 + 12B \longrightarrow 2[Co(B)_6][Co(CO)_4]_2 + 8CO \quad (1)$$

where B is water, methanol, ethanol, ammonia, pyridine or *o*-phenanthroline. It has now been found that no carbon monoxide is evolved when excess dimethylamine is condensed onto cobalt octacarbonyl at −80° and the mixture allowed to warm to room temperature. Analysis of the reaction product showed that two moles of cobalt carbonyl anion was formed per mole of cobalt(II) ion, as required by equation 1, and that dimethylformamide was present along with small amounts of tetramethylurea. Evidently the carbon monoxide usually given off as gas (equation 1) reacted with dimethylamine to yield dimethylformamide as the principal reaction product according to equation 2

$$3[Co(CO)_4]_2 + 20(CH_3)_2NH \longrightarrow 2[Co[(CH_3)_2NH]_6][Co(CO)_4]_2 + 8HCON(CH_3)_2 \quad (2)$$

As no carbon monoxide was evolved in this reaction and as dimethylamine is a gas at room temperature, it was possible, by weighing the reaction product, to determine the amount of dimethylamine absorbed per mole of dicobalt octacarbonyl. By this method it was found that instead of 20 moles of dimethylamine (equation 2), 24 moles of dimethylamine was absorbed or 8 moles per mole of dicobalt octacarbonyl. As will be shown later, this excess

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[1] Presented before the Organic Division at the 121st meeting of the American Chemical Society, March 24-27, 1952, Buffalo, N. Y.

[2] I. Wender, H. W. Sternberg and M. Orchin, THIS JOURNAL, **74**, 1216 (1952).

amount of dimethylamine appeared in the product because of complex formation between the carbonyl groups of cobalt carbonyl anion and dimethylamine. Based on these results the reaction between dicobalt octacarbonyl and dimethylamine may now be represented by equation 3.[3] In equation 3 the

$$3[\mathrm{Co(CO)_4}]_2 + 24(\mathrm{CH_3})_2\mathrm{NH} \longrightarrow 2[\mathrm{Co}[(\mathrm{CH_3})_2\mathrm{NH}]_6][\mathrm{Co(CO)_4}]_2 + 8\mathrm{HCON(CH_3)_2} + 4(\mathrm{CH_3})_2\mathrm{NH}\ (\text{complexed}) \quad (3)$$

cation is shown coördinated only with dimethylamine; it is conceivable, however, that the cobalt cation is also coördinated with dimethylformamide. That dimethylformamide is capable of coördinating with cobalt(II) ion was shown by an experiment in which dicobalt octacarbonyl was treated with this compound. The amount of carbon monoxide evolved and the amount of anion formed were consistent with equation 1 where B is dimethylformamide.

According to equation 3, stoichiometric amounts of dicobalt octacarbonyl are needed to furnish the carbon monoxide required for the conversion of dimethylamine to dimethylformamide. However, if it were possible to reverse equation 1 by employing a high partial pressure of carbon monoxide, dicobalt octacarbonyl might function as a transfer agent for carbon monoxide, and only catalytic quantities of the carbonyl might be required. This possibility was realized when the carbonylation of dimethylamine was achieved as follows: dimethylamine was treated with one mole per cent. of dicobalt octacarbonyl in the presence of 200 atm. (initial pressure) of carbon monoxide at 200–220°. Dimethylformamide was obtained smoothly and without side products in 60% yield. Mass spectrometric analysis of the reaction product showed no dimethylamine and no tetramethylurea. The yield of 60% represents a minimum yield because of probable losses of dimethylamine during the sealing and flushing of the bomb. In an extension of the reaction, the experiment was repeated with piperidine in place of dimethylamine; the yield of N-formylpiperidine was 78% of the theoretical.

Mechanism of the Reaction.—When excess dimethylamine is condensed onto dicobalt octacarbonyl at atmospheric pressure and −80° and the mixture allowed to warm to room temperature, the original dark, brown-black solution slowly changes to light greenish-yellow and finally to dark red as, the excess amine evaporates. These two color changes correspond to two steps of the reaction. The dark brown color at the start of the reaction is due to the intense color which dicobalt octacarbonyl imparts to its solutions. The light greenish-yellow color which appears as the solution approaches the boiling point of dimethylamine (7.4°) is caused by formation of the salt I according to equation 4[4]

$$[\mathrm{Co(CO)_4}]_2 + (\mathrm{CH_3})_2\mathrm{NH} \longrightarrow \underset{\mathrm{I}}{[(\mathrm{CH_3})_2\mathrm{NHCo(CO)_4}]^+[\mathrm{Co(CO)_4}]^-} \quad (4)$$

To show that a salt such as I is formed in the presence of excess dimethylamine, dicobalt octacarbonyl was allowed to react with an excess of a saturated solution of dimethylamine in toluene. Analysis of the reaction product showed that half of the amount of dicobalt octacarbonyl was present as cobalt carbonyl anion, $[\mathrm{Co(CO)_4}]^-$. The change from the initial color to the characteristic dark red of the final product is due to formation of a salt of the type $[\mathrm{Co(B)_6}][\mathrm{Co(CO)_4}]_2$, where B is a base.

The fact that all the carbon monoxide available from the decomposition of dicobalt octacarbonyl according to equation 1 was consumed in the formation of dimethylformamide suggests that the transfer of carbon monoxide from the carbonyl to the dimethylamine is achieved by means of an intermediate complex and that free carbon monoxide is never available as such.

That the carbonyl group in metal carbonyls forms complexes involving hydrogen bonds was demonstrated by preparation of a complex between dimethylamine and iron pentacarbonyl. This complex, containing 4 to 5 moles of dimethylamine per mole of iron pentacarbonyl, is stable at room temperature. Its infrared spectrum (Fig. 1) is radically different from the spectra of the individual

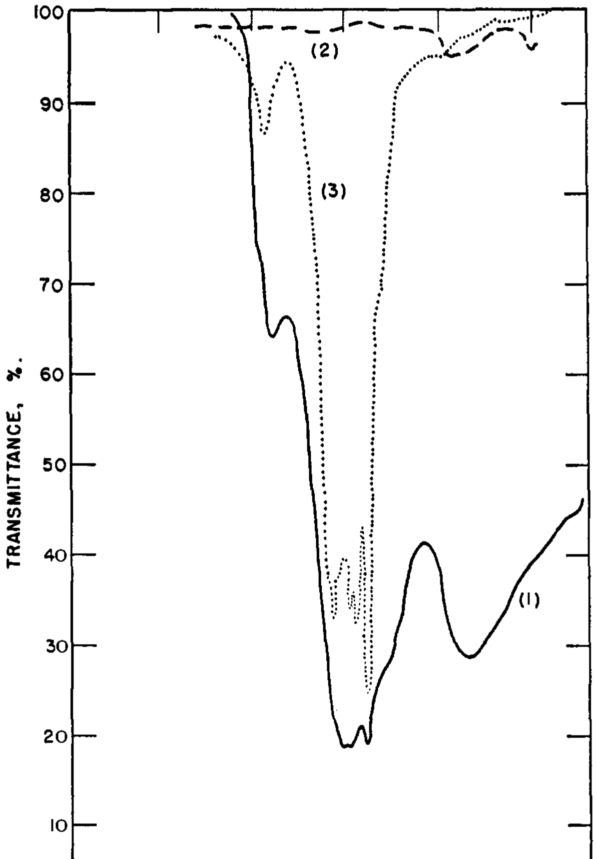

Fig. 1.—Infrared spectra illustrating complex formation: (1) —, iron pentacarbonyl-dimethylamine complex; (2) -----, iron pentacarbonyl; (3).........., dimethylamine (saturated $\mathrm{CCl_4}$ solution) (see Experimental).

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[3] The amount of tetramethylurea is too small to account for the weight of the reaction product above that postulated in equation 2.

[4] The formation of an analogous salt in the presence of excess piperidine has been shown previously.[5]

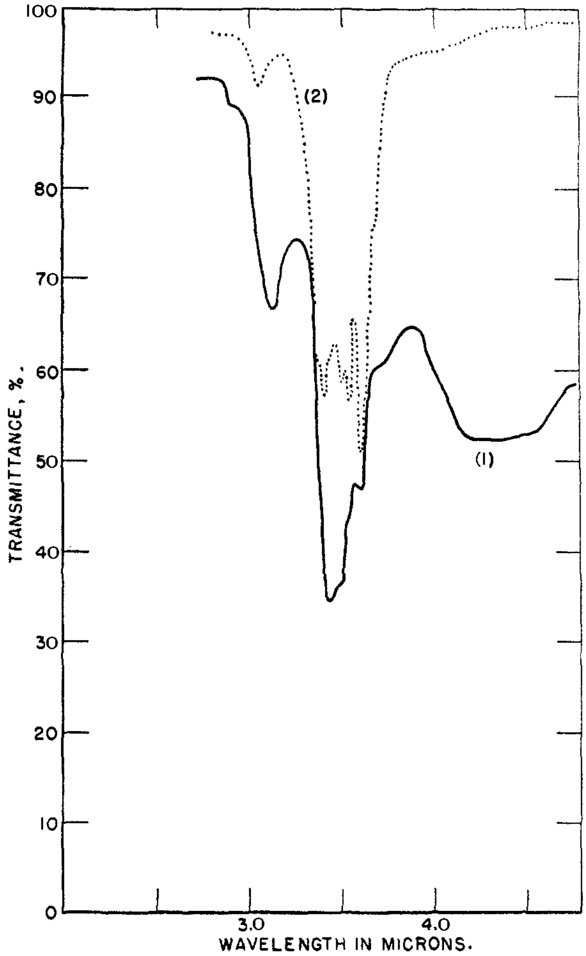


Fig. 2.—Infrared spectra illustrating complex formation: (1) —, reaction product obtained according to equation 2; (2) ...., dimethylamine (saturated CCl_4 solution) (see Experimental).

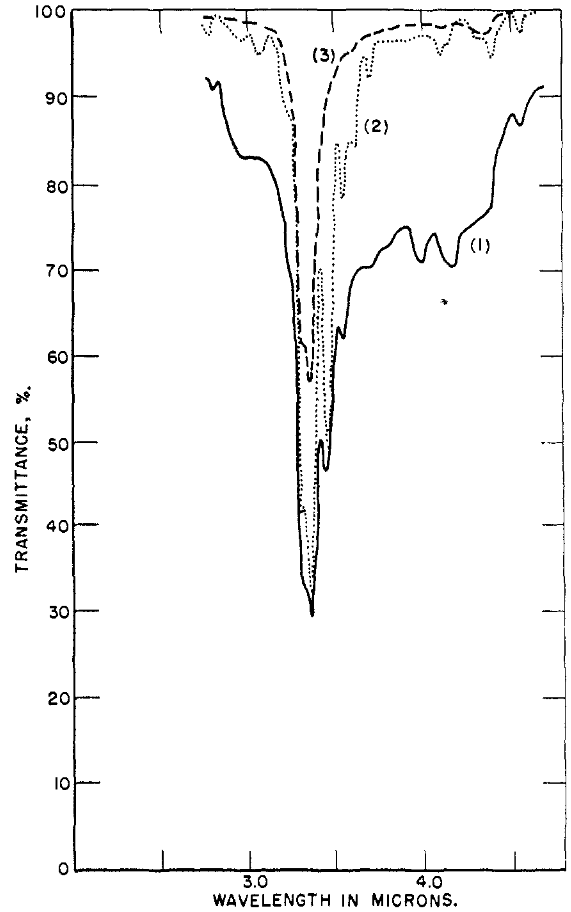
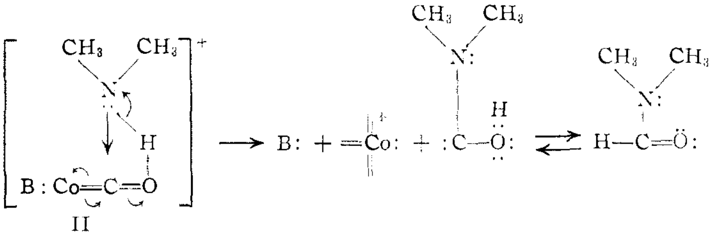


Fig. 3.—Infrared spectra illustrating complex formation: (1) —, $[Co(Pyr)_6][Co(CO)_4]_2$-piperidine complex in pyridine solution; (2) ......, solution of piperidine in pyridine in same molar ratio as in curve (1); (3) - - - - - - - -, $[Co(Pyr)_6][Co(CO)_4]_2$ in pyridine solution (see Experimental).

components, indicating hydrogen bonding and perhaps other bonds. Figure 2 shows the spectrum of the reaction product obtained according to equation 3 and Fig. 3 the spectrum of a pyridine solution containing one mole of piperidine per mole of $[Co(Pyr)_6][Co(CO)_4]_2$. These spectra indicate that complex formation takes place between the carbonyl groups of cobalt carbonyl anion $[Co(CO)_4]^-$ and the -NH group of dimethylamine (Fig. 2) and piperidine (Fig. 3), respectively. The excess dimethylamine in the reaction product, therefore, (equation 3) can probably be attributed to coördination through complex formation.

It is reasonable to assume that complex formation also occurs between dimethylamine and the cation $[(CH_3)_2NHCo(CO)_4]^+$ (equation 4). Thus, it seems likely that in the light greenish-yellow solution of I (equation 4) in excess dimethylamine, all carbonyl groups are complexed with dimethylamine. The fact that carbon monoxide is not liberated as such but appears in dimethylformamide may be due to a mechanism such as the following where II is the cation $[BCo(CO)_4]^+$ complexed with dimethylamine (only one carbonyl-amine complex shown) and B is dimethylamine



II

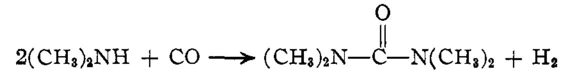
On warming to room temperature and evaporation of the excess dimethylamine, the less stable[1] cation complex II disproportionates to cobalt(II) ion, dimethylformamide, and cobalt carbonyl anion. This decomposition may be represented by equation 5 where B is dimethylamine and where, for the purpose of simplification, the complexed amine has been omitted.

$$2[BCo(CO)_4]^+ \longrightarrow 2B + 2Co^{++} + 8CO + 2e^- \quad (5a)$$

$$[BCo(CO)_4]^+ + 2e^- \longrightarrow B + [Co(CO)_4]^- \quad (5b)$$

$$3[BCo(CO)_4]^+ \longrightarrow 3B + 2Co^{++} + [Co(CO)_4]^- + 8CO \text{ (as } HCON(CH_3)_2) \quad (5)$$

The formation of tetramethylurea from dimethylamine and dicobalt octacarbonyl must arise from some type of over-all dehydrogenation.



$$2(CH_3)_2NH + CO \longrightarrow (CH_3)_2N{-}\overset{\overset{\large O}{\|}}{C}{-}N(CH_3)_2 + H_2$$

Such dehydrogenations have been shown to occur in the presence of dicobalt octacarbonyl,[5] probably by the formation and decomposition of cobalt hydrocarbonyl, $HCo(CO)_4$. Whether the same mechanism is applicable here cannot be determined from the present work; this problem is now under investigation.

Experimental

Reaction of Dicobalt Octacarbonyl with Dimethylamine at Atmospheric Pressure and Temperature.—Dry dimethylamine was prepared by dropping an aqueous solution containing about 50% of the hydrochloric acid salt (Eastman Kodak Co.) on excess NaOH. The gas was swept with nitrogen through two drying towers (filled with soda lime) into a flask provided with an inlet and outlet tube. The outlet tube was closed by a mercury valve. The flask contained a weighed amount of dicobalt octacarbonyl and was immersed in a Dry Ice bath. After an excess of amine had been condensed in the flask the inlet tube was closed, the bath removed and the amine allowed to evaporate until no more gas was given off at room temperature.

In a tared flask 1.57 g. of dicobalt octacarbonyl (4.59 millimoles) was treated with excess amine as described above. After removal of the Dry Ice bath, the inlet tube was closed and the outlet tube connected to a gas buret filled with aqueous 10% sulfuric acid. A mass spectrometric analysis of the gas not absorbed by the acid solution showed that it consisted of nitrogen and 10 ml. (N.T.P.) of carbon monoxide. If all of the carbon monoxide contained in the dicobalt octacarbonyl had been liberated 823 ml. (N.T.P.) would have been evolved. After no more gas was given off at room temperature, the flask was stoppered and weighed. The increase in weight was 1.75 g. corresponding to 39 millimoles of dimethylamine. Thus, 8.5 millimoles of dimethylamine had been adsorbed per mole of dicobalt octacarbonyl. Mass spectrometric analysis of the reaction product indicated the presence of dimethylamine, dimethylformamide and tetramethylurea, the last-named compound being present in an amount corresponding to about 10% of the amount of dimethylformamide present. The reaction product gave the spectrum shown in Fig. 2. A micro-distillation of a few drops of the reaction product at atmospheric pressure and a bath temperature of 150–200° gave a distillate which contained 33.5% dimethylformamide, 3.5% tetramethylurea and appreciable percentages of dimethylamine and water, as determined by mass spectrometric analysis.

In a second experiment the amount of cobalt carbonyl anion was determined with nickel *o*-phenanthroline chloride solution by a method described previously.[6] Dicobalt octacarbonyl (0.833 g., 2.43 millimoles) treated with excess dimethylamine as described above gave 0.533 g. (3.11 millimoles) of cobalt carbonyl anion, *i.e.*, 1.28 moles of anion per mole of dicobalt octacarbonyl. This result is in good agreement with equation 3 which requires the formation of 1.33 moles of anion per mole of dicobalt octacarbonyl.

Reaction of Dicobalt Octacarbonyl with Dimethylamine at 200 Atm. of Carbon Monoxide and 200–220°.—An ice-cooled solution of benzene (115 ml.) saturated with dimethylamine and containing 15.5 g. of dimethylamine (345 millimoles) was poured into an ice-cooled bomb, and 10 ml. of benzene containing 1.26 g. (3.7 millimoles) of dicobalt octacarbonyl was added. The bomb was flushed three times with nitrogen before being pressured to 200 atm. with carbon monoxide. The sealing and flushing operation took four minutes, during which time some dimethylamine may have escaped. The yield given below thus represents a minimum figure. The reaction took place at 200–210°, as judged by the pressure drop. The reaction product was a clear-yellow liquid which contained no dimethylamine and no tetramethylurea, as determined by mass spectrometric analysis. The bulk of the benzene was distilled and the residue fractionated from a small Claisen flask. The boiling ranges, yields and compositions of the fractions as determined by mass spectrometric analysis are given below.

Fraction	Temp., °C.	Yield, g.	Composition, g. Dimethylformamide	Composition, g. Benzene
I	60–84	84.0	0.84	83.16
II	84–146	14.7	3.81	10.89
III	146–154	10.3	10.28	0.02
			14.93	

The total amount of dimethylformamide in the reaction products (14.93 g., 205 millimoles) represents a 59.4% yield based on dimethylamine.

Reaction of Dicobalt Octacarbonyl with Piperidine at 200 Atm. and 200–220°.—A solution of piperidine (1 mole) and 30 ml. of benzene containing 5.1 g. (0.015 mole) of dicobalt octacarbonyl was subjected to 200 atm. of carbon monoxide pressure, heated to 220° and kept at this temperature for four hours. After cooling, the autoclave was opened and the products were removed. Benzene was evaporated from the reaction product at 40° and 20 mm. The residue was distilled to dryness at 20 mm. Redistillation yielded 88 g. of a constant-boiling (70° at 5 mm.) distillate, which was identified as N-formylpiperidine by its complex with mercuric chloride.[7] The yield of constant-boiling distillate was 88 g. or 78%.

Reaction of Dicobalt Octacarbonyl with Dimethylformamide.—Treatment of dicobalt octacarbonyl (0.8160 g., 2.39 millimoles) with 20 ml. of dimethylformamide in an apparatus described previously[8] evolved 135.5 ml. (6.05 millimoles) of carbon monoxide, *i.e.*, 2.52 millimoles of carbon monoxide per mole of dicobalt octacarbonyl. Analysis of the reaction product by a gasometric procedure[6] showed that it contained 0.526 g. (3.08 millimoles) of cobalt carbonyl anion, *i.e.*, 1.29 moles of anion per mole of dicobalt octacarbonyl. These data are consistent with equation 1 (where B is dimethylformamide), which requires liberation of 2.66 moles of carbon monoxide and formation of 1.33 moles of anion per mole of dicobalt octacarbonyl.

Reaction of Dicobalt Octacarbonyl with Excess Dimethylamine in Toluene Solution.—The reaction vessel consisted of a 300-ml. erlenmeyer flask provided with a magnetic stirrer, a stopper fitted with a dropping funnel and an outlet tube dipping in a mercury pool to prevent access of air. Ten ml. of toluene containing 0.5981 g. (1.75 millimoles) of dicobalt octacarbonyl was placed in the erlenmeyer flask, the stopper inserted, and nitrogen passed through the dropping funnel to displace the air in the flask. The flask was placed in a Dry Ice bath and 12 ml. of toluene containing 1.28 g. (28 millimoles) of dimethylamine added. The Dry Ice bath was removed and the liquid stirred while warming to room temperature. The solution turned light yellow, and a brownish-yellow oil separated. Twenty ml. of water placed in the separatory funnel and forced into the flask under pressure of nitrogen readily dissolved the oil. Fifty ml. of aqueous nickel *o*-phenanthroline chloride was added[6b] to precipitate the anion $[Co(CO)_4]^-$ as $[Ni(o\text{-}Phthr)_3][Co(CO)_4]_2$. The precipitate was filtered, washed with benzene and water and the amount of carbon monoxide determined.[6] The amount of carbon monoxide corresponded to 0.276 g. (0.807 millimole) of dicobalt octacarbonyl or 46% of the amount of original dicobalt octacarbonyl.

Reaction of Iron Pentacarbonyl with Dimethylamine.—Iron pentacarbonyl (4.25 g., 22 millimoles) was treated with excess dimethylamine at −80° and the excess amine evaporated as described for dicobalt octacarbonyl. The weight increase was 4.35 g. (97 millimoles), *i.e.*, 4.4 moles of amine per mole of iron pentacarbonyl. Figure 1 shows the infrared spectum of the reaction product.

Infrared Spectra.—The spectra were determined in a Perkin-Elmer Model 21 spectrophotometer. All samples containing metal carbonyls were placed in demountable

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[5] (a) G. Natta, P. Pino and R. Ercoli, THIS JOURNAL, **74**, 4496 (1952); (b) I. Wender, H. Greenfield, S. Metlin and M. Orchin, *ibid.*, **74**, 4079 (1952).

[6] H. W. Sternberg, I. Wender and M. Orchin, *Anal. Chem.*, **24**, 174 (1952).

[7] M. W. Farlow and H. Adkins, THIS JOURNAL, **57**, 2222 (1935).

[8] I. Wender, H. W. Sternberg and M. Orchin, *ibid.*, **74**, 1216 (1952).

rock-salt cells because of the formation of insoluble reaction products.

Figures 1 and 2.—The carbon tetrachloride solution saturated with dimethylamine contained approximately 10% by weight of dimethylamine.

Figure 3.—Three ml. of pyridine was added to 3.0 millimoles (1.03 g.) of dicobalt octacarbonyl, care being taken to prevent access of air to the reaction mixture. To the reaction mixture, which according to equation 1, contained 2 millimoles of $[Co(Pyr)_6][Co(CO)_4]_2$ there was added two millimoles (0.17 g.) of piperidine.

The solution of piperidine in pyridine was prepared by adding two millimoles of piperidine to 3 ml. of pyridine.

The solution of $[Co(Pyr)_6][Co(CO)_4]_2$ in pyridine was prepared by adding 3 ml. of pyridine to 3 millimoles (1.03 g.) of dicobalt octacarbonyl as described above.

Bruceton, Pa.

[Contribution from the Department of Chemistry, Purdue University]

The Preparation and Reactions of Fluorine-containing Acetoacetic Esters

By E. T. McBee, O. R. Pierce, H. W. Kilbourne[1] and E. R. Wilson[1]

Received November 14, 1952

New fluorine-containing acetoacetic esters were prepared by the Claisen reaction of fluorine-containing acetate esters using sodium hydride as the condensing agent. The acetoacetic esters were found to decarboxylate in the presence of aqueous sulfuric acid to form the corresponding fluorine-containing acetones. Both the esters and ketones demonstrated a strong tendency to form addition complexes which are decomposed with difficulty.

Only two fluorine-containing acetoacetic esters have been reported previously. Ethyl γ,γ,γ-trifluoroacetoacetate[2,3] and ethyl γ,γ-difluoroacetoacetate[3,4] were prepared by a Claisen condensation of ethyl acetate with ethyl trifluoroacetate or ethyl difluoroacetate, respectively, using sodium ethoxide as the condensing agent. When this method was extended to the self-condensation of ethyl difluoroacetate, no acetoacetic ester was obtained.[5]

In this Laboratory, it was found that a Claisen condensation could be effected between fluorine-containing acetate esters by using sodium hydride as the condensing agent at reaction temperatures in the range of 30–70° and a comparatively short reaction time of 6–8 hours. The fluorine-containing acetoacetic esters were obtained in 75–85% yield with the exception of the pentafluoroacetoacetic ester which was formed in 65% yield. In the latter case, it was necessary to employ a reaction time of 24 hours and a higher reaction temperature (90°) which was achieved by using butyl rather than the ethyl esters. The effectiveness of sodium hydride in these reactions may be attributed, primarily, to the irreversibility of the first step of the Claisen reaction, that of conversion of the ester to a carbanion and that a stronger base is generally effective in ion formation.[5–7]

An important observation is that only one acetoacetic ester was obtained in those cases in which two or more were possible, *i.e.*, the reaction of ethyl difluoroacetate with ethyl fluoroacetate. In this case, four possible acetoacetic esters could be formed but the only product obtained was ethyl α,γ,γ-trifluoroacetoacetate. This may be explained by the fact that the reaction was conducted at a temperature below which ethyl difluoroacetate reacts with itself in an excess of this ester, thus favoring the formation of a carbanion from ethyl fluoroacetate in an excess of ethyl difluoroacetate. Other reactions of this type were conducted similarly and resulted in only one product.

The reaction product, in most cases, appeared to be the hemi-ketal of the acetoacetic ester rather than the ester itself. In the case of pentafluoroacetoacetic ester the addition compound with butanol was sufficiently stable to be distilled at atmospheric pressure without decomposition, but in others it was observed that the reaction product decomposed on heating, liberating the free alcohol. The effect of increased fluorine substitution should enhance the formation of such hemi-ketal structures,[2] and this proved to be the case.

The addition compound of ethanol with ethyl $\alpha,\alpha,\gamma,\gamma$-tetrafluoroacetoacetate was quite acidic in aqueous solutions. A solution of the acetoacetic ester in ethanol was sufficiently acidic to liberate hydrogen from sodium borohydride and no reduction of the beta ketone could be effected under these conditions.

The fluorine-containing acetoacetic esters were hydrolyzed by refluxing in aqueous acid solutions. In strong contrast to the non-fluorinated acetoacetic acids which decompose slowly in aqueous solutions at room temperature and very fast at higher temperatures, the polyfluorinated acetoacetic acids were quite stable under these conditions. Both hydrolysis and decarboxylation of the esters took place with increasing difficulty as more fluorine was substituted in the molecule. The tetrafluoro- and pentafluoroacetoacetic acids were isolated and distilled without decomposition. It was necessary to remove the last traces of water from the acids by azeotropic distillation of the water with benzene.

By using strongly acidic solutions such as 40% sulfuric acid and refluxing the mixture, it was possible to hydrolyze and decarboxylate the fluorine-containing acetoacetic esters. The fluorine-containing acetones produced in this manner were water soluble and could be removed from the aqueous solutions by continuous extraction with ether for a

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(1) Taken, in part, from the Doctoral dissertations of H. W. Kilbourne and E. R. Wilson, Purdue University. Presented before the Fluorine Symposium, Fall Meeting of the American Chemical Society, Atlantic City, N. J., 1952.

(2) F. Swartz, *Bull. soc. chim. Belg.*, **35**, 412 (1926).

(3) A. L. Henne, This Journal, **69**, 1819 (1947).

(4) Y. Desirant, *Bull. sci. acad. roy. Belg.*, **15**, 966 (1929).

(5) C. R. Hauser and W. B. Renfrow, This Journal, **59**, 1823 (1937).

(6) F. W. Swamer and C. R. Hauser, *ibid.*, **68**, 2647 (1946).

(7) W. L. Hansley and P. J. Carlisle, *Chem. Eng. News*, **23**, 1332 (1945).