<u>5-Chloro-5-chloromethyl-3,3-dioxolan-4-one (V).</u> Into a reaction vessel with stirrer, thermometer, bubbler, and calcium chloride tube were inserted 10 g (0.1 mole) of compound IV [4], 20 ml carbon tetrachloride, and free-radical polymerization inhibitors. At  $-5^{\circ}$ C 7.5 g (0.107 mole) chlorine was passed in, and the mixture was maintained with stirring at room temperature for 4 h. Completion of reaction was determined chromatographically according to the disappearance of initial dioxolanone IV. The solvent was removed under vacuum, and 16.3 g (95%) crude dioxolanone V was obtained, which on heating decomposed with the formation of tarry products. In a subsequent synthesis it was used without purification.

<u>5-Chloromethylene-1,3-dioxolan-4-one (VII)</u>. Into a reaction vessel with stirrer, dropping funnel, thermometer, and calcium chloride tube were inserted 10.6 g (0.105 mole) triethylamine and 20 ml benzene. At 20-25°C a solution of 17.1 g (0.1 mole) dioxolanone V in 30 ml benzene was further added. The mixture was maintained for 5 h; then triethylamine hydrochloride salt was filtered off, and the filtrate was washed successively with 5% solutions of hydrochloric acid and sodium carbonate, and then with water. The solvent was removed, and 9.5 g (71%) was obtained, mp 7.52-73.0°C (from an ether-n-hexane mixture in the presence of grade A activated carbon). IR spectrum: 1817, 1805 cm<sup>-1</sup> (C=O), 1680 cm<sup>-1</sup> (C=C). Found: C 35.9; H 2.3; Cl 26.5%; MW 138.5. C<sub>4</sub>H<sub>3</sub>ClO<sub>3</sub>. Calculated: C 35.7; H 2.2; Cl 26.4%; MW 134.5.

## LITERATURE CITED

- 1. P. Salomaa and S. Laiho, Acta Chem. Scand., 17, 103 (1963).
- 2. M. I. Khramushina, V. R. Likhterov, V. S. Étlis, and D. K. Chuprov, USSR Inventor's Certificate No. 609,290; Byull. Izobret., No. 6, 215 (1984).
- 3. E. Bear and H. Fischer, J. Biol. Chem., <u>180</u>, 145 (1949).
- 4. V. R. Likhterov, V. S. Étlis, L. A. Balandina, and S. A. Arzhakov, USSR Inventor's Certificate No. 606,313; Byull. Izobret., No. 6, 215 (1984).

REACTION OF 2-METHYL-5,6-DIHYDRO-2H-PYRAN WITH DICHLOROCARBENE

UDC 547.811.542.955: 543.422:541.634

U. G. Ibatullin, T. F. Petrushina, R. R. Gataullin, and M. G. Safarov

Upon treatment of 2-methyl-5,6-dihydro-2H-pyran with dichlorocarbene there are formed products of addition to the double bond and insertion at the C-H bond giving cis- and trans-7,7-dichloro-2-methyl-3-oxabicyclo[4.1.0]heptane and 2-dichloromethyl-2-methyl-5,6-dihydro-2H-pyran.

The reaction of dihalocarbenes with alkenes usually yields the corresponding adduct via addition to the double bond (including 5- and 6-membered cyclic vinyl ethers [1, 2]).

We have found that three compounds are formed from 2-methyl-5,6-dihydro-2H-pyran (I) in 37% overall yield: cis- (III) and trans- (IV) 7,7-dichloro-2-methyl-3-oxabicyclo[4.1.0]- heptane and 2-dichloromethyl-5,6-dihydro-2H-pyran (V) in the ratio 1.0:5.7:3.3.



It can be proposed that the C-H insertion product appearing together with the adducts III and IV is due to the allyl structure of I, the same course of reaction having earlier been observed in the case of 2,5-dihydrofuran [3].

Bashkir State University, Ufa 450074. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 2, pp. 190-191, February, 1986. Original article submitted October 8, 1984; revision submitted May 16, 1985.

TABLE 1. Mass Spectra of the Products of Reaction of Dichlorocarbene with 2-Methyl-5,6-dihydro-2H-pyran\*

Compound	m/z value (% of maximum ion)
111	180 (0,3), 138 (5,8), 136 (9,8), 125 (10,4), 124 (16,2), 123 (16,5), 122 (26,5), 103 (5,6), 101 (21,0), 97 (6,3), 89 (5,4), 87 (18,7), 79 (6,6), 77 (7,0), 65 (20,8), 53 (5,0), 51 (9,6), 43 (100,0), 4i (21,0)
IV	180 (0,2), 145 (6,6), 138 (19,5), 136 (31,0), 125 (30,8), 124 (17,0), 123 (46,5), 122 (24,4), 115 (6,3), 103 (10,5), 101 (34,9), 89 (10,1), 87 (30,6), 79 (14,0), 77 (15,3), 71 (10,5), 65 (31,7), 53 (8,9), 51 (15,9), 43 (100,0), 41 (30,9)
v	167 (3,2), 165 (5,5), 98 (6,4), 97 (100,0), 79 (5,9), 77 (6,1), 65 (6,0), 53 (6,5), 43 (57,7), 41 (19,4)

## \*Ion peaks greater than 5% given.

It is known, however, that another allyl isomer (4-methyl-5,6-dihydro-2H-pyran (VI)) gives only the corresponding adduct in ~70% yield under the same conditions. In all probability the different behavior of dihydropyrans I and VI is due to the high lability of the 2H in pyran I as well as the lower reactivity of the di-substituted double bond when compared with the trisubstituted one in pyran VI.

The elemental composition of the mixture of III and IV agrees well with the empirical formula  $C_{7}H_{10}Cl_{2}O$ . In the PMR spectrum there are signals characteristic of the tetrahydropyran ring together with signals for the protons of the double bond (5.81 ppm) and the dichloromethyl group (5.52 ppm). The III/V mixture contains 35% of olefine (ozonolysis) pointing to the dihydropyran V.

Compounds III and IV are extremely unstable towards electron impact (molecular ion intensity 0.2-0.3%) and they break down by several routes. On the whole their mass spectra are very similar. The spectrum of dihydropyran V is significantly simpler and markedly different from III and IV. The molecular ion is absent but there are fragments at M-CH<sub>3</sub> (m/z 165 and 167) and for CHCl<sub>2</sub> (m/z 83 and 85). The most intensive peak is seen for M-CHCl<sub>2</sub> (m/z 97) (see Table 1).

In connection with the difficulty of separating III-V the stereochemistries are not established. However, as is known for norbornene [5], dichlorocarbene adds to six-membered olefines with a preferred formation of the trans isomer. Hence, in our case we can propose that the predominant product is trans-7,7-dichloro-2-methyl-3-oxabicyclo[4.1.0]heptane (IV)

## EXPERIMENTAL

GCMS analysis was carried out on a Finnegan-4021 instrument with glass capillary column (30 m  $\times$  0.25 mm, SE-30) with temperature programming from 50 to 180°C (5°C/min) at 68-70 eV and a scan velocity of 1 spectrum/second. PMR spectra were recorded in a Tesla BS-467C (80 MHz) instrument in CCl<sub>4</sub>. Double bond analysis was performed on an ADS-4M.

The reaction was carried out using the method [4] of generating dichlorocarbene from CHCl<sub>3</sub> under phase transfer catalytic conditions to give an isomer mixture in 37% yield with mp 97°C,  $n_D^{20}$  1.5010. Found: C 46.2; H 5.2; Cl 39.2%. C<sub>7</sub>H<sub>10</sub>Cl<sub>2</sub>O. Calculated: C 46.6; H 5.5; Cl 39.2%.

When the system potassium tert-butylate/chloroform was used the yield of products fell to 2%.

## LITERATURE CITED

- 1. E. E. Schweizer and W. E. Parham, J. Amer. Chem. Soc., 82, 4085 (1960).
- 2. J. C. Anderson and D. J. Lindsay, Tetrahedron, 20, 2021 (1964).
- 3. J. C. Anderson and C. B. Reese, Chem. Ind., No. 3, 575 (1963).
- 4. A. A. Gevorkyan, N. M. Khizantsyan, P. I. Kazaryan, and G. A. Panosyan, Khim. Geterotsikl Soedin., No. 2, 167 (1981).
- 5. V. Kirmse, Chemistry of Carbenes [Russian translation], Mir, Moscow, (1966), p. 201.