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+ 363. C17H21N3O4S. Calculated: C 56.2; H 5.8%; M 363.

\( \gamma \)-(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+ 248. C14H10O4. Calculated: C 67.7; H 6.5%; M 248.

Lactone of \( \gamma \)-(2-methyl-5-methoxybenzofuryl-3)-\( \gamma \)-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+ 246. C14H14O4. Calculated: C 68.3; H 5.7%; M 246.

LITERATURE CITED

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

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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-di-substituted pyrazolines, the N=N bond is usually retained [1, 2, 4]. The infrared spectrum of the spirene II shows absorption due to stretching vibrations at 1565 cm\(^{-1}\) (N=N) [5] and at 1810 cm\(^{-1}\) (C=O) [6], while no absorption is seen in the region 3270-3305 cm\(^{-1}\) (NH) [5].

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-spiro-cyclopropane (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-hydroxycyclopropanecarb0xylic 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),