displace the dissociation equilibrium and lower the concentration of acetyl ions by the common ion effect. This should then cause a reduction in the exchange rate of acetyl hexafluoroarsenate. Unfortunately those hexafluoroarsenates which are soluble in sulfur dioxide exist almost entirely as the ion pair in solution. Therefore a negative result would not disprove the mechanism but a reduction in rate would be confirming evidence. It was found that addition of an equimolar quantity of tetra-*n*-butylammonium hexafluoroarsenate had no effect on the rate of exchange.

If the two different states of the acetyl ion involve a change in solvation the mechanism or rate of the reaction might change upon changing solvent. Acetyl hexafluoroarsenate is essentially insoluble in CH_2Cl_2 and SO_2F_2. A minor change in solvent was attempted by addition of another salt, tetra-*n*-butylammonium perchlorate. A rearrangement reaction occurred to yield acetyl perchlorate as neutral molecules. Its proton resonance peak is in the same position as those previously reported for acetyl complexes.[6] No exchange reaction was observed between acetyl perchlorate and acetyl fluoride at temperatures where the previous exchange reaction was rapid.

Experimental Section

Proton resonance spectra were obtained at 100 MHz on a Varian Associates HR100 spectrometer. Probe temperatures were calibrated with a copper–constantan thermocouple in a dummy sample tube. Methylene chloride, purified and stored over Linde Molecular Sieve 4A in a container on the vacuum line, was used as internal reference. Tetramethylsilane is unsuitable since it slowly reacts with arsenic pentafluoride to yield trimethylsilyl fluoride. Arsenic pentafluoride (Ozark-Mahoning) and anhydrous sulfur dioxide (Matheson) were stored over P_2O_5 in bulbs on the vacuum line. Acetyl fluoride was prepared according to the literature[10] and kept frozen when not being used. It was necessary to carefully bake the vacuum system prior to sample preparation in order to get adequately pure samples. If this precaution is not followed eq 1 is not obeyed, presumably because of other exchange pathways for the acetyl ion. Throughout this investigation only samples which obeyed eq 1 were used. The occasional sample which deviated was discarded and another prepared. The extent of agreement with eq 1 is shown in part by Table I. The data were fitted by least-square techniques and the listed errors are standard deviations.

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(10) C. W. Tullock and D. D. Coffman, *J. Org. Chem.*, **25**, 2016 (1960).

The Reaction of Organomercuric Halides with Dicobalt Octacarbonyl. A New Ketone Synthesis[1]

Dietmar Seyferth and Ralph J. Spohn[2]

Contribution from the Department of Chemistry, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139. *Received January 9, 1969*

Abstract: Many organomercuric halides react with dicobalt octacarbonyl in tetrahydrofuran solution at room temperature to give the ketone ($R_2C{=}O$) derived from R in RHgX, $Hg[Co(CO)_4]_2$, Co(II) halide, and carbon monoxide. The reaction proceeds rapidly and is of good preparative utility. The scope and limitations of this new ketone synthesis have been defined and the probable mechanism involves the following steps: solvent-induced redox disproportionation of dicobalt octacarbonyl to give $THF\cdot Co(CO)_4^+$ and $Co(CO)_4^-$; nucleophilic displacement of halide ion from mercury by the latter; electrophilic cleavage of the C–Hg bond in the $RHgCo(CO)_4$ formed (or in its disproportionation product, R_2Hg) by $THF\cdot Co(CO)_4^+$, forming $RCo(CO)_4$; organic group migration in the latter, producing $RCOCo(CO)_3$; and reaction of the latter with $RCo(CO)_4$ to give the ketone and cobalt carbonyl. Diphenylmercury also reacts with dicobalt octacarbonyl in THF to give benzophenone and $Hg[Co(CO)_4]_2$.

During a study of the possible extension of our recently observed dihalocarbene insertion into the Sn–Sn bond of hexamethylditin[3] to other metal–metal bond systems, the reaction of phenyl(trichloromethyl)mercury with dicobalt octacarbonyl was investigated.[4] The products obtained were $Hg[Co(CO)_4]_2$, chloromethinyltricobalt enneacarbonyl, cobalt(II) chloride, chloroform, and benzophenone. The presence of chloroform in the reaction mixture spoke for a CCl_3^- displacement from mercury at some stage during this reaction, nucleophilic displacement of CX_3^- from mercury being known to be a very facile process.[5,6] Further reaction of chloroform with dicobalt octacarbonyl no doubt was responsible for the small amount of chloromethinyltricobalt enneacarbonyl produced.[7] The formation of benzophenone suggested to us that organocobalt intermediates were involved and raised the question if the process exemplified by this reaction might not be of synthetic utility. Accordingly, a more detailed investigation was undertaken. Since the trichloromethyl group did not seem to be essential to the process to be studied and since nucleophilic displacement of halide ion from mercury occurs very readily under mild conditions,[8] it was decided to devote our further attention to a study of the action of dicobalt octacarbonyl on organomercuric halides.

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(1) Preliminary communication: D. Seyferth and R. J. Spohn, *J. Am. Chem. Soc.*, **90**, 540 (1968).

(2) National Institutes of Health Predoctoral Fellow, 1966 to present.

(3) (a) D. Seyferth and F. M. Armbrecht, Jr., *J. Am. Chem. Soc.*, **89**, 2790 (1967); (b) D. Seyferth, F. M. Armbrecht, Jr., and B. Schneider, *ibid.*, **91**, 1954 (1969).

(4) D. Seyferth, J. Y.-P. Mui, and R. J. Spohn, unpublished work.

(5) D. Seyferth, M. E. Gordon, J. Y.-P. Mui, and J. M. Burlitch, *J. Am. Chem. Soc.*, **89**, 959 (1967).

(6) D. Seyferth, M. E. Gordon, and R. Damrauer, *J. Org. Chem.*, **32**, 469 (1967).

(7) (a) W. T. Dent, L. A. Duncanson, R. G. Guy, W. H. B. Reed, and B. L. Shaw, *Proc. Chem. Soc.*, 169 (1961); (b) G. Bor, L. Markó, and B. Markó, *Chem. Ber.*, **95**, 333 (1962).

(8) *E.g.*, D. Seyferth and R. H. Towe, *Inorg. Chem.*, **1**, 185 (1962).

Results and Discussion

When a slurry of phenylmercuric bromide in tetrahydrofuran (THF) was added to an equimolar quantity of dicobalt octacarbonyl in THF (under nitrogen), moderate gas evolution commenced and a color change from red-brown to deep green was observed at the end of the addition. After 2 hr, work-up of the reaction mixture gave $Hg[Co(CO)_4]_2$ (79.5%, based on available mercury) and benzophenone (83%, based on available phenyl groups), as well as cobalt(II) bromide. This work-up procedure, which involved several extraction and crystallization steps, was tedious and for this reason a new procedure was devised. The known great insolubility of $Hg[Co(CO)_3PPh_3]_2$[9] was utilized to separate the $Hg[Co(CO)_4]_2$. An excess of triphenylphosphine was added to the benzene extracts of the reaction mixture to precipitate this triphenylphosphine substitution product quantitatively, and subsequent addition of methyl iodide served to remove the excess triphenylphosphine as the insoluble methyltriphenylphosphonium iodide. This left a solution containing some methyl iodide and the ketone produced. Isolation of the latter then was easily effected. This procedure served excellently in the isolation of benzophenone in 80% yield from such a reaction mixture.

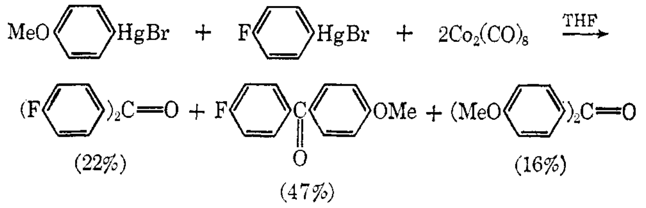
Having established that dicobalt octacarbonyl reacts with phenylmercuric bromide to give benzophenone, further experiments were carried out with other organomercuric halides. The RHgX compounds to be investigated were chosen with the aim of obtaining as much information as possible concerning the scope and mechanism of this new reaction in a minimum of experiments.

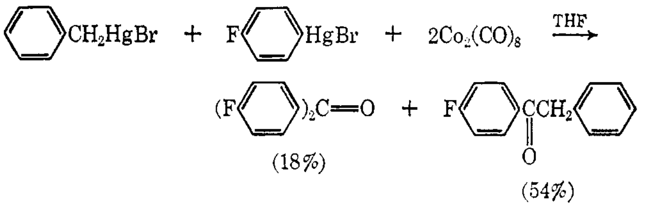
Simple, *para*-substituted arylmercuric bromides or chlorides reacted with dicobalt octacarbonyl in THF at room temperature to give the corresponding diaryl ketone in excellent yield. Prepared in this manner were 4,4′-dimethylbenzophenone (86%), 4,4′-dimethoxybenzophenone (84%), 4,4′-difluorobenzophenone (93%), and 4,4′-dichlorobenzophenone (89%). Completely different results were obtained in the case of C_6F_5HgBr and C_6Cl_5HgCl; no ketones were formed and only the diarylmercurials, $(C_6F_5)_2Hg$ (65%) and $(C_6Cl_5)_2Hg$ (98%), and $Hg[Co(CO)_4]_2$ could be isolated from the reaction mixtures. Intermediate behavior was found with *o*-tolymercuric bromide, the products of its reaction with dicobalt octacarbonyl being 2,2′-dimethylbenzophenone (38%) and di(*o*-tolyl)mercury (25%). Mesitylmercuric chloride, on the other hand, gave only dimesitylmercury in 78% yield, in addition to minor amounts (5%) of the δ-chlorobutyl ester of 2,4,6-trimethylbenzoic acid.

Further experiments extended the scope of this new ketone synthesis to the preparation in moderate yield of dialkyl ketones from alkylmercuric halides. Thus ethylmercuric chloride and cyclopropylmercuric bromide reacted with dicobalt octacarbonyl in THF to give 3-pentanone and dicyclopropyl ketone in yields of 60 and 66%, respectively. A similar reaction of isomerically pure *n*-butylmercuric bromide was of special interest in that *n*-butyl *sec*-butyl ketone (3-methyl-4-octanone) was produced in 14% yield in addition to the expected di-*n*-butyl ketone (5-nonanone) in 42% yield. Benzylmercuric bromide also presented complications. Dibenzyl ketone (51%) was obtained, but minor by-products included phenylacetaldehyde (4%), benzyl alcohol (8%), and bibenzyl (7%). With allylmercuric bromide the product isolated was an organocobalt compound, π-allylcobalt tricarbonyl (45% yield), rather than the expected diallyl ketone.

Of interest in terms of its relation to the initial finding which led to this investigation was the case of trichloromethylmercuric chloride. Here trichloromethyl anion displacement appeared to compete rather effectively with chloride ion displacement from mercury; chloroform was produced, as well as the product of its further reaction with dicobalt octacarbonyl, chloromethinyltricobalt enneacarbonyl, in 23% yield.

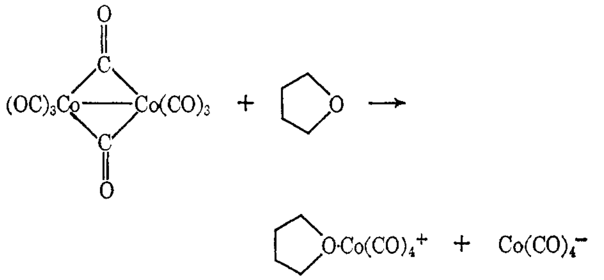
When two different organomercuric halides were allowed to react with dicobalt octacarbonyl (1:1:2 ratio), both the symmetrical ketones and the unsymmetrical ketone were produced. Random distribution of the organic groups in the ketones produced would give the two possible symmetrical ketones and the unsymmetrical ketone in 1:1:2 ratio. In the first case shown above, the product yields do not deviate very far from this ratio.





Further remarks concerning the synthetic utility of this new procedure for ketone synthesis will be made later in this paper, but first a discussion of the probable mechanism of this reaction is in order.

For the RHgX + $Co_2(CO)_8$ reaction in THF we propose the sequence of steps shown in eq 1-5: sol-



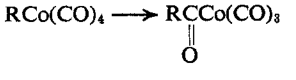
(1)

$$RHgX + Co(CO)_4^- \longrightarrow RHgCo(CO)_4 + X^- \quad (2)$$

$$RHgCo(CO)_4 + THF{\cdot}Co(CO)_4^+ + Co(CO)_4^- \longrightarrow RCo(CO)_4 + Hg[Co(CO)_4]_2 + THF \quad (3)$$

$$2\,RHgCo(CO)_4 \longrightarrow R_2Hg + Hg[Co(CO)_4]_2 \quad (3a)$$

$$R_2Hg + THF{\cdot}Co(CO)_4^+ + Co(CO)_4^- \longrightarrow RCo(CO)_4 + RHgCo(CO)_4 + THF \quad (3b)$$



$$RCo(CO)_4 \longrightarrow R\underset{\underset{O}{\|}}{C}Co(CO)_3 \quad (4)$$

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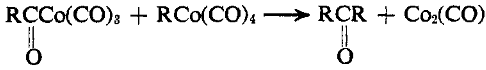
[9] W. Hieber and R. Breu, *Chem. Ber.*, 90, 1259 (1957).



$$R\underset{\underset{O}{\|}}{C}Co(CO)_3 + RCo(CO)_4 \longrightarrow R\underset{\underset{O}{\|}}{C}R + Co_2(CO)_7 \qquad (5)$$

vent-induced redox disproportionation of dicobalt octacarbonyl (eq 1), nucleophilic displacement of halide from mercury by $Co(CO)_4^-$ (eq 2), electrophilic cleavage of the C–Hg bond by $THF \cdot Co(CO)_4^+$ (eq 3), or a less direct sequence, symmetrization of $RHgCo(CO)_4$ (eq 3a), followed by electrophilic cleavage of the C–Hg bond in R_2Hg by $THF \cdot Co(CO)_4^+$ (eq 3b), migration of the organic group from cobalt to carbon (eq 4), ketone formation (eq 5). All of these steps are quite reasonable in terms of observations made during the course of this study or of previous work by others in the literature.

Reaction 1 is well known; many organic Lewis bases are known to induce such redox disproportionation of dicobalt octacarbonyl.[10,11] While the action of a Lewis basic solvent on dicobalt octacarbonyl leads ultimately to the degradation reaction of the stoichiometry shown in eq 6, the first step in this process is

$$3Co_2(CO)_8 + 12B\colon \longrightarrow 2[CoB_6^{2+}][Co(CO)_4^-]_2 + 8CO \qquad (6)$$

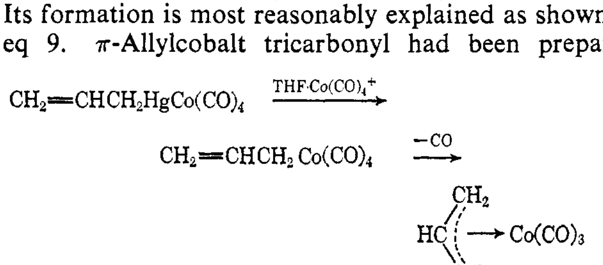
believed to be the formation of $[B\colon Co(CO)_4^+][Co(CO)_4^-]$, and it was suggested that the stability of the $B\colon Co(CO)_4^+$ ion depends upon the donor properties of the Lewis base, B:. Since THF, compared to tertiary amines and phosphines, is a relatively weak Lewis base, the $THF \cdot Co(CO)_4^+$ ion should be relatively resistant to further degradation by displacement of carbon monoxide by THF.

Reaction 2 is quite plausible. As mentioned, in the case of $PhHgCCl_3$ in acetone one of the products is chloroform and this is usually the major product when nucleophilic displacement of CCl_3^- from mercury occurs.[5,6] The $Co(CO)_4^-$ ion is known to be a good nucleophile. For instance, it displaces iodide ion from carbon[12] (eq 7) and, more to the point, halide ion from organometallic halides (*e.g.*, eq 8).[13] However, compounds of type $RHgCo(CO)_4$ are not well known. A brief note has mentioned the preparation of $CH_3HgCo(CO)_4$ by reaction of $Na[Co(CO)_4]$ with excess methylmercuric chloride in methanol, but no details or properties other than the C≡O stretching frequencies were reported.[14] One wishes that this compound had been more adequately characterized, especially in view of the later report by Mays and Robb[15] that $RHg\text{-}M(CO)_nL$ systems (*e.g.*, $\pi\text{-}C_5H_5Mo(CO)_3HgCH_3$) appear to be generally unstable with respect to disproportionation to the symmetrical species, R_2Hg and $Hg[M(CO)_nL]_2$. Our own attempts to prepare and isolate an arylmercurycobalt tetracarbonyl were unsuccessful, $ArHgBr + Na[Co(CO)_4]$ reactions giving the diarylmercury compound and $Hg[Co(CO)_4]_2$ in high yield in the cases examined. However, in the $RHgX + Co_2(CO)_8$ reaction it is sufficient that the $RHgCo(CO)_4$ compounds be only transiently stable species, and as has been indicated in eq 3a and 3b, product formation in some or even in all cases may involve disproportionation of $RHgCo(CO)_4$ to R_2Hg and $Hg[Co(CO)_4]_2$ before cleavage of the R–Hg bond. In any case, it was found that diphenylmercury will react with dicobalt octacarbonyl in THF at room temperature to give benzophenone and $Hg[Co(CO)_4]_2$ in good yield, and thus the alternate path to reaction 3, the reaction sequence 3a, 3b, most certainly can be followed. If the cleavage of the R–Hg bond by $THF \cdot Co(CO)_4^+$ is very facile, the reaction sequence leading to ketone formation may be (1, 2, 3, 4, 5); if, on the other hand, cleavage of the R–Hg bond occurs at a rate slower than symmetrization of $RHgCo(CO)_4$, the reaction sequence would be (1, 2, 3a, 3b, 4, 5). One can conceive of cases where steric and/or electronic factors operate to completely hinder R–Hg cleavage, or to retard it to such an extent that a significant proportion, or even all, of the $THF \cdot Co(CO)_4^+$ species is consumed by further reaction with solvent to give unreactive cobalt species. In such cases substantial amounts of R_2Hg compounds would be present at the end of the reaction period and the ketone yields would range from low down to zero. We have found several examples interpretable in terms of such behavior. With *o*-tolylmercuric bromide both the ketone and the diarylmercurial were formed. In the case of mesitylmercuric bromide access by the $THF \cdot Co(CO)_4^+$ electrophile to the $Hg\text{-}C_{aryl}$ bond must have been prevented completely by the two *o*-methyl groups and *only* dimesitylmercury was obtained. With C_6F_5HgBr and C_6Cl_5HgCl only the diarylmercurials were obtained, and electronic factors as well as steric factors serve to explain this result, since it is known that the $C_6F_5\text{–}Hg$ and $C_6Cl_5\text{–}Hg$ bonds are relatively resistant toward electrophilic cleavage. Thus, the action of HCl on $C_6H_5HgC_6F_5$ resulted in preferential cleavage of the phenyl group, giving C_6H_6 and C_6F_5HgCl,[16] while HCl cleavage of $C_6H_5HgC_6Cl_5$ gave C_6H_6 and C_6Cl_5HgCl.[17] Hence in the $C_6F_5HgBr + Co_2(CO)_8$ and the $C_6Cl_5HgCl + Co_2(CO)_8$ reactions the process shown in eq 2 is followed by reaction 3a; reaction of $THF \cdot Co(CO)_4^+$ with the THF solvent then occurs more rapidly than, and to the exclusion of, (3b).

$$Co(CO)_4^- + CH_3I \longrightarrow CH_3Co(CO)_4 + I^- \qquad (7)$$

$$2Co(CO)_4^- + (CH_3)_2SnCl_2 \longrightarrow (CH_3)_2Sn[Co(CO)_4]_2 + 2Cl^- \qquad (8)$$

Two of our experiments provide evidence that $RCo(CO)_4$ compounds are intermediates in the $RHgX + Co_2(CO)_8$ reaction. First, in the case of allylmercuric bromide, an organocobalt compound, π-allylcobalt tricarbonyl, was the product isolated. Its formation is most reasonably explained as shown in eq 9. π-Allylcobalt tricarbonyl had been prepared previously by reaction of allyl bromide with $Na[Co(CO)_4]$ in diethyl ether, and an unstable σ-allylcobalt



(9)

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(10) I. Wender, H. W. Sternberg, and M. Orchin, *J. Am. Chem. Soc.*, **74**, 1216 (1952).

(11) W. Hieber and J. Sedlmeier, *Chem. Ber.*, **87**, 25 (1954).

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

(13) W. Hieber and R. Breu, *Chem. Ber.*, **90**, 1270 (1957).

(14) O. Kahn, J. Henrion, and G. Bouquet, *Bull. Soc. Chim. France*, 3547 (1967).

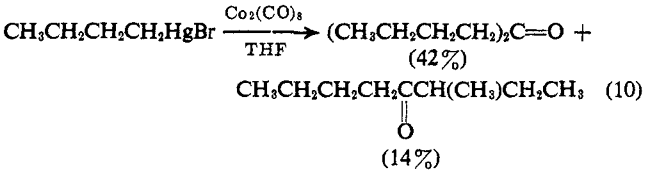
(15) M. J. Mays and J. D. Robb, *J. Chem. Soc., A*, 329 (1968).

(16) R. D. Chambers, G. E. Coates, J. G. Livingstone, and W. K. R. Musgrave, *ibid.*, 4367 (1962).

(17) F. E. Paulik, S. I. E. Green, and R. E. Dessy, *J. Organometal. Chem.*, **3**, 229 (1965).

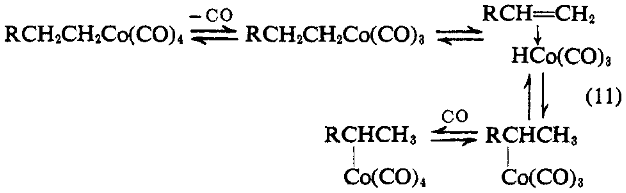
tetracarbonyl intermediate was implicated in this reaction.[18]

Also to be noted as evidence for the intervention of $RCo(CO)_4$ intermediates is the isomerization which occurred in the case of *n*-butylmercuric bromide (eq 10).



$$CH_3CH_2CH_2CH_2HgBr \xrightarrow[THF]{Co_2(CO)_8} \underset{(42\%)}{(CH_3CH_2CH_2CH_2)_2C{=}O} + \underset{(14\%)}{CH_3CH_2CH_2CH_2\underset{\overset{\|}{O}}{C}CH(CH_3)CH_2CH_3} \quad (10)$$

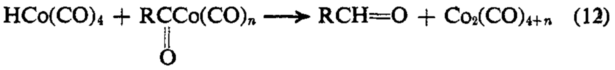
Alkylcobalt tetracarbonyls are known to undergo isomerization of the alkyl groups and the process shown in eq 11 is believed responsible.[19] Since alkylmercury compounds are stable with respect to such isomerization, alkylcobalt compounds are the only intermediates in our proposed reaction sequence which could serve to explain the result shown in eq 10. Such isomerizations, it should also be noted, can occur under very mild conditions.[20]



(11)

Reaction 4, the $RCo(CO)_4$ to $RCOCo(CO)_3$ conversion, is a well-known process and constitutes one of the key steps of the cobalt carbonyl catalyzed hydroformylation of olefins.[19,21]

Finally, the ketone-forming step (reaction 5) proposed also finds support in a previous study by Jonassen, *et al.*,[22] devoted to the formation of ketones in the hydroformylation reaction. It was pointed out by these authors that when R in $RCo(CO)_4$ was small in size (*e.g.*, when R = Et), the reaction shown in eq 5 can compete rather effectively with the aldehyde-producing reaction (eq 12). An example was given in which gaseous cobalt tetracarbonyl hydride was passed into an excess of 1-butene in pentane at −8° and the resulting reaction mixture then was heated to 125°. The product mixture obtained contained ketones and aldehydes in 9:1 ratio, and, among the former, 5-nonanone, 3-methyl-4-octanone, and 3,5-dimethyl-4-heptanone were identified. However, absolute yields or even molar ratios of these components were not reported by these authors. The decomposition of methylcobalt tetracarbonyl was found by Hieber and his coworkers[12,23] to give acetone, and thus the formation of ketones from $RCo(CO)_4$ (*via* eq 4 and 5) seems to be a well-established process, and it should be particularly effective in the absence of free $HCo(CO)_4$. It is perhaps significant that in our case, the $n\text{-}C_4H_9HgBr + Co_2(CO)_8$ reaction, only ketones and no aldehydes were formed. This would appear to be indirect evidence that *free* cobalt tetracarbonyl hydride is not involved in the *n*-butyl to *sec*-butyl isomerization process, in agreement with the process shown in eq 11. Also of interest is the difference in the conditions in the two $(C_4H_9)_2C{=}O$-producing experiments under discussion. In the 1-butene + $HCo(CO)_4$ reaction, a heating period seemed necessary to effect decomposition of the organocobalt species, but in the case of the $n\text{-}C_4H_9HgBr + Co_2(CO)_8$ reaction, essentially complete decomposition was observed at room temperature. This difference, if real (*i.e.*, was the 125° heating period really necessary?), could reflect a synthetically useful solvent effect, since pentane was used in the first case and THF in the second.



$$HCo(CO)_4 + R\underset{\overset{\|}{O}}{C}Co(CO)_n \longrightarrow RCH{=}O + Co_2(CO)_{4+n} \quad (12)$$

To provide still further evidence in favor of a reaction scheme for the RHgX + $Co_2(CO)_8$ ketone synthesis involving $RCo(CO)_4$ intermediates, we investigated the reaction of benzyl bromide with $Na[Co(CO)_4]$ in THF. This should give benzylcobalt tetracarbonyl as the initial product and hence the same final products as the reaction of benzylmercuric bromide with dicobalt octacarbonyl. This prediction was confirmed; the major product obtained was dibenzyl ketone and the other minor products of the $PhCH_2HgBr + Co_2(CO)_8$ reaction also were produced.

In summary, the reaction sequences (1, 2, 3, 4, 5) and/or (1, 2, 3a, 3b, 4, 5) seem to provide the best explanation for the course of the RHgX + $Co_2(CO)_8$ ketone synthesis. The consideration of our experimental results together with these conclusions concerning mechanism now provides a good indication of the scope of this synthesis. One may thus make the following comments concerning the synthetic utility of the RHgX + $Co_2(CO)_8$ reaction.

(a) The reaction is rapid, almost complete by the end of the RHgX addition as indicated by the color change from red-brown to green, and it proceeds under very mild conditions. Worth stressing again are the generally good yields (excellent in many cases) and the very simple and rapid work-up procedure which has the advantage of not requiring a hydrolysis step.

(b) It should be excellently applicable to the preparation of a wide variety of symmetrical diaryl ketones, provided that the aryl groups are not too hindered at the *ortho* positions or of such a nature that their electrophilic cleavage from mercury will be hindered because of electronic factors. This procedure should be especially attractive for the preparation of diaryl ketones in view of the facility with which such a great diversity of aromatic and heterocyclic compounds is mercurated directly.[24,25] Thus, a very direct route for the conversion of aromatic hydrocarbons to the respective diaryl ketone is available.

(c) This procedure should be cleanly applicable to the synthesis of only those dialkyl ketones where carbon skeleton rearrangements of the alkylcobalt tetracarbonyl

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[18] R. F. Heck and D. S. Breslow, *J. Am. Chem. Soc.*, **82**, 750 (1960); **83**, 1097 (1961).

[19] (a) R. F. Heck, *Advan. Organometal. Chem.*, **4**, 243 (1966); (b) R. F. Heck in "Organic Syntheses via Metal Carbonyls," Vol. 1, I. Wender and P. Pino, Ed., Interscience Division of John Wiley and Sons, Inc., New York, N. Y., 1968, pp 373–403; (c) A. J. Chalk and J. F. Harrod, *Advan. Organometal. Chem.*, **6**, 119 (1968).

[20] G. L. Karapinka and M. Orchin, *J. Org. Chem.*, **26**, 4187 (1961).

[21] C. W. Bird, "Transition Metal Intermediates in Organic Synthesis," Logos Press, London, 1967, Chapter 6.

[22] J. A. Bertrand, C. L. Aldridge, S. Husebye, and H. B. Jonassen, *J. Org. Chem.*, **29**, 790 (1964).

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

[24] W. Kitching, *Organometal. Chem. Rev.*, [A], **3**, 35 (1968).

[25] L. G. Makarova and A. N. Nesmeyanov, "The Organic Compounds of Mercury" (English translation), North Holland Publishing Co., Amsterdam, 1967, Chapter 5.

intermediates would not complicate matters (*e.g.*, diethyl and dicyclopropyl ketones, as shown in this study). However, in the case of most alkylmercuric halides, rearrangements would be expected; the abundant literature concerning the hydroformylation reaction would be a valuable guide in this connection.

(d) Not very much is known concerning the reactivity of $Co(CO)_4^-$ toward organic functional groups, but one would expect those functional groups particularly sensitive to nucleophilic attack to cause complications.

(e) This procedure can be used to prepare unsymmetrical ketones if a mixture of two different organomercuric halides is used, but yields of *ca.* 50% are the best to be expected, and all three possible ketones usually should be formed. Other routes to unsymmetrical ketones clearly are preferable (*e.g.*, RCOX + $[R'_2Cd + MgX_2]$).

(f) For many ketones the RX + $Na[Co(CO)_4]$ reaction, demonstrated here in the case of benzyl bromide, could possibly be a more directly applicable alternative, and we are at present examining this general reaction in greater detail. However, if the organic halide is not susceptible to nucleophilic attack by $Co(CO)_4^-$ (*e.g.*, most aryl and vinyl halides), the RHgX + $Co_2(CO)_8$ is of excellent utility.

The RHgX + $Co_2(CO)_8$ reaction represents a stoichiometric utilization of dicobalt octacarbonyl. This reaction would, of course, be considerably more attractive if it could be carried out with only catalytic quantities of the cobalt carbonyl, using carbon monoxide as the stoichiometric reagent. Further research in these laboratories is directed toward this end. In this connection, the recent work of Heck,[26] published after our preliminary communication,[1] concerning the synthesis of diaryl ketones by the reaction of arylmercuric halides in the presence of palladium(II) or rhodium(III) catalysts is of interest. σ-Arylpalladium and σ-arylrhodium intermediates undoubtedly were involved in these reactions, but it must be noted that the yields of ketones were not high.

Other ketone syntheses based on RX + metal carbonyl reactions have been reported recently. For instance, nickel tetracarbonyl reacts with benzyl halides in N,N-dimethylformamide to give dibenzyl ketone in high yield,[27a] and the reaction of benzyl halides with $Fe_3(CO)_{12}$ in THF also gave dibenzyl ketone, but in much lower yields.[27b] To these can now be added the benzyl bromide + $Co_2(CO)_8$ reaction in THF, which we have studied briefly and which also gives dibenzyl ketone.

Experimental Section

General Comments. All reactions were carried out under an atmosphere of prepurified nitrogen. Infrared spectra were recorded using a Perkin-Elmer Model 237 grating infrared spectrophotometer, nmr spectra with a Varian Associates T60 spectrometer. Chemical shifts are given in δ units (ppm) downfield from internal TMS. Thin layer chromatography (tlc) was performed using Eastman Chromatogram Sheet No. 6060 Type K301-R. The sheet was developed using 20% benzene in cyclohexane and organomercury compounds were visualized by treatment with iodine vapors followed by spraying with 10% aqueous sodium sulfide. In gas-liquid partition chromatographic (glpc) analyses, the MIT isothermal unit was used with a glass column 4 ft × 12 mm o.d. containing 20% Dow Corning silicone oil DC-710 on Johns-Manville Chromosorb P. F & M gas chromatographs, Models 700, 720, and 5754, also were used. Yields were determined by the internal standard procedure. A list of columns used follows: column A, 12 ft aluminum (0.25 in. o.d.), 20% General Electric Co. SE-30 silicone rubber gum on Chromosorb P (F & M 700); column B, 4 ft aluminum, 25% SE-30 on Chromosorb P (F & M 700); column C, 4 ft, 10% UC-W98 on Chromosorb P (F & M 5754); column D, 6 ft, 20% Carbowax 20M on Chromosorb P (F & M 700); column E, 3 ft, 20% SE-30 on Chromosorb W (F & M 720); column F, 4 ft, 7.5% SE-30 on Chromosorb P (F & M 700); column G, 6 ft, 20% Carbowax M on Chromosorb P (F & M 700).

Dicobalt octacarbonyl was purchased from Strem Chemical Co. and stored in a freezer under nitrogen. Tetrahydrofuran (THF) was distilled from sodium benzophenone ketyl immediately before use.

Organomercuric Halides. Most of the organomercuric halides used were prepared by the Grignard procedure. Trichloromethylmercuric chloride was obtained by cleavage of phenyl(trichloromethyl)mercury with hydrogen chloride in benzene solution,[28] allyl- and cyclopropylmercuric bromides by cleavage of the appropriate tetraorganotin compound with mercuric bromide in diethyl ether.[29] The mercurials used in this study included: C_6H_5HgCl, mp 257° (lit.[30] mp 256–258°); C_6H_5HgBr, mp 283° (lit.[30] mp 283–285°); *p*-FC_6H_4HgBr, mp 303–305° (sealed tube; sublimes at 240° in an open capillary) (lit.[31] mp 240°); *p*-MeC_6H_4HgCl, mp 231–232° (lit.[32] mp 231°); *p*-$MeOC_6H_4HgBr$, mp 254–255° (lit.[33] mp 258°); *p*-ClC_6H_4HgBr, mp 241–242° (lit.[34] mp 239°); *o*-MeC_6H_4HgBr, mp 167–169° (lit.[32] mp 168°); 2,4,6-$Me_3C_6H_2HgCl$, mp 204–204.5° (lit.[35] mp 202°); C_6Cl_5HgCl, mp 264–265° (lit.[17] mp 264°); C_6F_5HgBr, mp 152–154° (lit.[16] mp 155°); $C_6H_5CH_2HgBr$, mp 117–119° (lit.[36] mp 119°); EtHgCl, mp 190–192° (lit.[37] mp 192–194°); *n*-BuHgBr, mp 129–130° (lit.[38] mp 130°); Cl_3CHgCl, mp 191.5–192° (lit.[28] mp 191°); $CH_2{=}CHCH_2HgBr$, mp 116–117° (lit.[39] mp 116–118°); *c*-C_3H_5HgBr, mp 196–197° (lit.[29] mp 196.5–197.5°). Because of the discrepancy between our observed melting point and that in the literature, *p*-fluorophenylmercuric bromide was analyzed. *Anal.* Calcd for C_6H_4BrFHg: C, 19.15; H, 1.08. Found: C, 19.28; H, 1.30.

Also analyzed was mesitylmercuric bromide. *Anal.* Calcd for $C_9H_{11}BrHg$: C, 30.43; H, 3.12. Found: C, 30.58; H, 3.11.

Reaction of Phenylmercuric Bromide with Dicobalt Octacarbonyl. Isolation of Reaction Products. Dicobalt octacarbonyl (7.1 g, 20.8 mmoles) was charged into a 100-ml three-necked flask equipped with a reflux condenser topped with a nitrogen-inlet tube, a pressure-equalizing addition funnel, and a magnetic stirring unit under an atmosphere of dry nitrogen and thirty milliliters of dry THF was added. A slurry of 6.80 g (19 mmoles) of phenylmercuric bromide in 20 ml of THF was added *via* the addition funnel, slowly with stirring, over a 55-min period at room temperature. Carbon monoxide was evolved during the addition, and near the end, the initially red-brown reaction solution turned dark green. The reaction mixture was stirred at room temperature for 2 hr. Carbon monoxide evolution had ceased shortly after the last of the phenylmercuric bromide had been added. The solvent was removed at reduced pressure and the dark green residue was extracted with 150 ml of hexane, until the extracts no longer were red-brown. Cooling the extracts to 0° resulted in crystallization of 3.6 g of red-brown needles. This material, mp 80.5–82.5° dec, was identified as Hg-

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(26) R. F. Heck, *J. Am. Chem. Soc.*, **90**, 5546 (1968).

(27) (a) E. Yoshisato and S. Tsutsumi, *J. Org. Chem.*, **33**, 869 (1968); (b) I. Rhee, N. Mizuta, M. Ryang, and S. Tsutsumi, *Bull. Chem. Soc. Japan*, **41**, 1417 (1968).

(28) D. Seyferth, J. Y.-P. Mui, L. J. Todd, and K. V. Darragh, *J. Organometal. Chem.*, **8**, 29 (1967).

(29) D. Seyferth and H. M. Cohen, *Inorg. Chem.*, **2**, 652 (1963).

(30) D. Seyferth and J. M. Burlitch, *J. Organometal. Chem.*, **4**, 129 (1965).

(31) A. E. Borisov, I. S. Savel'eva, and S. R. Serdyuk, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 924 (1965).

(32) E. L. Hill, *J. Am. Chem. Soc.*, **50**, 167 (1928).

(33) J. C. Sipos, H. Sawatzky, and G. F. Wright, *ibid.*, **77**, 2759 (1955).

(34) D. Spinelli and A. Salvemini, *Ann. Chim.* (Rome), **51**, 1296 (1961); *Chem. Abstr.*, **56**, 15530 (1962).

(35) R. F. Heck, *J. Am. Chem. Soc.*, **90**, 5518 (1968).

(36) K. C. Bass, *J. Organometal. Chem.*, **4**, 92 (1965).

(37) L. H. Werner and C. R. Scholz, *J. Am. Chem. Soc.*, **76**, 2453 (1954).

(38) B. C. Curran, *ibid.*, **64**, 830 (1942).

(39) O. A. Reutov and M. A. Besprozvannyi, *Dokl. Akad. Nauk SSSR*, **80**, 765 (1951).

$[Co(CO)_4]_2$ (lit.[40] mp 81–82° dec) by comparison of its infrared spectrum with that in the literature.[41] Analysis gave 17.61% carbon (calcd 17.70%). Several subsequent careful concentration and cooling steps gave additional $Hg[Co(CO)_4]_2$; the total yield was 7.85 g (15.1 mmoles). The hexane was removed from the mother liquor at reduced pressure, leaving 1.4 g (81% yield, based on available phenyl groups) of light brown benzophenone, mp 46–47°. Sublimation at 40° (0.01 mm) gave white crystals, 1.25 g (73%), mp 46–47°, whose mixture melting point with authentic material was not depressed.

The blue-green solids left after the hexane extraction were dissolved in acetone to give a deep blue solution. The solution became pink when water was added. A small sample of the solution gave a positive halide ion test with silver nitrate. The uv spectrum of the aqueous solution showed a band at 510 mμ with a shoulder on the low-frequency side, characteristic of the $Co(H_2O)_6^{2+}$ ion.[42] Removal of the solvents at reduced pressure left 2.1 g of $CoBr_2 \cdot 6H_2O$.

Preparation of Diaryl Ketones by the Reaction of Arylmercuric Halides with Dicobalt Octacarbonyl. Recommended Procedure. The preparation of 4,4′-difluorobenzophenone is given as an example of the procedure used.

A solution of 1.85 g (5.4 mmoles) of dicobalt octacarbonyl in 20 ml of dry THF was prepared in a 100-ml three-necked flask equipped with reflux condenser topped with a nitrogen-inlet tube, a pressure-equalizing addition funnel and a magnetic stirring unit. To this was added slowly with stirring a solution of 2.03 g (5.4 mmoles) of *p*-fluorophenylmercuric bromide in 20 ml of THF during a 15-min period. Carbon monoxide was evolved and near the end of the addition the initially red-brown solution turned green. Tlc analysis 1 hr after completion of the addition showed that all of the starting mercurial had been consumed. The THF was removed at reduced pressure and the green residue was extracted with 100 ml of hot benzene. Triphenylphosphine (5 g, 19 mmoles) was added to the warm benzene extracts. Carbon monoxide was evolved and a solid (dec pt 205–210°) precipitated. Filtration was followed by addition of 5 ml of methyl iodide to the filtrate to precipitate unconverted triphenylphosphine as methyltriphenylphosphonium iodide. The mixture was allowed to stand at room temperature for 1 hr and then was filtered to remove the phosphonium iodide. Removal of the volatiles from the filtrate at reduced pressure left a residue, sublimation of which at 60° (0.05 mm) gave 0.501 g (93%) of 4,4′-difluorobenzophenone, mp 103–105° (lit.[43] mp 105–106°), $\nu_{C=O}$ 1663 cm^{-1}.

This procedure was used to prepare benzophenone in 80% yield from phenylmercuric chloride, 4,4′-dimethylbenzophenone (86%) from *p*-tolylmercuric chloride, 4,4′-dimethoxybenzophenone (84%) from *p*-anisylmercuric bromide, and 4,4′-dichlorobenzophenone (89%) from *p*-chlorophenylmercuric bromide. All ketones had melting points in agreement with those recorded in the literature and infrared spectra which agreed well with those in the Sadtler Standard Spectra file for these ketones.

Reaction of *o*-Tolylmercuric Bromide with Dicobalt Octacarbonyl. A solution of 5.62 g (16.4 mmoles) of dicobalt octacarbonyl in 65 ml of dry THF in a 200-ml reaction flask (equipped in the usual manner) was prepared under nitrogen and 6.0 g (16.2 mmoles) of *o*-tolylmercuric bromide in 65 ml of THF was added with stirring during 35 min at room temperature. As usual, carbon monoxide was evolved and the reaction mixture turned green. The mixture was stirred overnight and then the THF was removed at reduced pressure. The oily residue was extracted with 120 ml of benzene and the extracts were treated with 6.0 g (23 mmoles) of triphenylphosphine. The mixture was stirred for 2 hr and filtered to remove 11.65 g of solid. To the filtrate was added 6 ml of methyl iodide and the methyltriphenylphosphonium iodide which was produced was filtered off 1 hr later. The filtrate was evaporated at reduced pressure and the residue sublimed at 125° (0.05 mm). The oily sublimate, obviously a mixture of compounds, was dissolved in THF. Glpc analysis of the THF solution (column C, 100–210°, 6°/min temperature program) showed the presence of three components besides solvent. A sample of this solution was saved for later yield analysis and the remainder was distilled at 0.07 mm. Two fractions were collected: (A) bp 95–97°, (B) bp 97–100°.

Fraction A contained one component which was identified as 2,2′-dimethylbenzophenone. Its infrared spectrum was identical with that reported for this compound[44] and its nmr spectrum (in CCl_4) showed the expected singlet at 2.4 ppm and multiplet centered at 7.2 ppm in the proper ratio. Fraction B contained a mixture of this ketone and two other components which were collected by glpc (column B, 100–200°, 10°/min temperature program). The major component was identified as di-*o*-tolylmercury by tlc and its melting point of 103–105° (lit.[45] mp 107°). Its nmr spectrum showed a singlet at 2.36 ppm and a multiplet centered at 7.13 ppm in the appropriate ratio. (We recognize that had any *o*-tolylmercuric bromide been present at the point when triphenylphosphine was added, it would have been symmetrized by this reagent to di-*o*-tolylmercury and $HgBr_2 \cdot 2Ph_3P$.[46] However, in the case of the mesityl-, pentachlorophenyl-, and pentafluorophenylmercuric halides, the Ar_2Hg compounds were obtained in a work-up procedure which did not involve a triphenylphosphine treatment. Also, in the present case, not enough triphenylphosphine was added to accomplish precipitation of all cobalt carbonyl species and symmetrization of 25% of the *o*-tolylmercuric bromide.)

The minor component was identified as δ-bromobutyl *o*-toluate on the basis of its $\nu_{C=O}$ at 1722 cm^{-1}, a positive Beilstein test for halogen, and its mass spectrum which showed a parent ion at *m/e* 270–272 (1 : 1), characteristic of the presence of a bromine atom.

Glpc analysis (column C, 100–210°, 6°/min program) using *n*-valerophenone as internal standard established that 2,2′-dimethylbenzophenone and di-*o*-tolylmercury had been formed in yields of 38 and 25%, respectively.

Reaction of Mesitylmercuric Chloride with Dicobalt Octacarbonyl. A solution of 7.10 g (20.0 mmoles) of mesitylmercuric chloride in 65 ml of THF was added to 6.90 g (20.5 mmoles) of dicobalt octacarbonyl in 60 ml of THF in the usual manner. Some gas was evolved during the 40-min addition period, but the reaction solution remained red-brown. A small amount of green solid was, however, present. The reaction mixture was concentrated to approximately 30 ml at reduced pressure. The solid phase, 3.0 g of crude dimesitylmercury, was filtered. Further quantities of this compound were obtained by concentration and cooling of the mother liquor. The combined solids thus obtained were recrystallized from THF to give 3.05 g of white needles, mp 241–243° (lit.[47] mp 235° for dimesitylmercury), and 0.38 g of discolored dimesitylmercury, a total yield of 78%; nmr (in $DCCl_3$), 2.30 (3) s, 2.52 (6) s, 7.04 (2) s ppm. *Anal.* Calcd for $C_{18}H_{22}Hg$: C, 49.25; H, 5.05. Found: C, 49.07; H, 4.80.

The remaining THF was removed at reduced pressure and the residue was extracted with 50 ml of benzene. Addition of 5.0 g (19 mmoles) of triphenylphosphine to the benzene solution resulted in precipitation of 10.5 g of solid. The filtrate from the removal of this solid was treated with 5 ml of methyl iodide for 1 hr and filtered to remove the precipitated phosphonium salt. The filtrate was evaporated at reduced pressure and the residue sublimed at 150° (0.1 mm). The oily sublimate was dissolved in diethyl ether. Glpc analysis of this solution (column E, 180°) showed the presence of several minor components. The one present in largest quantity was collected and identified as the δ-chlorobutyl ester of 2,4,6-trimethylbenzoic acid: $n^{25}D$ 1.5128; nmr (in CCl_4), 1.75 (4) m, 2.03 (9) s, 3.43 (2) m, 4.20 (2) m, 6.75 (2) s ppm. The infrared spectrum (neat film) showed $\nu_{C=O}$ at 1725 cm^{-1}.

Anal. Calcd for $C_{14}H_{19}O_2Cl$: C, 66.01; H, 7.52. Found: C, 65.66; H, 7.20.

Reaction of Pentachlorophenylmercuric Chloride with Dicobalt Octacarbonyl. A solution of 2.30 g (4.75 mmoles) of C_6Cl_5HgCl in 30 ml of THF was added to 1.64 g (4.80 mmoles) of dicobalt octacarbonyl in 30 ml of THF in the usual manner. During the 40-min addition period white needles precipitated and the solution remained red-brown. Tlc analysis after 5.5 hr showed that all of the C_6Cl_5HgCl had been consumed. Filtration of the reaction mixture gave 1.63 g (98%) of white needles.

Recrystallization from nitrobenzene gave material with mp 375–377°. The melting point reported for $(C_6Cl_5)_2Hg$ is 383°.[17]

Reaction of Pentafluorophenylmercuric Bromide with Dicobalt Octacarbonyl. A solution of 7.45 g (16.6 mmoles) of C_6F_5HgBr in

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[40] R. B. King, *Organometal. Syn.*, **1**, 101 (1965).

[41] G. Bor and L. Markó, *Spectrochim. Acta*, **16**, 1105 (1960).

[42] O. G. Holmes and D. S. McClure, *J. Chem. Phys.*, **26**, 1686 (1957).

[43] W. Funusaka, T. Ando, K. Kondo, and S. Kodama, *Kûi Gosei Kagaku Kyôkai Shi*, **17**, 717 (1959); *Chem. Abstr.*, **55**, 2248 (1961).

[44] "The Sadtler Standard Spectra," Sadtler Research Laboratories, Philadelphia, Pa., Spectrum No. 4863.

[45] K. A. Kocheshkov and M. M. Nad, *J. Gen. Chem. USSR*, **5**, 1158 (1935).

[46] G. E. Coates and A. Lauder, *J. Chem. Soc.*, 1857 (1965).

[47] G. A. Razuvaev, Yu. A. Ol'dekop, and M. N. Karleva, *Zh. Obshch. Khim.*, **21**, 650 (1951).

75 ml of THF was added to 5.74 g (16.7 mmoles) of dicobalt octacarbonyl in 50 ml of THF in the usual manner. An infrared spectrum of the reaction solution taken 30 min after the 30-min addition period showed no C=O absorption characteristic of the expected ketone ($\nu_{C=O}$ for $(C_6F_5)_2C{=}O$ is 1725 cm^{-1} [48]). Tlc analysis gave evidence only for the presence of $Hg[Co(CO)_4]_2$, $(C_6F_5)_2Hg$, and Co^{2+} salts. The solvent was removed under reduced pressure, leaving a green oil. Extraction of the latter with 150 ml of hot benzene was followed by addition of 6 g of triphenylphosphine to the benzene extracts. The precipitate which resulted was filtered and the filtrate was evaporated under reduced pressure. Sublimation of the residue (140° at 0.15 mm) gave 2.90 g (65%) of bis(pentafluorophenyl)mercury, mp 138–140° (lit.[16] mp 142°).

Reaction of Ethylmercuric Chloride with Dicobalt Octacarbonyl. A solution of 1.95 g (7.3 mmoles) of ethylmercuric chloride in 30 ml of THF was added to 2.50 g (7.3 mmoles) of dicobalt octacarbonyl in 30 ml of THF in the usual manner. After the 40-min addition period, the reaction mixture was stirred at room temperature for 1 hr and subsequently trap-to-trap distilled at 0.1 mm (pot temperature to 70°). Glpc analysis (MIT isothermal unit, 56°) of the distillate showed that one component in addition to solvent was present. It was collected and identified as the expected 3-pentanone by comparison of its glpc retention time and its infrared spectrum with those of an authentic sample purchased from Eastman. Glpc analysis (toluene internal standard) showed the ketone yield to be 60%.

Reaction between Cyclopropylmercuric Bromide and Dicobalt Octacarbonyl. A solution of 6.72 g (21.0 mmoles) of cyclopropylmercuric bromide in 65 ml of THF was added to 7.30 g (21.3 mmoles) of dicobalt octacarbonyl in 65 ml of THF during 40 min in the usual manner. At the end of the addition, tlc analysis showed that a small quantity of the organomercuric bromide still was present. The reaction mixture was stirred at room temperature for 12 hr and between 35 and 45° for another 2 hr. Trap-to-trap distillation at 0.05 mm (pot temperature to 85°) of the reaction mixture was followed by glpc analysis (column B, 50°) of the yellow distillate. The presence of one component besides solvent was indicated. Most of the solvent was distilled from the distillate using a 12-in. Vigreux column and the solution which remained was trap-to-trap distilled once again.

The residue from the first trap-to-trap distillation was extracted with 100 ml of hot benzene and the benzene extracts were treated with 7 g of triphenylphosphine to give 15.15 g of solid. Trap-to-trap distillation (95° at 0.05 mm) followed an initial distillation of much of the benzene. Glpc analysis of the distillate showed the presence of one component other than solvent. Isolation of this product by glpc (column B, 50°) showed it to be dicyclopropyl ketone, $n^{26}\mathrm{D}$ 1.4642 (lit.[49] $n^{25}\mathrm{D}$ 1.4654). Its infrared spectrum also was in good agreement with the published spectrum of this ketone.[49] Glpc yield analysis (column B, 50°, chlorobenzene internal standard) showed the dicyclopropyl ketone yield (total in both solutions obtained above) to be 66%.

Reaction of *n*-Butylmercuric Bromide with Dicobalt Octacarbonyl. A solution of 5.07 g (15.0 mmoles) of *n*-butylmercuric bromide in 65 ml of THF was added to 5.15 g (15.0 mmoles) of dicobalt octacarbonyl in 60 ml of THF during 30 min in the usual manner. Tlc analysis after completion of the addition indicated that almost all of the mercurial had been consumed. A trap-to-trap distillation at 0.1 mm (pot temperature to 80°) removed most of the volatiles. The residue was dissolved in 100 ml of benzene, triphenylphosphine (6 g) was added, and the 12.2 g of solid which precipitated was filtered. Addition of 6 ml of methyl iodide served to remove the unconverted triphenylphosphine. The filtrate was concentrated by distillation using a 12-in. Vigreux column. A small amount of hexane was added to the liquid residue to precipitate more solid. The filtrate from this operation and the trap-to-trap distillate were combined and analyzed by glpc (column C, 90°). Two major components were found to be present, retention times 4.5 and 6.0 min. These were identified as 3-methyl-4-octanone and 5-nonanone, respectively, by comparison of their glpc retention times and infrared spectra with those of authentic samples purchased from Aldrich and Eastman, respectively. Glpc yield analysis (column C, 90°, 1,2,4-trichlorobenzene internal standard) showed 5-nonanone to have been obtained in 42% yield, 3-methyl-4-octanone in 14% yield.

Reaction of Benzylmercuric Bromide with Dicobalt Octacarbonyl. A solution of 12.75 g (34.3 mmoles) of benzylmercuric bromide in 65 ml of THF was added to 11.79 g (34.5 mmoles) of dicobalt octacarbonyl in 60 ml of THF during 23 min in the usual manner. Carbon monoxide was evolved and the initially red-brown solution turned green. The reaction mixture was stirred at 45° for 3 hr and subsequently the THF was removed at reduced pressure. The residue was extracted with benzene. Triphenylphosphine (12 g) was added to the benzene extracts; the solid which precipitated was filtered and the filtrate was concentrated using a 12-in. Vigreux column. The liquid residue was trap-to-trap distilled at 0.1 mm (pot temperature to 160°). Glpc analysis (column B, 80–200°, 7.5°/min program) of the distillate showed that four components were present in addition to the solvent. These were collected and identified as phenylacetaldehyde (4%), benzyl alcohol (8%), 1,2-diphenylethane (7%), and dibenzyl ketone (51%) (α-methylnaphthalene internal standard) by comparison of their glpc retention times and infrared spectra with those of authentic samples.

Reaction of Allylmercuric Bromide with Dicobalt Octacarbonyl. A solution of 8.70 g (27.0 mmoles) of allylmercuric bromide in 65 ml of THF was added to 9.21 g (26.9 mmoles) of dicobalt octacarbonyl in 60 ml of THF during 30 min in the usual manner. Gas evolution was observed and the initially red-brown reaction mixture turned green. An infrared spectrum of an aliquot of the reaction mixture showed strong absorptions at 2065 and 1988 cm^{-1}. (π-Allylcobalt tricarbonyl has CO stretching frequencies at 2065 and 1985 cm^{-1}.[50]) Distillation of the reaction mixture at 0.1 mm afforded a small sample of a red-brown liquid, and its infrared spectrum was identical with that reported for π-allylcobalt tricarbonyl.[50]

Another such reaction was carried out between allylmercuric bromide and dicobalt octacarbonyl. The reaction mixture then was trap-to-trap distilled at 0.1 mm (pot temperature to 70°). The distillate was treated with 6 g of triphenylphosphine and the THF was removed at reduced pressure. The orange residue was dissolved in benzene and 6 ml of methyl iodide was added. The solution was stirred for 3 hr, then filtered through Celite. The benzene was stripped at reduced pressure, leaving 3.7 g (46%) of yellow-orange π-$C_3H_5Co(CO)_2PPh_3$, mp 150–152° dec. Recrystallization from methylene chloride–pentane gave material of mp 150–152° dec. The melting point of this compound has been reported by Heck to be 132° dec[18] and 119° dec.[51] The infrared spectrum of our product (in CCl_4) showed the following absorptions: 3070 (w), 3055 (w), 3000 (vw), 2060 (w), 1990 (vs), 1940 (vs), 1478 (m), 1434 (s), 1380 (vw), 1305 (vw), 1225 (w), 1183 (w), 1118 (w), 1092 (m), 1068 (w), 1027 (w), 1012–995 (w), and 975 (w) cm^{-1}; this spectrum is in good agreement with that reported by Heck and Breslow.[18]

Anal. Calcd for $C_{23}H_{20}O_2PCo$: C, 66.03; H, 4.82. Found: C, 66.29; H, 5.03.

Reaction of Trichloromethylmercuric Chloride with Dicobalt Octacarbonyl. A solution of 9.55 g (27 mmoles) of trichloromethylmercuric chloride in 75 ml of THF was added to 9.35 g (27.3 mmoles) of dicobalt octacarbonyl in 50 ml of THF during 30 min in the usual manner. During the addition of the first third of the mercurial solution, gas evolution was vigorous and the solution changed from red-brown to purple. Addition of the remaining two-thirds of the mercurial solution caused only little gas evolution. The reaction mixture was stirred at 40–43° for 90 min after completion of the addition. Tlc analysis of the reaction mixture showed the presence of Co^{2+} salts, Cl_3CHgCl, possibly some $Hg(CCl_3)_2$, $Hg[Co(CO)_4]_2$, and chloromethinyltricobalt enneacarbonyl.

Volatiles were removed from the reaction mixture by trap-to-trap distillation at 0.1 mm (pot temperature to 60°), giving a light purple distillate. Analysis by glpc (column G, 30°) of the latter demonstrated the presence of chloroform (identified by its glpc retention time and by peak enhancement with an authentic sample). The residue from the distillation was extracted with 200 ml of hot hexane. The hexane extracts were treated with 5 g of triphenylphosphine (an infrared spectrum of a test solution containing triphenylphosphine, $Hg[Co(CO)_4]_2$, and chloromethinyltricobalt enneacarbonyl at room temperature having shown that the phosphine reacts preferentially with $Hg[Co(CO)_4]_2$ under these conditions); after 2 hr, 9.85 g of solid was filtered. The filtrate was evaporated, leaving 3.0 g (23% yield, based on available CCl_3 groups) of chloromethinyltricobalt enneacarbonyl, mp 131–133° dec (lit.[7b] 131–

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(48) A. K. Barbour, M. W. Buxton, P. L. Coe, R. Stephens, and J. C. Tatlow, *J. Chem. Soc.*, 808 (1961).

(49) H. Hart and O. E. Curtis, *J. Am. Chem. Soc.*, **78,** 112 (1956).

(50) W. R. McClellan, H. H. Hoehn, H. W. Cripps, E. L. Muetterties, and B. W. Howk, *ibid.*, **83,** 1601 (1961).

(51) R. F. Heck, *ibid.*, **90,** 317 (1968).

133° dec), whose infrared spectrum was in complete agreement with that reported for this compound by Italian workers.[52]

Sublimation of the green, hexane-insoluble solid at 100° (0.1 mm) gave 3.05 g (32% recovery) of trichloromethylmercuric chloride, mp 190–191°. The nonsublimable residue was extracted with water to leave 5.75 g of insoluble brown powder. The aqueous extracts were evaporated to give 2.80 g of $CoCl_2 \cdot 6H_2O$.

Use of the Organomercuric Halide–Dicobalt Octacarbonyl Reaction in the Preparation of Unsymmetrical Ketones. (a) 4-Fluoro-4′-methoxybenzophenone. A solution of 1.69 g (4.5 mmoles) of *p*-fluorophenylmercuric bromide and 1.75 g (4.5 mmoles) of *p*-anisylmercuric bromide in 30 ml of THF was added to 3.09 g (9.03 mmoles) of dicobalt octacarbonyl in 30 ml of THF during 40 min in the usual manner. The THF was removed from the green reaction mixture at reduced pressure and the residue was extracted with 125 ml of hot benzene. The usual treatment with triphenylphosphine (6 g) and methyl iodide (6 ml) followed. Evaporation of the final filtrate left a residue which was sublimed at 110° (0.05 mm) to give a mixture of solid ketones. Glpc analysis of this mixture (column F, 190°) showed the presence of three products. In order of increasing retention time these were 4,4′-difluorobenzophenone, 4-fluoro-4′-methoxybenzophenone, and 4,4′-dimethoxybenzophenone. The symmetrical ketones were identified by comparison of their glpc retention times and infrared spectra with those of the products from the experiments described above. The unsymmetrical ketone had mp 91–93° (lit.[53] mp 94.5–95.5°) and its infrared spectrum was that expected for this structure. The C═O stretching frequency of the unsymmetrical ketone (1658 cm^{-1} in CCl_4) was intermediate between those of the 4,4′-difluoro- (1664 cm^{-1}) and 4,4′-dimethoxybenzophenone (1654 cm^{-1}). Glpc yield analysis (column C, 200–250°, 8°/min program) established the following yields: 4,4′-difluorobenzophenone, 22%; 4-fluoro-4′-methoxybenzophenone, 47%; 4,4′-dimethoxybenzophenone, 16%. 1-Chloronaphthalene was used as internal standard.

(b) Benzyl *p*-Fluorophenyl Ketone. A solution of 4.90 g (13.0 mmoles of *p*-fluorophenylmercuric bromide and 4.82 g (13.0 mmoles) of benzylmercuric bromide in 65 ml of THF was added to 8.90 g (26.0 mmoles) of dicobalt octacarbonyl in 30 ml of THF at room temperature under nitrogen in the usual manner. The green reaction mixture was kept at room temperature overnight and then was evaporated at reduced pressure. The residue was extracted with 150 ml of benzene and the extracts were treated with triphenylphosphine (9 g) and methyl iodide (9 ml) as usual. Evaporation of the last filtrate left a residue which was sublimed at 70° (0.1 mm) to give 2 g of mixed ketones. These were dissolved in THF and analyzed by glpc (column B, 200°). Two components were present: 4,4′-difluorobenzophenone (17.5%) and benzyl *p*-fluorophenyl ketone (54%). The latter had mp 82–84° (lit.[54] mp 86°). Its C═O stretching frequency was observed at 1700 cm^{-1} in CCl_4 solution, and its nmr spectrum also was in agreement with this structure: 4.22 (2) s, 7.30 (7) m, 8.10 (2) m ppm. Dibenzyl ketone ($\nu_{C=O}$ 1725 cm^{-1}) was not present. Glpc yield analysis was carried out using column C at 140–270° (6°/min program), with 1-chloronaphthalene as internal standard.

Reaction of Diphenylmercury with Dicobalt Octacarbonyl. A solution of 4.75 g (13.4 mmoles) of diphenylmercury in 65 ml of THF was added rapidly to 4.60 g (13.4 mmoles) of dicobalt octacarbonyl at room temperature. No gas was evolved and the reaction solution remained red-brown. The reaction mixture was stirred at room temperature under nitrogen for 2 hr. Then oxygen was blown through the still red-brown solution to destroy unconverted cobalt carbonyl. Six grams of triphenylphosphine was added to the now brownish reaction mixture and, after 1 hr, 9.1 g of solid was filtered off. The filtrate was trap-to-trap distilled at 0.1 mm (pot temperature to 40°) and the distillate showed no volatile products upon glpc analysis. Sublimation of the distillation residue at 125° (0.1 mm) gave first an oil and subsequently an oily solid. The former solidified on being cooled. Recrystallization from hexane gave 1.70 g (70% yield, based on both phenyl groups of diphenylmercury) of benzophenone, mp 45–46°. The oily solid, mp 115–117°, was mainly diphenylmercury (5% recovery), contaminated with some benzophenone.

Reaction of *p*-Fluorophenylmercuric Bromide with Sodium Tetracarbonylcobaltate(−1). A solution of *ca.* 12.3 mmoles of $Na[Co(CO)_4]$ in 60 ml of THF was prepared[55] from sodium amalgam and 2.1 g (6.15 mmoles) of dicobalt octacarbonyl in a 200-ml three-necked flask equipped with an addition funnel and a nitrogen-inlet tube. This solution then was transferred to an addition funnel on a 500-ml three-necked flask containing 4.13 g (11.1 mmoles) of *p*-fluorophenylmercuric bromide in 250 ml of THF, under nitrogen and cooled to −78°. The $Na[Co(CO)_4]$ solution was added slowly to the cold mercurial solution. Upon completion of the addition, the THF was stripped off at reduced pressure while the reaction mixture was kept chilled. An infrared spectrum (in Nujol) of the residue showed only C≡O bands characteristic of $Hg[Co(CO)_4]_2$: 2068 (s), 2018 (w), and 2003 (s) cm^{-1}. Tlc analysis showed the presence only of this compound, bis(*p*-fluorophenyl)mercury, and a trace of *p*-fluorophenylmercuric bromide. The residue was dissolved in benzene and 3.5 g (13.4 mmoles) of triphenylphosphine was added. Filtration gave 5.2 g (84%) of $Hg[Co(CO)_3PPh_3]_2$. The filtrate was treated with 4 ml of methyl iodide, the phosphonium iodide was filtered off, and the resulting filtrate was evaporated at reduced pressure. Sublimation of the residual solid gave 1.72 g (82%) of bis(*p*-fluorophenyl)mercury, mp 148–149°. Recrystallization from THF–hexane raised the melting point to 150–152° (lit.[31] mp 153.5°).

Characterization of $Hg[Co(CO)_3PPh_3]_2$. This compound was precipitated often during the course of this study, but only on a few occasions were efforts made to establish its identity. The samples isolated decomposed at 210–215° and an infrared spectrum (KBr pellet) showed the following bands: 3074 (vw), 3057 (vw), 1992 (w), 1944 (s), 1585 (vw), 1570 (vw), 1479 (m), 1434 (m), 1330 (vw), 1305 (vw), 1182 (w), 1157 (vw), 1117 (vw), 1091 (m), 1068 (vw), 1024 (w), 995 (w), 745 (m), 720 (w), 704 (m), 690 (m) cm^{-1}.

Manning[56] has reported mp 212–214° dec and found $\nu_{C=O}$ at 1989 and 1946 cm^{-1} in chloroform solution.

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[52] R. Ercoli, E. Santambrogio, and G. T. Casagrande, *Chim. Ind.* (Milan), **44**, 1344 (1962).

[53] B. Fluksik, Z. Eckstein, and W. Sobotka, *Bull. Acad. Polon. Sci., Ser. Sci., Chim. Geol. Geograph.*, **2**, 803 (1959); *Chem. Abstr.*, **54**, 21005 (1960).

[54] B. Hoi, N. Hoan, and P. Jacquignon, *Rec. Trav. Chim.*, **68**, 781 (1949).

[55] R. B. King, *Organometal. Syn.*, **1**, 153 (1965).

[56] A. R. Manning, *J. Chem. Soc., A*, 1018 (1968).