spectrum (CF_3COOH, HDMS): 3.20 (3H, singlet, NCH_3), 3.23 (3H, singlet, NCH_3), 4.02-4.90 ppm (5H, multiplet, SCH and $2NCH_2$).

2-[(8-Bromo-3-methyl-7-xanthinyl)methyl]-2,3-dihydro-8-methylthiazolo[2,3-f]xanthine (IIIc). The compound had mp >330°C (with decomposition, from acetic acid). Mass spectrum: m/z 482 and 480 ($M^{+\cdot}$).

The data of elemental analysis of compounds IIIa-c corresponded to the calculated values.

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REGIOSELECTIVE ADDITION OF DICHLOROCARBENE TO 2-VINYLOXY-3,4-DIHYDROPYRANS

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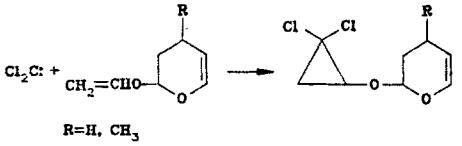
UDC 547.812.6'512:542.97'3

We have found that the reaction (temperature ~10°C, time ~2.5 h) between 2-vinyloxy-3,4-dihydropyrans and dichlorocarbene (generated from chloroform and the two-phase system CH_2Cl_2–50% NaOH) in the presence of triethylbenzylammonium chloride (TEBA) gives 3,4-dihydro-2-(2,2-dichlorocyclopropoxy)pyrans (the products of addition to the vinyloxy group) only:



Increasing the temperature and the reaction time failed to afford the products of addition to the endocyclic double bond. Omission of the methylene chloride from this system results in the partial formation of the diadduct.

To a mixture of 6.3 g of 2-vinyloxy-3,4-dihydropyran, 0.2 g of TEBA, 10 ml of CH_2Cl_2 and 16 ml of 50% NaOH was added at 10°C over 0.5 h with vigorous stirring a solution of 8 ml of chloroform in 10 ml of CH_2Cl_2. The mixture was stirred for 2 h at 10°C, and worked up in the usual way to give 5.95 g (57%) of 3,4-dihydro-2-(2,2-dichlorocyclopropoxy)pyran, bp 89°C (15 mm), n_D^{20} 1.4860, d_4^{20} 1.2370. PMR spectrum ($CDCl_3$), δ: 6.22 (1H, d, 6-H), 5.23 (1H, m, 2-H), 4.79 (1H, m, 5-H), 3.66 (1H, d.d, 1'-H), 1.92 (4H, m, 3- and 4-H), 1.62 ppm (2H, m, 3'-H). According to [1], bp 65°C (1 mm), n_D^{20} 1.4860, d_4^{20} 1.2368.

Obtained similarly was 3,4-dihydro-2-(2,2-dichlorocyclopropoxy)-4-methylpyran, bp 81°C (1 mm), n_D^{20} 1.4883, d_4^{20} 1.2312, yield 49%. PMR spectrum ($CDCl_3$), δ: 6.17 (1H, d, 6-H), 5.37 (1H, m, 2-H), 4.60 (1H, m, 5-H), 3.60 (1H, d.d, 1'-H), 1.87 (3H, m, 3- and 4-H), 1.58 (2H, m, 3'-H), 1.07 ppm (3H, d, 4-CH_3).

Elemental analytical data agreed with that calculated.

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CYCLIZATION OF 3-HYDROXY-3-ALKYL-2-(2-HYDROXYETHYLTHIO)-1-BUTENECARBONITRILES TO 5-AMINOFURAN-3-ONES

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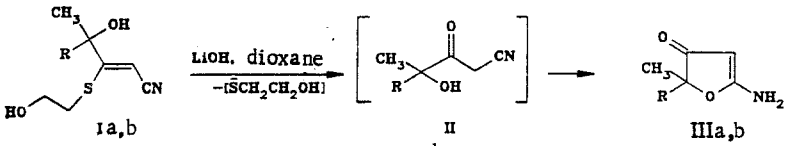
UDC 547.722.6.07'339'269.1.04

3-Hydroxy-3-methyl-2-propylthio-1-butenecarbonitrile, obtained by the reaction between tertiary cyanoacetylenic alcohols and propanethiol, is highly stable, and does not undergo changes (isomerization or cyclization) either on keeping or on heating [1].

We have found that the sulfides (I), obtained from the same cyanoacetylenic alcohols and 2-mercaptoethanol, are very different in their chemical properties and undergo intramolecular cyclization to give, instead of the expected 1,3-oxathiolanes or iminodihydrofurans [2, 3], the 5-amino-2,2-dialkyl-2,3-dihydrofuran-3-ones (III).



Ia,b II IIIa,b

I, III a R=CH_3; b R=C_2H_5

An intermediate in the conversion of (I) into (III) appears to be the hydroxyketonitrile (II), formed by hydrolytic cleavage of the sulfide moiety. A similar cyclization has been observed when (I) is kept at room temperature (50 days).

5-Amino-2,3-dihydro-2,2-dimethylfuran-3-one (IIIa). A mixture of 0.3 g (1.6 mmole) of the sulfide (Ia), 0.03 g of LiOH, and 6 ml of dioxane was stirred for 3 h at 50°C. The dioxane was then removed under reduced pressure, and the residue dissolved in acetone and the solution filtered. Removal of the acetone gave 0.1 g (50%) of the aminofuranone (IIIa), mp 228-230°C (sublimes). ^{1}H NMR spectrum (DMSO-D_6), δ: 7.76 (2H, s), 4.28 (1H, s), 1.29 ppm (6H, s). ^{13}C NMR spectrum (DMSO-D_6): 178.29 [$C_{(5)}$], 87.87 [$C_{(4)}$], 198.17 [$C_{(3)}$], 75.79 [$C_{(1)}$], 23.51 ppm (CH_3). IR spectrum (chloroform): 980...1050 (C–O–C), 1600 (C=CH), 1680 (C=O), 3420, 3450 cm^{-1} (NH_2).

5-Amino-2,3-dihydro-2-methyl-2-ethylfuran-3-one (IIIb) was obtained similarly in 68% yield, mp 205-206°C (sublimes). PMR spectrum (DMSO-D_6), δ: 7.80 (2H, s), 4.30 (1H, s), 1.50 (2H, q), 1.30 (1H, s), 0.99 ppm (3H, t). IR spectrum (chloroform): 980...1070 (C–O–C), 1600 (C=CH), 1680 (C=O), 3420, 3450 cm^{-1} (NH_2).

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