

ADDITION OF ESTERS OF CHLOROACETIC ACIDS TO 1,3-BUTADIENE CATALYSED BY COPPER COMPLEXES

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The addition of alkyl trichloro- and dichloroacetates to 1,3-butadiene catalysed by copper complexes has been studied. The reactivity of the chloroacetates increased with increasing number of chlorine atoms in their molecule and with decreasing number of the carbon atoms of the alkyl of their ester group. The addition of trichloroacetates gave the products (1 : 1 adducts) in around 80 per cent yields while the less reactive dichloroacetates afforded the adducts in 35% yields. The 1 : 1 adducts were the products of both 1,4- and 1,2-addition, the relative proportion of which depended especially on the type of the ligand of copper complexes.

Addition reactions of 1,3-butadiene have so far been studied with tetrachloromethane¹⁻⁴, halogenoacetic acids⁵ and their esters^{6,7}, chloroacetonitrile⁸, chloroform⁹, and 1,1,1,4-tetrachloropropane¹⁰. The additions were both initiated by organic peroxides¹ or UV light⁶ and catalysed by the systems based on copper chlorides^{2,3,5,8,9} or copper oxides⁷, Fe chlorides^{5,9} or iron carbonyls¹⁰ as well as by dichloro-tris(triphenylphosphine)ruthenium⁴. In the presence of organic peroxides or under UV irradiation, the addition proceeded by radical chain mechanism which has often been proposed also for the other methods of initiation. The most thoroughly studied addition was the reaction of 1,3-butadiene with tetrachloromethane which with dichloro-tris(triphenylphosphine)ruthenium⁴ and copper compounds^{2,3} as catalysts gave 1 : 1 adducts in high yields (86–90%). However, with organic peroxides as initiators the addition was accompanied by polymerisation of the diene¹ and afforded 1 : 1 adduct in only 15% yield. The main product was 1 : 1 adduct which was formed exclusively by 1,4-addition of tetrachloromethane. The exclusive 1,4-addition has been observed also in the additions of ethyl tribromoacetate⁶ or trichloroacetate⁷ to 1,3-butadiene. On the other hand, analogous reactions of chloroacetonitrile⁸ and 1,1,1,4-tetrachloropropane¹⁰ gave also 1,2-adducts in small amounts, the 1,4-addition being again the main reaction path.

In the present work we report on the investigation of the catalytic activity and selectivity of copper-amine complexes in the additions of esters of chloroacetic acids to 1,3-butadiene with respect to optimal conditions for synthesis of 1 : 1 adducts.

EXPERIMENTAL

Chemicals

Ethyl trichloroacetate, methyl chloroacetate, methyl dichloroacetate (all Fluka AG), and diethylamine (Laborchemie Apolda, G.D.R.) were purified by rectification prior to using. Acetonitrile (Croft Laboratories, Ltd.) was distilled twice over P_2O_5 and potassium carbonate. Methyl trichloroacetate, n-butyl trichloroacetate and ethyl dichloroacetate were prepared by esterification of the acids with the appropriate alcohols. Cuprous oxide was obtained by the reduction of copper(II) sulphate with glucose¹¹. Cuprous chloride (Lachema Brno) was purified as described earlier¹². 1,3-Butadiene (Kaučuk Kralupy) and 1,10-phenanthroline monohydrate (Lachema Brno) were used as obtained.

Analytical Methods

GLC analysis of reaction mixtures was carried out on Chrom 4 instrument equipped with FID detector and CI 100 integrator (Laboratorní přístroje, Prague). The column was packed with 3% Silicone OV-17 on Gas-Chrom Q (2 m long, i.d. 3 mm, 80 mesh), over temperature 100 to 140°C. The 1,4- and 1,2-adducts used as standards were isolated by preparative GLC made on Chrom 3 instrument using 2.4 m-column (i.d. 8 mm) packed with 5% Silicone OV-17 on Gas-Chrom Q at 140°C. ¹H NMR and ¹³C NMR spectra were recorded on BS 467 Tesla 60 and Varian XL 200 spectrometers (CDCl₃ solutions). Chemical shifts (δ) are in ppm relative to TMS or HMDSO.

General Procedure for Addition of Esters of Chloroacetic Acids to 1,3-Butadiene

In 20 ml Pyrex ampoule closed with a septum, 0.0164 g (0.166 mmol) of cuprous chloride were dissolved in 3 ml of acetonitrile and after cooling with dry ice/ethanol, the liquid 1,3-butadiene (1.8 g, 33 mmol), an amine (0.332 mmol) and a trichloroacetate (33 mmol) were added. In the additions with ethyl dichloroacetate, 1.66 mmol of cuprous chloride or cuprous oxide and 3.32 mmol of an amine were used. Then, the reaction mixture was allowed to warm up to room temperature (in about 20 min), the ampoule was placed in an oil bath heated to the reaction temperature (45–130°C) and the ampoule was shaken with a vibration agitator. During the reaction, samples were withdrawn and analysed by GLC. The reaction products were isolated after washing the reaction mixture twice with 20 ml of water by vacuum distillation, using mantle flask.

The reactivity of individual esters was determined from initial reaction rates at low ester conversion ($x < 0.2$). At high ester conversions ($x > 0.5$), such as in preparative experiments, butadiene dimerization to 4-vinylcyclohexene was found to be side reaction. However, the dimerization proceeded only to small extent (less than 5%).

Ethyl 2,2,6-trichloro-4-hexenoate, b.p. 135°C/1.33 kPa. For C₈H₁₁Cl₃O₂ (209.16) calculated: 39.13% C, 4.52% H, 43.32% Cl; found: 39.27% C, 4.57% H, 41.82% Cl. ¹H NMR (δ) 4.1 (CH₂Cl—), 5.8 (—CH=CH—), 3.1 (—CH₂—), 4.3 (—OCH₂—), 1.3 (—CH₃). ¹³C NMR (δ) 44.1 (CH₂Cl—), 126.5 (—CH=), 132.7 (=CH—), 47.5 (—CH₂—), 82.7 (—CCl₂—), 165.4 (—CO—), 63.9 (—OCH₂—), 13.8 (—CH₃).

Ethyl 2,2,4-trichloro-5-hexenoate, b.p. 100–105°C/1.33 kPa. Isolated in 90% purity by preparative GLC. ¹H NMR (δ) 5.2 (CH₂=), 5.8 (=CH—), 4.6 (—CHCl—), 3.0 (—CH₂—), 4.2

(—OCH₂—), 1.3 (—CH₃). ¹³C NMR (δ) 118.1 (CH₂=), 136.5 (=CH—), 57.8 (—CHCl—), 52.0 (—CH₂—), 81.9 (—CCl₂—), 165.1 (—CO—), 64.0 (—OCH₂—), 13.7 (—CH₃).

Ethyl 2,6-dichloro-4-hexenoate, b.p. 114–116°C/1.40 kPa. ¹H NMR (δ) 4.0 (CH₂Cl—), 5.8 (—CH=CH—), 2.7 (—CH₂—), 4.3 (—CHCl), 4.2 (—OCH₂—), 1.3 (—CH₃).

TABLE I

Reactivity of chloroacetates in their addition to 1,3-butadiene catalysed by CuCl–diethylamine complex at 100°C

Ester	Reaction rate mol h ⁻¹ g ⁻¹
ClCH ₂ COOCH ₃	0.00 ^a
Cl ₂ CHCOOCH ₃	0.02
Cl ₃ CCOOCH ₃	0.94
Cl ₃ CCOOC ₂ H ₅	0.66
Cl ₃ CCOOC ₄ H ₉	0.52

^a The addition product was not formed in measurable amounts.

TABLE II

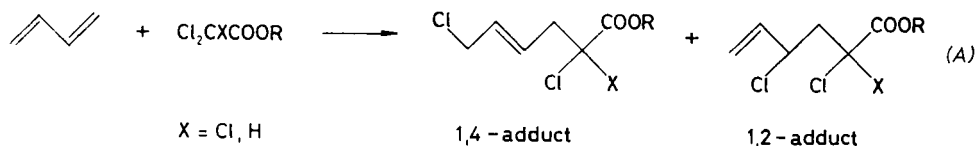
Effect of catalysts on selectivity of additions of ethyl trichloroacetate and ethyl dichloroacetate to 1,3-butadiene

Ester	Catalyst ^a	Ester conversion, x	Selectivity, % ^b		Isolated yield, %
			1,4-addition	1,2-addition	
Cl ₃ CCOOCH ₃ ^c	CuCl	0.26	95	5	—
	CuCl–DEA	0.95	95	5	80
	CuCl–phen ^d	0.33	94	6	25
Cl ₂ CHCOO. C ₂ H ₅ ^e	CuCl	0.31	89	11	—
	CuCl–DEA	0.37	83	17	—
	CuCl–phen	0.50	67	33	27
	Cu ₂ O–phen	0.69	75	25	35

^a phen = 1,10-phenanthroline, DEA = diethylamine, ^b selectivity (1,4- to 1,2-adduct ratio) did not depend on ester conversion, ^c 100°C/1.5 h, 0.5 mol % catalyst (with respect to the ester, ^d 1 : 1 adducts were accompanied by greater amounts of polymers, ^e 130°C/5 h, 5 mol % catalyst (with respect to the ester).

RESULTS AND DISCUSSION

In the reactions of ethyl trichloro- and dichloroacetate with 1,3-butadiene catalysed by copper complexes, the main route is 1,4-addition. In both cases the addition is accompanied by formation of the isomeric 1,2-adducts (Equation (A)).



As expected, the rate of the addition increases markedly with increasing number of chlorine atoms of the acetates (Table I). The reason is obviously the weakening of the neighbouring C—Cl bond which facilitates the cleavage due to the negative induction effect. The reactivity of the esters decreases with increasing number of carbon atoms in the ester alkyl group. However, this effect is less significant due to the greater distance between the alkyl group and the reaction centre.

As for the catalytic activity of copper complexes, the most pronounced effect on the rate increase in the trichloroacetate addition was exhibited by cuprous chloride–diethylamine complex while with phenanthroline this influence was less important. On the other hand, in the addition of dichloroacetates, 1,10-phenanthroline formed the most active copper complexes (Table II).

The effect of the copper catalysts on the selectivity (*i.e.* 1,4- to 1,2-adduct ratio) of the addition of ethyl trichloroacetate and ethyl dichloroacetate to 1,3-butadiene is presented in Table II. With cuprous chloride as catalyst, conversions of the esters were low and with dichloroacetate polymerization of the diene was the main reaction. The coordination of amine ligands to copper atom increased markedly activity of the catalysts and suppressed polymer formation in ethyl dichloroacetate addition. While with ethyl trichloroacetate, the 1,4- to 1,2-adduct ratio was around 95 : 5 irrespective of the type of amine ligand, in the addition of ethyl dichloroacetate this ratio varied from 89 : 11 to 67 : 33, depending on the ligand.

Of other factors, the reaction temperature exerted much less effect on the selectivity of additions under study. In the case of ethyl trichloroacetate addition, the increase in reaction temperature from 45 to 130°C resulted in only 3% increase in the 1,2-adduct formation (from 3 to 6%). The same situation has been encountered also in the ethyl dichloroacetate addition.

In the addition of ethyl trichloroacetate, the catalytic systems used made it possible to suppress completely polymer formation and to obtain the 1 : 1 adduct in 80% yield. With the less reactive ethyl dichloroacetate, side reactions could not be fully suppressed and the isolated yields of the 1 : 1 adducts did not exceed here 35 per cent.

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