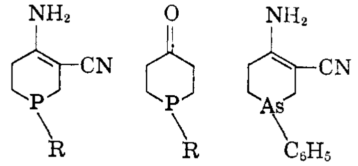
The procedure consisted of cyclizing bis-(2-cyanoethyl)-phosphines (II) to the corresponding 4-amino-1,2,5,6-tetrahydrophosphorin-3-carbonitriles (III) using sodium *t*-butoxide,[3] followed by hydrolysis and decarboxylation to the 4-phosphorinanones in refluxing 6 *N* hydrochloric acid. We also prepared an arsenic carbonitrile (IV) using the same condensing agent.

$(NCCH_2CH_2)_2PR$



IIa, $R = C_2H_5$ b, $R = C_6H_5$

IIIa, $R = C_2H_5$ b, $R = C_6H_5$

Ia, $R = C_2H_5$ b, $R = C_6H_5$

IV

The infrared spectra of the three carbonitriles showed them to have predominantly the enamine structure, as does their carbocyclic analog, 2-amino-2-aminocyclopentene-1-carbonitrile.[4] They resinified upon heating, like 3-cyano-1-methyl-4-piperidone.[5]

The 4-phosphorinanones, I, were stable to distillation. They formed semicarbazones and methyl iodide salts in the manner normal for ketones and tertiary phosphines.

3,3′-(Phenylphosphinidene)-dipropionitrile[6] (IIb), heated with one equivalent of sodium *t*-butoxide for 3 hours in refluxing toluene, gave 4-amino-1,2,5,6-tetrahydro-1-phenylphosphorin-3-carbonitrile (IIIb) in 80% yield; m.p. 135–138°. After chromatography on alumina, the m.p. was 139.5–140°. Calcd. for $C_{12}H_{13}N_2P$: C, 66.66; H, 6.06; N, 12.96; P, 14.33: mol. wt., 216. Found: C, 66.41: H, 6.31: N, 12.81: P, 14.29; mol. wt., 218. Infrared bands at 2170 cm.$^{-1}$ (β-amino unsaturated nitrile), 3400, 3320 and 1645 cm.$^{-1}$ ($-NH_2$ group) and 1605 cm.$^{-1}$ (olefin). Hydrolysis in refluxing 6 *N* hydrochloric acid for 10 hours gave 1-phenyl-4-phosphorinanone (Ib) in 21% yield: b.p. 185–190° (1 mm.): $n^{24}\text{D}$ 1.6051 (supercooled): m.p. 43–44°. Calcd. for $C_{11}H_{13}OP$: C, 68.74: H, 6.82; P, 16.12. Found: C, 68.34: H, 6.84; P, 16.100. Infrared band at 1695 cm.$^{-1}$; m.p. of semicarbazone[7] (93% yield), 155.5–156.5°; m.p. of 1-methyl-4-oxo-1-phenyl-phosphorinanium iodide[7] 155–156°.

3,3¹-(Ethylphosphinidene)-dipropionitrile[8] (IIa) gave4-amino-1-ethyl-1,2,5,6-tetrahydrophosphorin-3-carbonitrile (IIIa) in 83% yield; m.p. 68–71°. After chromatography, the m.p. was 74.5–75°. Calcd. for $C_8H_{13}N_2P$: C, 57.13; H, 7.79; N, 16.66; P, 18.42; mol. wt., 168. Found: V, 57.14; H, 7.80; N, 16.60; P, 18.49; mol. wt., 163. Infrared bands at 3450, 3360, 2175, 1647 and 1605 cm.$^{-1}$. Hydrolysis gave 1-ethyl-4-phosphorinanone (Ia) in 23% yield; b.p. 92° (7 mm.), $n^{25}\text{D}$ 1.5180. Calcd. for $C_7H_{13}OP$: C, 58.32; H, 9.10; P, 21.49. Found: C, 58.09; H, 9.16; P, 21.25. Infrared band at 1715 cm.$^{-1}$; m.p. of semicarbazone,[7] 167–169°: m. p. of methyl iodide salt,[7] 213–214°.

3,3′-(Phenylarsylene)-dipropionitrile[9] gave 4 amino-1,2,5,6-tetrahydro-1-phenylarsenin-3-carbonitrile (IVb); m.p. 65–67°. Calcd. for $C_{12}H_{13}N_2As$: C, 55.40; H, 5.04; N, 10.77; As, 28.20; mol. wt., 260. Found: C, 55.40; H, 5.04; N, 10.58; As, 28.70: mol. wt., 277. Infrared bands at 3480, 3380, 2180, 1643 and 1605 cm.$^{-1}$.

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[3] Q. E. Thompson, THIS JOURNAL, **80**, 5483 (1958).

[4] C. F. Hammer and R. A. Hines, *ibid.*, **77**, 3649 (1955).

[5] A. H. Cook and R. J. Reed, *J. Chem. Soc.*, 399 (1945).

[6] M. M. Rauhut, *et al.*, THIS JOURNAL, **81**, 1103 (1959).

[7] Analysis was satisfactory.

[8] M. Grayson, P. T. Keough and G. A. Johnson, THIS JOURNAL, **81**, 4803 (1959).

[9] R. C. Cookson and F. G. Mann, *J. Chem. Soc.*, 618 (1947).

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RECEIVED JULY 8, 1960

REACTIONS OF ALKYL- AND ACYL-COBALT CARBONYLS WITH TRIPHENYLPHOSPHINE

Sir:

The preparation and isolation of rather unstable alkyl- and acyl-cobalt carbonyls have been reported.[1,2] It has now been found that stable derivatives can be formed from these compounds by reaction with triphenylphosphine.

Thus, acetylcobalt tetracarbonyl reacts with triphenylphosphine in ether at 0° to evolve CO. Addition of *n*-pentane and chilling yields acetylcobalt tricarbonyl triphenylphosphine as a yellow, crystalline compound, m.p. 123° (dec.). *Anal.* Calcd.: C, 61.6; H, 4.05. Found: C, 61.6; H, 4.44. Similarly, 3-butenoylcobalt tetracarbonyl yields 3-butenoylcobalt tricarbonyl triphenylphosphine, m.p. 82° (dec.). *Anal.* Calcd.: C, 63.3; H, 4.25; Co, 12.4. Found: C, 63.8; H, 4.63; Co, 11.7. The corresponding propionyl (m.p. 98–100° (dec.). *Anal.* Calcd.: C, 62.4; H, 4.36. Found: C, 62.8; H, 4.42) and isobutyryl (m.p. 101° (dec.). *Anal.* Calcd.: C, 63.0; H, 4.66. Found: C, 63.5: H, 4.78) compounds were prepared in the same manner. These compounds are stable at room temperature; the solids can be handled for short periods of time in air, but solutions oxidize rather rapidly. Proton magnetic resonance spectra are in accord with the assigned structures. All the compounds have a peak at 5.9–6.0μ in the infrared which we attribute to the acylcarbonyl group, the previously reported[1] 5.8-μ peak being shifted 0.1–0.2μ to longer wave length by the triphenylphosphine. The coördinated carbonyl bands at 5μ are shifted also by about the same amount. It is interesting that the use of a large excess of triphenylphosphine leads to the replacement of only one CO under these conditions. A limited amount of work indicates that triphenyl phosphite reacts analogously.

Several methods have been used to prepare these complexes, and in every case the reactions are in accord with the recently described chemistry of these compounds.[1,2] Thus, in the reaction of $RCOCo(CO)_4$, prepared by the acylation of $NaCo(CO)_4$ with acid halides or with alkyl halides and CO, one mole of CO per cobalt is evolved: $RCOCo(CO)_4 + P(C_6H_5)_3 \rightarrow RCOCo(CO)_3\text{-}P(C_6H_5)_3 + CO$. If $RCo(CO)_4$ is used, however, no CO is evolved, in agreement with our indications that this is in equilibrium with $RCOCo(CO)_3$.

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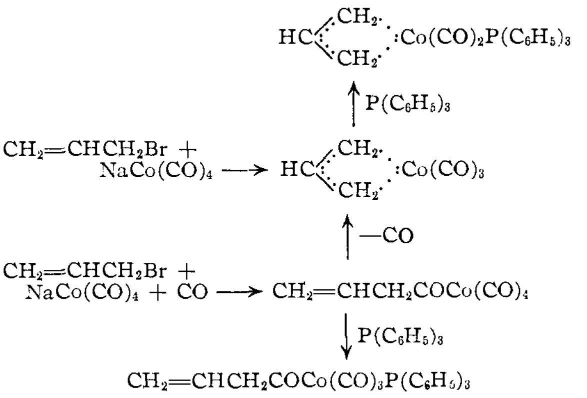
[1] R. F. Heck and D. S. Breslow, *Chem. & Ind.* (*London*), 467 (1960).

[2] R. F. Heck and D. S. Breslow, THIS JOURNAL, **82**, 750 (1960).

$RCo(CO)_4 \rightleftarrows RCOCo(CO)_3$ and $RCOCo(CO)_3 + P(C_6H_5)_3 \rightarrow RCOCo(CO)_3P(C_6H_5)_3$. This latter reaction constitutes a very convenient preparation of these complexes, an 86% yield of acetylcobalt tricarbonyl triphenylphosphine being obtained by treating excess methyl iodide with $NaCo(CO)_4$ at 0° in the presence of excess triphenylphosphine. $RCo(CO)_4$ should be formed as the primary product of the addition of $HCo(CO)_4$ to olefins; this reaction cannot be carried out in the presence of triphenylphosphine, because triphenylphosphine reacts with $HCo(CO)_4$ to give apparently $HCo(CO)_3P(C_6H_5)_3$, which is unreactive at 0°. The reaction of $HCo(CO)_4$ with a large excess of 1-pentene, followed by the addition of triphenylphosphine, has led to the isolation of a hexanoylcobalt tricarbonyl triphenylphosphine, m.p. 82–86° (dec.). *Anal.* Calcd.: C, 64.3; H, 5.20. Found: C, 64.5; H, 5.30. $HCo(CO)_4 + C_5H_{10} \rightarrow C_5H_{11}Co(CO)_4 \xrightarrow{P(C_6H_5)_3} C_5H_{11}COCo(CO)_3P(C_6H_5)_3$.

Allylcobalt tricarbonyl[2] reacts quite differently from simple alkylcobalt compounds. Treatment of it with triphenylphosphine liberates one mole of CO and yields allylcobalt dicarbonyl triphenylphosphine, m.p. 132° (dec.). *Anal.* Calcd.: C, 66.3; H, 4.85. Found: C, 66.3; H, 5.29. On the other hand, reaction of allyl bromide with $NaCo(CO)_4$ and CO in the presence of triphenylphosphine gives 3-butenoylcobalt tricarbonyl triphenylphosphine, identical with the product obtained from 3-butenoyl chloride, in spite of the fact that it has been shown[2] that 3-butenoylcobalt tetracarbonyl is converted on standing into allylcobalt tricarbonyl.



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RECEIVED JUNE 30, 1960

BOOK REVIEWS

Progress in Inorganic Chemistry. Volume Edited by F. ALBERT COTTON, Department of Chemistry, Massachusetts Institute of Technology, Cambridge, Massachusetts. Interscience Publishers, Inc., 250 Fifth Avenue, New York 1, N. Y. 1959. ix + 566 pp. 16 × 23 5 cm. Price, $14.50.

This is the first in an annual series of volumes devoted to "...maintaining effective, fruitful communication among the different branches of inorganic chemistry...". If the high standards generally typical of the contributions to this first volume are maintained, this series may well prove to be almost equally of interest and value to workers in the other fields of chemistry as well.

The seven largely unrelated topics reviewed in this volume are: Cyclopentadienyl and Arene Metal Compounds (G. Wilkinson and F. A. Cotton), Interstitial Compounds of Graphite (G. R. Henning), Uber Schwefel-Stickstoff-Verbindungen (M. Becke-Goehring), Metal-Ammonia Solutions (W. L. Jolly), Isocyanide Complexes of Metals (L. Malatesta), The Effect of Inner Orbital Splitting on the Thermodynamic Properties of Transition Metal Compounds and Coördination Complexes (P. George and D. S. McClure), and The Structure and Properties of Mixed Metal Oxides (R. Ward). It is an unfortunate but unavoidable fact that, owing to publication schedules, such discussions must always be incomplete relative to the current literature. For example, it is regrettable that the discussion of the structure of ferrocene and related species could not include more recent considerations of ionic models.

It is refreshing to find that, in accordance with stated editorial policy, these discussions reflect no efforts at oversimplification designed to appeal to a particular reader audience. At the same time, these discussions reveal only limited evidence of consciousness of a need to conform to the "sophisticated" approach.

The significance of this series to the literature of inorganic chemistry is best seen in context with the closely related series entitled "Advances in Inorganic Chemistry and Radiochemistry," Vol. 1 (Academic Press Inc., 1959) edited by Emelėus and Sharpe. Together these two new series provide ample evidence of the rapid postwar expansion and growth of the field of inorganic chemistry. It is to be hoped that editorial coöperation will minimize duplication of topics in succeeding volumes.

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Glutathione. Biochemical Society Symposium No. 17 held at Senate House, University of London on 15 February, 1958. Organized and Edited by E. M. CROOK, New York: Cambridge University Press, 32 East 57th Street, New York 22, N. Y. 1959. 115 pp. 16 × 25 cm. Price, $4.50.

"Glutathione," the subject of the Biochemical Society's 17th symposium, brings to the interested reader in condensed form both background and recent work on this ubiquitous substance, and supplements well the more comprehensive earlier American summary, "Glutathione: A Symposium," published in 1954. Different authors cover different facets of the subject.

Of special interest in the first chapter, "Chemistry and Biochemistry of Glutathione," by F. A. Isherwood, are considerations of the *pK* values of the different titratable groups in glutathione and speculations as to possible ring structures of the molecule which could explain certain of its properties. Pointed objections are made, however, by a discussant, N. W. Pirie. In the second chapter, "Techniques for Determining Glutathione," Christine G. Thomson and Heather Martin compare three selected methods and provide data to show their specificity, reliability and degree of concordance when applied to different test materials. Pirie makes the suggestion here that the method of deproteinizing used in analyses on tissue extracts may affect the values obtained for the proportions of the reduced and oxidized forms of glutathione. In the third chapter,