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ORGANIC SYNTHESES BY MEANS OF METAL COMPLEXES. I. CARBONYLATION OF OLEFINS WITH CARBON MONOXIDE AND CARBON TETRACHLORIDE CATALYZED BY BINUCLEAR METAL CARBONYLS

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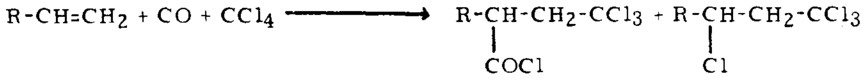
Transition metal carbonyls catalyze the carbonylation of olefins, and several types of the carbonylation reactions of olefins are known. This communication deals with a new type of metal carbonyl catalyzed reaction of olefins; namely the formation of 2-alkyl-4, 4, 4-trichlorobutanoyl chlorides by the addition reaction of carbon monoxide and carbon tetrachloride to olefins as shown below.



$$\mathrm{R\text{-}CH{=}CH_2 + CO + CCl_4} \longrightarrow \mathrm{R\text{-}}\underset{\mathrm{COCl}}{\underset{|}{\mathrm{CH}}}\mathrm{\text{-}CH_2\text{-}CCl_3} + \mathrm{R\text{-}}\underset{\mathrm{Cl}}{\underset{|}{\mathrm{CH}}}\mathrm{\text{-}CH_2\text{-}CCl_3}$$

The reaction is catalyzed by binuclear metal carbonyl complexes, and dicyclopentadienyldiiron tetracarbonyl ($[C_5H_5Fe(CO)_2]_2$, I), dicyclopentadienyldimolybdenum hexacarbonyl ($[C_5H_5Mo(CO)_3]_2$, II) and dicobalt octacarbonyl ($[Co(CO)_4]_2$, III) were found to be most active catalysts. The by-product of the reaction is 1, 1, 1, 3-tetrachloroalkanes.

A typical example is the following. Ethylene (30 atm.), carbon monoxide (170 atm.) and carbon tetrachloride (40 ml.) were allowed to react in a stainless steel autoclave (300 ml.) at 120° in the presence of II (1 g.). After 14 hrs., 4, 4, 4-trichlorobutanoyl chloride (15.4 g.) was isolated as a sole product by distillation, which showed an infrared absorption band at 1790 cm^{-1} due to acyl chloride. Then it was converted into amide by the treatment with ammonia (m.p. 88-89°, reported, 89-90° (1)). The amide showed a typical A_2B_2 pattern of a N.M.R. spectrum centered at τ7.03 and τ7.20. Some results of the reaction are shown in

Table I. The complexes I and II catalyze the reaction at temperatures below 100°. On the other hand, III is active above 100°. Various 1-olefins can be used for the reaction, except ethylene, which can be converted satisfactorily into 4, 4, 4-trichlorobutanoyl chloride by the catalytic action of the complex II.

TABLE I. Products of the Carbonylation

Olefins	Catalyst 1 g.	CO Press. atm.	Reaction Temp. °C	Reaction Time, hr.	Products g.
ethylene 30 atm.	I	170	120	15	$CCl_3CH_2CH_2COCl$(3. 3)
ethylene 30 atm.	II	170	120	15	$CCl_3CH_2CH_2COCl$(15. 4)
ethylene 30 atm.	III	170	135	15	$CCl_3CH_2CH_2Cl$(0. 3)
propylene 10 g.	I	200	53	14	$CCl_3CH_2CH(CH_3)COCl$(12. 0) $CCl_3CH_2CH(CH_3)Cl$(3. 0)
propylene 10 g.	II	200	95	3	$CCl_3CH_2CH(CH_3)COCl$(10. 0) $CCl_3CH_2CH(CH_3)Cl$ (9. 0)
propylene 10 g.	III	200	140	15	$CCl_3CH_2CH(CH_3)COCl$(11. 1) $CCl_3CH_2CH(CH_3)Cl$ (6. 6)
1-hexene 4. 2 g.	II	200	91	15	$CCl_3CH_2CH(n\text{-}C_4H_9)COCl$(3. 8) $CCl_3CH_2CH(n\text{-}C_4H_9)Cl$ (2. 5)
1-hexene 4. 2 g.	III	200	125	15	$CCl_3CH_2CH(n\text{-}C_4H_9)COCl$(4. 9) $CCl_3CH_2CH(n\text{-}C_4H_9)Cl$ (3. 6)
1-octene 7. 2 g.	I	200	118	15	$CCl_3CH_2CH(n\text{-}C_6H_{13})COCl$(7. 6) $CCl_3CH_2CH(n\text{-}C_6H_{13})Cl$ (3. 5)

The reactions were carried out with 40 ml. of CCl_4 in a glass vessel placed in an autoclave (300 ml.)

The formation of 1, 1, 1, 3-tetrachloroalkanes is competitive with the formation of the acid chlorides. It was found that the ratio of the acid chloride to the tetrachloroalkane increased with the increase of the carbon monoxide pressure. In the absence of carbon monoxide, these binuclear complexes catalyzed smoothly the telomerization of carbon tetrachloride and olefins. It is known that mononuclear metal carbonyls such as iron pentacarbonyl and molybdenum hexacarbonyl catalyze the telomerization of olefins and carbon tetrachloride (2). However it was confirmed that the catalytic activity of these mononuclear complexes for the addition reaction of carbon monoxide and carbon tetrachloride to olefins to form the acid chlorides was low.

Although it is premature to discuss the mechanism of the reaction from the present experimental data, it seems likely that the first step of the reaction is the splitting of the metal-metal bond of the binuclear complexes with carbon tetrachloride as shown below, followed by insertion of olefin into the metal-carbon bond.

$$CCl_4 + Co_2(CO)_8 \longrightarrow Cl\text{-}Co(CO)_4 + CCl_3\text{-}Co(CO)_4$$

In addition, a radical mechanism through the formation of $\cdot CCl_3$ or $\cdot Cl$ is another possibility. However, it was confirmed that hydroquinone did not inhibit the reaction catalyzed by the complexes I and II.

We have found that some radical generators such as azobisisobutyronitrile catalyze the similar carbonylation reaction (3). The difference in the catalytic activities of the radical generators and the binuclear metal carbonyls will be discussed in a forthcoming paper. Thus this reaction offers a convenient preparative method of 2-alkyl-4, 4, 4-trichlorobutanoyl chloride, from which various bifunctional compounds can be derived.

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