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Photochemical Ethoxycarbonylation, Formylation, and Ethoxymethylation of Ruthenocene in Ruthenocene–Polychloromethane–Ethanol Systems

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Similar to ferrocene the UV-irradiation of ruthenocene–polychloromethane–ethanol systems brings about substitution (ethoxycarbonylation for CCl_4, formylation for $CHCl_3$, and ethoxymethylation for CH_2Cl_2) and oxidation. When $CHCl_3$ and CH_2Cl_2 are used, substitution is dominant. In the irradiation of ruthenocene–CCl_4–ethanol system, $[Ru(C_5H_5)_2]^+[RuCl_4]^-$ and cyclopentenes substituted by chlorine and trichloromethyl are obtained. The excitation of the CT-complex between ruthenocene and polychloromethane initiates the reaction.

We have reported the photochemical substitution (ethoxycarbonylation, formylation, ethoxymethylation, and alkylation) in ferrocene–halogenated hydrocarbon–ethanol systems.[1] As to ruthenocene, a ferrocene analog, photochemical oxidation to ruthenocenium ions has been reported.[2,3] However, in these studies the photoreactions of ruthenocene in halogenated hydrocarbon–(alcohol) solutions have been studied mainly on the basis of UV- and visible spectral changes and the product analysis has not been done completely. We report here that the UV-irradiation of ruthenocene–polychloromethane–ethanol systems brings about the substitution similar to that of ferrocene in addition to the oxidation of ruthenocene.

Experimental

Materials. Ruthenocene(**1**) was synthesized from $RuCl_3$ and cyclopentadiene according to Pertici *et al.*[4] mp 198—199 °C.

UV-irradiation. A solution of ruthenocene (4×10^{-2} mol dm^{-3}) in polychloromethane–ethanol (1:1 v/v, 40 cm^3) in a quartz vessel was deaerated by the freeze-thaw method using a vacuum system. The solution was irradiated either with a low pressure or with a high pressure mercury lamp.

Photoproducts. During the irradiation of ruthenocene–CCl_4–ethanol system, a brown precipitate was formed. Other systems gave no precipitate. After the precipitate was filtered, the solvent was distilled off. The residue was extracted with benzene and the products were separated by means of TLC (on silica gel of Merck GF_{254}; developing solvent, benzene).

Ruthenocenium tetrachlororuthenate(III) was identified by the comparison of UV- and IR-spectra with those reported by Traverso *et al.*[2] (Found: C, 25.84; H, 2.64%).

*Ethyl Ruthenocenecarboxylate (**2a**)*[5]: Brownish yellow crystal; mp 77.5—79 °C; IR(KBr disk) 3110, 2960 (C–H), 1690 (C=O), 1130 (ester C–O), 1100 and 995 cm^{-1} (C–H deformation of C_5H_5 ring); NMR (CCl_4) δ=5.01 (2H, t, J=2.0 Hz, ring H at α-position), 4.59 (2H, t, J=2.0 Hz, ring H at β-position), 4.52 (5H, s, H at unsubstituted ring), 4.13 (2H, q, J=7.0 Hz, CH_2), and 1.27 (3H, t, J=7.0 Hz, CH_3); MS (70 eV), m/e (rel intensity), 306(56), 304(100), 303(56), 302(42), 301(38) (M^+); 278(38), 276(68), 275(37), 274(28), 273(27) ($(M-C_2H_4)^+$); 234(22), 233(19), 232(40), 231(48), 230(31), 229(29), 228(16) ($(M-COOC_2H_5)^+$ and $(M-COOC_2H_5+H)^+$); 169(18), 167(30), 166(19), 165(15), 164(14) ($(RuC_5H_5)^+$).

A mixture of chlorinated hydrocarbons was obtained. By means of TLC technique it could not be separated completely. However, by the consideration of the results of GC-MS and NMR spectra, two major components were assigned to 3,4,5-tris(trichloromethyl)cyclopentene and 4-chloro-3,5-bis(trichloromethyl)cyclopentene.

3,4,5-Tris(trichloromethyl)cyclopentene. NMR(CCl_4) δ= 6.14 (2H, s, olefinic), 4.03 (2H, d, H=2.0 Hz, H at 3- and 5-position), 3.66 (1H, t, J=2.0 Hz, H at 4-position); MS (20 eV), m/e (rel intensity), 350(6), 348(9), 346(9), 344(4) ($(M-2HCl)^+$); 303(31), 301(39), 299(20) ($(M-CCl_3)^+$); 269(20), 267(58), 265(91), 263(54) ($(M-HCl-CCl_3)^+$); 233 (11), 231(31), 229(43), 227(27) ($(M-2HCl-CCl_3)^+$); 185 (6), 183(16), 181(19) ($(M-H-2CCl_3)^+$); 149(6), 147(12), 145(18), 143(16) ($(M-HCl-H-2CCl_3)^+$); 121(15), 119 (48), 117(50) ($(CCl_3)^+$); 113(12), 111(66), 109(100) ($(M-2HCl-H-2CCl_3)^+$).

4-Chloro-3,5-bis(trichloromethyl)cyclopentene. NMR (CCl_4) δ=6.25 (2H, s, olefinic), 4.21 (2H, d, J=3.0 Hz, H at 3- and 5-position), and 3.85 (1H, t, J=3.0 Hz, H at 4-position); MS (20 eV), m/e (rel intensity), 301(2), 299(2) ($(M-Cl)^+$); 269(3), 267(7), 265(11), 263(7) ($(M-HCl-Cl)^+$); 231(4), 229(6), 227(4) ($(M-2HCl-Cl)^+$); 223(7), 221(36), 219(78), 217(62) ($(M-CCl_3)^+$); 185(31), 183(98), 181(100) ($(M-HCl-CCl_3)^+$); 150(3), 148(14), 146(22) ($(M-HCl-Cl-CCl_3)^+$); 149(8), 147(23), 145(29) ($(M-2HCl-CCl_3)^+$); 121(3), 119(12), 117(10) ($(CCl_3)^+$); 111 (11), 109(14) ($(M-H-2CCl_3)^+$).

*Formylruthenocene (**2b**).* Mp 99—100 °C lit,[6] 103—104 °C; IR and NMR spectra agreed with reported ones.

*(Ethoxymethyl)ruthenocene (**2c**).* Yellow oil, IR 3090, 2965, 2850(CH), 1080(C–O), 1090, and 990 cm^{-1} (deformation of ring hydrogen); NMR($CDCl_3$) δ=4.63 (2H, t, J= 1.7 Hz, ring H at α-position), 4.50 (7H, H at β-position of the substituted ring and of the unsubstituted ring), 4.05 (2H, s, CH_2), 3.48 (2H, q, J=7.0 Hz, $\underline{CH_2}-CH_3$), and 1.17 (3H, t, J=7.0 Hz, CH_3); MS (70 eV) m/e (rel intensity), 292(55), 290(100), 289(58), 288(44), 287(39) (M^+); 264(5), 263(11), 262(9), 261(22), 260(15), 259(13), 258(11) ($(M-C_2H_4)^+$ and $(M-C_2H_5)^+$); 248(34), 247(44), 246(61), 245 (95), 244(61), 243(49), 242(31) ($(M-C_2H_5O+H)^+$ and $(M-C_2H_5O)^+$); 234(24), 233(49), 232(57), 231(39), 230(35), 229(18) ($(M-C_2H_5OCH_2+H)^+$ and $(M-C_2H_5OCH_2)^+$); 169(38), 167(66), 166(38), 165(30), 164(29) ($(RuC_5H_5)^+$).

Spectroscopic Measurements. GC-MS analysis was carried out with a Shimadzu GC-MS Model 6020 equipped with a 2 m column of OV-17 (2% on chromosorb N; column temperature, 160—240 °C).

NMR and IR spectra were recorded on a Hitachi NMR spectrometer Model R-22 and a Hitachi IR spectrometer Model 125, respectively.

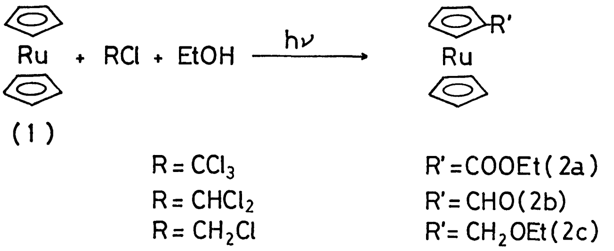
Table 1. Photochemical reactions of ruthenocene–polychloromethane–ethanol systems
RcH = Ruthenocene; [RcH] = 4×10^{-2} mol dm^{-3}; Solvent 1 : 1 v/v.

Solvent	Light source[a]	Irr. time h		Conversion %	Photoproduct	Yield[b] %
CCl_4-EtOH	LP	9		27	RcCOOEt (**2a**)	5.4
					$[Ru(C_5H_5)_2]^+[RuCl_4]^-$	10.3
	LP	10	Refluxed for 3 h after irradiation	28	RcCOOEt (**2a**)	6.4
					$[Ru(C_5H_5)_2]^+[RuCl_4]^-$	9.4
	HP	10		28	RcCOOEt (**2a**)	9.5
					$[Ru(C_5H_5)_2]^+[RuCl_4]^-$	4.0
	HP	12	Pyrex-filtered	12	RcCOOEt (**2a**)	2.3
					$[Ru(C_5H_5)_2]^+[RuCl_4]^-$	12
$CHCl_3$-EtOH	LP	15		21	RcCHO (**2b**)	57
	HP	15		20	RcCHO (**2b**)	39
	HP	42	Pyrex-filtered	19	RcCHO (**2b**)	6
CH_2Cl_2-EtOH	LP	10		31	$RcCH_2OEt$ (**2c**)	51
	HP	10		26	$RcCH_2OEt$ (**2c**)	20

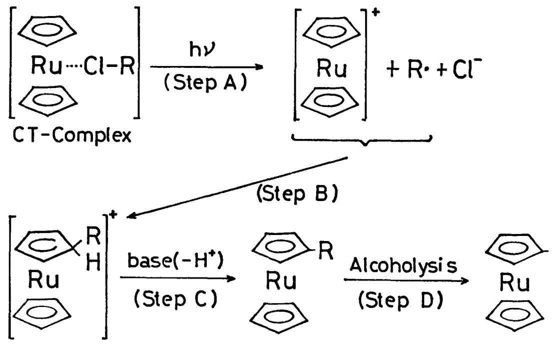
a) LP, Low pressure mercury lamp; HP, High pressure mercury lamp. b) Yield was measured by means of TLC and is based on the quantity of ruthenocene consumed.

Results and Discussion

Similar to ferrocene (**3**), ruthenocene (**1**) undergoes photochemical substitution, accompanying oxidation.



The type of the photo-substitution in ruthenocene–polychloromethane–ethanol systems is the same as that in ferrocene–polychloromethane–ethanol systems. The yields of the products under various irradiation conditions are shown in Table 1. Formylation in $CHCl_3$–EtOH and ethoxymethylation in CH_2Cl_2–EtOH occur effectively by UV-irradiation. In these reactions the color change that indicates the formation of ruthenocenium tetrachlororuthenate(III) (**4**), an oxidation product, was not observed. On the other hand, the photoreaction of the **1**–CCl_4–EtOH system shows a feature different from that of the **3**–CCl_4–EtOH system: UV-irradiation of ferrocene in a CCl_4–EtOH solution gives effectively the ethoxycarbonylation product, whereas that of ruthenocene gives a small amount of ethyl ruthenocenecarboxylate (**2a**) and considerable amounts of ruthenocenium tetrachlororuthenate(III) and cyclopentenes substituted by chlorine and trichloromethyl group ($C_5H_5Cl(CCl_3)_2$, $C_5H_5(CCl_3)_3$ *etc.*). Under the assumption that the average molecular weight of the cyclopentenes with chlorine and trichloromethyl is 338 (the molecular weight of $C_5H_5Cl(CCl_3)_2$), the yields of the halogenated compounds are estimated to be 40 and 34% for the irradiation with a low pressure mercury lamp and that with a high pressure mercury lamp, respectively.



Scheme 1. Mechanism of photo-substitution.

In the ruthenocene–polychloromethane–ethanol systems the irradiation with a low pressure mercury lamp (with shorter wavelength light) gives higher yields of the substitution products than that with a high pressure mercury lamp (with longer wavelength light) except for the **1**–CCl_4–EtOH system. The light of wavelength longer than 300 nm (pyrex-filtered light) was almost ineffective for the photo-substitution.

Similar to ferrocene, ruthenocene forms charge transfer complexes with halogenated hydrocarbons.[2,3] This fact and the similarity of the photoreactions of ruthenocene to those of ferrocene suggest the mechanism shown in Scheme 1.

The factors which determine the effectiveness of the photo-substitution are: 1) the efficiency of photo-induced electron transfer in the CT-complex between metallocene and polychloromethane (Step A), 2) the reactivity of metallocenium ions with polychloromethyl radicals (Step B), 3) the elimination of H$^+$ (Step C), and 4) the effectiveness of alcoholysis of chlorine on the side chain (Step D).

The fact that the CT-absorption bands are situated around 280 nm (CTTS-band for ruthenocene–CCl_4, 285 nm)[2,3] can explain the wavelength dependence of the photoreactions.

A remarkable difference between the photoreactions of the **1**–CCl_4–EtOH system and those of the **3**–CCl_4–EtOH system is the low yield of the photo-ethoxycarbonylated product for ruthenocene. This difference might be ascribed to the difference in the efficiencies of Step A: the CT-complex between **1** and CCl_4 is expected to be less stable than that between **3** and CCl_4 because of the higher ionization potential of **1** (I_p for ruthenocene, 7.45 eV; I_p for ferrocene, 6.88 eV$^{7)}$). However, the association constant for the CT-complex between **1** and CCl_4 was estimated to be similar to that for the complex between **3** and CCl_4 (association constant; for **1**–CCl_4, 0.012 $dm^3\,mol^{-1}$; for **3**–CCl_4, 0.015 $dm^3\,mol^{-1}$).$^{3)}$ Moreover, the less stable CT-complexes of **1**–$CHCl_3$ and **1**–CH_2Cl_2 give the substitution products in good yields. These facts indicate that the low efficiency of the photo-ethoxycarbonylation in the **1**–CCl_4–EtOH system can not be ascribed to the efficiency of Step A.

Step D is not the controlling step. It has been reported that the solvolysis rate at the carbon atom attached to ruthenocenyl group is greater than that at the carbon atom attached to ferrocenyl group.$^{8)}$

The low yield of the ester in the photoreaction of the **1**–CCl_4–EtOH system accompanies the formation of ruthenocenium tetrachlororuthenate(III) and cyclopentenes substituted by chlorine and trichloromethyl. The cyclopentene derivatives are composed mainly of $C_5H_5Cl(CCl_3)_2$ and $C_5H_5(CCl_3)_3$. This result suggests that the decomposition competes with Step C. If the decomposition occurs after the elimination of H^+, the decomposition products of the type $C_5H_4Cl_n(CCl_3)_{4-n}$ should be obtained.

The cationic intermediate formed by the addition of trichloromethyl to metallocenium ions would be destabilized owing to the electron attraction of the trichloromethyl group and would undergo the decomposition. The destabilization would be greater for the more electronegative ruthenium compound than for the iron compound.

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