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COBALT CARBONYL CATALYZED DEHALOGENATION AND COUPLING REACTIONS BY PHASE TRANSFER CATALYSIS

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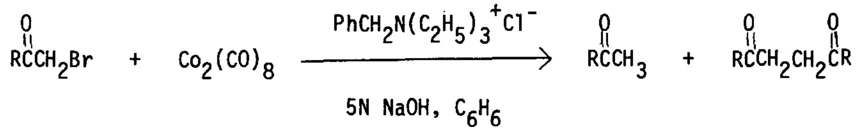
Recent investigations have demonstrated that phase transfer catalysis is an exceedingly useful technique in organometallic chemistry. The reduction of nitroarenes to anilines,[1] as well as the synthesis of cluster,[2] π-allyl,[2] ortho-metalated,[3] and Group VI metal carbonyl[4] complexes can be effected under mild conditions by phase transfer catalysis. This communication describes a simple and convenient method for the stoichiometric or catalytic dehalogenation of α-halo ketones.

Treatment of an α-bromo ketone (1) with an equimolar amount of dicobalt octacarbonyl [$Co_2(CO)_8$], 5N NaOH, benzene, and benzyltriethylammonium chloride as the phase



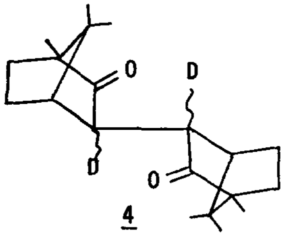
$$R\overset{\overset{O}{\|}}{C}CH_2Br + Co_2(CO)_8 \xrightarrow[5N\ NaOH,\ C_6H_6]{PhCH_2N(C_2H_5)_3{}^+Cl^-} R\overset{\overset{O}{\|}}{C}CH_3 + R\overset{\overset{O}{\|}}{C}CH_2CH_2\overset{\overset{O}{\|}}{C}R$$

1 2 3

transfer catalyst, for two hours at room temperature, affords the dehalogenated monoketone 2 in almost quantitative yield (e.g. R= p-$C_6H_5C_6H_4$, 98% yield; R= 2-naphthyl, 97% yield). While these results indicate the considerable potential of this reaction as a synthetic dehalogenation technique, it would be of much greater utility if the reaction is catalytic with respect to the metal carbonyl.

Use of a 20:1 ratio of α-bromo ketone:cobalt in the above reaction gave ketones(2) in fair to excellent yields (Table I). Although the yields are lower in the catalytic than in the stoichiometric reaction, they are nevertheless good and the catalytic process requires small amounts of dicobalt octacarbonyl. In addition, the stoichiometric or catalytic reactions occur under very gentle conditions, and are simple to work up. Product yields are low in the absence of the metal carbonyl. For example, 1, R= 2-naphthyl, reacts with 5N NaOH, C_6H_6, and the phase transfer catalyst to give 2, R= 2-naphthyl, in 11% yield, and the 1,4-diketone 3, R= 2-naphthyl, in 7% yield.

The monoketone 2 was the principal reaction product in most instances, with the coupled 1,4-diketone(3) formed as a by-product in some cases. Exceptions include 2-bromo acetophenone and α-bromocamphor, the latter affording the dideuterio-1,4-diketone (4) as the only product (using NaOD/D_2O as the aqueous phase).



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A possible pathway for the reaction is outlined in Scheme 1. The generation of the cobalt tetracarbonyl anion was described previously.[2] Electron transfer reaction of the organic substrate with the cobalt tetracarbonyl anion would generate the radicals 5 and 6, and regenerate the quarternary ammonium halide, which returns to the aqueous phase. Coupling of 5 and 6 would give the organocobalt tetracarbonyl complex 7, which on subsequent cobalt-carbon bond cleavage forms the ketone 2 and regenerates the cobalt tetracarbonyl anion. Self-coupling of radicals 5 and 6 would afford the 1,4-diketone(3) and dicobalt octacarbonyl, respectively. The formation of 3 as the major product from 1, R= C_6H_5, and α-bromocamphor may be due, at least in part, to the aqueous-organic phase distribution of one or more of the

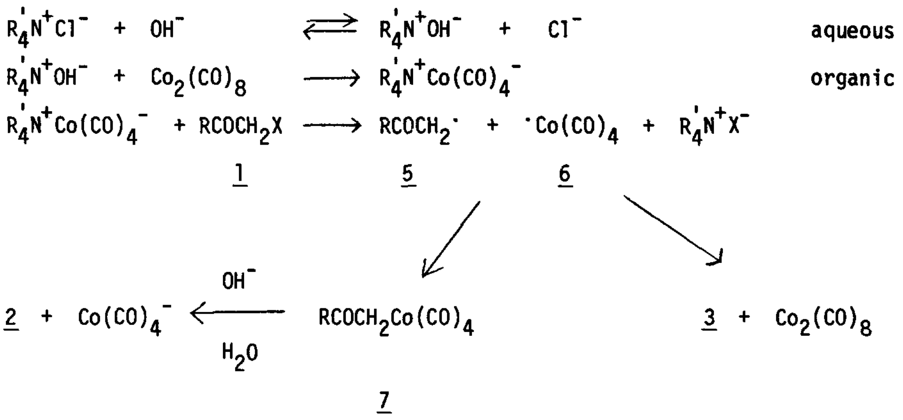
TABLE I

Products Obtained from Reaction of 1 with a Catalytic Amount of $Co_2(CO)_8$

1,R=	Product[a]	Yield(%)
1-adamantyl	2,R=1-adamantyl	58
2-naphthyl	2,R=2-naphthyl	66
p-PhC_6H_4	2,R=p-PhC_6H_4	64
p-BrC_6H_4	2,R=p-BrC_6H_4	69
	3,R=p-BrC_6H_4	28
p-$CH_3OC_6H_4$	2,R=p-$CH_3OC_6H_4$	25
	3,R=p-$CH_3OC_6H_4$	20
Ph	2,R=Ph	23
	3,R=Ph	55

[a] Products were identified by comparison of spectral data (ir,nmr,ms) with that for authentic samples, as well as by mixed melting points.

Scheme 1



$$R'_4N^+Cl^- + OH^- \rightleftharpoons R'_4N^+OH^- + Cl^- \quad \text{aqueous}$$

$$R'_4N^+OH^- + Co_2(CO)_8 \longrightarrow R'_4N^+Co(CO)_4^- \quad \text{organic}$$

$$R'_4N^+Co(CO)_4^- + \underset{1}{RCOCH_2X} \longrightarrow \underset{5}{RCOCH_2^{\cdot}} + \underset{6}{{}^{\cdot}Co(CO)_4} + R'_4N^+X^-$$

$$2 + Co(CO)_4^- \xleftarrow[H_2O]{OH^-} \underset{7}{RCOCH_2Co(CO)_4}$$

$$3 + Co_2(CO)_8$$

intermediates- i.e. solubility differences being significant when compared with the other cases.

The following general procedure was used (nitrogen atmosphere): To a benzene(10 ml.) solution containing the α-bromo ketone (1, 1.0mmol) and $Co_2(CO)_8$ (0.1 mmol) was added 5N NaOH (10 ml.) and benzyltriethylammonium chloride (0.11g., 0.5 mmol). The reaction mixture was vigorously stirred at room temperature for two hours. The layers were separated (centrifuge) and the organic layer was dried, concentrated to a few milliliters, and chromatographed on Florisil. Elution with benzene-petroleum ether gave 2, while the 1,4-diketone (3-if formed) was eluted with benzene-chloroform or benzene-methylene chloride.

ACKNOWLEDGMENT

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