CHEMISTRY LETTERS, pp. 1255-1258, 1982.

A FACILE SYNTHESIS OF α,α,γ-TRICHLOROALKANOIC ACIDS *VIA* THE Ru(II)-CATALYZED ADDITION OF TRICHLOROACETYL CHLORIDE TO OLEFINS

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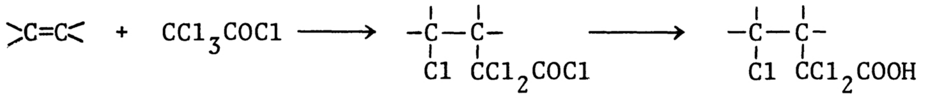
α,α,γ-Trichloroalkanoic acids were prepared with great ease by the dichlorotris(triphenylphosphine)ruthenium(II)-catalyzed addition of trichloroacetyl chloride to olefinic compounds followed by hydrolysis of the resulting 1:1 adducts, α,α,γ-trichloro-substituted acid chlorides.

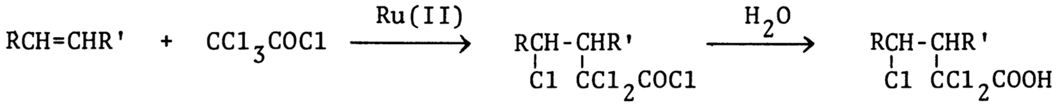
α,γ-Polychloroalkanoic acids are structurally closely related to antibiotic α-amino-γ-polychloroalkanoic acids¹⁾ and also have been reported to be useful as lubricating oil additives²⁾ and as activators for bleaching textiles with chlorites.³⁾ The reported synthesis of these acids involves acid-catalyzed hydrolysis of α,γ-polychloroalkanoates which are obtained from the radical addition of polychloroacetates to olefins.³⁾ However, acid-catalyzed hydrolysis of an ester is a reversible process⁴⁾ and it might be difficult to shift the equilibrium completely to the acid product side. Homolytic addition of trichloroacetyl chloride to olefins followed by hydrolysis of the resulting 1:1 adducts, α,α,γ-trichloroalkanoyl chlorides, would be an alternate and more recommendable route to α,γ-polychloroalkanoic acids (eqn. 1).



$$>C{=}C< \; + \; CCl_3COCl \longrightarrow -\underset{Cl}{\overset{|}{C}}-\underset{CCl_2COCl}{\overset{|}{C}}- \longrightarrow -\underset{Cl}{\overset{|}{C}}-\underset{CCl_2COOH}{\overset{|}{C}}- \qquad (1)$$

Only a few reports have appeared on the corresponding addition of trichloroacetyl chloride which is the key step in this conceptually unprecedented route. Thus, Kharasch and coworkers⁵⁾ reported that, in the presence of diacetyl peroxide, trichloroacetyl chloride reacted with 1-octene to give α,α,γ-trichlorodecanoyl chloride in 81% yield. However, it has been reported by Sakota and coworkers⁶⁾ that the reaction of the acetyl chloride with polymerizable olefins such as styrene and butyl acrylate gave only telomers of high molecular weights under free-radical conditions (*e.g.*, AIBN-initiation). Moreover, Martin and coworkers⁷⁾ have recently reported that trichloroacetyl chloride adds to $CClX{=}CH_2$ (X = H, Cl) in the presence of Cu_2Cl_2 (3 mol%) to afford the 1:1 adducts,

$CCl_2XCH_2CCl_2COCl$, in 32-45% yields. The reported reaction, however, was accompanied by the concurrent formation of significant amounts (18-35% yields) of the 1:2 adducts. Further, to the best of our knowledge, other examples of the Cu_2Cl_2-catalyzed addition of trichloroacetyl chloride to olefins have not yet been reported. We would like to report our new finding that chemoselective addition of trichloroacetyl chloride to carbon-carbon doulbe bonds can be most easily achieved by employing the ruthenium(II) complex, $RuCl_2(PPh_3)_3$,[8) as a catalyst and that hydrolysis of the resulting 1:1 adducts gives α,α,γ-trichloroalkanoic acids in high yields.



$$\mathrm{RCH{=}CHR' + CCl_3COCl \xrightarrow{Ru(II)} \underset{Cl\ \ CCl_2COCl}{RCH\text{-}CHR'} \xrightarrow{H_2O} \underset{Cl\ \ CCl_2COOH}{RCH\text{-}CHR'}} \qquad (2)$$

The addition reaction was simply performed by refluxing a toluene solution of a binary mixture of trichloroacetyl chloride (1.4-2.0 equiv.) and an olefin (1.0 equiv.) in the presence of the ruthenium(II) complex (0.003-0.006 equiv.) under nitrogen. Several examples of the reaction are given in Table 1. As seen from the Table, 1:1 adducts were obtained in good yields from both internal and terminal olefins. It is worthy to note that the addition works well similarly for an easily polymerizable olefin, *e.g.*, styrene.

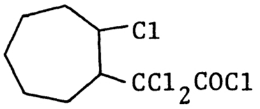
The hydrolysis of the resulting 1:1 adducts occurred spontaneously by mixing these compounds with water at room temperature to give the corresponding α,α,γ-trichloroalkanoic acids in almost quantitative yield. The results are summarized in Table 2.

These results indicate that our recipe provides an exceptionally workable route to α,γ-polychloroalkanoic acids. In this context, it might be anticipated that α,α,γ-trichloroalkanoic acids would be obtained directly from the homolytic addition of trichloroacetic acid to olefins. However, we have recently shown that the reaction in the presence of the ruthenium(II) complex affords α,α-dichloro-γ-butyrolactones instead of the chloroalkanoic acids.9)

A typical procedure is as follows. A solution of 21.0 g (150 mmol) of 1-decene, 54.1 g (297 mmol) of trichloroacetyl chloride, 0.850 g (0.87 mmol) of the ruthenium(II) complex, and 20 ml of toluene was refluxed for 12 h. GLC analysis showed that the reaction had given α,α,γ-trichlorododecanoyl chloride in 90% yield. Then, the reaction mixture was diluted with pentane, filtered, and distilled to afford 39.1 g (81% yield) of the 1:1 adduct: bp. 139-141°C/2 mmHg; IR (neat) 1790 cm^{-1} (ν, C=O); NMR (CCl_4) δ 0.56-2.10 (m, 17H, $CH_3(CH_2)_7$-), 2.72 (dd, 1H, $-C\underline{H}H-CCl_2-$, J = 5 and 14 Hz), 3.12 (dd, 1H, $-CH\underline{H}-CCl_2-$, J = 7 and 14 Hz), and 4.05 (m, 1H, -CHCl-); Anal. Found: C, 44.97%; H, 6.18%. Calcd for $C_{12}H_{20}Cl_4O_1$: C, 44.75%; H, 6.26%. The resulting adduct was hydrolyzed in the following manner. A sample of 3.22 g (10.0 mmol) of α,α,γ-trichlorododecanoyl chloride was mixed with 0.37 g (20 mmol) of water and the mixture was stirred at room temperature for 1 min. The reaction mixture was diluted with ether and dried over anhydrous magnesium sulfate. Removal of the solvent afforded

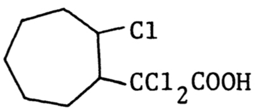
3.0 g (99% yield) of α,α,γ-trichlorododecanoic acid as a colorless liquid: IR (neat) 3700-2500 (ν, OH) and 1750 cm^{-1} (ν, C=O); NMR (CCl_4) δ 0.56-2.10 (m, 17H, $CH_3(CH_2)_7$-), 2.73 (dd, 1H, -C$\underline{H}$H-CCl_2-, J = 5 and 14 Hz), 3.08 (dd, 1H, -CH$\underline{H}$-CCl_2-, J = 7 and 14 Hz), 4.17 (m, 1H, -CHCl-), and 10.65 (s, 1H, -COOH).

Table 1. Addition of Trichloroacetyl Chloride to Olefins in the Presence of a Catalytic Amount of Dichlorotris(triphenylphosphine)ruthenium(II)[a]

Olefin	Time (h)	1:1 Adduct[b]		Yield,%[c]
1-Octene	10	n-$C_6H_{13}CHClCH_2CCl_2COCl$	$\underline{1}$	93
1-Decene	12	n-$C_8H_{17}CHClCH_2CCl_2COCl$	$\underline{2}$	90 (81)
Cycloheptene	10		$\underline{3}$ [d]	86 (72)
Styrene	6	$C_6H_5CHClCH_2CCl_2COCl$	$\underline{4}$	75

[a] Conditions: [olefin]/[CCl_3COCl]/[Ru] = 1/1.4-2.0/0.003-0.006; solvent = toluene; reflux under nitrogen. [b] Analyses and physical properties are consitent with the assigned structures(ref. 10). [c] Yields (via GLC) are based on the olefin charged. In parentheses are given isolated yields. [d] Stereochemistry was not determined.

Table 2. Conversion of 1:1 Adducts Obtained into α,α,γ-Trichloroalkanoic Acids by Hydrolysis[a]

Compound	Time (min)	Product[b]		Yield,%[c]
$\underline{1}$	1	n-$C_6H_{13}CHClCH_2CCl_2COOH$	$\underline{5}$	99
$\underline{2}$	1	n-$C_8H_{17}CHClCH_2CCl_2COOH$	$\underline{6}$	99
$\underline{3}$	120		$\underline{7}$	98
$\underline{4}$	1	$C_6H_5CHClCH_2CCl_2COOH$	$\underline{8}$	97

[a] Conditions: [acid chloride]/[H_2O] = 1/2; at room temperature. [b] Analyses and physical properties are consistent with the assigned structures(ref. 10). [c] Isolated yields.

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10) The spectral data of these compounds are as follows; 1: IR (neat) 1790 cm^{-1} (ν, C=O); NMR (CCl_4) δ 0.60-2.07 (m, 13H), 2.73 (dd, 1H, J = 5 and 14 Hz); 3.17 (dd, 1H, J = 8 and 14 Hz), and 4.15 (m, 1H). 3: IR (neat) 1790 and 1770 cm^{-1} (ν, C=O); NMR (CCl_4) δ 1.1-2.4 (m, 10H), 2.6-3.5 (m, 1H), and 4.4-4.9 (m, 1H). 4: IR (neat) 1790 (ν, C=O) and 1600 (ν, C=C) cm^{-1}; NMR (CCl_4) δ 3.15 (dd, 1H, J = 6 and 14 Hz), 3.54 (dd, 1H, J = 8 and 14 Hz), 5.20 (dd, 1H, J = 6 and 8 Hz), and 7.39 (s, 5H). 5: IR (neat) 3700-2500 (ν, OH) and 1740 cm^{-1} (ν, C=O); NMR (neat) δ 0.60-2.05 (m, 13H), 2.73 (dd, 1H, J = 5 and 14 Hz), 3.08 (dd, 1H, J = 7 and 14 Hz), 4.17 (m, 1H), and 10.64 (s, 1H). 7: IR (neat) 3700-2400 (ν, OH), and 1740 and 1710 cm^{-1} (ν, C=O); NMR (CCl_4) δ 1.0-2.4 (m, 10H), 3.0 (m, 1H), 4.55 (m, 0.8H), 4.83 (m, 0.2H), and 11.48 (s, 1H). 8: IR (KBr disk) 3600-2400 (ν, OH) and 1730 cm^{-1} (ν, C=O); NMR (CCl_4) δ 3.14 (dd, 1H, J = 6 and 14 Hz), 3.50 (dd, 1H, J = 8 and 14 Hz), 5.22 (dd, 1H, J = 6 and 8 Hz), 7.39 (s, 5H), and 8.82 (s, 1H).

(Received May 24, 1982)