# Radical Reactions in the Coordination Sphere. III.[1] Reactions of Dichloro- and Trichloroacetic Acid Esters with 1-Olefins Catalyzed by Dichlorotris(triphenylphosphine)ruthenium(II)

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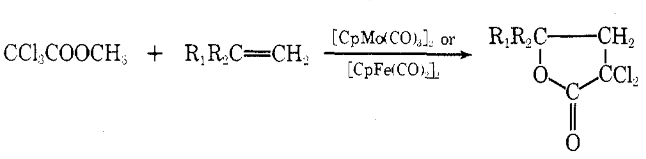
*Received April 1, 1975*

Although transition metal complex or salt catalyzed addition reactions of polyhaloalkanes with olefins give the 1:1 adducts which have a straight carbon-chain structure,[2] the course of addition reactions of polychloroacetic acid esters depends upon the type of the catalyst used for the reactions. Thus, under the catalytic influence of binuclear metal carbonyls of molybdenum and iron, methyl trichloroacetate undergoes lactonization reaction with olefins to afford 4-alkyl-2,2-dichloro-γ-butyrolactone,[3] whereas, in the presence of copper salts, methyl or ethyl trichloroacetate adds to olefins to give methyl or ethyl 2,2,4-trichlorocarboxylates as 1:1 adduct.[4] In the latter cases, the yields of the products were at best 40–60% based on the olefin charged.



(1)

$$\mathrm{CCl_3COOR' + RCH{=}CH_2 \xrightarrow{copper\ salts} RCHClCH_2CCl_2COOR'}$$
$$\mathrm{(R' = CH_3, C_2H_5)} \qquad (2)$$

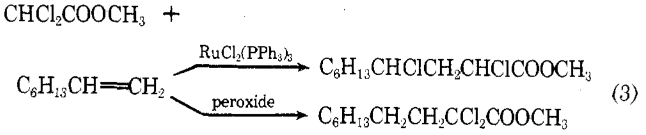
In the course of our investigation on the synthetic utility of the radical reactions brought about by the interaction between a transition metal homogeneous catalyst and an organic halide, we have found that, in the presence of dichlorotris(triphenylphosphine)ruthenium(II), the reaction of polyhalomethanes such as carbon tetrachloride and chloroform with olefins proceeded smoothly under mild conditions to give the corresponding 1:1 adducts in good yields.[1,5] We now report the results of the ruthenium complex catalyzed addition reactions of polychloroacetic acid esters with some 1-olefins. The general feature of the reactions is indicated by the results summarized in Table I.

Addition of methyl trichloroacetate to 1-octene was simply accomplished by heating a benzene solution of the halide, the olefin, and the ruthenium complex (molar ratio 1.7:1:0.004) in a sealed tube at 120°C for 23 hr. Thus, methyl 2,2,4-trichlorodecanoate was obtained in a yield of 95% (based on the olefin consumption) from this reaction. The reaction can be carried out without any added solvent, but the use of a solvent such as benzene gave somewhat better results. Under almost the same conditions, the reaction of ethyl trichloroacetate with 1-octene resulted in the formation of 93% yield of ethyl 2,2,4-trichlorodecanoate. Similarly, the reaction of methyl trichloroacetate with 1-hexene afforded methyl 2,2,4-trichlorocapryrate in 97% yield.

Although the reactions were conducted using benzene as solvent, which was said to be the best solvent for lactonization reaction,[3] no lactonization products could be detected in these reactions. Thus, the ruthenium catalyst favors the formation of esters over that of lactones in the reaction of chloro esters.

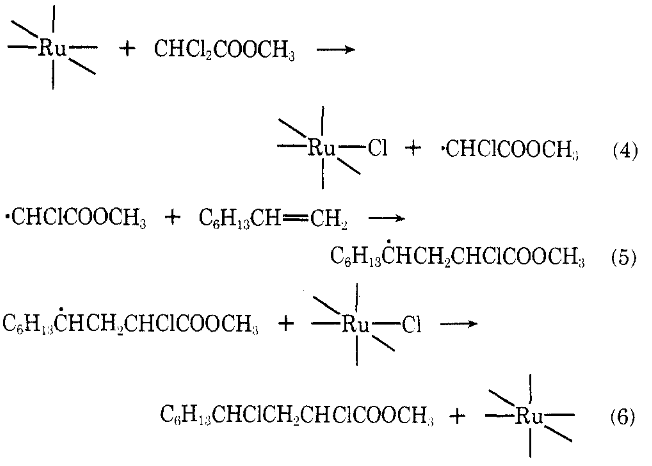
It was further found that the ruthenium complex catalyzed addition reaction can be extended to easily polymerizable olefins such as styrene, acrylonitrile, methyl methacrylate, and methyl vinyl ketone. The reactions could be carried out with considerable success using an equimolar mixture of ethyl trichloroacetate and the olefins, but we have obtained best results with a 2:1 mixture of the reactants. Thus, heating a 2:1 mixture of ethyl trichloroacetate and styrene with 0.5 mol % of the ruthenium complex at 120°C for 10 hr gave ethyl 2,2,4-trichloro-4-phenylbutyrate in 95% yield. Similarly, the reaction of the same halide with acrylonitrile, methyl methacrylate, and methyl vinyl ketone gave ethyl 2,2,4-trichloro-4-cyanobutyrate, ethyl 2,2,4-trichloro-4-carbomethoxyvalerate, and ethyl 2,2,4-trichloro-5-ketocaproate in a yield of 85, 80, and 80%, respectively.

When methyl dichloroacetate was allowed to react with 1-octene in the presence of 0.7 mol % of the ruthenium complex at 120°C for 20 hr, only methyl 2,4-dichlorodecanoate was obtained in 95% yield. Thus, the present reaction exhibits a striking contrast to the peroxide catalyzed reaction which finds chiefly methyl 2,2-dichlorodecanoate as an adduct.[6] This result can be rationalized in terms of the mechanism of the ruthenium catalysis (eq 4–6 in Scheme I). The reaction is likely to involve a ligand transfer process (eq 6) in which the adduct radical abstracts a chlorine atom from the ruthenium complex with at least one labile chlorine ligand in its coordination sphere.[2a,5] Hence the chlorine abstraction in the ruthenium catalysis is associated with lower energy requirements compared to the hydrogen abstraction from the starting ester. It follows that the formation of methyl 2,4-dichlorodecanoate will become a predominant pathway in the present case.



$$\mathrm{CHCl_2COOCH_3 + C_6H_{13}CH{=}CH_2 \xrightarrow{RuCl_2(PPh_3)_3} C_6H_{13}CHClCH_2CHClCOOCH_3}$$
$$\mathrm{C_6H_{13}CH{=}CH_2 \xrightarrow{peroxide} C_6H_{13}CH_2CH_2CCl_2COOCH_3} \qquad (3)$$

Scheme I



Supporting evidence for the homolytic nature of the present reaction comes from the result that the reaction was inhibited by adding a small amount of galvinoxyl to the reaction mixture (Figure 1).

The results accumulated in Table I indicate that the ruthenium complex catalyzed addition reaction has many advantages over the existing methods for the preparation of chloro esters of moderate molecular weight from polychloroacetic acid esters and olefins. E.g., (a) the reaction can afford the 1:1 adducts in high yields with 1-olefins including vinyl monomers. Peroxide catalysis gives predominantly

**Table I**
**Reactions of Trichloro- and Dichloroacetic Acid Esters with 1-Olefins in the Presence of Dichlorotris(triphenylphosphine)ruthenium(II)[a]**

| Chloro ester | Registry no. | Olefin | Registry no. | Conditions | Adduct[b] | Yield, %[c] | Conversion, %[d] |
|---|---|---|---|---|---|---|---|
| $CCl_3COOCH_3$ | 598-99-2 | 1-Octene | 111-66-0 | 120°C, 23 hr | $C_6H_{13}CHClCH_2CCl_2$-$COOCH_3$ (1) | 95 (88) | 100 |
| $CCl_3COOCH_2$-$CH_3$ | 515-84-4 | 1-Octene | | 120°C, 19 hr | $C_6H_{13}CHClCH_2$-$COOCH_2CH_3$ (2) | 93 (83) | 92 |
| $CCl_3COOCH_3$ | | 1-Hexene | 592-41-6 | 120°C, 21 hr | $C_4H_9CHClCH_2CCl_2$-$COOCH_3$ (3) | 97 (90) | 96 |
| $CCl_3COOCH_2$-$CH_3$[e] | | Styrene | 100-42-5 | 120°C, 10 hr | $C_6H_5CHClCH_2CCl_2$-$COOCH_2CH_3$ (4) | 95 (82) | 100 |
| $CCl_3COOCH_2$-$CH_3$[e] | | Acrylonitrile | 107-13-1 | 120°C, 20 hr | (CN)$CHClCH_2CCl_2$-$COOCH_2CH_3$ (5) | 84 (71) | 100 |
| $CCl_3COOCH_2$-$CH_3$[e] | | Methyl methacrylate | 80-62-6 | 120°C, 10 hr | ($COOCH_3$)($CH_3$)-$CClCH_2CCl_2$-$COOCH_2CH_3$ | 80 (62) | 100 |
| $CCl_3COOCH_2$-$CH_3$[e] | | Methyl vinyl ketone | 78-94-4 | 120°C, 10 hr | $CH_3COCHClCH_2CCl_2$-$COOCH_2CH_3$ (7) | 80 (64) | 100 |
| $CHCl_2COO$-$CH_3$[f] | 116-54-1 | 1-Octene | | 120°C, 20 hr | $C_6H_{13}CHClCH_2$-$CHClCOOCH_3$[g] (8) | 94 (89) | 100 |

[a] Reactions were carried out in benzene with a 1.5–1.7:1 mixture of a chloro ester and an olefin, the catalyst concentration being 0.4 mol % based on the olefin charged without otherwise indicated. [b] All new compounds in the table gave satisfactory elemental analyses. [c] Yields are based on the olefin consumed (via GLC). In parenthesis are given isolated yields. [d] Conversion is (moles of olefin consumed)/(moles of olefin charged). [e] A 2:1 mixture of a chloro ester and an olefin was used. The catalyst concentration was 0.5 mol %. [f] The catalyst concentration was 0.7 mol %. [g] This adduct was obtained as a 1:1 mixture of the diastereomers **8a** and **8b**.

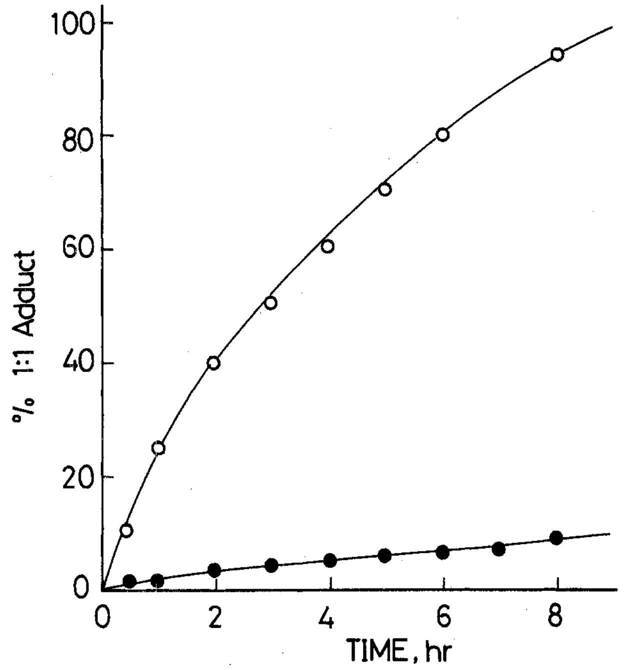


**Figure 1.** Formation of methyl 2,2,4-trichlorodecanoate from the addition reaction with 0.10 mmol of $RuCl_2(PPh_3)_3$ using (○) 10 mmol of 1-octene, 20 mmol of methyl trichloroacetate, and 3 ml of benzene; (●) 0.81 mmol of galvinoxyl added to the mixture.

telomers of high molecular weight in the reaction of the halides with vinyl monomers.[7] (b) For the addition of ethyl trichloroacetate to the olefins the ruthenium catalysis gives 60–80% isolated yields of the adducts, while copper salts catalyzed reactions give 10–40% yields.[4a]

## Experimental Section

Boiling points are uncorrected. Infrared spectra were recorded on a Hitachi Model EPI-G3 spectrophotometer with neat samples. NMR spectra were taken on a Varian Model A-60D instrument using tetramethylsilane as an internal standard in carbon tetrachloride solvent. GLC analyses were carried out with an Okura Model 802 gas chromatograph equipped with a thermal conductivity detector. Teflon columns (200 × 0.4 cm) packed with 20% Silicone KF-96, 20% Carbowax 20M, 25% DCQF-1, and 25% polydiethylene glycol adipate on 60–80 mesh Chromosorb W were utilized for analytical studies. Corrections were made for thermal conductivity of the various components.

Commercially available ethyl trichloroacetate, methyl trichloroacetate, methyl dichloroacetate, 1-octene, 1-hexene, styrene, acrylonitrile, methyl methacrylate and methyl vinyl ketone were purified by distillation under nitrogen prior to use. Dichlorotris(triphenylphosphine)ruthenium(II) was prepared by Wilkinson's procedure.[8]

The addition reactions were carried out in a sealed Pyrex tube containing a Teflon-covered stirring bar. Only typical examples are shown below.

**Reaction of Methyl Trichloroacetate with 1-Octene Catalyzed by Dichlorotris(triphenylphosphine)ruthenium(II).** A mixture of 6.25 g (58.2 mmol) of 1-octene, 15.65 g (102 mmol) of methyl trichloroacetate, 0.20 g (0.21 mmol) of the ruthenium complex, and 10 ml of benzene was introduced into a Pyrex tube, cooled in liquid nitrogen, degassed (two times) at 0.1 mm, sealed, and heated for 23 hr at 120°C with stirring. After the reaction, the tube was cooled in liquid nitrogen and then opened. GLC analysis of the resulting mixture indicated that the olefin had been almost completely consumed and that the 1:1 adduct had been produced in 95% yield based on the olefin consumption. The mixture was then diluted with 40 ml of *n*-pentane to precipitate the catalyst which was removed by filtration. The solvents were evaporated from the filtrate under reduced pressure and subsequent distillation gave 14.8 g (88% yield) of methyl 2,2,4-trichlorodecanoate in 97% purity, bp 112–113°C (1.2 mm). The structure of the product was confirmed by spectral data and elemental analysis. These data are shown in Table II.

**Reaction of Ethyl Trichloroacetate with Styrene Catalyzed by the Ruthenium Complex.** The addition reaction was carried out at 120°C for 10 hr using 2.24 g (21.6 mmol) of styrene, 8.55 g (44.6 mmol) of ethyl trichloroacetate, 0.10 g (0.10 mmol) of the ruthenium complex, and 5 ml of benzene as described above. GLC analysis of the resulting solution disclosed that the olefin had been almost completely consumed and that the 1:1 adduct had been produced in 95% yield. The mixture was then diluted with 30 ml of *n*-pentane and the precipitated catalyst was removed by filtration. After removal of the solvents, distillation gave 5.20 g (82% yield) of ethyl 2,2,4-trichloro-4-phenylbutyrate, bp 139–142°C (1.8 mm).

**Reaction of Methyl Dichloroacetate with 1-Octene Catalyzed by the Ruthenium Complex.** The addition reaction was carried out at 140°C for 20 hr using 4.01 g (35.8 mmol) of 1-octene, 10.91 g (76.3 mmol) of methyl dichloroacetate, 0.24 g (0.25 mmol) of the ruthenium complex, and 10 ml of benzene as described above. The resulting mixture was worked up as described above. Subsequent distillation gave 9.14 g (89% yield) of methyl 2,4-dichlorodecanoate as a 1:1 mixture of the diastereomers, bp 110–113°C (2.0 mm). The structure of each diastereomer was confirmed by spectral data and elemental analysis after isolation by preparative GLC.

**Acknowledgment.** Grateful acknowledgment is made for the support of this work through a grant from the Ministry of Education (Grant 947023).

**Registry No.**—**1**, 57196-88-0; **2**, 53781-38-7; **3**, 33037-20-6; **4**, 57196-89-1; **5**, 34405-09-9; **6**, 57196-90-4; **7**, 57196-91-5; **8a**, 57196-92-6; **8b**, 57196-93-7; $RuCl_2(PPh_3)_3$, 15529-49-4.

**Supplementary Material Available.** Table II, reporting the physical properties of adducts 1–8 (2 pages), will appear following these pages in the microfilm edition of this volume of the journal.

## References and Notes

(1) For part II of this series, see H. Matsumoto, T. Nikaido, and Y. Nagai, *Tetrahedron Lett.*, 899 (1975).
(2) (a) M. Asscher and D. Vofsi, *J. Chem. Soc.*, 1887 (1963); 3921 (1963); (b) S. Murai and S. Tsutsumi, *J. Org. Chem.*, **31**, 3000 (1966); (c) D. J. Burton and L. J. Kehoe, *Tetrahedron Lett.*, 5163 (1966); *J. Org. Chem.*, **35**, 1339 (1970); (d) T. Susuki and J. Tsuji, *Tetrahedron Lett.*, 913 (1968); *J. Org. Chem.*, **35**, 2982 (1970).
(3) Y. Mori and J. Tsuji, *Tetrahedron*, **28**, 29 (1972).
(4) (a) S. Murai, N. Sonoda, and S. Tsutsumi, *J. Org. Chem.*, **29**, 2104 (1964); (b) Y. Mori and J. Tsuji, *Tetrahedron*, **29**, 827 (1973).
(5) H. Matsumoto, T. Nakano, and Y. Nagai, *Tetrahedron Lett.*, 5147 (1973).
(6) M. S. Kharasch, W. H. Urry, and E. V. Jensen, *J. Am. Chem. Soc.*, **67**, 1626 (1945).
(7) No data are available on the reaction of trichloroacetic acid esters with vinyl monomers catalyzed by peroxides and our investigation has shown that there was obtained only quite low yield of the 1:1 adduct when a 3:1 mixture of ethyl trichloroacetate and styrene was heated in the presence of 2 mol % (based on the olefin charged) of benzoyl peroxide at 80°C for 15 hr.
(8) T. A. Stephenson and G. Wilkinson, *J. Inorg. Nucl. Chem.*, **28**, 945 (1966).

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# A Stereoselective Total Synthesis of *exo*- and *endo*-Brevicomin

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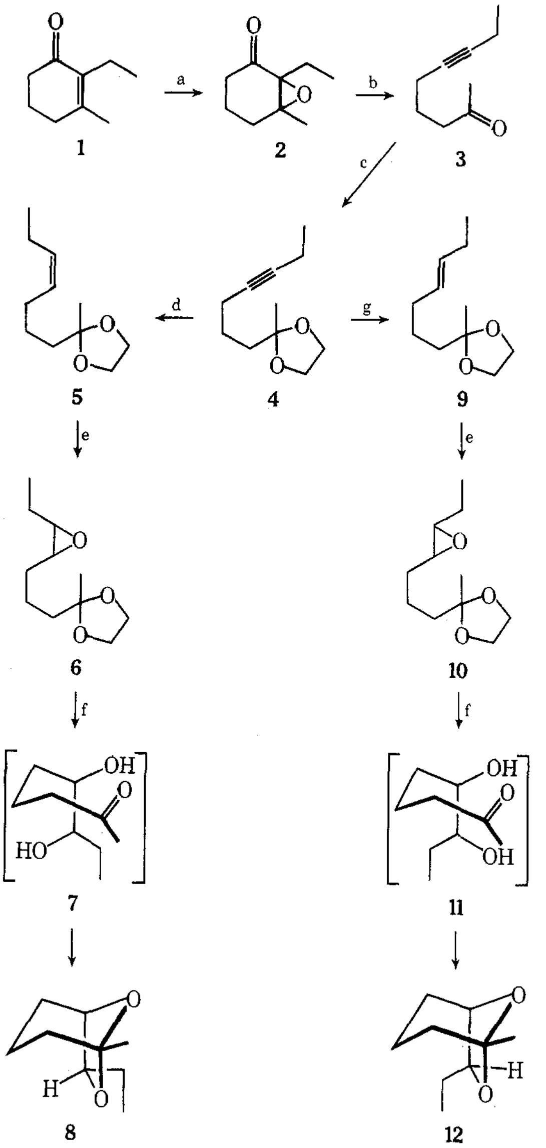
*Received August 13, 1975*

In 1968, Silverstein and co-workers[1] reported the structure determination of *exo*-brevicomin (8),[2] the principal sex attractant of the western pine beetle *Dendroctonus brevicomis*. The unusual 6,8-dioxabicyclo[3.2.1]octane skeleton has since been demonstrated in two other sex pheromones: frontalin, from the southern pine beetle *Dendroctonus frontalis*,[3] and multistriatin, from the elm bark beetle *Scolytus multistriatus*.[4] Since the use of *exo*-brevicomin for the manipulation of the mating habits of *D. brevicomis* may provide an ecologically advantageous means for the population control of this destructive insect,[5] we have developed a practical stereoselective synthesis of both *exo*-brevicomin (8) and the corresponding endo isomer 12[6] which should be amenable to large-scale preparation. With one exception,[8] previous syntheses of 8 are inefficient and/or nonstereoselective.[7-10]

The preparation of both *endo*- and *exo*-brevicomin required that our synthetic plan incorporate an intermediate which was sufficiently flexible to permit conversion to both products. The acetylenic ketal 4 seemed ideally suited for this purpose since stereoselective reductions of acetylenes to the requisite cis or trans olefins are well established.

Scheme I[a]



[a] a, $H_2O_2$–NaOH/MeOH; b, *p*-TsNHNH$_2$/CH$_2$Cl$_2$–HOAc; c, HOCH$_2$CH$_2$OH, H$^+$; d, BH$_3$·Me$_2$S–ether, HOAc; e, *m*-ClC$_6$H$_4$CO$_3$H; f, 0.1 *N* HClO$_4$; g, Na–NH$_3$.

Thus the fulcrum of the synthesis, 4, was prepared in three steps (73% overall) from the known cyclohexenone 1[11] as shown in Scheme I. Eschenmoser fragmentation[12] of the epoxy ketone 2 yielded 6-nonyn-2-one (3) which incorporated the carbon skeleton appropriately functionalized for eventual conversion to the desired products.

The *exo*-brevicomin (8) was prepared in 42% overall yield[13] from the acetylenic ketal 4 by a three-step sequence involving reduction of the acetylene with $BH_3 \cdot Me_2S$ followed by protonolysis to give first the cis olefin 5 (75%).[15] Epoxidation of 5 (73%) followed by stereospecific acid-catalyzed cleavage of the resultant cis epoxide 6[16] with concomitant hydrolysis of the ketal function afforded *exo*-brevicomin (8, 72%). No attempt was made to isolate or detect the presumed threo keto diol intermediate 7. The *exo*-brevicomin thus obtained was contaminated with <1% of the endo isomer 12 by VPC analysis.

Similarly, *endo*-brevicomin (12) was prepared in three steps (77% overall) from the acetylenic ketal 4 by Na–$NH_3$ reduction of 4 to the trans olefin 9 (96%).[15] Epoxidation of 9 (93%) followed by acid hydrolysis gave the intermediate erythro keto diol 11 which cyclized under the reaction con-