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REACTION OF CHLORAL WITH ALLYL ALCOHOLS. SYNTHESIS OF SUBSTITUTED 3,3,5-TRICHLORO-2-HYDROXYTETRAHYDROPYRANS

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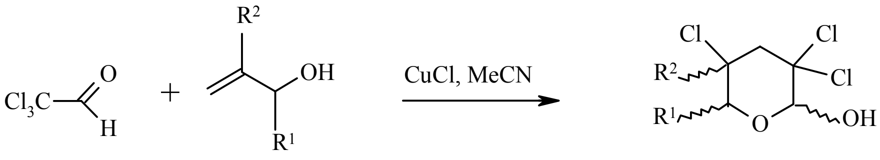
When heated with substituted allyl alcohols in acetonitrile in the presence of copper monochloride, chloral forms substituted 3,3,5-trichlorotetrahydropyrans as mixtures of diastereomers.

Keywords: allyl alcohols, 3,3,5-trichloro-2-hydroxytetrahydropyrans, chloral.

We have already reported [1] on the formation of 3,3,5-trichloro-2-hydroxytetrahydropyran in the reaction of chloral with allyl alcohol in the presence of copper monochloride. The structure of the obtained compound was confirmed by NMR spectroscopy [2].

We established that substances of similar structure – substituted 3,3,5-trichloro-2-hydroxytetrahydropyrans **3a-d** – are formed when the chloral (**1**) is heated with substituted allyl alcohols **2a-d** in acetonitrile in the presence of copper monochloride:



1 **2a–d** **3a–d**

2, 3 a R^1 = Me, R^2 = H, **b** R^1 = R^2 = Me, **c** R^1 = Et, R^2 = H, **d** R^1 = H, R^2 = Cl

The position of the substituents in the ring is determined by the structure of the initial alcohol. The composition and structure of the obtained compounds were confirmed by NMR spectroscopy and elemental analysis.

The same compounds are formed with similar yields when the semiacetals **4a-d** – specially synthesized products from addition of the allyl alcohols **2a-d** to the carbonyl group of chloral **1** – are brought into the reaction in the presence of copper monochloride:

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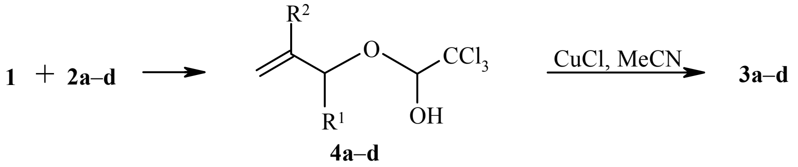
TABLE 1. The ^{1}H NMR Spectra of Compounds **3a-d**

Compound	^{1}H NMR spectrum, δ, ppm					
	OH	OCHOH	CH_2	R^2	CHR^1	R^1
3a	5.43	4.74; 4.86; 5.07	2.96; 3.04; 3.10	3.98; 4.03; 4.08	3.98; 4.03; 4.06; 4.09	1.38
3b	5.45	4.74; 4.86; 5.07	2.87; 2.92; 2.98	2.07; 2.10	3.98; 4.03; 4.06; 4.09	1.38
3c	5.46	4.64; 4.83; 4.98	2.43; 2.51; 2.54	4.03; 4.08	4.37; 4.41; 4.43	1.69 (2H); 1.01 (3H)
3d	5.44	5.01	3.12; 3.45	—	4.42; 4.05	



4 a R^1 = Me, R^2 = H, **b** R^1 = R^2 = Me , **c** R^1 = Et, R^2 = H, **d** R^1 = H, R^2 = Cl

The tetrahydropyrans **3a-d** are isolated from the reaction in the form of mixtures of diastereomers. In the ^{1}H NMR spectra it is possible to identify a series of characteristic groups of signals for the protons of the pyran ring: A singlet in the region of 4.74-5.07 ppm, belonging to the proton of the semiacetal group $C_{(2)}$; a singlet for the proton of the hydroxyl group in the region of 5.54 ppm; signals for the protons of the methylene group in the region of 2.96-3.95 ppm; a signal for the proton at the $C_{(6)}$ atom, attached to the oxygen, in the region of 3.98-4.43 ppm; signals for the proton at the carbon atom attached to the chlorine (except for compounds **3b** and **3d**, in which there is no hydrogen at $C_{(5)}$) in the region of 3.02-3.46 ppm. In the spectra of compounds **3a-c** there are also signals for the alkyl groups at $C_{(5)}$ and $C_{(6)}$ in the region characteristic of alkyl groups (1.01-1.68 ppm). The chemical shifts of the protons in the ^{1}H NMR spectra of compounds **3a-d** are given in Table 1.

EXPERIMENTAL

The NMR spectra were recorded in deuterochloroform on a Bruker WP-200 spectrometer (200 MHz). Gas-liquid chromatography was performed on a Chrom-5 instrument with a flame-ionization detector, carrier gas helium (30 cm^3/min), 3500×3 mm glass columns, 5% of XE-60 on Inerton-Super (0.20-0.25 mm), and thermostat temperature 200°C.

Chloral Semiacetals (4a-d) (General Procedure). To freshly distilled chloral **1** (0.1 mol) the respective allyl alcohol (0.1 mol) was added. The reaction mixture was heated to 80-90°C. After cooling to room temperature the mixture was kept for 2 h and distilled.

1-Methyl-2-propenyl Ether of Chloral Semiacetal (4a). Yield 73%; bp 110-111°C, n_D^{20} 1.4912. ^{1}H NMR spectrum, δ, ppm: 4.65 (2H, dd, CH_2); 6.18 (1H, m, CH=); 5.02 (1H, s, CHOHO); 3.38 (1H, m, CHO); 1.60 (1H, m, CH); 0.91 (2H, d, CH_3); 4.85 (1H, br. s, OH).

1,2-Dimethyl-2-propenyl Ether of Chloral Semiacetal (4b). Yield 69%; bp 115-116°C, n_D^{20} 1.4892. ^{1}H NMR spectrum, δ, ppm: 4.83, 5.11 (2H, dd, CH_2); 6.24 (1H, m, CH=); 4.96 (1H, s, CHOHO); 3.38 (1H, dt, CHO); 1.15 (3H, d, CH_3); 1.82 (3H, s, CH_3); 4.85 (1H, br. s, OH).

1-Ethyl-2-propenyl Ether of Chloral Semiacetal (4c). Yield 76%; bp 116-117°C, n_D^{20} 1.4919. ^{1}H NMR spectrum, δ, ppm: 4.83, 5.11 (2H, dd, CH_2); 6.24 (1H, m, CH=); 4.96 (1H, s, CHOOH); 3.38 (1H, dt, CHO); 1.60 (2H, m, CH_2); 0.91 (3H, t, CH_3); 4.85 (1H, br. s, OH).

2-Chloroallyl Ether of Chloral Semiacetal (4d). Yield 70%; bp 123-125°C, n_D^{20} 1.4924. ^{1}H NMR spectra, δ, ppm: 5.50, 5.24 (2H, d, CH_2); 3.92 (2H, s, CHOOH); 5.04 (1H, s, CHOHO); 4.85 (1H, br. s, OH).

Substituted 3,3,5-trichloro-2-hydroxytetrahydropyrans (3a-d) (General Procedure). A. Chloral (0.01 mol), allyl alcohol (0.01 mol), acetonitrile (10 ml), and copper monochloride (0.001 mol) were placed in a glass tube. The tube was sealed and heated at 130°C for 12 h. After cooling the tube was opened, and the reaction mixture was evaporated under vacuum. The residue was dissolved in ether (30 ml) and filtered. The filtrate was evaporated, and the residue was distilled under vacuum.

B. The respective semiacetal (0.01 mol), copper monochloride (0.001 mol), and acetonitrile (10 ml) were placed in a glass tube. The tube was sealed and heated at 130°C for 12 h. After cooling the product was treated as in method A.

3,3,5-Trichloro-2-hydroxy-6-methyltetrahydropyran (3a). Yields: A) 34%; B) 35%; bp 120°C (0.15 mm Hg). Found %: C 32.50; H 4.17. $C_6H_9Cl_3O_2$. Calculated %: C 32.83; H 4.13.

3,3,5-Trichloro-2-hydroxy-5,6-dimethyltetrahydropyran (3b). Yields: A) 32%; B) 32%; bp 124°C (0.12 mm Hg). Found %: C 35.97; H 4.72. $C_7H_{11}Cl_3O_2$. Calculated %: C 36.01; H 4.75.

3,3,5-Trichloro-6-ethyl-2-hydroxytetrahydropyran (3c). The yields were: A) 35%; B) 37%; bp 126 (0.11 mm Hg). Found %: C 36.04; H 4.96. $C_7H_{11}Cl_3O_2$. Calculated %: C 36.01; H 4.75.

3,3,5,5-Tetrachloro-2-hydroxytetrahydropyran (3d). Yields: A) 32%; B) 30%; bp 128°C (0.12 mm Hg), mp 48-49°C (ether–hexane). Found %: C 25.12; H 2.50. $C_5H_6Cl_4O_2$. Calculated %: C 25.22; H 2.52.

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