SYNTHESIS AND SOME TRANSFORMATIONS OF gem-DICHLOROCYCLOPROPYL VINYL ETHER

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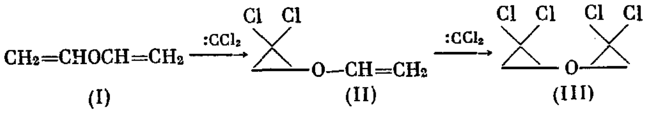
The preparation of the bisadducts of the dichloro- and dibromocarbenes to the unsubstituted divinyl and diisobutenyl ethers has been described, in which connection the monoadducts, the vinyl ethers of the gem-dihalocyclopropanols were not isolated [1]. Despite the interest that is associated with the use of the latter in organic synthesis, only the simpler members of this series are known [2-4].

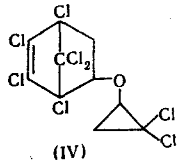
In the present paper we studied the reaction of divinyl ether (I) with dichlorocarbene (DCC) and a number of the chemical and physical properties of the formed adducts.

The reaction of DCC (generated from ethyl trichloroacetate by treatment with CH_3ONa in either petroleum ether or pentane at 0°) with (I), using even a slight excess of the latter, leads to the exclusive formation of the monoadduct, the gem-dichlorocyclopropyl vinyl ether (II). Better yields of (II) are achieved by using a five- to sixfold excess of (I) and adding the ethyl trichloroacetate slowly. The rapid addition of the latter lowers the yield of (II) with increase in the time of stirring. The yield of (II) is low when a twofold excess of ethyl trichloroacetate and CH_3ONa with respect to (I) is used, in which connection it was observed that the bisadduct of di-gem-dichlorocyclopropyl ether (III) is formed in ~1% yield. A noticeable amount of the bisadduct (III) is formed when (II) is used as a DCC acceptor. Bisadduct (III) can be isolated in 25% yield if a threefold excess of (II) is used.

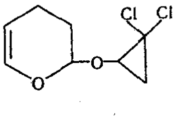


Compound (I) reacts differently with the DCC that is generated by the alkaline hydrolysis of $CHCl_3$ in a two-phase system in the presence of catalytic amounts of triethylbenzylammonium chloride [5]. In this case both the mono- and bisadducts are formed, in which connection their yields are determined by the ratio of the starting reactants (Table 1).

The presence of the vinyl group in (II) makes it possible to use it as the dienophile in the diene condensation. The reaction of (II) with hexachlorocyclopentadiene proceeds at 100°, while with acrolein it proceeds at 115°, and leads, respectively, to gem-dichlorocyclopropoxy-1,4,5,6,7,7-hexachlorobicyclo-[2.2.1]-5-heptene (IV) and 2-gem-dichlorocyclopropoxy-2,3-dihydropyran (V).



(IV)



(V)

Irkutsk Institute of Organic Chemistry, Siberian Branch, Academy of Sciences of the USSR. Translated from Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya, No. 8, pp. 1818-1823, August, 1974. Original article submitted December 4, 1973.

TABLE 1. Reaction of (I) with Dichlorocarbene in a Two-Phase System

Mole ratio of (I) and $CHCl_3$	Reaction temperature, °C	Yield, %*	
		(II)	(III)
1 : 1	0	44	2
1 : 1	25	24	0,7
2 : 1 †	0	21	1
1 : 2 †	0	53,6	17
1 : 3 †	0	23	55

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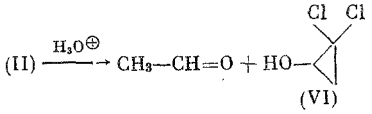
*When based on (I).

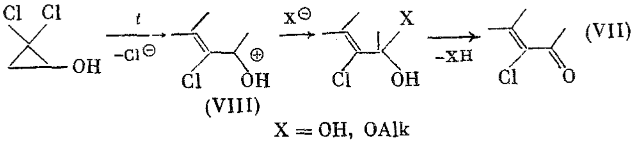
†The alkali was added in 4 h to a mixture of (I), $CHCl_3$, and the catalyst.

The ability of (II) to enter into the diene synthesis is expressed more weakly than for the unsubstituted cyclopropyl vinyl ether [2]. Nevertheless, (II) can be used to synthesize cyclic compounds that contain the gem-dichlorocyclopropoxy group.

The hydrolysis of (II) in acid medium at ≤50° for 1 h leads to a mixture of gem-dichlorocyclopropanol (VI) and acetaldehyde, from which (VI) was isolated in 87% yield.

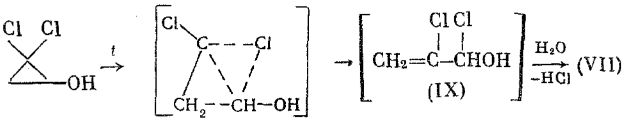


An increase in the hydrolysis time of (II) at the same temperature leads to a decrease in the yield of (VI), in which connection the accumulation of α-chloroacrolein (VII) in the reaction mixture is observed. When (VI) is heated for 2 h at 60° in the presence of 10% HCl solution it is converted completely to (VII). In alkaline medium (in either alcohol or aqueous solution in the presence of K_2CO_3 at 60°) the opening of the (VI) ring also leads to (VII) [identified as the 2,4-dinitrophenylhydrazone (DNPH)], probably via the scheme:

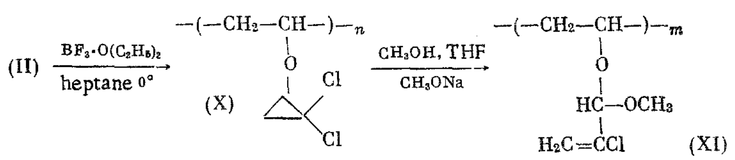


A similar scheme was proposed in [6] to explain the cleavage of gem-dichlorocyclopropyl ethers under the influence of alkoxy ions. The ease with which the chloride ion in (VI) is cleaved can be explained by the ability of the unshared electron pair of oxygen to increase the electron density of the cyclopropane ring, and in this way importantly change the polarization of the ring bonds and the C–Cl bonds.

Another possible mechanism of the reaction is the opening of the (VI) ring with the formation of the intermediate dichlorocarbinol (IX). This scheme was proposed for the isomerization of gem-dihalocyclopropane derivatives [7].



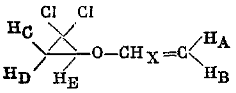
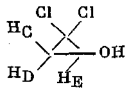
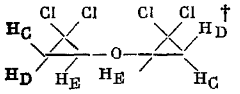
The polymerization of (II) under the influence of BF_3-etherate leads to polymer (X), which contains gem-dichlorocyclopropoxy groups that are attached directly to the ring. These groups retain the ability to undergo ring cleavage under the influence of alcoholic alcoholate solutions.



This method was used to obtain the modified polymer (XI), which contains α-chloroacrolein acetal groups attached to the ring.

The structure of compounds (II)-(VI) and polymers (X) and (XI) was confirmed by the IR and NMR spectra. The absorption bands in the 1015-1030, 3010-3030, and 3095-3100 cm^{-1} regions are due to the presence of the cyclopropane ring in (II)-(VI) and (X) [8, 9]. The double bond is confirmed by the presence of bands at 1625 and 3120 cm^{-1} in the spectrum of (II), at 1600 cm^{-1} for (IV), at 1660 and 3070 cm^{-1} for (V), and at 1640 and 3080 cm^{-1} for (XI). A strong band, characteristic for the OH group in (VI), was detected at 3320 cm^{-1}. As was to be expected, strong absorption bands are observed in the 2800-3000 cm^{-1} region in the spectra of polymers (X) and (XI), which testify to the presence of a polymeric chain. Characteristic bands in the 1060-1160 cm^{-1} region belong to the acetal groupings in (XI).

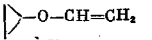
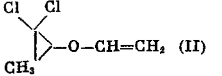
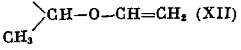
TABLE 2. Parameters of NMR Spectra

Compounds	Chemical shifts, ppm*							Spin-spin coupling constants J, Hz
	δ (X)	δ (A)	δ (B)	δ (E)	δ (C)	δ (D)	δ (OH)	
	6,43(q)	4,41 (q)	4,21 (q)	3,66(q)	1,50(q)	1,73(q)	—	$J_{AX}=14{,}0$; $J_{BX}=6{,}6$; $J_{AB}=2{,}6$; $J_{CD}=8{,}6$
	—	—	—	3,75(q)	1,44(q)	1,68(q)	4,84 (s)	$J_{CD}=8{,}6$; $J_{CE}=5{,}2$; $J_{DE}=7{,}8$
 †	—	—	—	3,74(q) 3,81 (q)	1,70(q) 1,71 (q)	1,54(q) 1,57(q)	—	—

*s = singlet, q = quartet.

†Based on the GLC data, a mixture of two diastereomers.

TABLE 3. Intensity of Lines of C =C Bonds in Raman Spectrum of Vinyl Ethers

Compound	$I^{\infty}_{C=C}$*	$I^{\infty}_{C=C}:I^{\infty}_{C=C}$ (XII)
$H_2C{=}CH{-}O{-}CH{=}CH_2$ (I)	700 †	2
	460	1,3
 (II)	360	1
 $(CH_3)_2CH{-}O{-}CH{=}CH_2$ (XII)	350	1

*Total $I^{\infty}_{C=C}$ of all of the rotational isomers.

†When based on one vinyl group.

The values of the chemical shifts and the spin–spin coupling constants are given in Table 2.

The NMR spectrum of polymer (X) consists of four broad signals. Two of the partially overlapping signals upfield, with an equal ratio of the intensities, belong to the methylene protons of the cyclopropane ring (δ 1.54 ppm) and the polymeric chain (δ 1.92 ppm). The two signals of equal intensity belong to the methine protons of the three-membered ring (δ 3.60 ppm) and the polymeric chain (δ 4.12 ppm) [10].

We studied the Raman spectra of (II) in comparison with the spectra of the model compounds. From the data in Table 3 it follows that the intensities of the lines of the C =C bond in the series of isopropyl, cyclopropyl, and gem-dichlorocyclopropyl vinyl derivatives relate as 1 : 1 : 1.3 : 2. This shows that replacing the H atoms of the cyclopropane ring by chlorine atoms leads to some decrease in the transfer effect of the conjugation of the cyclopropyl group and double bond through the ether oxygen atom.

The Raman spectrum of (II) contains two polarized bands in the region of the stretching vibrations of the C =C bond (1628 and 1643 cm^{-1}). Only one line of the vibrations of the C =C bond (1618 cm^{-1}) remains in the Raman spectrum of the crystalline (II). Consequently, the multiplet nature of the discussed bands is due to the presence of rotational isomers. This fact gives reason to assume that the decrease of $I^{\infty}_{C=C}$ in (II) can be the consequence of an increase in the portion of the out-of-plane rotamer when compared with cyclopropyl vinyl ether.

EXPERIMENTAL METHOD

The Raman spectra were recorded on a DFS-12 spectrometer, using the helium–neon laser line with λ = 6328 Å for excitation, and were planimetered in order to determine I^{∞} . Toluene was used as the external standard. The I^{∞} values were calculated as described in [11]. The IR spectra were taken on a UR-10 instrument, either as a microlayer of KBr pellets. The NMR spectra were obtained on a JNM-4H-100 spectrometer, using CCl_4 as the solvent and HMDS as the internal standard (δ-scale). The properties of the synthesized compounds are given in Table 4.

gem-Dichlorocyclopropyl Vinyl Ether (II). a) To a mixture of 262 g of (I) and 49 g of CH_3ONa in 150 ml of petroleum ether at 0°, in a current of dry nitrogen, was added 144 g of CCl_3COOEt in 3.6 h. The mixture was stirred at 0° for 1 h and then diluted with water. The organic layer was separated, and the aqueous layer was extracted with ether. The solvents and (I) were distilled from the combined organic layer and extracts, while the residue was heated with 200 ml of 10% KOH solution on the steam bath for 3 h.

TABLE 4. Properties of Synthesized Compounds

Compound	Bp, °C (p, mm of Hg)	n_D^{20}	d_4^{20}	Found, %			Empirical formula	Calculated, %		
				C	H	Cl		C	H	Cl
(II)	40 (22)	1,4625	1,2179	39,21	3,92	46,40	$C_5H_6Cl_2O$	39,58	4,17	46,66
(III) *	83 (3)	1,4992	1,4260	30,50	2,54	60,16	$C_6H_6Cl_4O$	30,31	2,67	60,48
(IV)	148 (1)	1,5550	—	28,10	1,40	66,60	$C_{10}H_6Cl_8O$	28,30	1,55	66,68
(V)	65 (1)	1,4860	1,2368	45,93	4,78	33,97	$C_9H_{10}Cl_2O_2$	46,13	4,72	34,27
(VI)	40 (3)	1,4825	1,4146	28,34	3,14	55,89	$C_3H_5Cl_2O$	28,66	3,24	55,01

* Mixture of two diastereomers.

The organic layer was separated, washed with water, and dried over $MgSO_4$. Fractional distillation in vacuo gave 34.5 g (30%) of (II).

b) In a similar manner, starting with 121 g of (I), 25.9 g of CH_3ONa, and 76.8 g of CCl_3COOEt in 150 ml of pentane, we isolated 12.0 g (19.5%) of (II).

c) A mixture of 35 g of (I), 60 g of $CHCl_3$, 100 ml of 50% aqueous NaOH solution, and 1.2 g of $[PhCH_2\overset{+}{N}Et_3\cdot]Cl^-$ was stirred at 0° for 4 h and then diluted with water. The organic layer was separated, and the aqueous layer was extracted with ether. After the usual workup we isolated 34 g of (II) and 2.3 g of (III). The results of the experiments using a variable ratio of the reactants are given in Table 1.

Raman Spectrum* ($\Delta\nu$, cm^{-1}): 215 (0), 233 (0), 256 (2), 299 (0), 329 (2), 463 (4), 535 (0.5), 620 (0.5), 768 (1), 799 (1), 836 (0), 905 (0.5), 927 (0.5 m), 1003 (0), 1024 (0), 1124 (0.5), 1240 (3), 1274 (0.5), 3122 (5), 1359 (0), 1401 (0.5), 1444 (0.5), 1491 (0), 1536 (0.5), 1628 (4), 1643 (2), 2866 (1), 3016 (1), 3049 (10), 3098 (1).

Di-gem-dichlorocyclopropyl Ether (III). a) From Divinyl Ether. Analogous to (II), starting with 39 g of (I) and 52.6 g of CH_3ONa in 200 ml of petroleum and 89.7 g of CCl_3COOEt, we isolated 1.5 g (1.3%) of (III), together with 3.5 g (4.9%) of (II).

Analogous to (II), starting with 17.5 g of (I), 90 g of $CHCl_3$, 1.8 g of $[PhCH_2\overset{+}{N}Et_3]Cl^-$, and 150 ml of 50% NaOH solution, we isolated 32.6 g (55%) of (III), together with 8.8 g (23%) of (II).

b) From gem-Dichlorocyclopropyl Vinyl Ether. Analogous to (II), starting with 91.8 g of (II) and 13.5 g of CH_3ONa in 200 ml of petroleum ether and 38 g of CCl_3COOEt, we isolated 12.1 g (25.8%) of (III).

2-gem-Dichlorocyclopropoxy-1,4,5,6,7,7-hexachlorobicyclo[2.2.1]-5-heptene (IV). A mixture of 5.46 g of hexachlorocyclopentadiene and 3.06 g of (II) in a sealed ampul was heated for 9 h at 100°. We obtained 4.7 g (85%) of (IV).

2-gem-Dichlorocyclopropoxy-2,3-dihydropyran (V). A mixture of 4.5 g of (II) and 2.5 g of acrolein in a sealed ampul was heated in the presence of hydroquinone for 25 h at 115°. We obtained 1.6 g (26%) of (V).

gem-Dichlorocyclopropanol (VI). A mixture of 7.65 g of (II) and 30 ml of 10% HCl solution was stirred at 50° for 1 h, after which it was extracted with ether. The extracts were dried over $MgSO_4$. Then the solvent was distilled off and the residue was fractionally distilled in vacuo. We isolated 5.5 g (87%) of (VI).

2,4-Dinitrophenylhydrazone of α-Chloroacrolein. a) A mixture of 4.6 g of (II) and 15 ml of 10% HCl solution was stirred at 60° for 12 h. After the usual workup, followed by distilling off the solvent, a part of the residue (0.5 g) was treated with 10 ml of alcohol and a solution of 0.5 g of 2,4-DNPH in 20 ml of alcohol containing conc. H_2SO_4. The mixture was heated up to the boil, and the obtained crystals were filtered, mp 168° (from ethyl acetate). The mixed melting point with the authentic 2,4-DNPH of α-chloroacrolein was not depressed.

b) A mixture of 2.5 g of (VI), 10 ml of CH_3OH, and 1.0 g of K_2CO_3 was stirred at 65° for 1.5 h, filtered, and the MeOH was distilled off. The residue was treated with 0.5 g of 2,4-DNPH in 20 ml of alcohol and heated up to the boil. Crystals with mp 167° were isolated after the workup described in the preceding experiment. The mixed melting point with an authentic specimen was not depressed. TLC in

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*The relative visual intensities are given in parentheses.

the system 1 : 3 ethyl acetate–hexane, R_f 0.46. The R_f of the obtained and authentic specimens coincided.

Polymerization of (II). To a stirred solution of 7.65 g of (II) in 30 ml of absolute heptane at 0°, in a current of dry nitrogen, was added two drops of $BF_3 \cdot O(C_2H_5)_2$. The cooling was removed and the mixture was stirred at ~20° in a nitrogen atmosphere for 90 h. The polymer was separated from the heptane, dissolved in ether, and a current of dry NH_3 was passed through the solution to remove the catalyst. The obtained precipitate was filtered, and the polymer was dissolved in ether, reprecipitated with heptane, and dried in vacuo to constant weight. We obtained 4.0 g (52%) of poly(vinyl gem-dichlorocyclopropyl ether) (X); mol. wt. 4000 (detd. as described in [12]). Found: C 39.25; H 4.06; Cl 42.72%. $C_5H_6Cl_2O$. Calculated: C 39.21; H 3.92; Cl 46.40%.

Acetalization of (X). A mixture of 1.1 g of (X), 1.0 g of CH_3ONa, 50 ml of THF, and 20 ml of MeOH was refluxed for 50 h, after which it was filtered and diluted with water. The obtained polymer was repeatedly reprecipitated from THF solution by pouring into water, and then dried in vacuo to constant weight. We obtained 0.6 g (46%) of polymer (XI), which is soluble in ether, dioxane or THF, and insoluble in $CHCl_3$ or CCl_4; mol. wt. 3900 (detd. as described in [12]).

CONCLUSIONS

1. A study was made of the reaction of dichlorocarbene with divinyl ether; the conditions for preparing the mono- and bisadducts were found.

2. A number of the chemical and physical properties of gem-dichlorocyclopropyl vinyl ether was studied.

3. gem-Dichlorocyclopropanol undergoes ring cleavage, with the formation of α-chloroacrolein, in both acid and alkaline media.

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