ORGANIC SYNTHESES BY MEANS OF METAL COMPLEXES VIII[1]

REACTIONS OF METHYL TRICHLOROACETATE WITH OLEFINS CATALYZED BY METAL CARBONYLS

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Abstract—Reactions of methyl trichloroacetate with olefins catalyzed by dicobalt octacarbonyl, cyclopentadienylmolybdenum tricarbonyl dimer and cyclopentadienyliron dicarbonyl dimer have been studied. Products varied depending on catalyst nature. Methyl-4-alkyl-2,2,4-trichlorobutyrate was obtained by the cobalt catalyst. 4-Alkyl-2,2-dichloro-γ-butyrolactone was the main product by the molybdenum and iron catalysts.

A NUMBER OF REPORTS on free radical addition reactions of polyhaloalkanes to olefins have been given. These reactions are initiated by organic peroxides,[2] copper or iron salts,[3] mononuclear metal carbonyls such as $Fe(CO)_5$,[4] or photochemically.[2] We have found that the dinuclear metal carbonyls such as $Co_2(CO)_8$ are active catalysts for the addition of CCl_4 to olefins.[5] We assume homolytic fission of the metal–metal bond in the dinuclear complexes by CCl_4 is the first step of this reaction as shown below.

$$M{-}M + CCl_4 \rightarrow Cl_3C{-}M + Cl{-}M$$

It is expected that polyhaloalkanes having the same or higher reactivity than CCl_4 might also cleave the metal–metal bond in the dinuclear metal carbonyls and add to olefins. Based on the fact that trichloroacetic acid is more active toward metal carbonyls than CCl_4 in polymerization of vinyl monomer,[6] the addition reaction of methyl trichloroacetate was undertaken. In this paper results of the reactions of methyl trichloroacetate with olefins catalyzed by dinuclear metal carbonyls are presented.

RESULTS AND DISCUSSION

The reaction of methyl trichloroacetate with olefins in the presence of a catalytic amount of $Co_2(CO)_8$ was first investigated. Addition of methyl trichloroacetate to olefins proceeded smoothly to give methyl 4-alkyl-2,2,4-trichlorobutyrate. Results of the reaction of methyl trichloroacetate with 1-hexene are shown in Table I.

There are two possible orientations for the addition. Actually, the product formed by addition of the $Cl_2CCO_2CH_3$ group to the terminal carbon was selectively obtained.

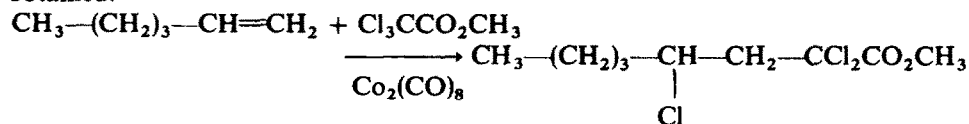$$CH_3{-}(CH_2)_3{-}CH{=}CH_2 + Cl_3CCO_2CH_3$$
$$\xrightarrow[\text{Co}_2(\text{CO})_8]{} CH_3{-}(CH_2)_3{-}\underset{\underset{\displaystyle Cl}{|}}{CH}{-}CH_2{-}CCl_2CO_2CH_3$$

Reaction Temp	methyl 2,2,4- trichlorocaprylate
150	16·10 g (73·8%)[b]
130	3·57 (16·4)
110	2·94 (13·5)

[a] The reactions were carried out with $CCl_3CO_2CH_3$
(20·0 g), 1-hexene (7·0 g), and $Co_2(CO)_8$ (0·5 g) for 16 hr.
[b] Yields based on 1-hexene.

Apparent from the table, the reaction should be carried out above 150° to secure a fairly good yield.

Then the reaction of methyl trichloroacetate with olefins catalyzed by $[CpMo(CO)_3]_2$ and $[CpFe(CO)_2]_2$ was investigated and somewhat different results obtained. One of the products (minor) was methyl 4-alkyl-2,2,4-trichlrobutyrate (I). The main product was 4-alkyl-2,2-dichloro-γ-butyrolactone (II).
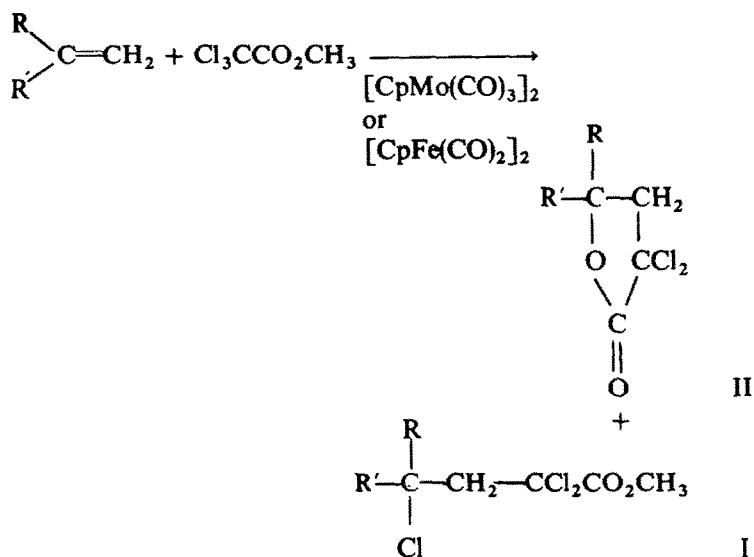
This result differs from the usual free radical addition reaction of trichloroacetic acid ester initiated by organic peroxide in which no lactonization occurs and the product is 4-alkyl-2,2,4-trichlorobutyric acid ester.[7] Therefore metal carbonyls seem to modify the nature of intermediate radical species by coordination or interaction. Results of the reactions of methyl trichloroacetate with propylene are shown in Table II. From the Table, it is clear that for the lactone synthesis $[CpMo(CO)_3]_2$ is superior to $[CpFe(CO)_2]_2$. It should be noticed that solvents have marked effect on the relative ratio of the products. Benzene is the best solvent for the lactone synthesis. Results of the reactions of methyl trichloroacetate with other 1-olefins in the presence of $[CpMo(CO)_3]_2$ are shown in Table III. The ratio of the ester to the lactone also changed depending on the olefin structure.

TABLE II. REACTIONS OF METHYL TRICHLOROACETATE WITH PROPYLENE CATALYZED BY [CpMo(CO)$_3$]$_2$ AND [CpFe(CO)$_2$]$_2$[a]

Catalyst[b]	Solvent	Products[d]		recovered CCl$_3$CO$_2$CH$_3$
		Lactone	Ester	
Mo[c]		23·11 g (81·5%)[e]	0·48 g (1·3%)	0·17 g
Fe[c]		13·48 g (46·1%)	3·83 g (13·1%)	6·33
Mo	MeOH	10·13 g (88·8%)	0·58 g (3·9%)	5·02
Mo	C$_6$H$_6$	13·22 g (98·7%)	trace	2·91
Mo	THF	12·10 g (75·2%)	4·30 g (20·5%)	0
Mo	CH$_2$Cl$_2$	12·81 g (79·4%)	0·32 g (1·5%)	0
Mo	n-hexane	9·01 g (70·0%)	trace	0

[a] Reactions were carried out with CCl$_3$CO$_2$CH$_3$ (17·0 g), propylene (20 ml), solvent (20 ml), and the catalyst (0·5 g) at 150° for 16 hr.
[b] Mo: [CpMo(CO)$_3$]$_2$ Fe: [CpFe(CO)$_2$]$_2$.
[c] Reaction was carried out with 30·0 g of CCl$_3$CO$_2$CH$_3$, 30 ml of propylene and 0·5 g of the catalyst at 150° for 16 hr.
[d] Lactone: 2,2-dichloro-4-methyl-γ-butyrolactone. Ester: methyl 2,2,4-trichlorovalerate.
[e] Yields based on the consumed CCl$_3$CO$_2$CH$_3$.

TABLE III. REACTIONS OF METHYL TRICHLOROACETATE WITH 1-OLEFINS IN THE PRESENCE OF [CpMo(CO)$_3$]$_2$[a]

R	R'		
CH$_3$—(CH$_2$)$_3$—	H	1·49 g (6·8%)	11·96 g (68·3%)
CH$_3$—CH$_2$—	H[b]	1·17 g (4·4%)[d]	10·48 g (50·8%)[d]
CH$_3$—(CH$_2$)$_5$—	H	1·16 g (10·2%)	6·85 g (73·8%)
(CH$_3$)$_2$CH—CH$_2$—	H	2·06 g (9·4%)	10·54 g (60·3%)
CH$_3$—	CH$_3$[b]	3·58 g (13·6%)[d]	8·69 g (42·1%)[d]

[a] The reactions were carried out with CCl$_3$CO$_2$CH$_3$ (20·0 g), olefin (7·0 g), [CpMo(CO)$_3$]$_2$ (0·5 g) at 150° for 16 hr.
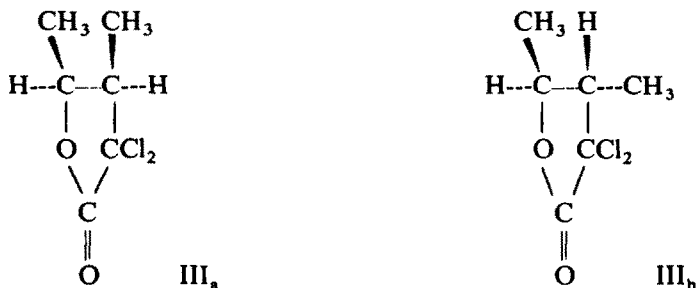[b] 20 ml of olefin was used.
[c] Yields based on the olefin.
[d] Yields based on the CCl$_3$CO$_2$CH$_3$.

The disubstituted olefin, isobutylene, showed lower selectivity compared to a monosubstituted olefin. This might be due to the steric influence by the two methyl group in the lactonization.

The reaction of methyl trichloroacetate with *cis*- and *trans*-2-butene in the presence of $[CpMo(CO)_3]_2$ was carried out. Methyl 2,2,4-trichloro-3-methylvalerate and 2,2-dichloro-3,4-dimethyl-γ-butyrolactone were obtained in about 10 and 50% yields from the butenes. The lactone contained *cis* (IIIa) and *trans* (IIIb) isomers.

$$
\begin{array}{cc}
\mathrm{CH_3\ CH_3} & \mathrm{CH_3\ H} \\
\diagdown\ \ \big| & \diagdown\ \ \big| \\
\mathrm{H\text{---}C\text{---}C\text{---}H} & \mathrm{H\text{---}C\text{---}C\text{---}CH_3} \\
\big|\ \ \big| & \big|\ \ \big| \\
\mathrm{O\ \ CCl_2} & \mathrm{O\ \ CCl_2} \\
\diagdown\diagup & \diagdown\diagup \\
\mathrm{C} & \mathrm{C} \\
\big\| & \big\| \\
\mathrm{O}\quad \mathrm{III_a} & \mathrm{O}\quad \mathrm{III_b}
\end{array}
$$

The ratio of the *trans* (IIIb) to the *cis* (IIIa) lactone obtained from *cis*- and *trans*-2-butene was 1·39 and 1·61 respectively. This means that the reaction did not proceed stereospecifically, namely, free rotation around the C—C bond occurred in the intermediate, and a larger amount of the thermodynamically more stable *trans* isomer was formed.

We propose the following mechanism for these reactions. The first step is the formation of the $CCl_2CO_2CH_3$ complex (IV) by reaction of the dinuclear metal complexes with methyl trichloroacetate. Addition of the $CCl_2CO_2CH_3$ complex (IV) to olefin forms complex V. Reaction of complex V with another molecule of methyl trichloroacetate gives methyl 4-alkyl-2,2,4-trichlorobutyrate (I) with regeneration of the $CCl_2CO_2CH_3$ complex (IV). 4-Alkyl-2,2-dichloro-γ-butyrolactone (II) is formed from complex V by cyclization.

$[Me(CO)_mL_n]_2 + CCl_3CO_2CH_3$

$\qquad\qquad\longrightarrow H_3CO_2CCl_2C\cdot Me(CO)_mL_n + Cl\cdot Me(CO)_mL_n$
$\qquad\qquad\qquad\qquad\qquad\qquad\text{IV}$

$R\text{---}CH{=\!=}CH_2 + H_3CO_2CCl_2C\cdot Me(CO)_mL_n$

$\qquad\qquad\qquad\qquad\longrightarrow R\text{---}CH\text{---}CH_2\text{---}CCl_2CO_2CH_3$

$\qquad\qquad\qquad\qquad\qquad\qquad Me(CO)_mL_n \qquad V$

$R\text{---}CH\text{---}CH_2\text{---}CCl_2\text{---}CO_2CH_3$
$\quad\ \cdot \qquad\qquad\qquad\qquad + Cl_3CCO_2CH_3$
$Me(CO)_mL_n$
$\qquad V$

$\qquad\qquad\qquad\longrightarrow R\text{---}\underset{\underset{\text{Cl}}{|}}{C}H\text{---}CH_2\text{---}CCl_2CO_2CH_3 + \qquad \text{IV}$
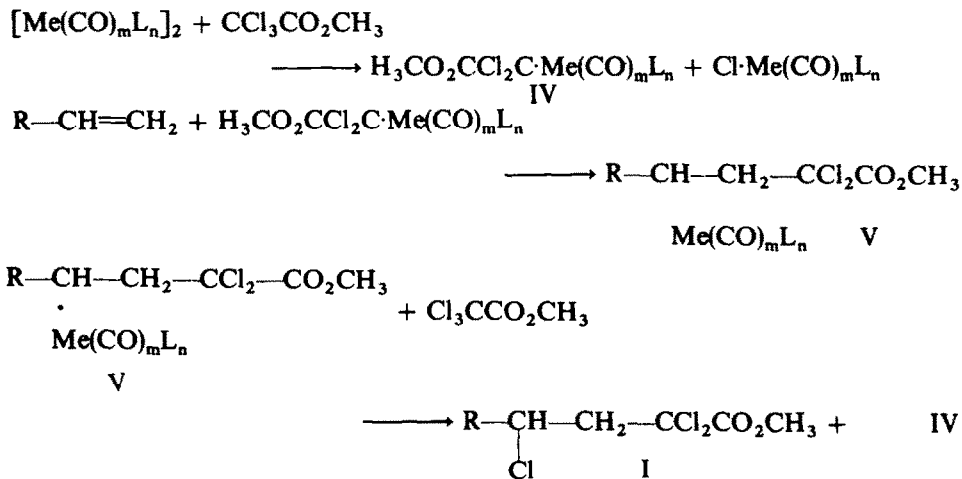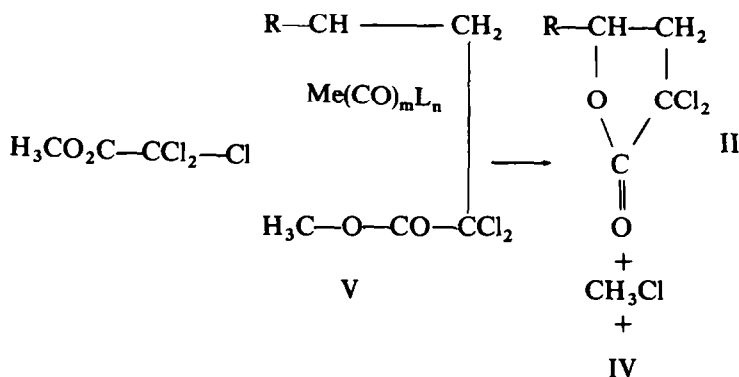$\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad \text{I}$

TABLE IV. PROPERTIES AND ANALYSIS OF METHYL 4-ALKYL-2,2,4-TRICHLOROBUTYRATE AND 4-ALKYL-2,2-DICHLORO-γ-BUTYROLACTONE

	b.p.		C(%)	H(%)	Cl(%)	MW(CHCl₃)	NMR spectrum
I, R = —(CH₂)₃— CH₃	96– 98/ 1 mm	Found	41·52	5·93	40·37	253	9·00 (3H, t), 7·90～8·80 (6H)
R′ = H		Calc.	41·37	5·75	40·61	261	7·20 (1H, q), 6·83 (1H, q)
							6·04 (3H, s), 5·73 (1H)
I, R = —CH₃	106–108/23 mm	Found	32·93	4·25	48·21	224	8·23 (3H, d), 7·07 (1H, q)
R′ = H		Calc.	32·88	4·11	48·40	219	6·72 (1H, q), 5·96 (3H, s)
							5·58 (1H)
I, R = —CH₂—CH₃	110–113/26 mm	Found	36·27	4·85	45·21	229	
R′ = —H		Calc.	36·05	4·72	45·49	233	
II, R = —CH₃ R′ = —H	124–125/23 mm	Found	35·77	3·77	41·78	173	8·44 (3H, d), 7·33 (1H, q)
		Calc.	35·50	3·55	42·01	169	6·70 (1H, q), 5·19 (1H)
II, R = —(CH₂)₅ —CH₃	118–120/ 2 mm	Found	50·08	6·92	29·88	232	9·12 (3H, t), 7·8～8·9 (10H)
R′ = H		Calc.	50·20	6·69	29·71	239	7·43 (1H, q), 6·81 (1H, q)
							5·42 (1H)
II, R = —(CH₂)₃—CH₃	148/23 mm	Found	45·68	5·82	33·41	205	9·02 (3H, t), 7·9～8·8 (6H)
R′ = H		Calc.	45·50	5·69	33·65	211	7·36 (1H, q), 6·76 (1H, q)
							5·38 (1H)
II, R = —CH₂—CH (CH₃ / \ CH₃)	144–146/28 mm	Found	45·72	5·81	33·38	207	9·02 (6H, d), 7·9～8·7 (3H)
		Calc.	45·50	5·69	33·65	211	7·40 (1H, q), 6·75 (1H, q)
R′ = H							5·35 (1H)
II, R = —CH₂—CH₃, R′ = H	110/5 mm	Found	39·52	4·43	38·62	179	
		Calc.	39·34	4·37	38·80	183	
II, R = R′ = —CH₃	118–120/29 mm	Found	39·61	4·49	38·53	189	8·43 (6H, s), 6·95 (2H, s)
		Calc.	39·34	4·37	38·80	183	

$$R—CH \text{———} CH_2 \qquad R—CH—CH_2$$

$$Me(CO)_mL_n \qquad \qquad O \quad CCl_2$$

$$H_3CO_2C—CCl_2—Cl \qquad \qquad \qquad \begin{array}{c} \backslash \ / \\ C \end{array} \quad II$$

$$H_3C—O—CO—CCl_2 \qquad \qquad O$$

$$V \qquad \qquad \qquad + \\ CH_3Cl \\ + \\ IV$$

The difference between the Co, Mo, and Fe catalysts toward the lactonization reaction seems to be due to the different degree of coordination or interaction of the methoxy carbonyl group with the metal carbonyls in the complex (V).
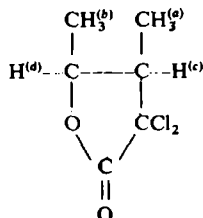
EXPERIMENTAL

NMR spectra were determined on a Varian A-60 spectrometer in CCl_4 and expressed in τ values. Analysis of the products were carried out by gas chromatography (silicone OV 17-108). $[CpMo(CO)_3]_2$ and $[CpFe(CO)_2]_2$ were synthesized from $Mo(CO)_6$ and $Fe(CO)_5$ by the known method.[8] All experiments were carried out using a glass tube equipped with a gas inlet capillary. The glass vessel was placed in an autoclave and the reaction was carried out by shaking. Only typical examples are shown.

Reaction of $CCl_3CO_2CH_3$ *with 1-hexene catalyzed by* $Co_2(CO)_8$. $CCl_3CO_2CH_3$ (20·0 g), 1-hexene (7·0 g), and $Co_2(CO)_8$ (0·5 g) were mixed in the glass vessel and placed in an autoclave and shaken at 150° for 16 hr. Distillation of product gave 16·10 g of methyl 2,2,4-trichlorocapryrate at 100-108°/2 mm. (IR spectrum: 1760 cm^{-1}).

Reaction of $CCl_3CO_2CH_3$ *with propylene catalyzed by* $[CpMo(CO)_3]_2$. $CCl_3CO_2CH_3$ (30·0 g) and $[CpMo(CO)_3]_2$ (0·5 g) were mixed in the glass vessel, which was placed in an autoclave. Propylene (30 ml) was introduced and the reaction was carried out at 150° for 16 hr. The product was distilled to give 0·17 g of $CCl_3CO_2CH_3$ recovered at 54–60°/23 mm. A mixture of methyl 2,2,4-trichlorovalerate and 2,2-dichloro-4-methyl-γ-butyrolactone (1:1, determined by gas chromatograph), 0·96 g, was obtained at 80–118°/23 mm. Further distillation gave 22·63 g of 2,2-dichloro-4-methyl-γ-butyrolactone at 118–125°/23 mm. (IR spectrum: 1800 cm^{-1}).

Reaction of $CCl_3CO_2CH_3$ *with cis-2-butene catalyzed by* $[CpMo(CO)_3]_2$. $CCl_3CO_2CH_3$ (20·0 g), MeOH (20 ml), and catalyst (0·5 g) were mixed in the glass vessel, and placed in an autoclave. *Cis*-2-butene (20 ml) was introduced and the autoclave shaken at 150° for 16 hr. Distillation of product gave first 4·47 g of $CCl_3CO_2CH_3$. Then a mixture of methyl 2,2,4-trichloro-3-methylvalerate and 2,2-dichloro-3,4-dimethyl γ-butyrolactone (ratio of the ester to the lactone was 1:1·5), 6·15 g, was obtained at 90–128°/26 mm. Further distillation afforded 5·83 g of 2,2-dichloro-3,4-dimethyl-γ-butyrolactone at 128–130°/26 mm. 2,2-Dichloro-3,4-dimethyl-γ-butyrolactone contained *cis*- and *trans*- isomers. Their configuration was determined by NMR.

$$\begin{array}{cc} CH_3^{(b)} & CH_3^{(a)} \\ | & | \\ H^{(d)}--C————C--H^{(c)} \\ | & | \\ O & CCl_2 \\ \backslash \quad / \\ C \\ \| \\ O \end{array}$$

Trans-lactone: 8·76 (CH$_3^{(a)}$- -, J_{ac}: 7 cps), 8·60 (CH$_3^{(b)}$--, J_{bd}: 6·5 cps), 6·87 (H$^{(c)}$, J_{ac}: 7 cps, J_{cd}: 7 cps) 5·07 (H$^{(d)}$, J_{bd}: 6·5 cps, J_{cd}: 7 cps). *Cis*-lactone: 8·68 (CH$_3^{(a)}$- -, J_{ac}: 6·5 cps), 8·53 (CH$_3^{(b)}$—, J_{bd}: 6 cps), 7·45 (H$^{(c)}$, J_{ac}: 6·5 cps, J_{cd}: 10 cps) 5·70 (H$^{(d)}$, J_{bd}: 6 cps, J_{cd}: 10 cps). The ratio of the *trans* to the *cis* was determined by gas chromatography and was 1·39:1.

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