

The Synthesis of 1, 1, 2-Trichlorobutadiene-1, 3

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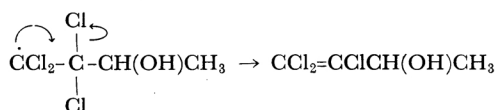
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Recently, 1, 1, 2-trichlorobutadiene-1, 3 has been synthesized by dehydrochlorination of 1, 1, 2, 4-tetrachlorobutene-1, which was prepared in the peroxide-induced addition reaction of tetrachloroethylene to ethylene.¹⁾ The yield of the monoadduct, however, was not satisfactory in the addition reaction. It was reported in a previous paper²⁾ that the radiation-induced addition of alcohols to tetrachloroethylene gave the monoadducts. The present paper is concerned with the preparation of 1, 1, 2-trichlorobutadiene-1, 3 from the monoadducts, which are obtained in the peroxide- as well as the radiation-induced addition reactions of ethanol to tetrachloroethylene.

The addition reactions gave a saturated monoadduct, 1, 1, 2, 2-tetrachlorobutane-3-ol and an unsaturated monoadduct, 1, 1, 2-trichloro-1-butene-3-ol in good yields. No telomer was detected. The reaction conditions and yield are shown in Table 1. In both the radiation- and peroxide-induced reactions, the products were the same and the yield of unsaturated adduct increased with the reaction temperature.

In the radiation-induced addition reactions of alcohols to 1, 2-dichlorotetrafluorocyclobutene³⁾ and of paradiroxane to tetrachloroethylene⁴⁾ at room temperature, the formation of unsaturated adducts has been observed. The mechanism has

been explained by dechlorination of the intermediate radical.³⁾ A similar mechanism may be applied to the present reaction as follows,



Since the *G*-values of this reaction were found to be 270 and 590 at 25°C and 60°C respectively, a radical chain mechanism, which involves the abstraction of a hydrogen from the substrate by the intermediate radical to give the saturated monoadduct, is plausible.

1, 1, 2-Trichloro-1-butene-3-ol was also prepared by dehydrochlorination of 1, 1, 2, 2-tetrachlorobutane-3-ol in an aqueous alkaline solution.

1, 1, 2-Trichlorobutadiene-1, 3 was prepared by dehydration of 1, 1, 2-trichloro-1-butene-3-ol with phosphorus pentoxide. Treatment of 1, 1, 2, 2-tetrachlorobutane-3-ol under a similar reaction condition gave 1, 1, 2-trichlorobutadiene-1, 3, together with small amounts of 2, 3, 4, 4-tetrachlorobutene-1.

The physical properties and analyses of the monoadducts, chlorobutene, and chlorobutadiene are shown in Table 2.

Experimental

Materials. Tetrachloroethylene and ethanol were purified by the conventional manner and redistilled before use. Organic peroxides supplied by Nippon Oils and Fats Co. were used without further purification: lauroyl peroxide (purity 99.6%), benzoyl peroxide (purity 98%), diisopropyl peroxy dicarbonate (40% xylene solution).

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3) H. Muramatsu and K. Inukai, *J. Org. Chem.*, **30**, 544 (1965).

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TABLE 1. ADDITION REACTION OF ETHANOL TO TETRACHLOROETHYLENE

Initiator dose $\times 10^{-6}$ or mol%	Reaction temp., $^{\circ}\text{C}$	Tetrachloro- ethylene consumed, %	Products yield, % ^{a)}	
			Satd. monoadduct	Unsatd. monoadduct
γ -ray (4.3)	25	34.0	53.8	10.7
γ -ray (1.1)	60	24.3	32.5	44.0
γ -ray (1.1)	80	21.3	30.8	49.1
DIPPC (0.6) ^{b)}	35	34.9	46.5	34.0
Lauroyl peroxide (1.0)	83	19.5	19.7	39.7
Benzoyl peroxide (0.4)	83	21.4	17.7	56.7

a) Percentage yield to each monoadduct based upon tetrachloroethylene consumed.

b) Diisopropyl peroxy dicarbonate.

TABLE 2. CHLORINE CONTAINING ALCOHOLS, BUTENE AND BUTADIENE

	Bp $^{\circ}\text{C}/15\text{ mmHg}$	n_D^{20}	d_4^{20}	MR _D		R_t min
				Calcd	Found	
$\text{CHCl}_2\text{CCl}_2\text{CH}(\text{OH})\text{CH}_3$	106	1.5130	1.536	41.66	41.47	9.5 ^{a)}
$\text{CCl}_2=\text{CClCH}(\text{OH})\text{CH}_3$	86	1.5150	1.440	36.33	36.74	4.4 ^{a)}
$\text{CHCl}_2\text{CCl}_2\text{CH}=\text{CH}_2$	62.5	1.5068	1.463	39.67	39.42	7.5 ^{b)}
$\text{CCl}_2=\text{CClCH}=\text{CH}_2$ ^{c)}	41	1.5290	1.373	34.34	35.04	4.1 ^{b)}

	C, %		H, %		Cl, %	
	Calcd	Found	Calcd	Found	Calcd	Found
$\text{CHCl}_2\text{CCl}_2\text{CH}(\text{OH})\text{CH}_3$	22.66	22.95	2.83	2.90	66.95	66.85
$\text{CCl}_2=\text{CClCH}(\text{OH})\text{CH}_3$	27.37	27.64	2.85	3.04	60.61	60.50
$\text{CHCl}_2\text{CCl}_2\text{CH}=\text{CH}_2$	24.77	25.04	2.06	2.03	73.17	73.00
$\text{CCl}_2=\text{CClCH}=\text{CH}_2$ ^{c)}	30.50	30.72	1.91	1.96	67.59	66.27

a), b) Retention time obtained with a Perkin-Elmer vapor fractometer Model-118 using a 2m-silicone grease packed column. Column temperature; a) 225 $^{\circ}\text{C}$, b) 150 $^{\circ}\text{C}$.c) Lit.¹⁾ bp 75 $^{\circ}\text{C}/80\text{ mmHg}$, n_D^{20} 1.5355, d_4^{20} 1.3733, MR_D 35.72.

General Procedure for Addition of Ethanol to Tetrachloroethylene. A mixture of ethanol and tetrachloroethylene in a molar ratio of 4 : 1 was refluxed with peroxide (lauroyl peroxide or benzoyl peroxide) in a flask under a nitrogen atmosphere, or heated in a deaerated glass tube with diisopropyl peroxy dicarbonate, or irradiated with ^{60}Co gamma-ray at a dose rate of 3×10^4 R/hr. Then, unchanged ethanol and tetrachloroethylene were distilled off and the remaining material was fractionally distilled at reduced pressure to give two fractions boiling at 86 $^{\circ}\text{C}/15\text{ mmHg}$ and 106 $^{\circ}\text{C}/15\text{ mmHg}$. The lower boiling fraction was identified to be 1, 1, 2-trichloro-1-butene-3-ol (II), and the higher boiling fraction to be 1, 1, 2, 2-tetrachlorobutane-3-ol (I). The infrared spectrum of I exhibited a free OH band at 3480 cm^{-1} (shoulder), a broad hydrogen bonded OH band at 3360 cm^{-1} , and C-Cl band at 780 cm^{-1} . With II, a sharp band due to the carbon carbon double bond stretching mode displayed at 1590 cm^{-1} .

Dehydrochlorination of 1, 1, 2, 2-Tetrachlorobutane-3-ol. Into an aqueous solution of 67 g (1.7 mol) sodium hydroxide, 159 g (0.75 mol) of 1, 1, 2, 2-tetrachlorobutane-3-ol was added dropwise over a period of 30 min. After 60 min heating of the reaction mixture at 90–95 $^{\circ}\text{C}$, the products were extracted with carbon tetrachloride. Distillation of the extract gave 128 g (yield 95%) of 1, 1, 2-trichloro-1-butene-3-ol,

bp 86 $^{\circ}\text{C}/15\text{ mmHg}$.

Preparation of 1, 1, 2-Trichlorobutadiene-1, 3. To 70 g (0.4 mol) of 1, 1, 2-trichloro-1-butene-3-ol there was added 85 g (0.6 mol) of phosphorus pentoxide. The reaction mixture was then heated in an oil bath up to about 200 $^{\circ}\text{C}$ and distilled under reduced pressure. The distillation gave 32 g (yield 51%) of 1, 1, 2-trichlorobutadiene-1, 3 (III). Under the similar condition, the reaction of 106 g (0.5 mol) of 1, 1, 2, 2-tetrachlorobutane-3-ol and 85 g (0.6 mol) of phosphorus pentoxide yielded 48 g of the crude product. The redistillation gave 30.7 g (yield 40%) of 1, 1, 2-trichlorobutadiene-1, 3, bp 39–41 $^{\circ}\text{C}/15\text{ mmHg}$, and 8.2 g (yield 8.4%) of 3, 3, 4, 4-tetrachlorobutene-1, bp 61–63 $^{\circ}\text{C}/15\text{ mmHg}$. The infrared spectrum of III exhibited two sharp bands at 1612 and 1550 cm^{-1} due to the carbon carbon double bond stretching modes, with a shift toward low frequencies due to a conjugation and chlorine substitution. In a region near 3000 cm^{-1} , the bands at 3050 and 3140 cm^{-1} due to the olefinic carbon hydrogen stretching modes displayed. The NMR spectrum showed two groups of peaks located at τ 3.1 and about τ 4.3, which could be assigned to non-terminal and terminal olefinic protons, respectively. The coupling constants between vicinal protons in a double bond were 17 cps for trans and 10 cps for cis, and these values were in good agreement with those reported previously.⁵⁾ The chemical shifts of the non-terminal olefinic proton, trans- and cis-terminal protons were τ 3.13, τ 4.22, and τ 4.54, respectively.

5) K. Karplus, *J. Chem. Phys.*, **30**, 11 (1959).