CYCLOPROPYL VINYL ETHER

S. M. Shostakovskii, A. V. Bobrov,
and A. N. Volkov

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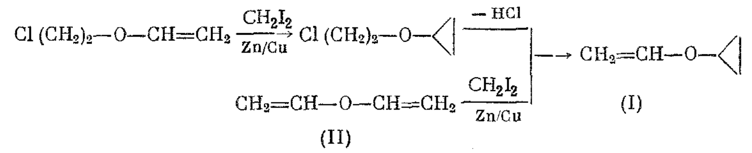
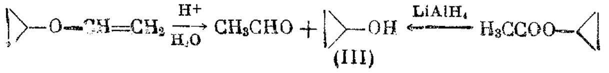
In a previous paper [1] we showed that aryl vinyl ethers can undergo Simmons-Smith reaction [2] with formation of the corresponding unsubstituted aryl cyclopropyl ethers. As a result of spectroscopic investigations on the aryl cyclopropyl ethers we established transmission of the conjugation effect between the cyclopropyl and aryl groups through the oxygen bridge. This gave us reason to suppose that an analogous effect would be found not only in such aromatic compounds, but also in cyclopropyl ethers containing other unsaturated groups (vinyl, carbonyl). It was therefore of interest to synthesize cyclopropyl vinyl ether and investigate some of its physical and chemical properties.

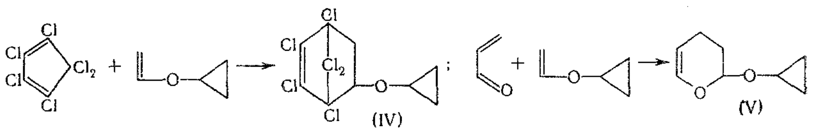
We synthesized cyclopropyl vinyl ether (I) by the Simmons-Smith reaction in two ways: methylenation of 2-chloroethyl vinyl ether with subsequent dehydrochlorination, and methylenation of divinyl ether (II) with 1 molecular proportion of reagent.



Methylenation goes more smoothly in the first case and leads to the adduct (I) in 20% yield. In the second case reaction is accompanied by considerable polymerization of divinyl ether, as a result of which the monoadduct (I) was isolated in only 7% yield. The samples of (I) obtained by the two methods were identical in their constants and retention times in GLC. We hope that compounds of type (I) will help to bring into relation two fields of organic chemistry – the chemistry of cyclopropanes and the chemistry of vinyl compounds – which have developed independently. In this investigation we carried out several reactions of (I) in which only the vinyl group took part. In an acid medium (I) readily hydrolyzes with formation of a mixture, which according to GLC consists solely of cyclopropanol (III) and acetaldehyde. (III) was identified by comparison with a known sample prepared by the reduction of cyclopropyl acetate with lithium tetrahydroaluminate [3].



In this case, unlike the hydrolysis of 2-alkoxycyclopropanecarboxylic acids [4], hydrolysis does not affect the three-membered ring. It should be noted that aryl cyclopropyl ethers are not hydrolyzed even when heated for 50 h with 2% H_2SO_4. (I) undergoes diene condensation with hexachlorocyclopentadiene at 100° and with acrolein at 180° with formation of the corresponding adducts: 1,2,3,4,7,7-hexachloro-5-cyclopropoxy-2-norbornene (IV) and 2-cyclopropoxy-3,4-dihydro-2H-pyran (V):



The ability of (I) to undergo diene condensations with preservation of the three-membered ring opens up the possibility of the synthesis of cyclic cyclopropoxy compounds of the most varied structure. The

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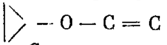
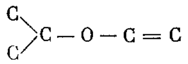
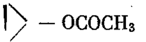
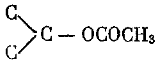
N. D. Zelinskii Institute of Organic Chemistry, Academy of Sciences of the USSR, and Irkutsk Institute of Organic Chemistry, Siberian Division, Academy of Sciences of the USSR. Translated from Izvestiya Akademii Nauk SSSR, No. 1, pp. 160-164, January, 1968. Original article submitted April 4, 1967.

TABLE 1. Intensities of C=C and C=O Lines and Their Ratios in Vinyl (I) and Cyclopropyl (II) Compounds to the Value in Isopropyl Compounds (III)*

Compound	$J^{\infty}_{C=C}$†	$\frac{J^{\infty}_{C=C}}{J^{\infty}_{C=C\,(III)}}$	$J^{\infty}_{C=O}$	$\frac{J^{\infty}_{C=O}}{J^{\infty}_{C=O(III)}}$
$C=C-O-C=C$	850‡	2	—	—
	520	1,3	—	—
	400	1	—	—
$C=C-O-CO-CH_3$	—	—	210	2
	—	—	150	1,35
	—	—	110	1

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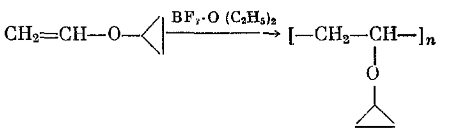
* Intensities of Raman lines on the cyclohexane scale: J^{∞} of the 802 cm^{-1} line of cyclohexane = 500 units. The contours of the Raman lines of the standard and the substance under investigation were recorded photometrically on a DFS-12 spectrophotometer and then planimetered to determine J^{∞}.

† The summation J^{∞} of all rotational isomers.

‡ Calculated for one vinyl group.

polymerization of (I) under the action of boron trifluoride ether complex leads to a polymer containing cyclopropoxy groups directly linked to the chain:



$$CH_2{=}CH{-}O{-}C_3H_5 \xrightarrow{BF_3\cdot O(C_2H_5)_2} [-CH_2-\underset{\underset{C_3H_5}{|}}{\underset{O}{\underset{|}{CH}}}-]_n$$

The IR spectrum of the polymer obtained contains lines due to the vibrations of the three-membered ring (ν, cm^{-1}: 1030, 1060), while bands due to C=C bonds are absent. It should be noted that the polymerization of (I) requires more severe conditions than the polymerization of alkyl vinyl ethers: it is not catalyzed by ferric chloride, usually used for this purpose.

Investigation of the Raman spectrum of (I) in comparison with the spectra of model compounds showed the occurrence of transmission of the conjugation effects of the cyclopropyl and vinyl groups through the ether oxygen atom. The transmission effect is somewhat smaller than in the case of the interaction of two vinyl groups (divinyl ether). An analogous effect is also observed in the case of cyclopropyl acetate. The intensity of the line of the vinyl group in vinyloxy derivatives and the intensity of the line of the carbonyl group in acetyl derivatives depend to an appreciable extent on the character of the unsaturation of the residue to which the group is attached.

It follows from the data in Table 1 that the intensities of the C=C and C=O lines in isopropyl, cyclopropyl, and vinyl derivatives are related as 1 : 1, 3 : 2, i.e., the relation is the same as that observed for the same series of aryl ethers [1]. The Raman spectra of cyclopropyl vinyl ether and divinyl ether contain two and three bands respectively in the region of the stretching vibrations of the C=C bond [1612 and 1633 cm^{-1} for (I) and 1624, 1641, and 1667 cm^{-1} for (II)]. The relative intensities of the bands are the same in the Raman and the IR spectra, and in the Raman spectra all the lines under discussion are polarized. In Raman spectra determined for (I) and (II) in the crystalline state only one line due to C=C stretch remains. In this case, therefore, the splitting of the C=C band is due to the presence of rotational isomers and to the separation of vibrations into symmetrical and antisymmetrical [5, 6].

EXPERIMENTAL

2-Chloroethyl Cyclopropyl Ether

Ethereal solutions (1 : 2) of 400 g of methylene iodide and 106 g of 2-chloroethyl vinyl ether were added simultaneously with stirring at a rate which maintained a uniform boil to a suspension of a zinc-copper couple [7], prepared from 100 g of zinc dust and 7 g of copper acetate, in 750 ml of ether. The reaction mixture was stirred for 70 h at the boiling point of ether. After the usual treatment the product was vacuum-distilled from the resinous residue and collected in a cooled receiver; it was dried over $CaCl_2$ and fractionated. We obtained 24.5 g (20%) of 2-chloroethyl cyclopropyl ether; bp 142°; n_D^{20} 1.4420; d_4^{20} 1.096. Found: C 49.78, 49.75; H 7.51, 7.53; Cl 29.45, 29.47%. C_5H_9ClO. Calculated: C 49.80; H 7.52; Cl 29.41%.

Cyclopropyl Vinyl Ether (I)

From 2-Chloroethyl Cyclopropyl Ether. 2-Chloroethyl cyclopropyl ether (36 g) was added dropwise with stirring to 120 g of KOH powder heated to 160-170°. The product distilled off through a column and was trapped in a cooled receiver. It was distilled over sodium, and we isolated 13.5 g (59%) of (I); bp 68°; n_D^{20} 1.4079; d_4^{20} 0.8452. Found: C 71.32, 71.29; H 9.55, 9.51%. C_5H_8O. Calculated: C 71.39; H 9.59%.

From Divinyl Ether. (I) was prepared analogously to 2-chloroethyl cyclopropyl ether from 1 mole each of the Simmons-Smith reagents (the couple was prepared from 65 g of zinc dust and 4.5 g of copper acetate) and 63 g of divinyl ether (II) (as a 1 : 2 ethereal solution). (II) and methylene iodide were added at room temperature in the course of 6 h, and the mixture was stirred further for 30 h. The reaction product was steam-distilled off and dried with potassium carbonate; ether was distilled off through a column of 20-plate efficiency. From the residue after distillation over sodium we isolated 5.3 g (7%) of (I), identical in constants and in behavior in GLC to the sample prepared by the first method.

Raman Spectrum ($\Delta\nu$, cm^{-1}):* 176(0), 194(0), 208(1), 228(0), 252(1), 264(1), 283(0), 348(1), 364(0), 385(2b), 412(1), 444(1), 480(0), 505(1), 540(0), 549(0), 590(1b), 620(0), 670(1), 700(0), 716(1), 739(2), 770(1), 801(2), 812(1), 872(0), 897(1), 908(2), 933(0), 946(1), 962(1), 993(1), 1016(0), 1041(1b), 1068(0), 1094(0), 1103(1), 1127(1), 1158(2), 1190(2), 1214(5), 1236(0), 1244(0), 1272(1), 1286(1), 1410(1), 1446(1), 1550(0), 1612(4), 1633(3), 2783(3), 2783(5), 2934(1), 2963(1), 3017(5), 3046(3), 3056(1), 3081(3), 3094(3).

IR Spectrum (ν, cm^{-1}):† 695 w, 739 m, 817 v.w, 826 v.s, 908 m, 957 s, 993 s, 1012 s, 1036 m, 1072 v.w, 1097 w, 1128 m, 1158 s, 1192 s, 1212 s, 1318 m, 1942 m, 1408 w, 1444 m, 1516 s, 1612 s, 1630 sh, 1644 sh, 1896 w.

Hydrolysis of (I)

A mixture of 1 g of (I) and 4 ml of 2% H_2SO_4 was shaken periodically and kept at room temperature until it no longer separated into layers. The homogeneous solution obtained was salted out with potassium carbonate and dried over Na_2SO_4. According to analysis by means of GLC‡ the upper layer was a mixture of acetaldehyde and cyclopropanol (III), which had the same retention time as a sample of (III) prepared in a parallel experiment by the reduction of cyclopropyl acetate with lithium tetrahydroaluminate [3].

1,2,3,4,7,7-Hexachloro-5-cyclopropoxy-2-norbornene (IV)

A mixture of 5.46 g of hexachlorocyclopentadiene and 1.7 g of (I) was heated in presence of hydroquinone in a sealed tube in a boiling water bath for 3.5 h. In distillation we isolated 3.06 g (80.5%) of the adduct (IV); bp 122° (1 mm); n_D^{20} 1.5431. Found: C 33.87, 33.58; H 2.25, 2.28; Cl 59.39, 59.63% $C_{10}H_8Cl_6O$. Calculated: C 33.65; H 2.25; Cl 59.61%.

IR Spectrum (ν, cm^{-1}): 699 m, 711 m, 766 s, 790 s, 822 w, 844 s, 870 w, 917 m, 970 m, 998 m, 1012 m, 1023 m, 1037 m, 1066 m, 1103 m, 1120 m, 1175 v.s, 1219 s, 1268 sh, 1280 m, 1334 s, 1380 v.w, 1421 w, 1448 m, 1460 m, 1610 s, 2936 w, 2960 sh, 3000 sh, 3012 w, 3094 w.

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* In the Raman spectra relative visual intensities are given.

† IR spectra were determined with UR-10 and Leitz IR spectrometers. Denotations: w, weak; m, medium strength; s, strong; v.s, very strong; sh, shoulder.

‡ LKhM-5 instrument, 2-m column, solid phase INZ-600, liquid phase Tween 80 10%, carrier gas helium.

2-Cyclopropoxy-3,4-dihydro-2H-pyran (V)

A mixture of 3.6 g of (I) and 3.36 g of acrolein was heated in a steel ampule at 180° for 1.5 h. By distillation we isolated 4.04 g (66.2%) of the adduct (V); bp 76.5-77° (26 mm); n_D^{20} 1.4627; d_4^{20} 1.024. Found: C 68.43; 68.70; H 859; 8.70%. $C_8H_{12}O_2$. Calculated: C 68.54; H 8.63%.

IR Spectrum (ν, cm^{-1}): 756 w, 769 v.w, 782 m, 821 sh, 830 sh, 842 s, 862 w, 898 s, 920 s, 951 s, 976 s, 1003 s, 1024 s, 1060 v.s, 1077 sh, 1108 s, 1140 m, 1172 s, 1201 sh, 1220 v.s, 1230 v.s, 1249 m, 1321 w, 1350 s, 1368 m, 1405 w, 1460 m, 1660 s, 1694 sh, 1744 w, 1770 sh, 1830 v.w, 2858 m, 2890 sh, 2940 s, 2968 w, 3014 m, 3069 m, 3092 w.

Polymerization of (I)

A mixture of 3 g of (I) and 11 ml of dry heptane was stirred in a stream of argon at –70°, and two drops of boron trifluoride ether complex were added. The cooling bath was removed, and the mixture was brought to room temperature in the course of 2 h and was left for 10 h in an atmosphere of argon. The polymer was separated from heptane and dissolved in ether, precipitated with heptane, and vacuum-dried to constant weight. We obtained 1.9 g (63%) of polymer of mol.wt. 10,000 (determined cryoscopically).

IR Spectrum (ν, cm^{-1}): 699 s, 736 s, 770 m, 865 sh, 883 sh, 943 w, 1007 w, 1030 w, 1060 m, 1080 w, 1092 m, 1150 s, 1180 w, 1270 m, 1300 sh, 1311 v.s, 1377 w, 1455 m, 1476 m, 1592 w.

Cyclopropyl Acetate

This was prepared by the method described in [2]. After distillation through a column of 50-plate efficiency it had: bp 110° (735 mm); n_D^{20} 1.4091; d_4^{20} 0.9746.

Raman Spectrum ($\Delta\nu$, cm^{-1}): 145(1), 295(0), 355(4), 400(2), 448(2), 502(0), 528(0), 628(6), 711(0), 749(3), 819(3b), 879(7), 955(3), 992(3), 1025(3), 1094(1b), 1154(2b), 1171(2), 1208(7), 1228(2), 1356(2), 1372(1), 1416(2), 1452(2), 1741(4), 2942(3), 3017(4), 3054(2), 3092(2).

Divinyl Ether (II)

This was prepared by the method described in [8]; bp 28.5°; n_D^{20} 1.3980.

Raman Spectrum ($\Delta\nu$, cm^{-1}): 145(1), 218(0), 284(1b), 398(0), 453(2b), 508(3b), 578(0), 705(0), 848(3b), 939(0), 1111(0), 1186(0), 1298(10), 1322(100, 1382(2), 1624(3), 1641(7), 1667(5), 3035(2).

CONCLUSIONS

1. Cyclopropyl vinyl ether was synthesized, and some of its chemical and physical properties were investigated. The polymerization of the ether and diene condensations with it lead to the preparation of new cyclopropoxy compounds.

2. It was shown that the conjugation effects of the cyclopropyl and vinyl groups are transmitted through the ether oxygen atom and that divinyl and cyclopropyl vinyl ethers show rotational isomerism.

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