composition of acetic anhydride is a truly unimolecular dissociation process forming ketene and acetic acid, and that the decomposition does not involve radicals. The vastly different nature of the decomposition of perfluorobutyric anhydride, for example, makes it likely, although not certain, that a radical mechanism is involved. Perfluorohexane may, accordingly, be formed as a result of the direct combination of the transient perfluoropropyl radicals in a ternary collision (with a solid or wall). Hodgins and Haines[14] have shown that the reaction between atomic sodium and iodotrifluoromethane in a diffusion flame apparatus results in the formation of hexafluoroethane from the combination of two trifluoromethyl radicals.

Finally, from a synthetic standpoint, the thermal degradations of silver salts or of anhydrides of perfluoro acids, $C_nF_{2n+1}COOH$, afford excellent methods for the preparation of higher molecular weight fluorocarbons of known structure, $C_{2n}F_{4n+2}$, possessing even-numbered carbon atoms.[15]

Acknowledgment.—The authors wish to express their thanks to Dr. A. V. Grosse for his advice and stimulating interest, and to Mr. C. S. Stokes for technical assistance.

---

[14] J. W. Hodgins and R. L. Haines, *Can. J. Chem.*, **30**, 473 (1952).

[15] For another, but less convenient, synthesis of this type see M. Hauptschein and A. V. Grosse, THIS JOURNAL, **74**, 4454 (1952).

PHILADELPHIA, PENNSYLVANIA

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, WASHINGTON UNIVERSITY]

The Reactions of Phenyl Esters of Phosphorous Acid with Iodine[1]

BY JAMES P. FORSMAN AND DAVID LIPKIN

RECEIVED AUGUST 28, 1952

The reactions of iodine with triphenyl phosphite, cyclohexyl diphenyl phosphite and 1,2:5,6-diisopropylidene-D-glucose 3-diphenylphosphite were investigated. In the case of all three esters an important reaction is the formation of phosphite polyiodides. Conditions for the reaction of the cyclohexyl ester were found, however, which lead to excellent yields of cyclohexyl iodide. Two phosphorus compounds of novel structure were obtained from the reaction of anhydrous ammonia with a solution of triphenyl phosphite and iodine.

Various investigators have studied the reactions of trialkyl phosphites with chlorine, bromine, iodine and cyanogen iodide.[2] The reactions are rapid and may be represented by the over-all equation

$$(RO)_3P + X_2 \longrightarrow (RO)_2P(O)X + RX \qquad (1)$$

The reactions of triaryl phosphites with halogens have been investigated less extensively.[3] The reaction of an aryl ester such as triphenyl phosphite with chlorine or bromine has been reported to yield the dichloride, $(C_6H_5O)_3PCl_2$, or dibromide, $(C_6H_5O)_3PBr_2$, respectively. The reaction of iodine with triaryl phosphites has not been reported previously in the literature. As a consequence of our interest in the synthetic possibilities of the reaction

$$(C_6H_5O)_2POR + I_2 \longrightarrow (C_6H_5O)_2P(O)I + RI \qquad (2)$$

we studied the reactions of iodine with triphenyl phosphite, cyclohexyl diphenyl phosphite and 1,2:5,6-diisopropylidene-D-glucose 3-diphenylphosphite.

Even in the case of the relatively simple triphenyl ester, the reaction with iodine is complex. Three unstable, crystalline products were isolated from this reaction, but only two of these could be identified. The latter proved to be the tetraiodide, $(C_6H_5O)_3PI_4$, and the enneaiodide, $(C_6H_5O)_3PI_9$. The expected diiodide, $(C_6H_5O)_3PI_2$, was not isolated and identified. The reaction of triphenyl phosphite with iodine in the presence of anhydrous ammonia, under conditions such that precipitation of polyiodides does not take place, also yielded two new crystalline compounds, $(C_{18}H_{15}O_3P)_2NI_3$ and $(C_{18}H_{15}O_3P)_2NI$.

Polyiodides of unknown composition are formed in the reaction of iodine with the other two esters. Under suitable conditions, however, cyclohexyl diphenyl phosphite and iodine react almost quantitatively according to equation (2). On the other hand, reaction conditions leading to the formation of 3-iodo-3-deoxy-1,2:5,6-diisopropylidene-D-glucose from the glucose phosphite and iodine were not found.

Experimental[4]

Because of the nature of the reactions involved, scrupulously anhydrous conditions and equipment were used throughout this work. The chloroform and ethyl ether also were treated to remove alcohol. The petroleum ether used was a fraction boiling at 32–37° and the ligroin was a fraction boiling at 65–68°.

Preparation of Diphenyl Chlorophosphite.—To 857 g. (5.60 moles) of phenol (Mallinckrodt A. R. grade) in a round-bottom flask fitted with a dropping funnel, thermometer and condenser filled with Dry Ice, was gradually added 513 g. (3.74 moles) of phosphorus trichloride (Mallinckrodt A. R. grade). After the addition of the acid chloride to the phenol was completed (1–3 hr.), the funnel was replaced by a gas inlet tube through which a slow stream of dry nitrogen was introduced. The reaction mixture was then heated during the course of four hours to a temperature of 175° and kept at this temperature for one hour. Distillation at a rapid rate of the resulting mixture yielded 428 g. of a colorless liquid, b.p. 101–125° (0.15 mm.). Redistillation[5] of this fraction through a one-meter column packed with glass helices gave 350 g. (50% yield based on phenol) of diphenyl chlorophosphite, b.p. 146.5–148.0° (4 mm.), $n^{25}D$ 1.5789.

---

[1] The material herein presented is taken from the Ph.D. thesis (Washington University, September, 1952) of James P. Forsman.

[2] (a) R. B. Fox and L. B. Lockhart, "The Chemistry of Organophosphorus Compounds," Naval Research Laboratory, Washington, D. C., 1948, p. 62; (b) W. Gerrard and N. H. Philip, *Research*, **1**, 477 (1948); (c) G. M. Kosolapoff, "Organophosphorus Compounds," John Wiley and Sons, Inc., New York, N. Y., 1950, pp. 197–198.

[3] Reference 2c, pp. 325 and 329.

[4] All boiling points are uncorrected. Melting points are corrected.

[5] Since diphenyl chlorophosphite disproportionates to phosphorus trichloride, phenyl dichlorophosphite and triphenyl phosphite, even on storage at −20°, it was always redistilled just prior to use.

The boiling point is in good agreement with extrapolated literature values.[6]

Preparation of Triphenyl Phosphite.—This was prepared by the usual method[7] from phenol and phosphorus trichloride; b.p. 200–206.5° (5 mm.), $n^{20}D$ 1.5912. A yield of 71% was obtained.

Reaction of Triphenyl Phosphite with Iodine.[8]—A solution of 7.8 g. (0.025 mole) of triphenyl phosphite in 150 ml. of benzene was added dropwise to a well-stirred mixture of 14.0 g. (0.055 mole) of iodine (Mallinckrodt A. R. grade) and 200 ml. of benzene. After the addition of the phosphite solution was completed, another 13.0 g. (0.051 mole) of solid iodine was added to the reaction mixture. This dissolved with the formation of a glistening, crystalline solid. The precipitate was removed by filtration, washed with petroleum ether and rapidly dried. The product (28.7 g., 77% yield based on iodine) consisted of emerald-green, stubby prisms, m.p. (sealed tube) 89–90°.

Anal. Calcd. for $C_{18}H_{15}I_9O_3P$: C, 14.88; H, 1.04; P, 2.13. Found: C, 15.09; H, 1.02; P, 2.04.

The enneaiodide is very soluble in chloroform, chlorobenzene or acetonitrile; moderately soluble in benzene or hot carbon tetrachloride; and insoluble in petroleum ether. It is best stored under dry petroleum ether; when the dry solid is stored in a desiccator, it decomposes with the evolution of iodine vapor. In moist air it is rapidly converted to a dark red oil.

A weighed sample of the enneaiodide was treated with a measured volume of 0.1 *N* sodium arsenite, excess sodium bicarbonate and a small amount of carbon tetrachloride. The mixture was stirred until the solid dissolved and the mixture became colorless. The excess arsenite was then back-titrated with 0.1 *N* iodine solution. The calculated equivalent weight for seven reducible iodine atoms in $C_{18}H_{15}I_9O_3P$ is 206; found, 199, 202.

Another sample of the enneaiodide (0.97 g.) was dissolved in a dioxane–water mixture containing excess sodium bicarbonate and allowed to stand overnight. The yield of triphenyl phosphate isolated from this reaction mixture was 0.21 g. (95%), m.p. 48.5–49°. The mixed melting point with authentic triphenyl phosphate was unchanged.

A solution of 5.08 g. (0.020 mole) of iodine in 200 ml. of benzene was added slowly to 6.20 g. (0.020 mole) of triphenyl phosphite dissolved in 100 ml. of petroleum ether. Green crystals began to form at the bottom of the reaction flask toward the end of the addition of the iodine solution. After the addition was completed, the dark supernatant was decanted from the green solid through a filter funnel. On the filter there remained a sizeable quantity of golden-brown platelets. Even in a dry atmosphere these turned to a dark reddish-brown oil within a few minutes. It was not possible, therefore, to obtain any analytical data on this compound. On allowing the filtrate to stand, a small quantity of dark red prisms separated. These were removed by filtration, washed with petroleum ether and rapidly dried.

Anal. Calcd. for $C_{18}H_{15}I_4O_3P$: C, 26.43; H, 1.85. Found: C, 26.43; H, 1.83.

In moist air this tetraiodide is converted within a few minutes to a dark red oil. Because of its unstable nature, it was not further characterized. The green solid which was obtained in this experiment was transferred to a filter, washed with petroleum ether and rapidly dried. It is presumably the enneaiodide, since it melted at 83.5–85.5° without further purification.

Reaction of Triphenyl Phosphite with Iodine and Anhydrous Ammonia.—Anhydrous ammonia was passed at a very slow rate into a well-stirred solution of 12.7 g. (0.050 mole) of iodine and 15.5 g. (0.050 mole) of triphenyl phosphite in 200 ml. of chloroform for a total of about 8 hours. At the end of this time the solution was a light tan and a precipitate consisting of a white powder and red prisms was present. The solids were filtered off and dried. On extraction with water the solid decreased in weight by 9.0 g. (ammonium iodide). The remaining water-insoluble red crystals, after drying, weighed 9.2 g. (54% yield). Recrystallization from acetonitrile gave reddish-brown prisms, m.p. 160.1–160.2°.

Anal. Calcd. for $C_{36}H_{30}I_3NO_6P_2$: C, 42.58; H, 2.98; P, 6.09; N, 1.38; I, 37.50. Found: C, 42.70; H, 2.94; P, 6.07; N (Kjeldahl), 1.24; I, 37.17.

This red substance (compound A) is stable in air. It is unaffected by cold, concentrated sulfuric acid or by cold, alcoholic potassium hydroxide. It is insoluble in water and fairly insoluble in most organic solvents. It is, however, moderately soluble in cold acetone, hot acetonitrile or hot chloroform.

The chloroform filtrate obtained after removing by filtration the ammonium iodide and the above triiodide from the reaction mixture was evaporated at reduced pressure. An oily, reddish solid remained (13.3 g.) which was triturated first with 100 ml. of ligroin and then with 100 ml. of benzene. The 4.5 g. of insoluble solid which remained was extracted with water and dried. An amorphous, tan-colored powder was thus obtained (4.2 g.) which was triturated with cold acetone. The residue (2.2 g.), on recrystallization from a hot chloroform–benzene mixture, gave colorless platelets, m.p. 184.0–184.8°.

Anal. Calcd. for $C_{36}H_{30}INO_6P_2$: C, 56.78; H, 3.97; P, 8.12; N, 1.84; I, 16.7. Found: C, 56.62; H, 3.65; P, 7.90; N (Kjeldahl), 1.93; I, 17.4.

This moniodide (compound B) is insoluble in hydrocarbons, acetone and carbon tetrachloride. It is fairly soluble in hot, absolute alcohol and very soluble in chloroform or acetonitrile. It has an absorption peak in the ultraviolet at 250 mμ (ϵ 12,000).

To a sample of the monoiodide (compound B) in a small amount of chloroform was added a solution of iodine in the same solvent. On adding ligroin to the resulting solution, a red precipitate was formed. It was filtered off and air-dried; m.p. 159.5–160°, unchanged on admixture with a sample of the triiodide (compound A).

Preparation of Cyclohexyl Diphenyl Phosphite.—A mixture of 78.6 g. (0.79 mole) of cyclohexanol, 3.1 g. (0.039 mole) of pyridine and 300 ml. of ether was added dropwise over a 2.5-hour period to an ice-cooled, well-stirred solution of 198.5 g. (0.79 mole) of diphenyl chlorophosphite and 62.1 g. (0.79 mole) of pyridine in 400 ml. of ether. The reaction mixture was then allowed to warm to room temperature overnight while stirring was continued. At the end of this time the pyridine hydrochloride was removed by filtration, washed well with ether, and discarded. The combined filtrate and ether washings[9] were evaporated at reduced pressure and the cloudy, pale yellow, sirupy residue which remained was rapidly distilled at low pressure. A colorless, odorless liquid (219 g., 88% yield) was collected as the second fraction, b.p. 148–153° (0.3 mm.), $n^{20}D$ 1.5559.

Anal. Calcd. for $C_{18}H_{21}O_3P$: C, 68.34; H, 6.69; P, 9.79. Found: C, 68.38; H, 6.60[10]; P, 9.56.

Reaction of Cyclohexyl Diphenyl Phosphite with Iodine.—To a mixture of 13.9 g. (0.055 mole) of iodine and 80 ml. of benzene was added rapidly, while stirring, a solution of 17.0 g. (0.054 mole) of cyclohexyl diphenyl phosphite in 80 ml. of benzene. After the addition was completed, stirring was continued for 24 hours. The dark reddish-brown solution was then washed with a solution of sodium thiosulfate and sodium bicarbonate. The resultant colorless benzene layer was dried and anhydrous ammonia then bubbled through it for a half hour.[11] The entire mixture, including the white

---

(6) Reference 2c, p. 200.

(7) E. Noack, *Ann.*, **218**, 85 (1883).

(8) In addition to the three crystalline products described in this section, dark red, dense oils, which are undoubtedly also triphenyl phosphite polyiodides, were frequently obtained from the reaction of triphenyl phosphite with iodine.

(9) Since cyclohexyl diphenyl phosphite is very sensitive to moisture, it was found that washing of the ether solution with aqueous solutions, for the purpose of removing pyridine hydrochloride and unchanged pyridine, is best eliminated.

(10) Attempts to determine carbon in this compound by the usual combustion technique were unsuccessful. The samples exploded and left black, refractory residues in the combustion tube. It was found that acceptable analyses could be obtained, however, if the sample was mixed with dry copper oxide and burned first at 350° and then again at 900°.

(11) In some of our preliminary experiments the reaction mixture containing cyclohexyl iodide and diphenyl iodophosphate was washed with an alkaline, aqueous solution in order to convert the latter to diphenylphosphoric acid. This compound was actually isolated from the aqueous washes and identified. The ammonolysis procedure described is much more satisfactory, however, since it is a rapid and quantitative reaction whereas the hydrolysis of the iodophosphate is surprisingly slow.

precipitate which formed on treatment with ammonia, was concentrated at reduced pressure to a small volume. The residue was diluted with several volumes of petroleum ether and the mixture filtered. The solid on the filter was washed with petroleum ether and dried. The filtrate and washings were combined and distilled. Cyclohexyl iodide (9.8 g., 87% yield) was obtained as a clear, colorless liquid, b.p. 85–90° (31 mm.), $n^{20}D$ 1.5471. Previously reported values for these constants are b.p. 96° (40 mm.),[12] $n^{20}D$ 1.54765.[13] The dried solid (18.3 g.) was washed with water until free of halogen and again dried. This water-insoluble, white solid weighed 11.3 g. (85% yield), m.p. 149.5–150.0°, undepressed in admixture with authentic diphenyl amidophosphate. The 7.0 g. (90% yield) of water-soluble material gave positive tests for ammonia and iodide.

It is also possible to prepare cyclohexyl diphenyl phosphite and to carry out the reaction with iodine without isolating the ester itself. A solution of 12.6 g. (0.050 mole) of diphenyl chlorophosphite in 50 ml. of benzene was added dropwise, during one hour, to an ice-cooled, well-stirred mixture of 5.01 g. (0.050 mole) of cyclohexanol, 5.00 g. (0.060 mole) of sodium bicarbonate, 15.0 g. of freshly dried Drierite and 100 ml. of benzene. The reaction mixture was warmed to room temperature and stirring was continued for 17 hours. At the end of this time, 12.6 g. (0.050 mole) of solid iodine was added in two portions. From the reaction mixture, after decolorization by shaking with sodium thiosulfate–sodium bicarbonate solution followed by ammonolysis, there was isolated 5.1 g. (48% yield) of crude cyclohexyl iodide, b.p. 85–97° (46 mm.), 3.21 g. (44% yield) of ammonium iodide, and 3.86 g. (31% yield) of diphenyl amidophosphate, m.p. 149.5–150.5°, unchanged in admixture with an authentic sample.

Preparation of 1,2:5,6-Diisopropylidene-D-glucose 3-Diphenylphosphite.—A solution of 16.4 g. (0.063 mole) of 1,2:5,6-diisopropylidene-D-glucose[14] and 5.5 g. (0.07 mole) of pyridine in 200 ml. of ether was added during a half-hour period to an ice-cooled, stirred solution of 15.9 g. (0.063 mole) of diphenyl chlorophosphite in 100 ml. of ether. The reaction mixture was then warmed to room temperature and stirring was continued for 17 hours. At the end of this time the pyridine hydrochloride was removed by filtration and washed with ether. A cloudy, viscous, colorless residue remained after the combined ether filtrate and washings were concentrated at reduced pressure. This residue was distilled in a pot-type molecular still. A clear, colorless, very viscous sirup (13.6 g., 45% yield) was collected as product at a bath temperature of 137–158° and a pressure of 10^{-5} mm., $n^{20}D$ 1.5253, $[\alpha]^{23}D$ −41.4° (C_6H_6, *c* 3.87).

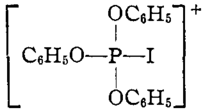
Anal. Calcd. for $C_{24}H_{29}O_8P$: C, 60.50; H, 6.14; P, 6.50. Found: C, 60.11; H, 6.04; P, 6.13.

In a similar preparation, a quantitative yield of crude ester was obtained after removal of the solvent at reduced pressure. The undistilled material had $n^{20}D$ 1.5242, $[\alpha]^{25}D$ −39.1° (C_6H_6, *c* 3.75).

Reaction of 1,2:5,6-Diisopropylidene-D-glucose 3-Diphenylphosphite with Iodine.—This reaction was carried out in a manner similar to the analogous reaction of the cyclohexyl ester. Chloroform, benzene or ether was used as solvent. With ether as solvent, but not with benzene or chloroform, dark red oils separated which were probably polyiodides. Ammonolysis of the reaction mixtures in the various solvents gave quantitative yields of ammonium iodide, but no diphenyl amidophosphate or 3-iodo-3-deoxy-1,2:5,6-diisopropylidene-D-glucose.

Discussion

The tetraiodide and enneaiodide obtained by the reaction of triphenyl phosphite with iodine are believed to have in common the cation



$$\left[\begin{array}{c} \quad\quad\quad OC_6H_5 \\ C_6H_5O—P—I \\ \quad\quad\quad OC_6H_5 \end{array}\right]^+$$

I

The crystalline tetraiodide is presumably the triiodide of I. The enneaiodide probably should be represented by the molecular formula $C_{36}H_{30}O_6P_2I_{18}$[15] and hence the crystal may be pictured as made up of cations of the above structure and equal numbers of the polyiodide anions I_7^- and I_9^-.[16] The evidence which has led us to these structures is as follows: First, the enneaiodide has an equivalent weight which indicates that seven of the nine iodine atoms are reduced by arsenite. Second, the enneaiodide is hydrolyzed almost quantitatively to triphenyl phosphate. Thus, none of the iodine atoms are substituted in the benzene rings. Third, addition of more iodine to reaction mixtures containing both the red and green crystalline solids brings about the conversion of the red tetraiodide to the green enneaiodide. Fourth, the reaction of anhydrous ammonia with triphenyl phosphite plus iodine may be represented as follows, although this is certainly not the only possible path by which the reaction may take place: $2(C_6H_5O)_3\overset{+}{P}I + 3NH_3 \rightarrow 2N\overset{+}{H_4} + 2I^- + (C_6H_5O)_3\overset{+}{P}—NH—\overset{+}{P}(OC_6H_5)_3 \xrightarrow{NH_3} N\overset{+}{H_4} + (C_6H_5O)_3P{=}N—\overset{+}{P}(OC_6H_5)_3$.

The two crystalline solids isolated from the reaction of anhydrous ammonia with iodine plus triphenyl phosphite can best be represented by rather novel structures. The red compound A is the triiodide and the white compound B the monoiodide of a cation which can be represented by the four resonance structures

$$(C_6H_5O)_3P{=}N—\overset{+}{P}(OC_6H_5)_3$$
II

$$(C_6H_5O)_3\overset{+}{P}—N{=}P(OC_6H_5)_3$$
III

$$(C_6H_5O)_3P{=}\overset{+}{N}{=}P(OC_6H_5)_3$$
IV

$$(C_6H_5O)_3\overset{+}{P}—\overset{-}{N}—\overset{+}{P}(OC_6H_5)_3$$
V

Structures IV and V are relatively unimportant, however, compared to the two equivalent structures II and III. It was readily demonstrated that the two compounds bear the relationship to each other of monoiodide–triiodide. Addition of iodine to the white compound converted it to the red one. Further, the absorption spectrum of compound A is essentially identical with that of triiodide ion in anhydrous acetonitrile.[17]

---

[12] W. Markownikov, *Ann.*, **302**, 12 (1898).

[13] A. I. Vogel, *J. Chem. Soc.*, 1809 (1948).

[14] Prepared by the method of H. V. Gruenenberg, C. Bredt and W. Freudenberg, THIS JOURNAL, **60**, 1507 (1938).

[15] The molecule $C_{18}H_{15}O_3PI_9$ contains an odd number of electrons and should show paramagnetic resonance absorption. A sample of the enneaiodide was examined in the microwave apparatus described in "Paramagnetic Resonance of Free Radicals," First Progress Report, Washington University, Dec., 1951, ONR Contact N6onr-20205. Since no absorption was found it is probable that the compound should be represented by the doubled formula. It is still possible, however, that the substance has such a broad resonance absorption that it escaped detection in the apparatus used.

[16] It has been suggested—N. V. Sidgwick, "Chemical Elements and Their Compounds," Vol. 2, Clarendon Press, Oxford, 1950, p. 1198—that CsI_4 is probably a crystal aggregate of CsI_3 and CsI_5.

[17] The absorption spectrum of triiodide ion in anhydrous acetonitrile was obtained by measuring (1.00-cm. quartz cells, Beckman Model *DU* spectrophotometer) the absorption of a solution containing equimolar amounts (3×10^{-5} *M*) of sodium iodide and iodine. This spectrum is identical with the one reported by R. E. Buckles, J. P. Yuk and A. I. Popov—THIS JOURNAL, **74**, 4379 (1952)—for a solution of

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.

ST. LOUIS 5, MISSOURI

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

$$3[\mathrm{Co(CO)_4}]_2 + 12\mathrm{B} \longrightarrow 2[\mathrm{Co(B)_6}][\mathrm{Co(CO)_4}]_2 + 8\mathrm{CO} \tag{1}$$

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

$$3[\mathrm{Co(CO)_4}]_2 + 20(\mathrm{CH_3})_2\mathrm{NH} \longrightarrow 2[\mathrm{Co}[(\mathrm{CH_3})_2\mathrm{NH}]_6][\mathrm{Co(CO)_4}]_2 + 8\mathrm{HCON(CH_3)_2} \tag{2}$$

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

[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).