

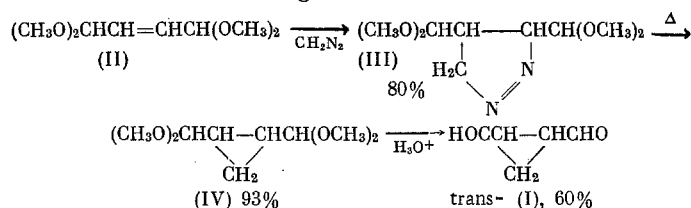
SYNTHESIS OF 1,2-DIFORMYLCYCLOPROPANE

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1,2-Diformylcyclopropane (I) is of considerable interest as the starting product for the synthesis of various symmetrical and unsymmetrical functionally substituted cyclopropanes, especially with unsaturated side chains. However, up to now this compound has been difficultly available and hardly studied, although the synthesis of (I) was attempted in [1, 2].

The trans (I) was synthesized in the following manner:



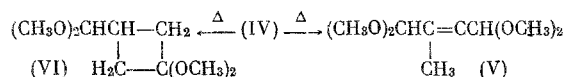
The available bis-dimethyl acetal of fumaraldehyde (II) [3] is reacted with CH_2N_2 in ether at $\sim 20^\circ\text{C}$ for 10–15 days to give the bis-dimethyl acetal of 3,4-diformyl- Δ^1 -pyrazoline (III) in 75–80% yield. The structure of (III) was confirmed by the NMR spectrum, in which were detected signals that correspond to the protons of the OCH_3 groups at 3.21 and 3.39 ppm, the CH_2 group at 4.42 and 4.52 ppm, and the CH groups in the 1.98–2.37 ppm region (multiplet); 3.70 and 3.79; 3.99 and 4.04; 4.10, 4.16, 4.18, and 4.20 ppm in a ratio of 12:2:1:1:1:1. Acids isomerize (III) to the bis-dimethyl acetal of 3,4-diformyl- Δ^2 -pyrazoline, the structure of which was also confirmed by the NMR spectrum: signals at 3.25 and 3.30 ppm, and a multiplet in the 3.34–3.50 ppm region; 3.84; 3.97; 4.05; 4.18 ppm (2 doublets) and 5.35 ppm (singlet); 5.98 and 6.00 ppm in a ratio of 12:2:2:1:1, corresponding to the protons of the OCH_3 , CH_2 , CH, and NH groups. The attempted acid hydrolysis of the Δ^2 -pyrazoline to the corresponding dialdehyde proved unsuccessful, and the Δ^2 -pyrazoline was recovered unchanged.

The pyrolysis of (III) was run under the conditions described for the diethyl acetal of 4-formyl- Δ^1 -pyrazoline [4], i. e., at 450°C and 2–3 mm of pressure. Under these conditions the yield of the product was 93%. Based on the composition, the product corresponded to the formula $\text{C}_9\text{H}_{18}\text{O}_4$, and, based on the GLC data, besides the main component (76%), included two minor components (amount 18 and 6%). Analysis of the NMR spectrum of a sample revealed that the main component of the mixture is the sought bis-dimethyl acetal of 1,2-diformylcyclopropane (IV) (signals of the protons of the cyclopropane ring in the 0.48–0.60 and 0.92–1.12 ppm regions (multiplets) and the signals of the protons of the $\text{CH}(\text{OCH}_3)$ groups in the 4.03 and 4.10 ppm regions in a 4:2 ratio; the signal of the protons of the OCH_3 groups in the 3.20 ppm region). The minor components apparently are the bis-dimethyl acetal of 2-methyl-2-butendial (V) (signals of protons of CH_3 groups in 1.57 and 1.60 ppm regions, signals of the $=\text{CH}$ protons in the region 5.02; 5.14; 5.44; 5.54 ppm (2 doublets), signals of the protons of $(\text{CH}_3\text{O})_2\text{CH}$ in the 4.40 and 4.96 ppm regions in a 3:1:2 ratio, and the signals of the protons of the OCH_3 group in the 3.20 ppm region) and the bis-dimethyl acetal of 1-formyl-3-cyclobutanone (VI) (signals of the protons of the CH_2 group in the regions 2.34 and 2.60; 2.85; 2.88 ppm, signals of the protons of the $\begin{array}{c} \text{CH} \\ \diagup \\ \text{CH} \end{array}$ grouping at 4.88 and 4.96 ppm in a 4:2 ratio, and the signals of the protons of the OCH_3 groups in the 3.20 ppm region). Compounds (V) and (VI) can be formed by

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the thermal cleavage and isomerization of (III) and (IV). Reactions of this type are widely known for cyclopropanes [5, 6].



The hydrolysis of (IV) could be accomplished by heating with 6% H_3PO_4 solution, with a simultaneous removal of the formed methanol by distillation. The conditions recommended in [4] for the hydrolysis of the bis-diethyl acetal of 1-formylcyclopropane by heating with 1 N aqueous trichloroacetic acid solution for 5-6 h proved to be unsuitable for (IV), which decomposes here. A complex mixture was obtained as a hydrolysis result, which could not be separated by fractional distillation, although the main component of the mixture was the sought (I). Besides (I), the mixture contained 2-methyl-2-butenal (VII), 1-formyl-3-cyclobutanone (VIII), and apparently the partial hydrolysis products of the acetals. This composition of the mixture is confirmed by its IR, UV, NMR, and mass spectra.

The IR spectrum of the mixture had absorption bands in the regions 1708 cm^{-1} (α, β -unsaturated aldehyde (VII) and (or) its monoacetal) and 1725 cm^{-1} [dialdehyde (I)], and a weak band at 1770 cm^{-1} [(VIII) and (or) its monoacetal].

In the NMR spectrum were detected the signals of the protons of (I) (0.98-1.23 and 1.42-1.70 ppm (multiplets) and 9.20; 9.21; 9.24; 9.25 ppm (doublets) in a 2:2:2 ratio, which belong to the cyclopropane ring and the CHO groups), the signals of the protons of (VII) at 2.12 and 2.14 ppm (singlets), 6.40; 6.41; 6.44; 6.46 and 6.51; 6.52; 6.55; 6.57 ppm (doublets); 9.63 and 10.02; 10.04 ppm in a 3:1:1:1 ratio, which belong to the CH_3 , CH, and CHO groups. In addition the NMR spectrum contains signals at 3.26 ppm, which belong to the OCH_3 groups, 9.49 ppm, which can be assigned to $\text{HOC}-\underset{\text{CH}_3}{\text{C}}=\text{CH}-\text{CH}-(\text{OCH}_3)_2$, and 2.25-2.52

ppm (multiplet), and also a poorly resolved quartet at 9.52, 9.57, 9.55, and 9.60 ppm, which evidently belong to the protons of the CH_2 and CHO groups in compound (VIII). The presence of (VII) as an impurity is also detected by the absorption in the UV spectrum ($\lambda_{\text{max}} 225\text{ nm}$ ($\epsilon 3320$), in alcohol). Analysis of the mass spectrum of the hydrolysis product of (IV) indicates that the mixture contains, besides the components with mol. wt. 98 [mainly (I), contaminated with (VII) and (VIII)], the starting diacetal (IV) as impurity, and also (V) and (VI) ($m/e 159$), and possibly the monoacetal ($m/e 113$).

From the ratio of the integral intensities of the aldehyde protons in the NMR spectrum the amount of aldehydes in the mixture can be approximately estimated to be 77% of (I), 14% of (VII), 3% of (VIII), and 6% of unidentified aldehydes, apparently the partial hydrolysis products of the bis-acetals. Employing GLC [Khrom-2, 50 m \times 0.3 mm capillary column, poly(ethylene glycol)], four components are also detected in the mixture of hydrolysis products, of which one is the main component, while the other three are present in small amount, with a close retention time, which does not permit determining the amount of the components with sufficient accuracy.

Compound (I) was converted by oxidation with aqueous KMnO_4 solution to the known trans-1,2-cyclopropanedicarboxylic acid [7], which serves as chemical proof for the configuration of I.

EXPERIMENTAL

Bis-dimethyl acetal of 3,4-Diformyl- Δ^1 -pyrazoline (III). An ether solution (0.13 mole) of CH_2N_2 was added in drops to a stirred and ice-cooled solution of fumaraldehyde diacetal (0.065 mole) in ether. The stirring was continued for 1.5 h, and the other solution was poured into a cooled vessel, sealed tightly, and allowed to stand at $\sim 20^\circ\text{C}$ for 10-15 days. After distilling off the solvent the residue was vacuum-distilled. We obtained (III) in 80% yield, bp $102-104^\circ\text{C}$ (0.2 mm); $n_D^{20} 1.5405$. Infrared spectrum (CCl_4): 1560 cm^{-1} ($-\text{N}=\text{N}-$). Found: C 49.53; H 8.37; N 12.95%; mol. wt. 218. $\text{C}_9\text{H}_{18}\text{O}_4\text{N}_2$. Calculated: C 49.53; H 8.31; N 12.84%.

Bis-dimethyl Acetal of 1,2-Diformylcyclopropane (IV). A sample of (III), heated in advance, was placed in a dropping funnel, equipped with a tube for equalizing the pressure, which was installed in the upper part of a column, filled to a height of 20 cm with broken Pyrex glass. A trap with a coil, cooled in ice, was connected to the lower part of the column, followed by another trap, which was cooled in Dry Ice. The column was heated up to 450°C , the residual pressure in the system was established at 2-3 mm, and pyrazoline (III) was slowly added in drops. The obtained mixture of pyrolysis products was vacuum-distilled at $75-77^\circ\text{C}$ (7 mm); $n_D^{19} 1.4320$; mol. wt. 190; yield 93%.

1,2-Diformylcyclopropane (I). With vigorous stirring, excess 6% H_3PO_4 solution was added to the bisdimethyl acetal of 1,2-diformylcyclopropane (IV), which was heated on the steam bath. The methanol began to distill in 2-3 min. After distilling off the alcohol the stirring was continued for another 30 min. The flask contents were cooled, solid CaCO_3 and CH_2Cl_2 were added, the mixture was stirred for 40 min, filtered, separated, and dried over MgSO_4 . The solvent was distilled off, and the residue was vacuum-distilled. We obtained (I) in 60% yield, bp $71-73^\circ\text{C}$ (7 mm), n_D^{16} 1.4728. Found: C 61.50; H 6.40%; mol. wt. 98. $\text{C}_5\text{H}_6\text{O}_2$. Calculated: C 61.21; H 6.17%.

trans-1,2-Cyclopropanedicarboxylic Acid. With stirring, a solution of 1.9 g (0.012 mole) of KMnO_4 in 75 ml of water was added in drops to 0.57 g (0.006 mole) of (I) in 25 ml of water, and the mixture was allowed to stand overnight. Then it was filtered, the filtrate was evaporated to 1/4 volume, diluted with methanol until colorless, extracted with ether (50 ml \times 2), the ether was evaporated, and the residue was recrystallized from hexane. We obtained trans-1,2-cyclopropanedicarboxylic acid with mp 172°C (literature data, mp 175°C).

CONCLUSIONS

A convenient method was developed for the synthesis of trans-1,2-diformylcyclopropane.

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