chromatographed on a KSK column (chloroform). The second fraction was collected and yielded 0.63 g (57.7%). Found: C 56.2; H 5.7%; $M^{+\cdot}$ 363. $C_{17}H_{21}N_3O_4S$. Calculated: C 56.2; H 5.8%; M 363.

γ-(2-Methyl-5-methoxybenzofuryl-3)butyric acid (XV) was prepared in the same way as compound III; yield 67%, mp 79-81°C. Found: C 67.8; H 6.5%; $M^{+\cdot}$ 248. $C_{14}H_{16}O_4$. Calculated: C 67.7; H 6.5%; M 248.

Lactone of γ-(2-methyl-5-methoxybenzofuryl-3)-γ-hydroxybutyric acid (XVI) was obtained from compound X, using the same conditions as for the preparation of compound IV, in 50.4% yield, mp 116-117°C (from methanol). Found: C 62.2; H 5.5%; $M^{+\cdot}$ 246. $C_{14}H_{14}O_4$. Calculated: C 68.3; H 5.7%; M 246.

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DIPOLAR ADDITION OF DIAZOMETHANE TO 5-METHYLENE-1,3-DIOXOLAN-4-ONE

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UDC 547.729.7'772.2'642

The reactions of 1-pyrazoline-3-spiro-4'-(1',3'-dioxolan-5'-one) were studied; this compound is the product of the 1,3-dipolar addition of diazomethane to 5-methylene-1,3-dioxolan-4-one. Depending on the conditions, thermolysis of the spiro compounds proceeds either with destruction of the pyrazoline ring, or with cleavage of the dioxolane ring, followed by rearrangement to give 1(2)-hydroxymethyl-3(5)-pyrazolecarboxylic acid.

The formation of a cyclic compound by the 1,3-dipolar addition of a diazoalkane addend to a vinylidene compound, in which one carbon atom is substituted with two groups with opposing mesomeric effects, proceeds readily [1, 2].

Of interest is the dipolar addition to 5-methylene-1,3-dioxolan-4-one (I) which we reported earlier [3]; in this compound, the gem-substituents at the carbon–carbon double bond are component parts of a heterocyclic ring, and exert identical I- and opposite M-effects.

The reaction of diazomethane with compound I proceeds smoothly even at room temperature. The first product of cyclization is 1-pyrazoline-3-spiro-4'-(1', 3'-dioxolan-5'-one) (II); the structure of this compound, which is obtained in high yield, was confirmed by elemental analysis and infrared spectroscopic data. It is known that in the formation of 3,3-disubstituted pyrazolines, the N=N bond is usually retained [1, 2, 4]. The infrared spectrum of the spirane II shows absorption due to stretching vibrations at 1565 cm^{-1} (N=N) [5] and at 1810 cm^{-1} (C=C) [6], while no absorption is seen in the region 3270-3305 cm^{-1} (NH) [5].

Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 9, pp. 1182-1184, September, 1985. Original article submitted October 2, 1984.

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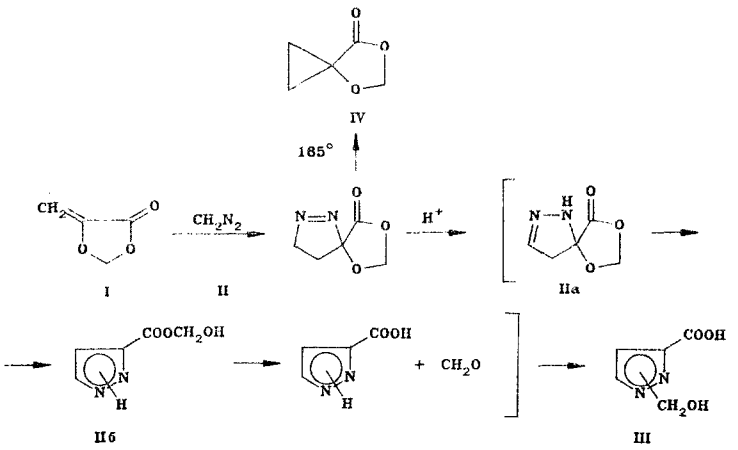

The spirane II is a colorless liquid which can be distilled in vacuum. On heating to 55°C in the presence of an acid, or on standing at room temperature for 7 days, it is converted to 1(2)-hydroxymethyl-3(5)-pyrazolecarboxylic acid (III), the structure of which was confirmed by elemental analysis, IR spectroscopy, and by proving its identity with material obtained by an alternate route. The infrared spectrum contains a band at 1695 cm^{-1} (C=O), characteristic of dimeric aromatic and vinylic acids.

The formation of compound III apparently proceeds via the prototropic isomerization of the spiran II to give the intermediate IIa. Under the action of acids, 3,3-disubstituted 1-pyrazolines are known to rearrange to the isomeric 5-pyrazolines, which are stable compounds [4]. However, the presence of a halogen, methoxy, or acetoxy group at position 3 facilitates the splitting off of a hydrogen halide, methyl alcohol or acetic acid to give the ester of 3(5)-pyrazolecarboxylic acid [1, 2]. It is proposed that the dioxolanone ring of compound IIa is opened at the acetal oxygen-spiroatom bond, and that the activating effect of the carbonyl group assists in the separation of a proton to the pyrazoline ring; the intermediate unstable hydroxymethyl ester IIb then splits to give an equimolar mixture of 3(5)-pyrazolecarboxylic acid and formaldehyde. This assumption is supported by the reported [7] instability of hydroxymethyl esters of carboxylic acids. On the other hand, pyrazoles unsubstituted at the nitrogen atom react smoothly with formaldehyde to form 1-hydroxymethyl derivatives [8]. The reaction of 3(5)-pyrazolecarboxylic acid with formaldehyde apparently takes place in the same way to give compound III.

To verify this, we carried out the reaction between 3(5)-pyrazolecarboxylic acid and formalin at room temperature and obtained compound III in high yield. The infrared spectrum of the compound obtained from the spiran II, was identical with that of an authentic sample.

It is known that 3,3-disubstituted pyrazolines, when heated to 150-200°C, are converted to cyclopropane derivatives, resulting from the splitting off of a nitrogen molecule [1, 9, 10]. Under these conditions, the spiran II is converted to 1,3-dioxolan-5-one-4-spirocyclopropane (IV) in high yield. In order to avoid the explosive evolution of nitrogen during the reaction, the spiran II was added in small portions of the heated reaction vessel, in which were first placed small pieces of porcelain.

The presence of the dioxolane ring was confirmed by the infrared spectrum which contains a peak at 1810 cm^{-1} (C=O) and a group of four peaks at 1310-880 cm^{-1}. It is a colorless, readily distilled liquid, which on hydrolysis gave 1-hydroxycyclopropanecarboxylic acid (V), analogous to that previously prepared [11] from 1,2-bis(trimethylsiloxy)-1-cyclobutene.

EXPERIMENTAL

Infrared spectra were taken on a UR-20 spectrophotometer: liquids were prepared as thin films between KBr plates, solids in KBr pellets.

1-Pyrazoline-3-spiro-4'-(1',3'-dioxolan-5'-one) (II). A solution of 4.4 g (105 mmoles) of diazomethane [12] in 180 ml of ether at 0°C was added to 10 g (100 mmoles) of the dioxolanone I [3] in 20 ml of diethyl ether, and the mixture allowed to stand at room temperature for 24 h. The solvent was removed at 45°C and the residue distilled *in vacuo* on a warm water bath at a temperature below 97°C to give 12.1 g (85%) of the spiran II, bp 82-83°C (1.33 hPa),

n_D^{20} 1.4740. Found: C 42.6; N 20.1%; M 139.5. $C_5H_6N_2O_3$. Calculated: C 42.2; H 4.2; N 19.8%; M 142.0.

1(2)-Hydroxymethyl-3(5)-pyrazolecarboxylic Acid (III). A. To a reaction vessel, fitted with a stirrer and reflux condenser, was added 14.2 g (100 mmoles) of the spiran II, 30 ml of benzene, and a few drops of acetic acid. The mixture was heated at 50-55°C for 4 h. The crystalline material which separated out on cooling was filtered off to yield 13 g (91%) of III, mp 158.5-159°C (from water). Found: C 42.5; N 4.6; N 20.2%; E 144. $C_5H_6N_2O_3$. Calculated: C 42.2; H 4.2; 19.8%; E 142.

B. To a solution of 0.28 g (2.5 mmoles) of 3(5)-pyrazolecarboxylic acid obtained by the hydrolysis of 3(5)-carboxymethoxypyrazole [2], in 9 ml of water, was added 0.2 ml (2.5 mmoles) of a 37% solution of formalin. The mixture was kept at room temperature for 18 h, and the water then removed *in vacuo* at 50°C to give 0.7 g (98%) of III, mp 159-160°C (from water). A sample on admixture with a sample obtained by method A gave no melting point depression.

1,3-Dioxolane-5-one-4-spirocyclopropane (IV). Some small pieces of porcelain were placed in a reaction vessel fitted with a dropping funnel, reflux condenser with water trap, and thermometer. The vessel was placed in an oil bath at 165°C, and 11.5 g (84 mmoles) of the spiran II was added dropwise over a period of 1 h. The reaction was complete when the evolution of nitrogen ceased. When cool, the reaction product was distilled *in vacuo* to give 7.2 g (89%) of IV, bp 38°C (4 gPa), n_D^{20} 1.4459, d_4^{20} 1.1790. Found: C 52.9; H 5.2%; M 117. $C_5H_6O_3$. Calculated: C 52.6; H 5.3%; M 114.

1-Hydroxycyclopropanecarboxylic Acid (V). A mixture of 1.14 g (10 mmoles) of IV and 6 ml of 10% NaOH solution was heated at 50°C for 30 min, cooled, acidified with 10% HCl to pH 3, and extracted with ether (5 × 5 ml). The ether extract was dried over Na_2SO_4, and the solvent evaporated at 45°C to give 0.87 g (85%) of the acid V, mp 107-108°C (from toluene); literature 105-108°C [11].

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