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The Reaction of Organic *gem*-Dihalides with Zerovalent Transition Metal Complexes. An Approach to Organic Synthesis

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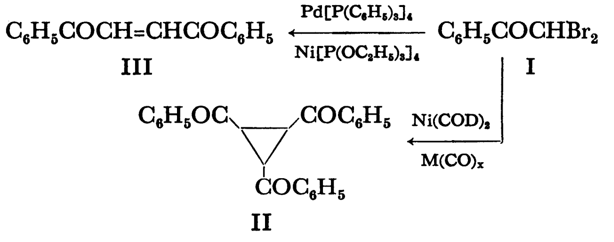
Synopsis. The reaction of ω,ω-dibromoacetophenone with $Ni(COD)_2$ (COD=1,5-cyclooctadiene), $Fe(CO)_5$, or $Co_2(CO)_8$ gave *trans*-1,2,3-tribenzoylcyclopropane, while the reaction with $Pd[P(C_6H_5)_3]_4$ or $Ni[P(OC_2H_5)_3]_4$ gave *trans*-1,2-dibenzoylethylene. Phenyl isocyanide dichloride was dechlorinated by metal carbonyls to give phenyl isocyanide-substituted metal carbonyls.

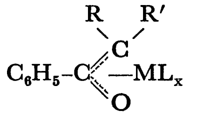
Carbon-carbon bond formation by means of low-valent transition metal complexes is of current interest, and a variety of regio- or stereospecific reactions have been developed.[1] Reactions of *gem*-dihalides with iron carbonyls are known; in them a transiently formed carbenoid is assumed to be the intermediate.[2,3] To find versatile applications of organotransition metals to organic synthesis, several organic dihalides were allowed to react with metal complexes.

Results and Discussion

It has been reported that the reaction of ω,ω-dibromoacetophenone (I) with zinc-copper gives 1,3-diphenyl-2-buten-1-one.[4] The reaction of I with $Ni(COD)_2$, $Fe(CO)_5$, or $Co_2(CO)_8$ in benzene at 80 °C was found to afford *trans*-1,2,3-tribenzoylcyclopropane (II) as the sole organic product. Bis(cyclooctadiene)nickel, $Ni(COD)_2$, was superior to the metal carbonyls, because $NiBr_2$ was more easily separated from the product by filtration. On the other hand, when dimethyl maleate or methyl sorbate was added to the system, these olefinic compounds did not participate in the reaction, and II was formed. This is a rare example of cyclopropane formation by the dehalogenation of an organic halide by transition metals.



If the debromination occurs by a step-by-step mechanism, an intermediate oxo-allyl complex might be isolated. In fact, the reaction of α-haloketones with $Fe_2(CO)_9$ affords the oxo-allyl complex (IVa).[5] A similar complex (IVb) has been prepared by the reaction of diazoacetophenone with bis(benzonitrile)palladium dichloride.[6] The isolation of the oxo-allyl complex from the reaction of I with tetrakis(triphenylphosphine)palladium $Pd[P(C_6H_5)_3]_4$ was not achieved even at 0 °C, but *trans*-1,2-dibenzoylethylene (III) was obtained in a high yield. The palladium was recovered as bis(triphenylphosphine)palladium dibromide $PdBr_2[P(C_6H_5)_3]_2$. The reaction with tetrakis(triethyl phosphite)nickel $Ni[P(OC_2H_5)_3]_4$ gave similar results. The presence of donor ligands such as phosphine or phosphite appears to suppress the formation of the cyclopropane. The ligands seem to alter the nature of the intermediate (presumably "carbenoid") electronically or sterically.



IV a; R=R′=H, M=Fe
b; R=H, R′=Cl, M=Pd

In relation to the above reaction, dimethyl dibromosuccinate was treated with $Fe(CO)_5$ with the expectation of gaining insight into the stereochemistry of the dehalogenation, because there is a possibility that II or III is formed by a step-by-step dehalogenation after the coupling of the bromoacetophenone moiety. This debromination proceeded smoothly in benzene at 80 °C. The *dl*(*racemic*)-, and *meso*-isomers gave dimethyl fumarate predominately. Under these conditions, the isomerization of the double bond occurs.[7] Therefore, the specificity, if any, is obscured by the *cis-trans* isomerization.

Contrary to the case with the reaction with I, ethyl dichloroacetate was difficult to be dechlorinated under similar conditions. No appreciable organic product was formed. The dechlorination of phenyl isocyanide dichloride $C_6H_5NCCl_2$ (V) required a higher temperature. On refluxing in toluene, the reaction with 2 mol of $Fe(CO)_5$ gave $(C_6H_5NC)Fe(CO)_4$ in a 67% yield. The reaction with $Ni(CO)_4$ gave pale-yellow solid with IR absorptions at 2040 and 1990 cm^{-1},[8] they are assigned to ν_{NC} of $Ni(C_6H_5NC)_4$.

Experimental

ω,ω-Dibromoacetophenone,[9] *dl*- and *meso*-dimethyl dibromosuccinate,[10] phenyl isocyanide dichloride,[11] $Ni(COD)_2$,[1] $Pd[P(C_6H_5)_3]_4$,[12] and $Ni[P(OC_2H_5)_3]_4$[13] were prepared by the known methods. Commercially available $Fe(CO)_5$, $Co_2(CO)_8$, and $Cr(CO)_6$ were used without further purification. Benzene and toluene were purified by distillation in the presence of sodium ketyl under an atmosphere of argon.

The following procedures are typical examples of the reactions. The amounts of material used are shown in Table 1.

Reaction of I with $Fe(CO)_5$. A test tube fitted with a three-way stopcock was filled with argon by evacuating and filling it with argon several times. To a benzene solution (3 ml) of I (1.0 mmol) was added $Fe(CO)_5$ (1.2 mmol) and the solution was heated at 80 °C with stirring. The precipitate was separated by filtration, and the filtrate was percolated

Table 1. Reactions of *gem*-dihalides with zerovalent metal complexes

Dihalide mmol		Complex mmol		Conditions			Product[b],	Yield[c] %
				Solv.[a]	°C	hr		
$C_6H_5COCHBr_2$,	1	$Ni(COD)_2$,	1.2	B,	80	10	II,	66
$C_6H_5COCHBr_2$,	1	$Co_2(CO)_8$,	1.2	B,	80	10	II,	51
$C_6H_5COCHBr_2$,	1	$Fe(CO)_5$,	1.2	B,	80	10	II,	28
$C_6H_5COCHBr_2$,	1	Pd-black,	1.2	B,	80	10	No reaction	
$C_6H_5COCHBr_2$,	1	$Pd(PPh_3)_4$,	1.2	B,	80	10	III,	77
$C_6H_5COCHBr_2$,	1	$Pd(PPh_3)_4$,	1.2	B,	0	24	III,	53
$C_6H_5COCHBr_2$,	1	$Ni[P(OEt)_3]_4$,	1.2	B,	80	10	III,	n.d.
$C_6H_5NCCl_2$,	10	$Fe(CO)_5$,	20	T,	110	10	$Fe(CO)_4L$[d],	67
$C_6H_5NCCl_2$,	5	$Cr(CO)_6$,	10	T,	110	10	$Cr(CO)_5L$[d],	55
$C_6H_5NCCl_2$,	8	$Ni(CO)_4$,	10	B[e],	80	10	Not isolated	

a) B, In benzene (3 ml); T, in toluene (30 ml). b) II, *trans*-1,2,3-Tribenzoylcyclopropane; III, *trans*-1,2-dibenzoylethylene. c) Based on the dihalides used. d) L, C_6H_5NC. e) In benzene (30 ml).

through a thin layer of alumina. The concentrated solution was poured into petroleum ether. A colorless compound, II, was thus obtained in a 28% yield. It was identified by comparing its spectral data with those of an authentic sample.[14]

Reaction of I with $Pd[P(C_6H_5)_3]_4$. To a benzene solution (3 ml) of I (1.0 mmol) was added $Pd[P(C_6H_5)_3]_4$ (1.2 mmol) under an atmosphere of argon. The reaction mixture was kept at 80 °C with stirring. The precipitate was identified as $PdBr_2[P(C_6H_5)_3]_2$ by comparing its infrared spectrum with that of the reported substance.[15]

The filtrate was concentrated, and the formation of III (in 77% yield) was confirmed by comparing its infrared spectrum with that of an authentic sample.[14]

Reaction of V with Metal Carbonyls. Phenyl isocyanide dichloride (V) was allowed to react with metal carbonyls under the conditions summarized in Table 1. After the reaction, the metal chloride thus precipitate was separated by filtration. The evaporation of the solvent gave isocyanide-substituted metal carbonyls.

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