in formic acid,[9] p-RC$_6$H$_4$C(CH$_3$)$_2$CH$_2$OBs in acetic acid,[10] and p-RC$_6$H$_4$CH$_2$C(CH$_3$)$_2$Cl and p-RC$_6$H$_4$C(CH$_3$)$_2$C(CH$_3$)$_2$Cl in 80% aqueous ethanol,[7c] where R is H, CH$_3$, and OCH$_3$, a virtually perfect correlation is found between log k (rate constant) and the ionization potential of RC$_6$H$_5$. These correlations are gathered into a single Figure 2 by plotting log (k/k^0) where k^0 is the rate for R = H. Since we have established the linear relationship for R = H, CH$_3$, and CH$_3$O between the ionization potential and (p-RC$_6$H$_5$CH$_2$)$_3$B charge-transfer transition energy, Figure 2 is also a correlation of log (k/k^0) with E_{CT}. It should be noted that the slopes of the correlation lines in Figure 2 correspond to that expected from relative importance of neighboring group participation by the phenyl ring in the solvolysis transition states. The correlation in Figure 2, which involves 12 points, implies that the mechanism by which R stabilizes the excited state of (p-RC$_6$H$_4$CH$_2$)$_3$B is similar to that by which the solvolysis transition state of the β-phenylalkyl tosylates, etc., are stabilized. Although each of the four linear relationships in Figure 2 is defined by only three points, no other substituent parameter such as Hammett σ or σ^+ places the CH$_3$O on the lines defined by H and CH$_3$.

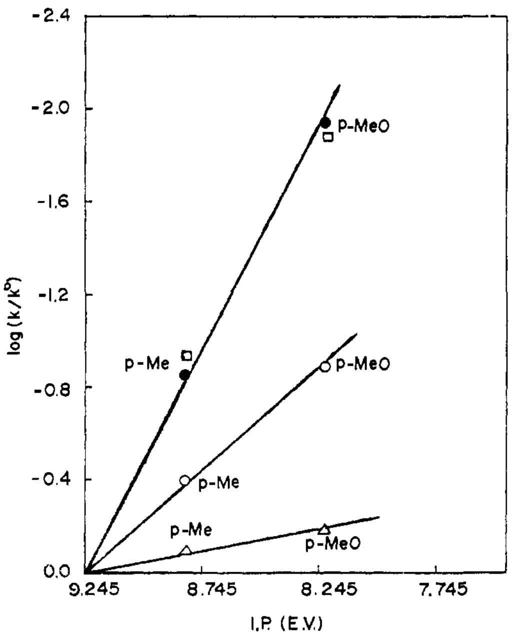

Figure 2. A plot of log (k/k^0) for the solvolysis rates of p-RC$_6$H$_4$-C(CH$_3$)$_2$CH$_2$OBs (●), p-RC$_6$H$_4$CH$_2$CH$_2$OTs (□), p-RC$_6$H$_4$C(CH$_3$)$_2$C(CH$_3$)$_2$Cl (○), and p-RC$_6$H$_4$CH$_2$C(CH$_3$)$_2$Cl (△) against the ionization potential (eV) of RC$_6$H$_5$ (R = H, CH$_3$, OCH$_2$).

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A Convenient High Yield Dicobalt Octacarbonyl Catalyzed Synthesis of Diaryl Ketones from Diarylmercury Compounds and Carbon Monoxide

Sir:

Recently we reported a synthesis of symmetrical ketones by the reaction of organomercuric halides or diorganomercurials with dicobalt octacarbonyl at room temperature in THF solution.[1] The yields of ketones were in general quite good, and in the case of diaryl

$$\mathrm{RHgX} \xrightarrow{\mathrm{Co_2(CO)_8}} \mathrm{R_2C{=}O + Hg[Co(CO)_4]_2 + CoX_2 + CO} \quad (1)$$

$$\mathrm{R_2Hg} \xrightarrow{\mathrm{Co_2(CO)_8}} \mathrm{R_2C{=}O + Hg[Co(CO)_4]_2 + CO} \quad (2)$$

ketones they were excellent. A mechanism involving organocobalt intermediates was indicated

$$\mathrm{Co_2(CO)_8 + THF \longrightarrow THF\cdot Co(CO)_4^+ + Co(CO)_4^-}$$

$$\mathrm{RHgX + Co(CO)_4^- \longrightarrow RHgCo(CO)_4 + X^-}$$

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

or

$$\mathrm{RHgCo(CO)_4 \longrightarrow {}^1/_2R_2Hg + {}^1/_2Hg[Co(CO)_4]_2}$$

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

$$\mathrm{RCo(CO)_4 \longrightarrow RCOCo(CO)_3}$$

$$\mathrm{RCo(CO)_4 + RCOCo(CO)_3 \longrightarrow R_2C{=}O + Co_2(CO)_7}$$

Reactions 1 and 2 represent a stoichiometric utilization of dicobalt octacarbonyl. More practical and economical would be a reaction in which the stoichiometric reagent is carbon monoxide and the relatively expensive dicobalt octacarbonyl is used in only catalytic quantities (eq 3). We report here concerning the realization of such a ketone synthesis.

$$\mathrm{R_2Hg + CO} \xrightarrow{\mathrm{[Co_2(CO)_8]}} \mathrm{R_2C{=}O + Hg} \quad (3)$$

Our new catalytic ketone synthesis is based upon our previously developed reaction of diorganomercurials with dicobalt octacarbonyl (eq 2). In order to make this process catalytic, a method for the conversion of the unreactive Hg[Co(CO)$_4$]$_2$ to the active reagent, Co$_2$(CO)$_8$, must be available. Italian workers[2] have reported photochemical reactions of Hg[Co(CO)$_4$]$_2$ with acetylenes, in which photolysis of the mercury compound served to release dicobalt octacarbonyl; *e.g.*, eq 4. This observation suggested to us that reaction 1 or 2 could be made catalytic in dicobalt octacarbonyl by irradiating the reaction mixture with an ultraviolet source while the reaction progressed. Our subsequent experiments showed that such was the case.

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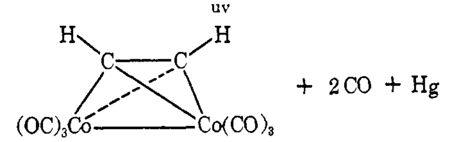
Table I. Cobalt Carbonyl Catalyzed Carbonylation of Diarylmercury Compounds

Ar in Ar_2Hg	Catalyst	Ar_2Hg/catalyst molar ratio	Reaction time, hr	Product (% yield)	Mercury, % yield
Ph	$Co_2(CO)_8$	37.3	123	$Ph_2C{=}O$ (91)	95
Ph	$Hg[Co(CO)_4]_2$	94	141	$Ph_2C{=}O$ (88)	99
Ph	$Hg[Co(CO)_4]_2$	470	21 days	$Ph_2C{=}O$ (74)	100
p-FC_6H_4	$Co_2(CO)_8$	46	120	$(p\text{-}FC_6H_4)_2C{=}O$ (87)	97
p-ClC_6H_4	$Co_2(CO)_8$	22.4	233	$(p\text{-}ClC_6H_4)_2C{=}O$ (85)	78
p-$CH_3C_6H_4$	$Hg[Co(CO)_4]_2$	88	36.5	$(p\text{-}CH_3C_6H_4)_2C{=}O$ (62)	98
p-$CH_3OC_6H_4$	$Hg[Co(CO)_4]_2$	48	113	$(p\text{-}CH_3OC_6H_4)_2C{=}O$ (52)	98

We were unsuccessful in our attempts to achieve a $Co_2(CO)_8$-catalyzed synthesis of ketones from organomercuric halides and carbon monoxide. However, such a synthesis based on diarylmercury compounds could be realized.



(4)

The preparation of benzophenone is described as an example of the procedure used. A 150-ml one-necked quartz flask containing a stirbar was fitted with an Allihn condenser. A solvent-resistant $^1/_8$-in. plastic tube was inserted through the condenser to within 1 in. of the flask bottom and connected to a carbon monoxide tank. The flask was charged with 10.0 g (28.2 mmol) of diphenylmercury and 100 ml of dry THF. The system was flushed with carbon monoxide and 0.50 g (1.46 mmol) of $Co_2(CO)_8$ was added. While the reaction mixture was stirred with a magnetic stirrer and carbon monoxide was continually and slowly passed through, the flask was irradiated externally with a Hanovia utility (100 W) high-pressure ultraviolet lamp. A closely placed fan provided cooling. The progress of the reaction was monitored by thin layer chromatography.[3] The flow of carbon monoxide was stopped after 123 hr at room temperature, after tlc showed that the diphenylmercury had been consumed. The reaction mixture was flushed with nitrogen and decanted from 5.40 g (95%) of metallic mercury. Further work-up of the filtrate followed our previous procedure.[1] Triphenylphosphine (3.8 mmol) was added after the THF had been replaced with benzene. After filtration of the precipitated $Hg[Co(CO)_3PPh_3]_2$, 1 ml of methyl iodide was added to remove unconverted triphenylphosphine. The final benzene solution was evaporated and the residue crystallized to give 4.7 g (91% yield) of benzophenone, mp 45–47°, whose ir spectrum was identical with that of an authentic sample.

The 37:1 mole ratio of diphenylmercury to cobalt carbonyl catalyst is by no means the practical limit. In another reaction 1 molar equiv of catalyst served to convert 470 molar equiv of diphenylmercury to benzophenone (74% yield) and metallic mercury (100%) during a reaction time of 21 days. Active catalyst was still present at the end of this time, so more benzophenone could have been made by adding more diphenylmercury to the reaction mixture. While $Co_2(CO)_8$ is the actual catalyst and may be used to start out the reaction, it is more convenient to use the stable and more easily handled $Hg[Co(CO)_4]_2$ as the initially charged catalyst. In a reaction where this was done (Ph_2Hg to $Hg[Co(CO)_4]_2$ ratio of 94; 141-hr reaction time), an 88% yield of benzophenone was obtained. Table I summarizes our initial results.

This new catalytic reaction does not appear to be applicable to the synthesis of dialkyl ketones from dialkylmercury compounds, most likely because of the well-known photolability of the alkyl–Hg bond. Such a reaction of 27.0 mmol of di-*n*-butylmercury with carbon monoxide in THF in the presence of 0.3 mmol of $Hg[Co(CO)_4]_2$ gave the expected[1] di-*n*-butyl ketone and *n*-butyl *sec*-butyl ketone, but the yields were only 17% and 5%, respectively. However, metallic mercury was isolated in 94% yield. A reaction time of 232 hr was required to completely consume the starting mercurial.

The reaction which we describe in this communication could find useful synthetic applications. Diarylmercury compounds are easily prepared and most attractive is their synthesis *via* direct mercuration of an aromatic compound followed by redistribution of the ArHgX compound obtained. This cobalt carbonyl catalyzed carbonylation of diarylmercury compounds proceeds under exceptionally mild conditions (room temperature and atmospheric pressure; neutral reaction medium). The metallic mercury produced is easily recycled and isolation of the ketone product is easily achieved. In contrast, the ketone synthesis of Heck[4] based on Pd(II)- or Rh(III)-catalyzed carbonylation of arylmercuric halides does not proceed cleanly and does not give good yields of product.

Further work in these laboratories is directed toward a more detailed study of reaction variables and a more varied and broader utilization of the basic reaction described in this communication.

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(5) National Institutes of Health Predoctoral Fellow, 1966–1969.

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