

benzene than in the more polar nitrobenzene. Similar solvent effects were also found in some phosphine exchanges of nickel-carbonyl-phosphine complexes.<sup>10</sup>

The extent of reaction 1 in these systems seems to depend more on the base strength of the entering ligand than on its ability to  $\pi$ -bond. For example the reaction of  $\text{Mn}(\text{CO})_5\text{Br}$  with  $\text{P}(\text{C}_6\text{H}_5)_3\text{Cl}_2$  goes to completion but  $\text{PCl}_3$  does not react. This is the order of decreasing base strength but increasing  $\pi$ -bonding tendency for the phosphorus compounds.<sup>11</sup>

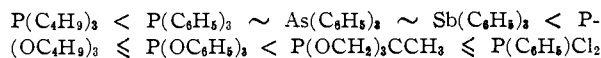
Likewise aniline, *o*- and *p*-toluidine which are not expected to  $\pi$ -bond significantly react completely. No reaction was observed for *p*-nitroaniline. Not only does there appear to be a lower limit of basicity below which this reaction does not take place at these conditions but also an upper limit above which a different reaction occurs. Stronger bases such as cyclohexylamine, dimethylamine and diethylamine react very rapidly with  $\text{Mn}(\text{CO})_5\text{X}$  to displace  $\text{X}^-$  rather than  $\text{CO}$ . No

(10) L. S. Meriwether and M. L. Fiene, *J. Am. Chem. Soc.*, **81**, 4200 (1959).

(11) E. A. Magnuson, *Revs. Pure and Appl. Chem. (Australia)*, **7**, 195 (1957).

further study has as yet been made of this reaction.

The infrared spectra of some  $\text{Mn}(\text{CO})_4\text{LX}$  compounds in the C-O stretching region are similar but show an increase in wave number of absorption with changes in L in the order



This same order has been found in the tetrahedral nickel-carbonyl-phosphine complexes<sup>10,12</sup> and has been correlated with the  $\pi$ -bonding ability of the phosphine, the best  $\pi$ -bonding phosphines yielding complexes with the highest carbonyl absorption frequencies.

**Acknowledgments.**—We wish to thank the Koppers Company and Lubrizol Company for fellowships to R.J.A. This research was supported in part by a National Science Foundation grant, NSF-G12872. We wish to thank Professor R. G. Pearson and Dr. A. J. Poe for helpful discussions.

(12) M. Bigorgne, "Advances in the Chemistry of Coordination Compounds," S. Kirschner, Ed., The Macmillan Co., New York, N. Y., 1961, pp. 199-208.

[CONTRIBUTION FROM THE RESEARCH CENTER, HERCULES POWDER COMPANY, WILMINGTON 99, DELAWARE]

## Acylcobalt Carbonyls and their Triphenylphosphine Complexes<sup>1</sup>

BY RICHARD F. HECK AND DAVID S. BRESLOW

RECEIVED AUGUST 31, 1961

A number of acylcobalt tetracarbonyls have been prepared by reaction of sodium cobalt tetracarbonyl with acyl halides or with alkyl halides and CO. The properties of these unstable compounds are described. Acylcobalt tricarbonyl triphenylphosphines have been prepared from acylcobalt tetracarbonyls and triphenylphosphine or in one step from alkyl halides, sodium cobalt tetracarbonyl and triphenylphosphine. These relatively stable, crystalline, high-melting derivatives have been isolated and characterized. Several unusual reactions of acylcobalt complexes containing functional groups have been described.

### Introduction

Three methods have been reported for the synthesis of acylcobalt tetracarbonyls,  $\text{RCOCo}(\text{CO})_4$ : reaction of an acyl halide with cobalt tetracarbonyl anion, reaction of an alkyl halide with cobalt tetracarbonyl anion and CO, and the addition of cobalt hydrocarbonyl and CO to an olefin.<sup>2-6</sup> The purpose of this work was to study in greater detail the preparation and properties of simple acylcobalt compounds, the effect of various functional groups on their chemistry and the preparation of stable triphenylphosphine adducts.

(1) A preliminary account of a portion of this work appeared in *J. Am. Chem. Soc.*, **82**, 4438 (1960).

(2) D. S. Breslow and R. F. Heck, *Chem. & Ind. (London)*, 467 (1960).

(3) R. F. Heck and D. S. Breslow, *Actes du Deuxième Congrès International de Catalyse*, Vol. I, Editions Technip, Paris, 1960, p. 671.

(4) R. F. Heck and D. S. Breslow, *J. Am. Chem. Soc.*, **83**, 1097 (1961).

(5) R. F. Heck and D. S. Breslow, "Advances in the Chemistry of the Coordination Compounds," edited by S. Kirschner, Macmillan Co., New York, N. Y., 1961, p. 281.

(6) R. F. Heck and D. S. Breslow, *J. Am. Chem. Soc.*, **83**, 4023 (1961).

### Discussion

The acyl halide procedure is the most generally useful one for the preparation of acylcobalt tetracarbonyls. Yields are generally high, providing the reactions are carried out in dilute solution at low temperatures with acid-free acyl halides under anhydrous conditions.<sup>7,8</sup> The alkylation of sodium cobalt tetracarbonyl in the presence of CO is a less useful procedure, operating well only with active alkylating agents, such as methyl


(7) Free acid reacts with sodium cobalt tetracarbonyl to form hydrocarbonyl, which is known to reduce acylcobalt carbonyls to aldehydes.<sup>5,6</sup>

(8) Trifluoroacetic anhydride yielded trifluoroacetylcobalt tetracarbonyl as an unusually stable acylcobalt compound in agreement with the recent report of Hieber, Beck and Lindner.<sup>9</sup> McClellan<sup>10</sup> reported that perfluoroacylcobalt tetracarbonyls lose CO spontaneously below 0° and cannot be isolated. Inasmuch as McClellan used perfluoroacyl halides instead of the anhydrides, it would appear that in these cases traces of either hydrogen halide or perfluorocarboxylic acid catalyze the elimination of CO to give perfluoroalkylcobalt tetracarbonyls.

(9) W. Hieber, W. Beck and E. Lindner, *Z. Naturforsch.*, **16b**, 229 (1961).

(10) W. R. McClellan, *J. Am. Chem. Soc.*, **83**, 1598 (1961).

TABLE I  
 ACYLCOBALT TRICARBONYL TRIPHENYLPHOSPHINE COMPLEXES  $\text{RCOCo}(\text{CO})_3\text{P}(\text{C}_6\text{H}_5)_3$ 

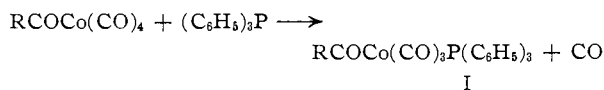
R	Method of prep. <sup>a</sup>	M.p., °C. (dec.)	Formula	Analyses			
				Calcd.		Found	
				% C	% H	% C	% H
CH <sub>3</sub> -	A, B	123	C <sub>23</sub> H <sub>18</sub> O <sub>4</sub> PCo	61.62	4.05	61.56	4.44
C <sub>2</sub> H <sub>5</sub> -	A	98-100	C <sub>24</sub> H <sub>20</sub> O <sub>4</sub> PCo	62.35	4.36	62.79	4.42
(CH <sub>3</sub> ) <sub>2</sub> CH-	B	101	C <sub>25</sub> H <sub>22</sub> O <sub>4</sub> PCo	63.03	4.66	63.45	4.78
CH <sub>3</sub> (CH <sub>2</sub> ) <sub>4</sub> -	B	95-98	C <sub>27</sub> H <sub>26</sub> O <sub>4</sub> PCo	64.29	5.20	64.57	5.41
C <sub>6</sub> H <sub>5</sub> -	B	119-122	C <sub>28</sub> H <sub>20</sub> O <sub>4</sub> PCo	65.89	3.95	66.02	4.17
<i>p</i> -CH <sub>3</sub> OC <sub>6</sub> H <sub>4</sub> -	B	120-130	C <sub>29</sub> H <sub>22</sub> O <sub>4</sub> PCo	64.45	4.10	63.73	4.23
	B	...	C <sub>30</sub> H <sub>34</sub> O <sub>4</sub> P <sub>2</sub> Co <sub>2</sub>	63.71	3.64	63.21	4.02
CF <sub>3</sub> - <sup>16</sup>	C	170-175	C <sub>23</sub> H <sub>15</sub> O <sub>4</sub> PF <sub>3</sub> Co	55.00	3.01	55.50	3.02
CH <sub>3</sub> OCH <sub>2</sub> -	A	150	C <sub>24</sub> H <sub>20</sub> O <sub>5</sub> PCo	60.26	4.22	60.65	4.48
C <sub>6</sub> H <sub>5</sub> OOCCH <sub>2</sub> -	A	63.5-65.5	C <sub>28</sub> H <sub>22</sub> O <sub>5</sub> PCo	60.02	4.26	60.15	4.42
CH <sub>3</sub> OOCCH <sub>2</sub> CH <sub>2</sub> -	B	115-117	C <sub>26</sub> H <sub>22</sub> O <sub>5</sub> PCo	60.02	4.26	59.99	4.53
ClCH <sub>2</sub> -	B	88-90	C <sub>23</sub> H <sub>17</sub> ClO <sub>4</sub> PCo	57.23	3.55	57.63	3.87
Cl(CH <sub>2</sub> ) <sub>3</sub> -	B	115-120	C <sub>25</sub> H <sub>21</sub> ClO <sub>4</sub> PCo	58.78	4.14	59.43	4.44

<sup>a</sup> A, from alkyl halide in one step; B, from acyl halide; C, from anhydride.

iodide, benzyl chloride, chloromethyl methyl ether, triethyloxonium fluoroborate, etc.<sup>11</sup> The reaction undoubtedly proceeds *via* the intermediate formation of alkylcobalt tetracarbonyl, which is in equilibrium with acylcobalt tricarbonyl, the latter adding CO to give the product.<sup>3,9</sup> The addition of cobalt hydrocarbonyl and CO to olefins is of limited utility. Often isomeric mixtures are obtained, and side reactions are difficult to avoid.<sup>6</sup>

Acylcobalt tetracarbonyls, in contrast to acylmanganese<sup>13,14</sup> and rhenium pentacarbonyls,<sup>14</sup> are thermally unstable, often decomposing below 0°, and are unstable to air. Although they are therefore not ordinarily isolated as such,<sup>15</sup> they can be identified quite readily by their infrared absorption spectra. There are usually three or four resolvable coordinated CO bands at  $4.72 \pm 0.02 \mu$  (m),  $4.85 \pm 0.05 \mu$  (s) and  $4.95 \pm 0.05 \mu$  (vs), as well as a very characteristic carbonyl band at  $5.8$ – $6.0 \mu$  depending upon the nature of the acyl group. The carbonyl band is at a slightly shorter wave length than in either the acylmanganese or rhenium carbonyls.<sup>14</sup>

Because of the inconvenience in handling the acylcobalt tetracarbonyls, a search was made for a more stable derivative. It was found that triphenylphosphine reacts with the tetracarbonyls to displace one CO and to form acylcobalt tricarbonyl triphenylphosphines (I) as thermally and moderately air-stable, high-melting compounds.



(11) Chloroacetone and phenacyl bromide reacted rapidly with sodium cobalt tetracarbonyl, but the products decomposed under the reaction conditions into dicobalt octacarbonyl and unidentified organic material. The reduction of  $\alpha,\beta$ -unsaturated aldehydes and ketones under oxo conditions<sup>12</sup> may be related to the apparent instability of compounds containing cobalt and carbonyl groups attached to the same carbon atom.

(12) H. Adkins and G. Krsek, *J. Am. Chem. Soc.*, **71**, 3051 (1949).

(13) R. D. Closson, J. Kozikowski and T. H. Coffield, *J. Org. Chem.*, **22**, 598 (1957).

(14) W. Beck, W. Hieber and H. Tengler, *Chem. Ber.*, **94**, 862 (1961).

(15) Acetylcobalt tetracarbonyl<sup>12,13</sup> and trifluoroacetylcobalt tetracarbonyl<sup>9</sup> have been isolated and identified.

Only one CO is displaced, irrespective of the amount of triphenylphosphine used, and the reaction appears to be essentially quantitative. Triphenylphosphite reacts analogously. The same derivatives can be obtained from alkylcobalt tetracarbonyls and triphenylphosphine without any CO evolution. Inasmuch as alkyl halides react with



sodium cobalt tetracarbonyl more rapidly than with triphenylphosphine, the phosphine adducts can be made in one step by reacting the three ingredients at 0°; at higher temperatures triphenylphosphine reacts with sodium cobalt tetracarbonyl to form the cobalt tricarbonyl triphenylphosphine dimer. By this procedure methyl iodide gave an 86% yield of acetylcobalt tricarbonyl triphenylphosphine in 30 minutes at 0°. The triphenylphosphine complexes which have been prepared are listed in Table I.

It is rather surprising, in view of the fact that bis-phosphines generally form more stable complexes than monophosphines,<sup>17</sup> that ethylenebis-(diphenylphosphine) formed a complex with acetylcobalt carbonyl in which only one phosphorus group reacted readily and that reaction of the second phosphorus, presumably intramolecularly, led to an unstable product.

The infrared spectra of acylcobalt tricarbonyl triphenylphosphines are very similar to those of the tetracarbonyls, except for a very characteristic shift of all the bands assigned to carbonyl groups attached to cobalt approximately  $0.1 \mu$  to longer wave lengths.

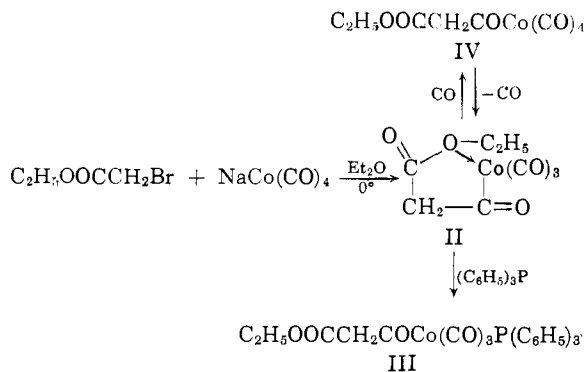
Alkyl substitution on the  $\alpha$ -carbon atom of acetylcobalt tetracarbonyl has some effect on the thermal stability of the compounds, trimethylacetylcobalt tetracarbonyl being less stable than the *n*-hexanoyl compound. Although the decomposition product from the trimethylacetyl derivative was not identified,<sup>18</sup> treatment of the

(16) Prepared also by Hieber, Beck and Lindner<sup>9</sup> from trifluoroacetic anhydride and sodium cobalt tricarbonyl triphenylphosphine, m.p. 172°.

(17) J. Chatt and F. A. Hart, *J. Chem. Soc.*, 1378 (1960).

undecomposed material with iodine in methanol<sup>6</sup> yielded only methyl trimethylacetate, demonstrating that no isomerization of the *t*-butylboron— isobutylboron type occurs.<sup>19</sup> Trimethylacetyl-cobalt tricarbonyl triphenylphosphine could not be isolated, although the tetracarbonyl evolved one CO on treatment with triphenylphosphine and the infrared spectrum showed that the expected adduct had been formed. Presumably the bulky triphenylphosphine group introduces sufficient steric hindrance to make the compound unstable. Acylcobalt tetracarbonyls and tricarbonyl triphenylphosphines are quite stable; the latter can be isolated easily.

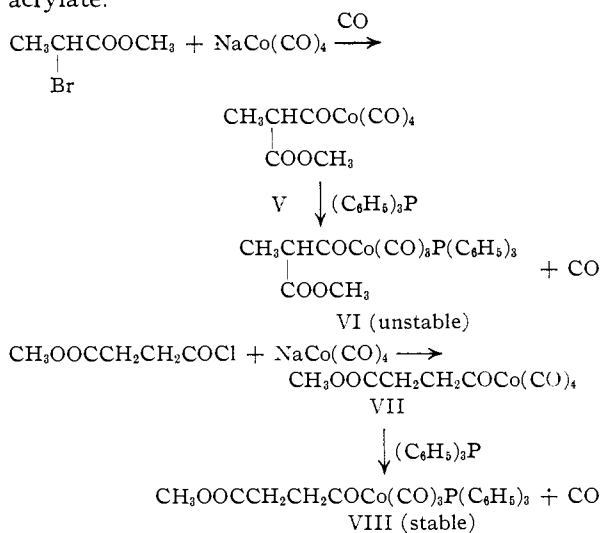
Unusual effects were observed with acylcobalt compounds containing certain functional groups. Ethyl bromoacetate reacted with sodium cobalt tetracarbonyl in the presence of CO to take up about 0.1 mole of gas. The infrared spectrum of the reaction mixture showed carbonyl bands, in addition to the usual coordinated CO bands, at 5.73 and 5.83  $\mu$ , indicating that an acylcobalt compound had been formed, probably carboethoxyacetyl-cobalt tricarbonyl (II) with one of the ester oxygens coordinated with cobalt. Triphenylphosphine reacted with this complex to displace the coordinated oxygen rather than CO, carboethoxyacetyl-cobalt tricarbonyl triphenylphosphine (III) being formed as a stable compound. The 0.1 mole of CO absorbed in the initial reaction probably formed some carboethoxyacetyl-cobalt tetracarbonyl (IV), probably in equilibrium with II under these conditions. The CO was evolved again when triphenylphosphine was added. In



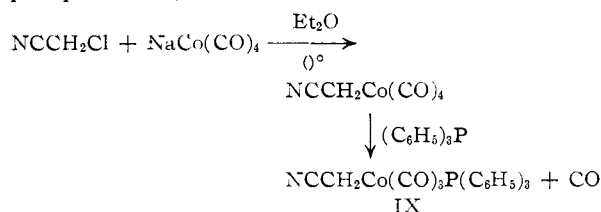
contrast, chloromethyl methyl ether reacted to form only methoxyacetyl-cobalt tetracarbonyl.

Methyl 2-bromopropionate reacted with sodium cobalt tetracarbonyl, but the product was relatively unstable. The infrared spectrum indicated that the expected acylcobalt compound (V) had been formed, but considerable decomposition apparently occurred. Reaction with triphenylphosphine gave a complex (VI) which was too unstable to be isolated. On the other hand, the half methyl ester-acid chloride of succinic acid reacted to give 3-

carbomethoxypropionylcobalt tetracarbonyl (VII), which yielded a stable triphenylphosphine complex (VIII). These compounds were also obtained by the addition of cobalt hydrocarbonyl to methyl acrylate.<sup>6</sup>



Chloroacetonitrile reacted with sodium cobalt tetracarbonyl differently from the haloacetate esters. Although here, too, little CO was absorbed, the absence of a 5.8- $\mu$  band in the spectrum indicated that an alkylcobalt rather than an acylcobalt compound had been formed. Reaction with triphenylphosphine led to the evolution of a mole of CO and the infrared spectrum confirmed the formation of cyanomethylcobalt tricarbonyl triphenylphosphine (IX).



This is the first example in which an alkylcobalt compound, other than a  $\pi$ -allyl type, has been reacted with triphenylphosphine to form an alkyl rather than an acylcobalt derivative.<sup>20</sup>

### Experimental

**Acylcobalt Tetracarbonyls from Acyl Halides.**—An approximately 0.07 *M* solution of sodium cobalt tetracarbonyl in ether<sup>22</sup> is stirred under N<sub>2</sub> or CO at 0° and a 10–20% excess of the acid chloride or bromide as a 1.0 *M* solution in ether is added. The reaction is complete when the 5.3- $\mu$  band of sodium cobalt tetracarbonyl disappears. *n*-Hexanoyl chloride requires about 1 hr. for completion, isobutyryl and benzoyl chlorides several hours and trimethylacetyl chloride 24 hr. or more.

**Acylcobalt Tetracarbonyls from Alkyl Halides.**—A two to tenfold excess of alkyl halide is added to a 0.07 *M* ethereal solution of sodium cobalt tetracarbonyl at 0° under one atmosphere of CO. The reaction is complete when gas absorption stops or when the 5.3- $\mu$  band disappears. Under

(18) According to Hieber, Beck and Lindner,<sup>9</sup> acetyl and trifluoroacetyl-cobalt tetracarbonyls can be decarbonylated to the corresponding alkylcobalt compounds, thus paralleling the manganese and rhenium compounds.<sup>12–14</sup> At elevated temperatures propionylcobalt tetracarbonyl yields ethylene and presumably cobalt hydrocarbonyl.<sup>6</sup>

(19) G. F. Hennion, P. A. McCusker, E. C. Ashby and A. J. Rutkowski, *J. Am. Chem. Soc.*, **79**, 5190 (1957).

(20) Recently, Hieber and Lindner<sup>21</sup> prepared methylcobalt tricarbonyl triphenylphosphine by the alkylation of sodium cobalt tricarbonyl triphenylphosphine.

(21) W. Hieber and E. Lindner, *Z. Naturforsch.*, **16b**, 137 (1961); *Chem. Ber.*, **94**, 1417 (1961).

(22) W. Hieber, O. Vohler and G. Braun, *Z. Naturforsch.*, **13b**, 192 (1958).

these conditions reactive halides, such as methyl iodide, benzyl chloride, ethyl bromoacetate and chloromethyl methyl ether, react completely in 0.5-2 hr. Less reactive halides, such as ethyl iodide, require days for complete reaction. The reaction can be accelerated in tetrahydrofuran by increasing the sodium cobalt tetracarbonyl concentration.

**Acylcobalt Tricarbonyl Triphenylphosphines from Acylcobalt Tetracarbonyls.**—A 10-50% excess of a 1.0 *M* triphenylphosphine solution in ether is added at 0° to an ethereal solution of acylcobalt tetracarbonyl prepared by either of the procedures above. Reaction is complete in a few minutes to a few hours as indicated by both gas evolution and the infrared spectrum. The reaction mixture is evaporated *in vacuo* below room temperature to remove excess halide, the crystalline yellow or orange residue is taken up in ether or tetrahydrofuran, centrifuged and concentrated to a small volume. Addition of *n*-pentane often leads to the separation of a small amount of amorphous solid. This is removed by centrifuging, the clear solution is cooled to -80°; more *n*-pentane is added and the crystals are separated. Two or three low-temperature recrystallizations from a mixture of ether, tetrahydrofuran or methylene chloride and *n*-pentane yield a pure product. All manipulations are carried out under nitrogen.

**Acylcobalt Tricarbonyl Triphenylphosphines from Alkyl Halides.**—Alkyl halide is reacted with sodium cobalt tetracarbonyl as described above at 0°, except that a 10-50% excess of triphenylphosphine in ether is added before the alkyl halide and the reaction is carried out under nitrogen. Completion is indicated by disappearance of the 5.3- $\mu$  band. The product is isolated in the same fashion as described above.

**Reaction of Acetylcobalt Tetracarbonyl with Triphenyl Phosphite.**—Acetylcobalt tetracarbonyl was prepared from 15 ml. of 0.07 *M* sodium cobalt tetracarbonyl and 1.0 ml. of methyl iodide in ether at 0° under CO. In 1 hr. 1.09 mmoles (104% of theory) of CO was absorbed. The addition of 0.5 ml. (1.9 mmoles) of triphenyl phosphite resulted in the evolution of 1.11 mmoles (106% of theory) of gas in 1.3 hr. The carbonyl spectrum was identical with that of

the corresponding triphenylphosphine complex. No attempt was made to isolate the complex.

**Reaction of Methylcobalt Tetracarbonyl with Ethylenebis-(diphenylphosphine).**—No reaction occurred between 15 ml. of 0.07 *M* sodium cobalt tetracarbonyl in ether and 2.5 ml. of 0.5 *M* ethylenebis-(diphenylphosphine)<sup>17</sup> in tetrahydrofuran in 30 minutes at 0°. Addition of 0.5 ml. of methyl iodide led to the formation of a pale yellow solution, but there was no change in gas volume in 2 hr. at 0°. The infrared spectrum was very similar to that of acetylcobalt tricarbonyl triphenylphosphine (bands at 4.85, 5.10 and 5.90  $\mu$ ). Warming the solution to 25° led to a very slow evolution of gas and the appearance of two new infrared bands at 5.2 and 6.15  $\mu$ . After standing at room temperature for several days, the solvent was evaporated and an attempt was made to recrystallize the reddish, crystalline product from tetrahydrofuran-*n*-pentane at -80°. Each attempt led to the formation of an insoluble yellow-red solid. The crude material had infrared bands at 5.05 (m), 5.20 (vs) and 6.15 (s)  $\mu$ .

**Cyanomethylcobalt Tricarbonyl Triphenylphosphine (IX).**—Ethereal solutions of sodium cobalt tetracarbonyl (30 ml. of 0.07 *M*) and chloroacetonitrile (3.0 ml. of 1 *M*) were mixed and stirred at 0° for 2.25 hr. under one atmosphere of CO; 7 ml. of gas was evolved. The infrared spectrum showed coordinated CO bands at 4.88 (vs), 4.98 (s) and 5.05 (vs)  $\mu$ , but no carbonyl band at 5.8  $\mu$ . Addition of 3.0 ml. of 1 *M* triphenylphosphine in ether at 0° led to gas evolution. After standing overnight at 0° the cold solution was evaporated to dryness and the residue was extracted with methylene chloride. Addition of ether and cooling to -80° yielded a yellow, crystalline powder. Recrystallization once more from methylene chloride-ether gave a product which decomposed at about 120° without melting.

The infrared spectrum in carbon tetrachloride had bands at 3.40 (w), 3.49 (vw), 4.51 (w), 4.86 (vw), 5.02 (s), 6.74 (w), 6.98 (w), 7.65 (w), 7.96 (w), 8.41 (w), 9.10 (s), 9.30 (w), 9.70 (w), 9.98 (w), 11.12 (w) and 14.6 (m)  $\mu$ .

*Anal.* Calcd. for C<sub>23</sub>H<sub>17</sub>O<sub>3</sub>NPCo: C, 62.04; H, 3.85. Found: C, 61.64; H, 3.95.

[CONTRIBUTION FROM THE SAVANNAH RIVER LABORATORY, E. I. DU PONT DE NEMOURS & Co., AIKEN, SOUTH CAROLINA]

## Conformation of Organophosphorus Compounds. I. Proton Magnetic Resonance Studies of Some Phosphinates, Phosphinic Acids, Phosphinyl Chlorides and Phosphonyl Dichlorides<sup>1</sup>

BY T. H. SIDDALL, III, AND C. A. PROHASKA

RECEIVED NOVEMBER 2, 1961

A number of alkylphosphonyl dichlorides and alkylarylphosphinic acids, -phosphinyl chlorides and -phosphinates were synthesized and their proton nuclear magnetic resonance spectra were obtained. Some of the compounds that contain a benzene ring attached to the phosphorus atom show a doubling of the proton resonances of the alkyl groups in the molecule. A theory is advanced to explain this doubling in terms of preferred rotational isomers.

### Introduction

There have been a number of studies of hindered rotation by use of nuclear magnetic resonance,<sup>2,3</sup> but no reports have been made of previous studies involving the phosphorus bonds in organophosphorus compounds. Preliminary results of the present investigation were reported elsewhere.<sup>4</sup> In that communication it was pointed out that

(1) The information contained in this article was developed during the course of work under contract AT(07-2)-1 with the U. S. Atomic Energy Commission.

(2) (a) J. J. Drysdale and W. D. Phillips, *J. Am. Chem. Soc.*, **79**, 319 (1957). (b) P. M. Nair and J. D. Roberts, *ibid.*, **79**, 4565 (1957).

(3) J. A. Pople, W. G. Schneider and H. J. Bernstein, "High-Resolution Nuclear Magnetic Resonance," McGraw-Hill Book Co., New York, N. Y., 1959.

(4) T. H. Siddall, C. A. Prohaska and W. E. Shuler, *Nature*, **190**, 903 (1961).

phenyl-substituted organophosphorus compounds in three categories showed a doubling of certain of the proton resonances. This doubling of resonances was attributed to hindered rotation around phosphorus bonds. A benzene ring in a molecule in this situation serves as an internal probe to indicate the relative position of other substituents in the molecule. Because of the diamagnetic anisotropy of the benzene ring, protons of other groups, if they are close to the ring, will resonate at a different value of the applied magnetic field than will otherwise identical protons that are far from the ring. Protons in the plane of the ring will resonate at a lower applied field, while protons axial to the ring will resonate at a higher applied field.