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Chlorination of Olefins with Thallium(III) Chloride Tetrahydrate[1]

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In CCl_4, $TlCl_3 \cdot 4H_2O$ reacted with mono- and diolefins to give *vic*-dichlorinated compounds (I) in 20—41% yields together with monochlorinated ones (II). The yields of I were intensely increased by adding $CuCl_2 \cdot 2H_2O$ or $FeCl_3$ and bubbling oxygen into the reaction system, although such additives alone gave none of I in CCl_4. In acetic acid, the reaction gave diacetoxylated compound. As to the *vic*-dichlorination, it was proposed that the reacting species was a polarized form of dimeric $TlCl_3$ and not free chlorine evolved from $TlCl_3 \cdot 4H_2O$.

Compared to a number of studies on the reactions of aromatic compounds with Lewis acid halides of metals or metalloids,[2] the study on the behavior of olefins toward such chlorides is limited to only two cases using $CuCl_2$[3-7] and $SbCl_5$[8] in liquid or gas phases. Recently, we have found that aromatic carboxylation and chlorination occur by heating aromatic compounds with $TlCl_3 \cdot 4H_2O$ in CCl_4 solvent.[9] An attempt to

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[1] Presented at the 24th Annual Meeting of the Chemical Society of Japan, Osaka, April, 1971.

[2] "Friedel-Crafts and Related Reactions," Vol. IV, ed. by G. A. Olah, Interscience Publisher, New York, N. Y. (1965), Chapter 48.

[3] J. K. Kochi, *J. Amer. Chem. Soc.*, **84**, 2121 (1962).

[4] M. L. Spector, H. Heinemann, K. D. Miller, *Ind. Eng. Chem. Process Des. Develop.*, **6**, 327 (1967).

[5] K. Ichikawa, S. Uemura, T. Hiramoto, and Y. Takagaki, *Kogyo Kagaku Zasshi*, **71**, 1657 (1968) and references therein.

[6] T. Koyano, This Bulletin, **43**, 1439 (1970).

[7] P. P. Nicholas and R. T. Carroll, *J. Org. Chem.*, **33**, 2345 (1968).

[8] S. Uemura, O. Sasaki, and M. Okano, *Chem. Commun.*, **1971**, 1064 and unpublished data.

[9] S. Uemura, O. Sasaki, and M. Okano, *ibid.*, **1970**, 1139.

TABLE 1. CHLORINATION OF OLEFINS WITH $TlCl_3 \cdot 4H_2O$ (25 mmol) IN CCl_4 SOLVENT (100 m*l*) AT 77°C

Olefin	(mmol)	React. time (hr)	Addeudum (mmol)	Products (mmol)		Tl^{1+}[a] (mmol)
				I	II	
Oct-1-ene	100	2		6.42	13.9[b]	15.7
Oct-2-ene[c]	100	2		5.14[d]	18.2[e]	18.9
cis-Oct-2-ene	50	2		1.46[f]	8.2[e]	15.9
Cyclohexene	100	2		4.35[g]	13.7	22.7
Cyclohexene	100	2	NaOAc (20)	trace	0.1	1.4
Cyclohexene	100	10	$CuCl_2 \cdot 2H_2O$(10)[h]	49.9[i]	17.0	—[j]
Cyclohexene	100	10	$FeCl_3$(10)[h]	16.0[k]	13.1	—[j]
Styrene	100	2		1.25[l]	0	15.6
Cyclooctene	100	2		trace	19.3	22.4
Cycloocta-1,5-diene	100	1		2.58[m]	—[j]	23.5
Buta-1,3-diene[n]	56	2		4.72[o]	trace	13.0

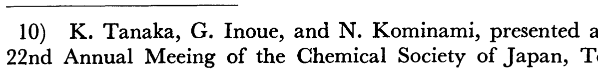
a) The amount of consumed Tl^{3+} was determined by iodometry. b) 2-Chlorooctane. c) Mixture of *cis* and *trans* isomers. d) *Erythro* 1.86 mmol, *threo* 3.28 mmol. e) Three components in which 2-chlorooctane is the major one. f) *Erythro* 0.29 mmol, *threo* 1.17 mmol; *i.e.*, *trans*/*cis*=4.05. g) *Trans* 4.25 mmol, *cis* 0.1 mmol; *i.e.*, *trans*/*cis*=42.5[8]. h) Oxygen was bubbled into the reaction mixture at a rate of 1 m*l*/sec throughout the reaction. i) *Trans* 46.6 mmol. *cis* 3.3 mmol. j) Not determined. k) *Trans* 16.0 mmol, *cis* trace. l) 1,3-Diphenyl-1-butene (11.5 mmol) was formed. m) *Trans* 1.73 mmol, *cis* 0.85 mmol. n) Buta-1,3-diene gas was bubbled into the reaction mixture for 2 hr. o) 1,2-Isomer 2.58 mmol, *cis*-1,4-isomer 0.51 mmol, and *trans*-1,4-isomer 1.63 mmol.

extend this reaction to olefins resulted in the formation of only chlorinated compounds. The characteristics of this chlorination of olefins are described in this report, with a comparison to the results of the reaction using $CuCl_2$ or $SbCl_5$. Although the fact has been known that $TlCl_3 \cdot 4H_2O$ can be used as a catalyst for the synthesis of propylene chlorohydrin from propylene in aqueous medium,[10] this is the first report of the chlorination of olefins with $TlCl_3 \cdot 4H_2O$.

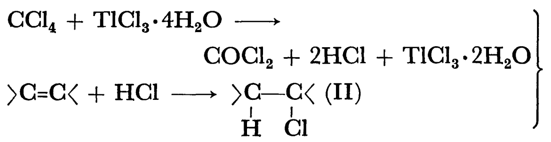
Results and Discussion

The reaction was carried out by adding or bubbling olefinic hydrocarbons into a stirred CCl_4 solution containing $TlCl_3 \cdot 4H_2O$ at refluxing temperature (77°C). Because of the low melting point (37°C) and the insolubility into CCl_4 of $TlCl_3 \cdot 4H_2O$, the solution was heterogeneous with the molten thallium salt. Dichlorinated (I) and monochlorinated hydrocarbons (II) were obtained as organic products, but none of hydrocarbons chlorinated at allylic position were found. Some typical data are summarized in Table 1. Because of the thallium(III) chloride-catalyzed hydrolysis of CCl_4,[11] this reaction accompanied the evolution of hydrogen chloride and phosgene regardless of the addition of olefinic component. I and II may be formed through Eqs. 1 and 2, respectively.

The formation of I occurred rather smoothly with 1- and 2-octenes, cyclohexene and buta-1,3-diene, and the



$$\rangle C{=}C\langle + TlCl_3 \longrightarrow \rangle\underset{Cl}{C}{-}\underset{Cl}{C}\langle \text{ (I)} + TlCl + 4H_2O \qquad (1)$$



$$\left.\begin{aligned} &CCl_4 + TlCl_3 \cdot 4H_2O \longrightarrow \\ &\qquad\qquad COCl_2 + 2HCl + TlCl_3 \cdot 2H_2O \\ &\rangle C{=}C\langle + HCl \longrightarrow \rangle\underset{H}{C}{-}\underset{Cl}{C}\langle \text{ (II)} \end{aligned}\right\} \qquad (2)$$

yields of which were 41, 27, 19, and 36%, respectively, on the basis of the amounts of the consumed Tl^{3+} salt. In the reaction with styrene, dimerization to yield 1,3-diphenyl-1-butene was the main reaction even at 50°C. In cases of cyclooctene and 1,3- and 1,5-cyclooctadienes, considerable amounts of II were formed but the yields of I were very poor. When buta-1,3-diene was used as a substrate, both 1,2- and 1,4-additions occurred and their ratio (1,4-dichloro-2-butene/3,4-dichloro-1-butene) was 0.83 for 2 hrs' reaction at refluxing temperature. It is premature to consider this ratio as a consequence of kinetic control, since a separate experiment showed that in this reaction condition 1,2-dichloroisomer readily converted to 1,4-one.[13] It must be noted here, however, that the 1,4-dichlorinated compound is consisted of *cis*- and *trans*-isomers in *ca.* 1 : 3 ratio, although usual chlorination with chlorine gas gives only stable *trans*-isomer.[14] This may suggest the participation of the species other than Cl_2 molecule. The formation of the *cis*-isomer was also observed in the chlorination of buta-1,3-diene with $SbCl_5$ in CCl_4.[8] In addition, both facts have been known that free chlorine is not involved in aromatic chlorination using $TlCl_3 \cdot 4H_2O$ in CCl_4[15] and that $TlCl_3 \cdot 4H_2O$ does not evolve chlorine gas by heating at 110°C.[16] Hence, it seems very unlikely that this

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[10] K. Tanaka, G. Inoue, and N. Kominami, presented at the 22nd Annual Meeing of the Chemical Society of Japan, Tokyo, April, 1969, Vol. IV, p. 2549.

[11] In one experiment using 25 mmol of $TlCl_3 \cdot 4H_2O$ and 100 m*l* of CCl_4 with stirring for 2 hr at 77°C, 29.7 mmol of phosgene and 141 mmol of hydrogen chloride were obtained. Details on the catalytic hydrolysis of trichloromethyl compounds were reported separately.[12]

[12] S. Uemura, F. Tanaka, O. Sasaki, and M. Okano, *Bull. Inst. Chem. Res. Kyoto Univ.*, **49**, 97 (1971).

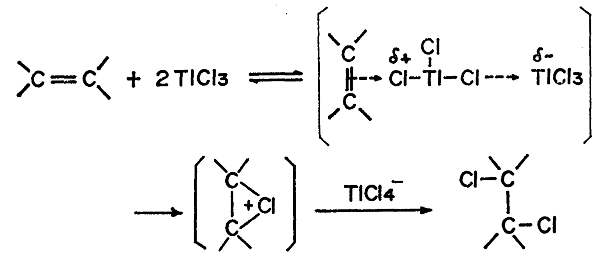
[13] A 6:1 mixture of 1,2- and 1,4-dichloroisomers (0.64 g) changed to a *ca.* 1:1 mixture (0.50 g) by heating at 77°C for 40 min in 50 m*l* of CCl_4 in the presence of $TlCl_3 \cdot 4H_2O$ (3 mmol) and TlCl (4 mmol).

[14] K. Mislow and H. M. Hellman, *J. Amer. Chem. Soc.*, **73**, 244 (1951); H. M. Hellman, J. W. Hellman, and K. Mislow, *ibid.*, **76**, 1075 (1954).

[15] S. Uemura, O. Sasaki, and M. Okano, to be submitted.

[16] F. M. McClenahan, *Amer. J. Sci.* (4), **18**, 104 (1904); J. W. Mellor, "A Comprehensive Treatise on Inorganic and Theoretical Chemistry," Vol. 5, Longmans, Green and Co., London (1924), p. 443.

reaction proceeds through addition of free chlorine evolved from $TlCl_3 \cdot 4H_2O$. The configurational analyses of I from cyclohexene and *cis*-2-octene (see Table 1) showed that this chlorination proceeds mainly in *trans* fashion as in the case of $CuCl_2$ chlorination in acetic acid or acetonitrile solvent.[5] Although a detailed mechanistic study was not carried out, a route involving the initial attack of a polarized $TlCl_3$ (probably in its dimeric form) on olefin would be reasonable.[17]



(3)

As thallium(III) chloride is reduced to thallium(I) chloride in this reaction, it is expected that the yield of I would increase if Tl^{1+} can be oxidized to Tl^{3+} by other metal salts. Thus, in the chlorination of cyclohexene with $TlCl_3 \cdot 4H_2O$, the addition of $CuCl_2 \cdot 2H_2O$ or $FeCl_3$ and the introduction of oxygen into the reaction system resulted in a significant increase in yields of I. Separate experiments showed that $CuCl_2 \cdot 2H_2O$ or $FeCl_3$ alone gave none of I in CCl_4 solvent, and it can safely be said that these chlorides oxidized Tl^{+1} to Tl^{+3} state as shown in Eq. 4. Since Cu^{1+} or Fe^{2+} salt formed here was readily oxidized to Cu^{2+} or Fe^{3+} state by oxygen respectively, probably under the coexistence of hydrochloric acid (see Eq. 2), the addition of an equivalent amount of these chlorides would not be required. As shown in Table 1, $CuCl_2 \cdot 2H_2O$ is more effective oxidant than $FeCl_3$ to TlCl.

$$\begin{array}{c} O_2\text{+aq. HCl} \\ TlCl + 2CuCl_2 \longrightarrow TlCl_3 + Cu_2Cl_2 \\ TlCl + 2FeCl_3 \longrightarrow TlCl_3 + 2FeCl_2 \\ O_2\text{+aq. HCl} \end{array} \qquad (4)$$

Although chlorination with $CuCl_2$ proceeded smoothly in acetic acid containing sodium acetate, alcohol or acetonitrile,[5] the reaction using $TlCl_3 \cdot 4H_2O$ in such solvents did not give any chlorinated product. In acetic acid containing sodium acetate (20 mmol) and $TlCl_3 \cdot 4H_2O$ (25 mmol), cyclohexene gave only a mixture of *cis*- and *trans*-1,2-diacetoxycyclohexane (8.75 mmol) for 2 hrs' reaction at 117°C. Similarly, styrene gave 1,2-diacetoxy-1-phenylethane (1.35 mmol), 1,3-diphenyl-1-butene (1.0 mmol) and a large amount of resinous residue. The formation of these products can be explained by the oxidation of olefins with thallium(III) acetate which might be formed in this reaction system. In acetonitrile, the formation of a complex $[TlCl_2(CH_3CN)_4TlCl_4]$[18] from $TlCl_3 \cdot 4H_2O$ and the solvent stopped the reaction.

Experimental

Materials. The organic materials were commercial products of the purest grade and were distilled and checked by gas chromatography. The inorganic metal chlorides were also commercial materials of an analytical grade and were used without purification.

Experimental Procedure. Olefinic substrates were added to mixtures of carbon tetrachloride and thallium(III) chloride tetrahydrate at refluxing temperature (77°C). After removing the evolved hydrogen chloride and phosgene by the stream of nitrogen into an ethereal solution of aniline, the reaction mixture were filtered from the resulting inorganic materials, and the filtrate was washed with water, dried over Na_2SO_4 and concentrated to *ca.* 10 m*l* by distillation of the solvent. The yields of the chlorinated products were calculated on the basis of the glc analysis of this residue using cyclohexanone or tetrachloroethylene as an internal standard. The amount of remaining Tl^{3+} salt was determined by iodometry.

Authentic Samples for Glc Analysis. Chlorocyclohexane, 3,4-dichloro-1-butene and 1,4-dichloro-2-butene were commercial products. 1,2-Dichlorooctane, 2,3-dichlorooctane (*erythro-threo* mixture), *trans*-1,2-dichlorocyclohexane, α,β-dichloroethylbenzene,[5] 1,2-dichlorocyclooctane, 5,6-dichlorocyclooctane (*trans-cis* mixture),[19] and α,β-diacetoxyethylbenzene[20] were prepared by the reported methods. 2-Chlorooctane was prepared from 2-octanol and thionyl chloride in pyridine;[21] bp 67—67.5°C/22 mmHg. *Threo*-2,3-dichlorooctane was prepared from the reaction of *cis*-2-octene with chlorine in chloroform; bp 104°C/25 mmHg, NMR τ 5.6—6.2 (m, 11H), 9.1 (t, 3H). *cis*-1,2-Dichlorocyclohexane was prepared from the reaction of *trans*-2-chlorocyclohexanol (bp 102—103°C/47 mmHg, prepared from cyclohexene[22]) and thionyl chloride in pyridine;[23] bp 68°C/6 mmHg, NMR: τ 5.5—5.8 (m, 2H), 7.5—8.8 (m, 8H). Chlorocyclooctane was isolated from the distillate (bp 82—90°C/21 mmHg) by preparative glc [PEG 6000 (25%)-Chromosorb-W 1.5 m column; carrier gas, He 120 m*l*/min at 150°C]; NMR: τ 5.6—6.0 (m, 1H), 7.75—8.2 (m, 4H), 8.2—8.65 (m, 10H). *cis*-1,4-Dichloro-2-butene was prepared as a mixture with *trans*-isomer (*trans*/*cis*=*ca.* 2) by the reaction of buta-1,3-diene with $SbCl_5$ in CCl_4;[8] bp 51—53°C/22 mmHg (Found: C, 37.64; H, 4.72%. Calcd for $C_4H_6Cl_2$: C, 38.44; H, 4.84%). NMR of *cis-trans* mixture: τ 3.95—4.3 (m, 2H), 5.8—6.0 (m, 4H). 1,2-Diacetoxycyclohexane (*trans-cis* mixture) was prepared as a mixture with cyclopentyl diacetoxymethane by heating cyclohexene and thallium(III) acetate in acetic acid at 70°C for 2 hr; bp 101—105°C/7 mmHg (reported[24] bp 112—120°C/12 mmHg).

Analytical Instruments. The IR and NMR spectra were measured with a Hitachi EPI-S2 apparatus and a Varian A-60 apparatus respectively. Gas chromatographies were carried out by Shimadzu 5APTF and 4APT [PEG 6000 (25%)-Chromosorb-W 3 m and Apiezon-L (30%) 1 m columns] apparatus.

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[17] See Ref. 2, p. 113. In the aromatic chlorination with this salt under similar conditions, we have recently obtained some results suggesting that an ionized form, $TlCl_2^+$, is preferable to the unionized one as actual attacking species.

[18] B. F. G. Johnson and R. A. Walton, *Inorg. Chem.*, **5**, 49 (1966).

[19] S. Uemura, A. Tabata, Y. Kimura, and K. Ichikawa, This Bulletin, **44**, 1973 (1971).

[20] S. Uemura and K. Ichikawa, *Nippon Kagaku Zasshi*, **88**, 893 (1967).

[21] F. C. Whitmor and F. A. Karnatz, *J. Amer. Chem. Soc.*, **60**, 2533 (1938).

[22] M. S. Newmann, *ibid.*, **67**, 233 (1945).

[23] B. Carrol, D. G. Kubler, H. W. Davis, and A. M. Whaley, *ibid.*, **73**, 5382 (1951).

[24] H. J. Kabbe, *Ann. Chem.*, **656**, 204 (1962).