

Organic Syntheses by Means of Metal Complexes. V.¹
Reactions of Olefins, Carbon Tetrachloride, and Carbon Monoxide
Catalyzed by Metal Carbonyls²

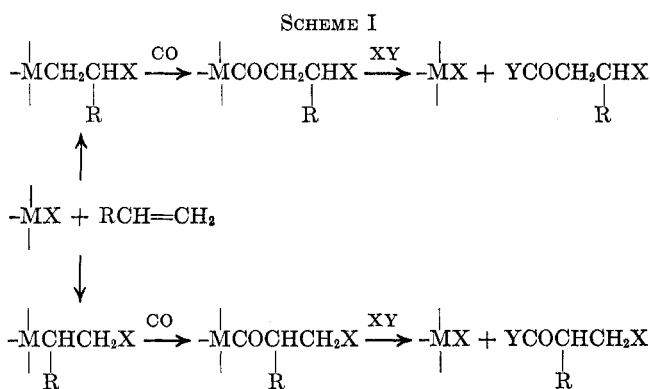
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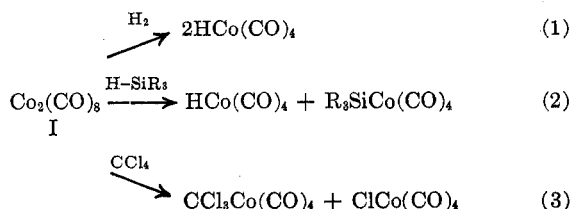
Received January 26, 1970

Dicobalt octacarbonyl, cyclopentadienyliron dicarbonyl dimer, and cyclopentadienylmolybdenum tricarbonyl dimer are effective catalysts for the addition reaction of carbon tetrachloride and carbon monoxide to olefins to form 2-alkyl-4,4,4-trichlorobutyl chloride. These dinuclear metal carbonyls are also active catalysts for the addition of carbon tetrachloride to olefins to form 1,1,1,3-tetrachloroalkane. The mechanism of these dinuclear metal carbonyl catalyzed reactions is discussed.

Metal carbonyls catalyze various reactions of olefins, among which carbonylations are the most important. In carbonylations, it is generally believed that an insertion of olefins into a metal σ bond to form an alkyl complex is followed by carbon monoxide insertion to form an acyl complex. Finally the acyl complex affords carbonyl compounds. This mechanism can be expressed by Scheme I.



In this mechanism, formation of σ -bonded complex is essential as a starting point. Dinuclear metal carbonyls such as $Co_2(CO)_8$ (I) react with some simple molecules with splitting of the metal-metal bond to form σ -bonded complexes. For example, in the I-catalyzed oxo reaction or hydrosilation,³ hydrogen or a silane reacts with I to form the following σ -bonded complexes (reactions 1 and 2), which then undergo olefin insertion.



(1) Part IV: T. Kajimoto and J. Tsuji, *Bull. Chem. Soc., Jap.*, **42**, 827 (1969).

(2) Preliminary communication: T. Susuki and J. Tsuji, *Tetrahedron Lett.*, 913 (1968).

(3) J. F. Harrod and A. J. Chalk, *J. Amer. Chem. Soc.*, **87**, 1133 (1965).

The reaction of CCl_4 with I to form $Co_2(CO)_9Cl$ is known,^{4,5} and the intermediate formation of the species $CCl_3Co(CO)_4$ and $ClCo(CO)_4$ has been assumed (reaction 3). Once the σ -bonded complex is formed from CCl_4 , olefin insertion into the σ bond to form an alkyl complex is expected. Based on this assumption, we attempted to apply this reaction of dinuclear metal carbonyls to a new catalytic carbonylation reaction of olefins.

The addition reaction of CCl_4 to olefins catalyzed by mononuclear metal carbonyls, such as $Fe(CO)_5$, $Mo(CO)_6$, or $Cr(CO)_6$, has been reported. Thus $Fe(CO)_5$ -catalyzed addition of CCl_4 to ethylene gave a mixture of telomer homologs, $CCl_3(CH_2CH_2)_nCl$ ($n = 1, 2, 3, 4$, and higher), in 70% conversion.⁶ From the above consideration, it is expected that dinuclear metal carbonyls should be better catalysts for the CCl_4 addition reactions. The dinuclear metal carbonyls are indeed very active catalysts for the addition reaction of CCl_4 and CO to olefins, as the catalyst I, $[C_5H_5Fe(CO)_2]_2$ (II), and $[C_5H_5Mo(CO)_3]_2$ (III) were found most effective.

The reaction of ethylene, carbon monoxide, and CCl_4 in methanol to give $CCl_3(CH_2CH_2)_nCO_2CH_3$ ($n = 1-3$) in 40% conversion using di-*t*-butyl peroxide as a catalyst at 1000 atm has been reported.⁷ Different from the reactions catalyzed by butyl peroxide and $Fe(CO)_5$, the reactions catalyzed by the dinuclear metal carbonyls are clean and selective without giving a mixture of homologs. The catalytic activity of metal carbonyls coordinated with a cyclopentadienyl group has scarcely been reported, although it was recently reported that II is an active catalyst for the oxo reaction.⁸ Further usefulness of the cyclopentadienyl-coordinated metal carbonyls was found in the present studies.

Results and Discussion

The reaction of CCl_4 with olefins in the presence of a catalytic amount of I was first investigated. Addition

(4) R. Ercoli, E. Santambrogio, and G. T. Casagrandi, *Chim. Ind. (Milan)*, **44**, 1344 (1962).

(5) G. Bor, L. Marko, and B. Marko, *Chem. Ber.*, **95**, 333 (1962).

(6) (a) A. N. Nesmeyanov, R. Kh. Freidlina, E. C. Chukovskaya, R. G. Petrova, and A. B. Belyavsky, *Tetrahedron*, **17**, 61 (1962). (b) E. T. Chukovskaya, A. A. Kamyshova, and R. Kh. Freidlina, *Dokl. Akad. Nauk SSSR*, **164**, 602 (1965), and the references cited therein.

(7) R. E. Foster, A. W. Larchar, R. D. Lipscomb, and B. C. Mukusick, *J. Amer. Chem. Soc.*, **78**, 5606 (1956).

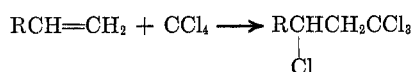
(8) J. Tsuji and Y. Mori, *Bull. Chem. Soc. Jap.*, **42**, 527 (1969).

TABLE I
 REACTION OF CARBON TETRACHLORIDE WITH OLEFINS IN THE PRESENCE OF $[\text{Co}(\text{CO})_4]_2$ (I)^a

Olefins	Temp, °C	Reaction Time, hr	Products (g)
Ethylene ^b (100 atm)	160	17	$\text{CCl}_3\text{CH}_2\text{CH}_2\text{Cl}$ (1.0) $\text{CCl}_3(\text{CH}_2)_4\text{Cl}$ (3.5)
Propylene (12 g)	150	15	$\text{CCl}_3\text{CH}_2\text{CH}(\text{CH}_3)\text{Cl}$ (4.2)
1-Butene (12 g)	160	16	$\text{CCl}_3\text{CH}_2\text{CH}(\text{C}_2\text{H}_5)\text{Cl}$ (8.0)
1-Butene (6 g)	160	1	$\text{CCl}_3\text{CH}_2\text{CH}(\text{C}_2\text{H}_5)\text{Cl}$ (4.3)
1-Hexene (7 g)	180	16	$\text{CCl}_3\text{CH}_2\text{CH}(n\text{-C}_4\text{H}_9)\text{Cl}$ (8.0)
1-Hexene (14 g)	20	48	$\text{CCl}_3\text{CH}_2\text{CH}(n\text{-C}_4\text{H}_9)\text{Cl}$ (1.5)
1-Octene (14 g)	160	15	$\text{CCl}_3\text{CH}_2\text{CH}(n\text{-C}_6\text{H}_{13})\text{Cl}$ (6.5)
<i>cis</i> -2-Butene (6 g)	160	16	$\text{CCl}_3\text{CH}(\text{CH}_3)\text{CH}(\text{CH}_3)\text{Cl}$ (3.0)
<i>trans</i> -2-Butene (6 g)	160	16	$\text{CCl}_3\text{CH}(\text{CH}_3)\text{CH}(\text{CH}_3)\text{Cl}$ (2.7)
2-Hexene (7 g)	160	16	$\text{CCl}_3\text{CH}(\text{C}_3\text{H}_7)\text{CH}(\text{CH}_3)\text{Cl}$ } $\text{CCl}_3\text{CH}(\text{CH}_3)\text{CH}(\text{C}_3\text{H}_7)\text{Cl}$ } (3.6)
Cyclohexene (16 g)	150	15	No sole product

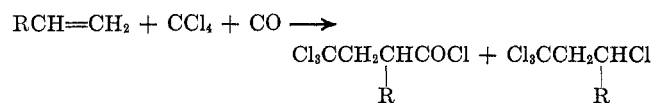
^a The reactions were carried out with 40 ml of CCl_4 and 1 g of the catalyst in a glass vessel placed in an autoclave (300 ml). ^b CCl_4 (20 ml) was used in a 100-ml autoclave.

of CCl_4 to various olefins was observed at about 160° and 1,1,1,3-tetrachloroalkanes were obtained. The results are shown in Table I. Ethylene is somewhat unusual and a mixture of 1:1 and 1:2 adducts was obtained showing that a successive ethylene insertion is possible. On the other hand, only 1:1 adduct was obtained with other olefins. Conversion was lower with internal olefins than terminal olefins. For 1 olefins, there are two possible orientations of the olefin additions. Actually, however, only products formed by addition of CCl_3 to the terminal carbon were obtained.



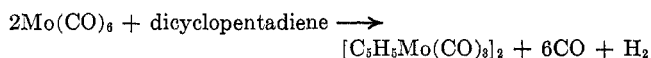
For example, only 1,1,1,3-tetrachloropentane was obtained selectively from 1-butene. This is the same result as obtained in the radical-initiated addition reaction of CCl_4 to olefins. It is clearly different from other I-catalyzed reactions such as the oxo reaction, in which two products derived from different additions to double bond are obtained in various ratios. As in the oxo reaction, only catalytic amounts of I are necessary. After the reaction was complete, CoCl_2 was recovered from the reaction mixture. The reaction can be applied to simple olefins, but not to butadiene. Acrylonitrile, methyl acrylate, and styrene polymerized with this catalyst.

The reaction under CO pressure was then investigated with the expectation that the CO insertion would follow olefin insertion to give carbonylated products. With 1 olefin, CCl_4 , and CO, the reaction proceeded smoothly to give 2-alkyl-4,4,4-trichlorobutyryl chloride. The formation of butyryl chlorides is competitive with simple addition of CCl_4 to olefins to form 1,1,1,3-tetrachloroalkanes.



A higher CO pressure and a lower reaction temperature tended to increase the ratio of the carbonylation to the simple addition. It should be noted that a simple CO insertion without olefin insertion to form trichloroacetyl chloride was not observed.

For this carbonylation reaction, mononuclear metal carbonyls, such as $\text{Fe}(\text{CO})_5$ or $\text{Mo}(\text{CO})_6$, were almost inactive. I is active, but higher activity was observed with dinuclear metal carbonyls derived from iron and molybdenum carbonyls. Mononuclear molybdenum and iron carbonyls can be converted into the dinuclear ones by coordination of a cyclopentadienyl group as a ligand.⁹



With these dimeric carbonyls, high yields of 2-alkyl-4,4,4-trichlorobutyryl chlorides were obtained, the reaction proceeding even at 50° with the iron catalyst. Results are shown in Table II. Another typical mononuclear carbonyl is $\text{Ni}(\text{CO})_4$ from which $[\text{C}_5\text{H}_5\text{Ni}(\text{CO})]_2$ can be derived; this, however, was found to be completely inactive. The catalytic action of I is somewhat different from that of the iron and molybdenum catalysts. For example, ethylene does not give the carbonylated product with I, but high yields of the carbonylated products were obtained with the other catalysts. Also, hydroquinone showed some inhibitory action with I and a little with III. There was no effect with II. The reaction carried out in ethanol produced corresponding esters in nearly the same yields as in the absence of the solvent. Thus, this carbonylation reaction is useful for the synthesis of 2-alkyl-4,4,4-trichlorocarboxylic acids from which various compounds can be derived by displacement or elimination of the chlorines.

We propose the following mechanism for this reaction. The first step is the formation of the trichloromethyl complex by reaction of the dinuclear carbonyls with CCl_4 (reaction 4). The insertion of olefin into the metal-trichloromethyl bond forms the 1-alkyl-3,3,3-trichloropropyl complex (reaction 5). Reaction of the propyl complex with another molecule of CCl_4 gives the 1,1,1,3-tetrachloroalkane with regeneration of the trichloromethyl complex (reaction 6). CO insertion into the propyl complex gives the acyl complex (reaction 7), which then reacts with CCl_4 to form 2-alkyl-4,4,4-trichlorobutyryl chloride with regeneration of the trichloromethyl complex (reaction 8).

(9) R. B. King, "Organometallic Syntheses," Vol. 1, Academic Press New York, N. Y., 1965, pp 109, 114.

TABLE II
REACTION OF OLEFINS, CCl₄ AND CO CATALYZED BY [Co(CO)₄]₂ (I), [C₅H₅Fe(CO)₂]₂ (II), AND [C₅H₅Mo(CO)₃]₂ (III)^a

Olefins	Catalyst, 1 g	CO pressure, atm	Reaction		Products ^b (g)
			Temp, °C	Time, hr	
Ethylene (30 atm)	II	170	119	15	CCl ₃ CH ₂ CH ₂ COCl (3.3)
Ethylene (30 atm)	III	170	120	15	CCl ₃ CH ₂ CH ₂ COCl (15.4)
Ethylene (30 atm)	I	170	135	15	CCl ₃ CH ₂ CH ₂ Cl (0.3) CCl ₃ (CH ₂) ₄ Cl (0.8)
Propylene (12 g)	II	200	53	14	CCl ₃ CH ₂ CH(CH ₃)COCl (12) CCl ₃ CH ₂ CH(CH ₃)Cl (3.0)
Propylene (12 g)	II	200	118	15	CCl ₃ CH ₂ CH(CH ₃)COCl (12) CCl ₃ CH ₂ CH(CH ₃)Cl (8.0)
Propylene ^c (12 g)	II	200	68	15	CCl ₃ CH ₂ CH(CH ₃)COOC ₂ H ₅ (11.2) CCl ₃ CH ₂ CH(CH ₃)Cl (2.7)
Propylene ^d (12 g)	II	200	67	15	CCl ₃ CH ₂ CH(CH ₃)COCl (13) CCl ₃ CH ₂ CH(CH ₃)Cl (3.0)
Propylene (12 g)	III	200	50	15	None
Propylene (12 g)	III	60	93	15	CCl ₃ CH ₂ CH(CH ₃)COCl (8.8) CCl ₃ CH ₂ CH(CH ₃)Cl (15)
Propylene (12 g)	III	200	95	3	CCl ₃ CH ₂ CH(CH ₃)COCl (10) CCl ₃ CH ₂ CH(CH ₃)Cl (9.0)
Propylene ^e (12 g)	III	150	103	4	CCl ₃ CH ₂ CH(CH ₃)COCl (1.1) CCl ₃ CH ₂ CH(CH ₃)Cl (1.8)
Propylene (10 g)	I	200	83	15	CCl ₃ CH ₂ CH(CH ₃)COCl (5.0) CCl ₃ CH ₂ CH(CH ₃)Cl (2.3)
Propylene ^c (10 g)	I	200	125	15	CCl ₃ CH ₂ CH(CH ₃)COOC ₂ H ₅ (9.0) CCl ₃ CH ₂ CH(CH ₃)Cl (6.4)
Propylene (10 g)	I	50	128	15	CCl ₃ CH ₂ CH(CH ₃)COCl (1.1) CCl ₃ CH ₂ CH(CH ₃)Cl (2.0)
Propylene ^f (10 g)	I	200	120	15	CCl ₃ CH ₂ CH(CH ₃)COCl (trace) CCl ₃ CH ₂ CH(CH ₃)Cl (trace)
1-Butene (12 g)	II	200	90	15	CCl ₃ CH ₂ CH(C ₂ H ₅)COCl (9.8) CCl ₃ CH ₂ CH(C ₂ H ₅)Cl (4.5)
1-Butene (12 g)	III	200	93	15	CCl ₃ CH ₂ CH(C ₂ H ₅)COCl (6.5) CCl ₃ CH ₂ CH(C ₂ H ₅)Cl (3.8)
1-Butene (12 g)	I	200	160	15	CCl ₃ CH ₂ CH(C ₂ H ₅)COCl (7.5) CCl ₃ CH ₂ CH(C ₂ H ₅)Cl (7.0)
1-Hexene (4 g)	III	200	91	15	CCl ₃ CH ₂ CH(<i>n</i> -C ₄ H ₉)COCl (3.8) CCl ₃ CH ₂ CH(<i>n</i> -C ₄ H ₉)Cl (2.5)
1-Hexene (7 g)	I	180	160	15	CCl ₃ CH ₂ CH(<i>n</i> -C ₄ H ₉)COCl (4.4) CCl ₃ CH ₂ CH(<i>n</i> -C ₄ H ₉)Cl (8.5)
1-Octene (7 g)	II	200	118	15	CCl ₃ CH ₂ CH(<i>n</i> -C ₆ H ₁₃)COCl (7.6) CCl ₃ CH ₂ CH(<i>n</i> -C ₆ H ₁₃)Cl (3.5)
1-Octene (7 g)	I	200	130	15	CCl ₃ CH ₂ CH(<i>n</i> -C ₆ H ₁₃)COCl (6.5) CCl ₃ CH ₂ CH(<i>n</i> -C ₆ H ₁₃)Cl (6.0)
<i>trans</i> -2-Butene (9 g)	III	200	120	15	CCl ₃ CH(CH ₃)CH(CH ₃)COCl (1.6) CCl ₃ CH(CH ₃)CH(CH ₃)Cl (1.8)
<i>trans</i> -2-Butene (6 g)	I	170	160	15	CCl ₃ CH(CH ₃)CH(CH ₃)Cl (2.0)
<i>cis</i> -2-Butene (12 g)	I	200	120	15	CCl ₃ CH(CH ₃)CH(CH ₃)COCl (1.7) CCl ₃ CH(CH ₃)CH(CH ₃)Cl (4.0)
Isobutene (9 g)	I	160	160	15	CCl ₃ CH ₂ C(CH ₃) ₂ Cl (2.0)
1,3-Butadiene (12 g)	II	200	74	6	None
1,3-Butadiene (12 g)	III	200	120	15	None
1,3-Butadiene (12 g)	I	200	120	15	CCl ₃ CH ₂ CH=CHCH ₂ COCl (0.6)

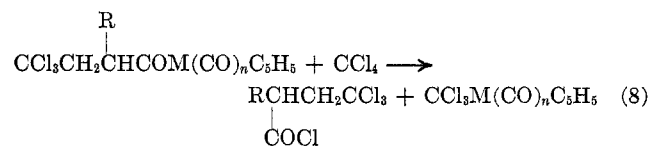
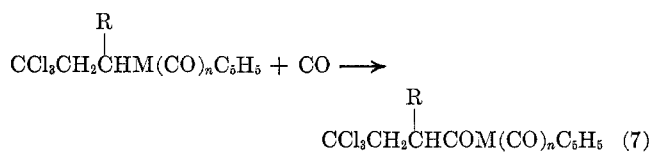
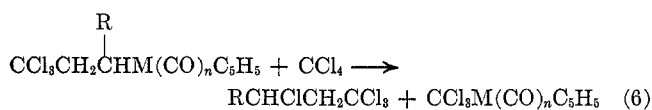
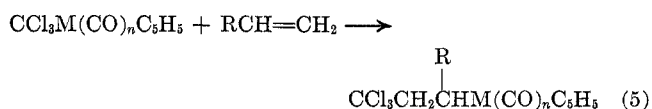
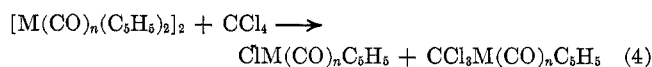
^a The reactions were carried out with 40 ml of CCl₄ in a glass vessel. ^b Amount of the acid chlorides was calculated from the weight of isolated acid amide. ^c The mixture of 20 ml of CCl₄ and 20 ml of ethanol was used. ^d Hydroquinone (1.0 g) was added. ^e Hydroquinone (0.86 g) was added. ^f Hydroquinone (1.27 g) was added.

TABLE III
PROPERTIES AND ANALYSES OF 1,1,1,3-TETRACHLOROALKANES

CCl ₃ CH—CHCl	R ¹ R ²	Registry no.	Bp, °C (mm)	Calcd, %			Calcd mol wt	Found, %			Found mol wt	Nmr spectrum
				C	H	Cl		C	H	Cl		
CH ₃	H	a	88–89 (53)	24.52	3.09	72.39	196	24.81	3.08	72.10	202.7	8.31 (d, 3), 6.79 (heptet, 2), 5.58 (m, 1)
C ₂ H ₅	H	b	80–83 (18)	28.60	3.84	67.55	210	28.65	3.80	67.25	213	8.86 (t, 3), 8.03 (m, 2), 6.79 (octet, 2), 5.77 (m, 1)
CH ₃	CH ₃	c	75 (15)	28.60	3.84	67.55		28.93	3.88	67.00		8.46 (t, 6), 6.85 (octet, 1), 5.10 (octet, 1)
<i>n</i> -C ₄ H ₉	H	d	119–120 (27)	35.33	5.08	59.59	238	35.59	5.11	59.30	243	9.05 (t, 3), 8.54 (m, 4), 8.14 (2), 6.81 (octet, 2), 5.72 (1)
<i>n</i> -C ₆ H ₁₃	H	e	73–75 (1)	40.64	6.06	53.31	266	41.19	6.12	53.10	279.9	9.08 (t, 3), 8.62 (m, 8), 8.14 (m, 2), 6.79 (octet, 2), 5.75 (m, 1)

TABLE IV
PROPERTIES AND ANALYSES OF AMIDES AND ESTERS DERIVED FROM 2-ALKYL-4,4,4-TRICHLOROBUTRYL CHLORIDES

X	C ₆ H ₅ CH-CHCOX		Registry no.	Mp or bp (mm), °C	Calcd, %			Found, %			Calcd mol wt	Found mol wt	Nmr spectrum		
	R ¹	R ²			C	H	N	Cl	C	H				N	Cl
NH ₂	H	H	a	88-89	25.22	3.18	7.35	55.85	190.5	25.34	3.25	7.20	56.00	185	7.20, 7.03
OC ₂ H ₅	H	H	b	110-115 (28)	32.83	4.13	48.46	219.5	33.21	4.18	48.10	216.3	205.7	8.76 (t, 3), 8.71 (d, 3), 7.6-6.4 (m, 3), 5.93(2)	
NH ₂	CH ₃	H	c	103-104	29.37	3.94	6.85	52.02	204.4	29.52	3.97	6.71	52.23	230	8.96 (t, 3), 8.36(2), 7.63-6.26 (m, 3)
OC ₂ H ₅	CH ₃	H	d	95-97 (12)	36.00	4.75	45.55	234	36.11	4.74	45.52	247.3	219	8.84-8.50 (double d, 6), 7.75-6.64 (m, 2)	
NH ₂	C ₂ H ₅	H	e	97-98	32.98	4.61	6.41	48.68	247.6	33.02	4.66	6.31	48.65	297	9.07 (t, 3), 8.57 (m, 6), 7.28(2), 6.55 (quartet, 1)
OC ₂ H ₅	C ₂ H ₅	H	f	120-130 (25)	38.81	5.29	42.97	247.6	38.65	5.18	43.45	247.3	219	6.89 (d, 2), 6.56 (d, 2), 4.11 (quintet, 2)	
NH ₂	CH ₃	CH ₃	g	56-57	32.98	4.61	6.41	48.68	219	33.14	4.66	6.55	48.54		
NH ₂	n-C ₄ H ₉	H	h	82-83	38.97	5.72	5.68	43.14	275.6	38.81	5.72	5.52	43.27		
OC ₂ H ₅	n-C ₄ H ₉	H	i	150-160 (25)	43.57	6.22	38.59	275.6	43.77	6.18	38.50	281.8			
NH ₂	n-C ₈ H ₁₇	H	j	87-88	43.73	6.61	38.79	275	43.59	6.42	4.93	38.64			
OC ₂ H ₅	n-C ₈ H ₁₇	H	k	127-130 (5)	47.47	6.97	35.01	303.6	47.51	6.92	35.00	297			
CCL ₃ CH ₂ CH=CHCONH ₂			l	94-97	33.29	3.72	6.47	49.13	216.5	33.77	3.95	5.89	48.89		



There is a close similarity, such as selective formation of only one product, between the metal carbonyl catalyzed addition of CCl₄ and radical-initiated reactions,⁷ and hence there is a possibility that a trichloromethyl radical, rather than the trichloromethyl complex shown above, is an active species. However, little or no inhibition by hydroquinone in the metal carbonyl catalyzed addition reactions weakens this possibility. Certainly metal-coordinated species, namely, σ-metal complexes or coordinated radicals, play an important role.

Bamford and others have published a series of papers dealing with the metal carbonyl initiated radical polymerization of vinyl monomers in the presence of CCl₄; they proposed that the polymerizations are initiated by a radical formed by the reaction of CCl₄ with metal carbonyls.¹⁰ In their polymerization, only monomeric metal carbonyls are reported to be active; dinuclear carbonyls such as I are not active. Under the present reaction conditions, however, styrene, acrylonitrile, and methyl acrylate polymerized with I.

Experimental Section

The nmr spectra were determined on a Varian high-resolution spectrometer Model HR-100 in CCl₄ and are expressed in τ values. The molecular weights were determined in benzene using the Mechrolab vapor pressure osmometer. II and III were synthesized by the known method.⁹ The addition and carbonylation reactions were carried out in a stainless steel autoclave with shaking. Only typical examples are shown below.

Reaction of Ethylene and CCl₄ Catalyzed by I.—CCl₄ (20 ml) and I (1 g) were mixed in a glass vessel equipped with a gas inlet capillary, which was placed in a 100-ml autoclave. The ethylene was introduced (100 atm). The reaction was carried out at 160° for 17 hr. Crude reaction product was isolated by distillation at 60-120° (25 mm). Redistillation gave 1,1,1,3-tetrachloropropane (1.0 g) and 1,1,1,5-tetrachloropentane (3.5 g).

Reaction of Propylene with CCl₄ and CO Catalyzed by II.—The catalyst (1 g) and CCl₄ (40 ml) were mixed in the glass vessel, which was placed in a 300-ml autoclave. Propylene (20 ml) was introduced, followed by CO (200 atm), and the reaction was carried out at 53° for 14 hr. Ir spectrum of the crude reaction mixture showed the presence of acyl chloride at 1780 cm⁻¹. The reaction mixture was treated with concentrated NH₃ and extracted with CH₂Cl₂. Distillation of the extract gave 1,1,1,3-

(10) C. H. Bamford, G. C. Eastmond, and D. Writtle, *J. Organometal. Chem.*, **17**, 33 (1969), and the references cited therein.

tetrachlorobutane (3 g) at 86–88° (50 mm) and the residue solidified. The solid was recrystallized from a CCl_4 -*n*-hexane mixture to give 4,4,4-trichloro-2-methylbutyramide (11 g). The amide (9 g) was dissolved in ethanolic HCl (40%, 50 ml) and refluxed for 3 hr. The solution was neutralized with ammonia and ethanol was evaporated. NH_4Cl was removed by filtration and the filtrate was subjected to distillation to give ethyl 4,4,4-trichloro-2-methylbutyrate at 95–97° (12 mm, 7.5 g).

Following derivatives of succinic acids were obtained by the hydrolysis of the trichloro esters formed from various olefins in concentrated H_2SO_4 and their melting points are shown (reported melting points): CH_3 -, 111–112° (111°); C_2H_5 -, 97° (98°); *n*- C_4H_9 -, 80° (81°); *n*- C_6H_{13} -, 83° (83–84°).

Properties of the other reaction products and their derivatives are shown in Tables III and IV.

Registry No.—Carbon tetrachloride, 56-23-5; carbon monoxide, 630-08-0; I, 10210-68-1; II, 12087-10-4; III, 12091-64-4; Table III—*a*, 13275-19-9; *b*, 19967-19-2; *c*, 20518-70-1; *d*, 13375-88-7; *e*, 1070-27-5; Table IV—*a*, 25236-71-9; *b*, 20101-80-8; *c*, 25236-73-1; *d*, 25236-74-2; *e*, 25236-75-3; *f*, 25236-76-4; *g*, 25236-77-5; *h*, 25236-78-6; *i*, 25236-79-7; *j*, 25236-80-0; *k*, 25236-81-1; *l*, 25236-82-2; ethylene, 74-85-1; propylene, 115-07-1; 1-butene, 106-98-9; 1-hexene, 592-41-6; 1-octene, 111-66-0; *cis*-2-butene, 590-18-1; *trans*-2-butene, 624-64-6; 2-hexene, 592-43-8; isobutene, 115-11-7; 1,3-butadiene, 106-99-0.

Zinc Reduction of γ Diketones

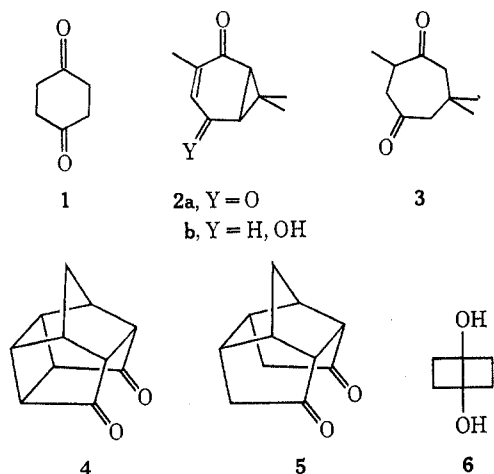
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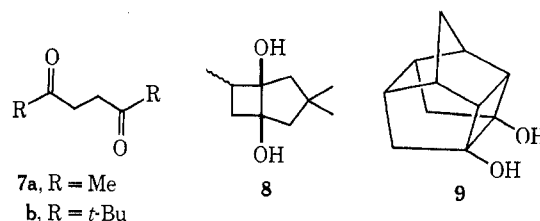
Received February 23, 1970

The reduction of cyclic γ diketones with amalgamated zinc and hydrochloric acid has been studied. While the eight- and seven-ring systems yield 1,2-glycols, cyclohexane-1,4-dione fragments into acyclic hexane-2,5-dione. Reduction of the latter produces 2-hexanol. The ease of reduction of 1,2-diacylethylenes, -cyclopropanes, and -cyclobutane is compared. A seven-membered-ring analog of the quinone-hydroquinone reduction-oxidation system is described.

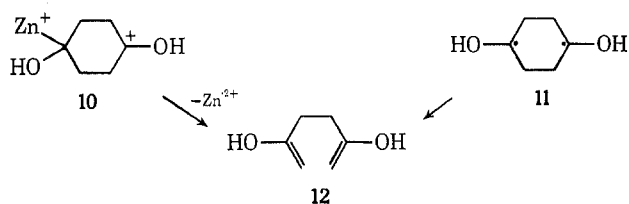
In continuation of a study of the Clemmensen reduction of diketones,¹ an investigation of the reaction of some cyclic γ diketones with amalgamated zinc in hydrochloric acid was undertaken. Diketones **1**, **3**, and **5** were chosen as six-, seven-, and eight-membered cyclic 1,4-dione representatives. The latter two substances were prepared by reduction of ketones **2a**² and **4**,³ respectively, with zinc in acetic acid.



The Clemmensen products were expected to be pinacols, although the high strain of potential pinacolic product **6** from **1** suggested that the reduction of the six-membered cyclic diketone might take a different course from that of its homologs. The Clemmensen reduction of cyclohexane-1,4-dione (**1**) yielded acetylacetone (**7a**), while the reduction of 2,6,6-trimethylcycloheptane-1,4-dione (**3**) gave the pinacol isomer pair **8** and that of **5** led to pinacol **9**. Periodate oxidation of the diols reverted them to their diketonic precursors.



The fragmentation of **1** is reminiscent of the conversion of 1,4-dibromocyclohexane or 1,4-diiodocyclohexane into diallyl on zinc reduction⁴ and can be envisaged to involve the breakup of the reduction intermediate(s) (**10**, **11**, or organozinc equivalents) into the dienol (**12**) of **7a**.⁵



The formation of products besides **7a** on reduction of **1** at elevated temperature led to a study of the Clemmensen reduction of acetylacetone (**7a**). The sole isolable product of a reaction at room temperature was 2-hexanol, while the latter and a mixture of stereoisomeric 2,5-dimethyltetrahydrofurans (**13a**) were obtained from a reaction at slightly elevated temperature and proved to be the products of overreduction of cyclohexane-1,4-dione (**1**).⁶ In view of the possibility of the

(4) C. A. Grob and W. Baumann, *Helv. Chim. Acta*, **38**, 594 (1955).

(5) (a) For a general discussion of heterolyses of this type, cf. C. A. Grob and P. W. Schiess, *Angew. Chem.*, **79**, 1 (1967). (b) For examples of homolyses of this type, cf. S. G. Cohen and R. Zand, *J. Amer. Chem. Soc.*, **84**, 586 (1962); W. R. Roth and M. Martin, *Tetrahedron Lett.*, 3865 (1967).

(6) An independent study of the Clemmensen reduction of acetylacetone and cyclohexane-1,4-dione under somewhat different conditions by J. G. St. C. Buchanan and B. R. Davis, *J. Chem. Soc. C*, 1340 (1967), has yielded related results. The authors are indebted to Dr. Davis for furnishing them information on this work prior to publication.

(1) E. Wenkert and E. Kariv, *Chem. Commun.*, 570 (1965).

(2) E. J. Corey and H. J. Burke, *J. Amer. Chem. Soc.*, **78**, 174 (1956).

(3) R. C. Cookson, E. Crundwell, and J. Hudec, *Chem. Ind. (London)*, 1003 (1958).