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SYNTHESIS OF 5-ALKENYL-1,3-DIOXANES

E. T. Lesnikova, S. S. Zlotskii, and D. L. Rakhmankulov

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Cyclic acetals containing alkenyl groups were obtained from 5-methyl-5-acyl-1,3-dioxane. The 1,3-dioxane fragment does not interfere in reduction of the carbonyl group, nor in participation of the carbonyl group in Wittig and Grignard reactions.

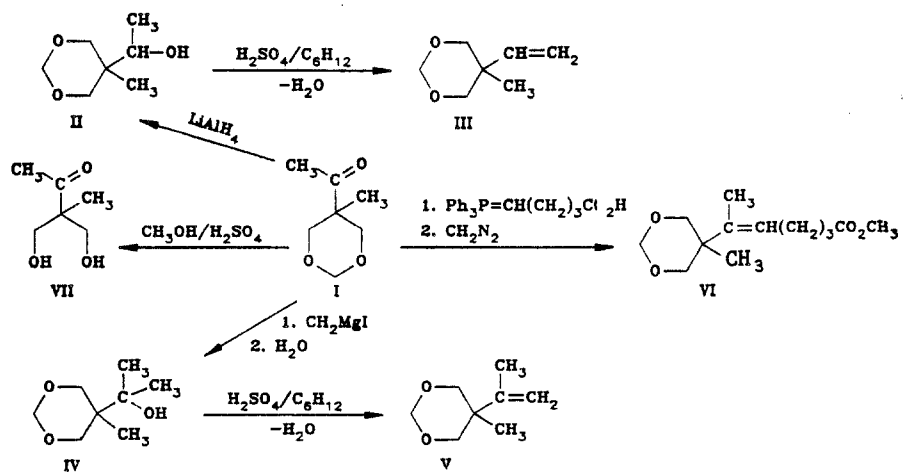
The synthesis of 2- and 4-alkenyl-1,3-dioxanes by acetalization of unsaturated aldehydes and by condensation of dienes with formaldehyde, respectively, has been described [1-3].

Because these compounds have been found to be of interest in the preparation of homo- and copolymers, the purpose of the present investigation is the development of different methods for preparation of cyclic acetals containing unsaturated substituents.

We synthesized 1,3-dioxanes containing alkenyl groups in the 5 position from a product of the condensation of methyl ethyl ketone with formaldehyde, namely 5-methyl-5-acyl-1,3-dioxane (I) [4].

The reduction of dioxane I to 5-methyl-5-(α-hydroxyethyl)-1,3-dioxane (II) and subsequent dehydration gave 5-methyl-5-vinyl-1,3-dioxane (III). In a reaction with CH_3MgI, ketone I formed tertiary alcohol 5-methyl-5-(α-methyl-α-hydroxyethyl)-1,3-dioxane (IV) in quantitative yield, and acid dehydration of (IV) gave 5-methyl-5-isopropenyl-1,3-dioxane (V). Wittig's reagent was used to obtain 5-methyl-5-[α-(methyloxycarbonylbutylidene)ethyl]-1,3-dioxane (VI).

During dehydration of dioxane alcohols II and IV, ring cleavage was practically not observed, and 3,3-bis(hydroxymethyl)-2-butanone (VII) was obtained in low yield (24%) only during acid methanolysis of I.



According to the obtained data, the cycloacetal fragment does not interfere in the occurrence of conversions at side functional groups, and 5-acyl-1,3-dioxanes can be used in the synthesis of polyfunctional cyclic acetals.

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EXPERIMENTAL

A Tesla BS-567 instrument was used to record PMR spectra in $CDCl_3$, and the standard was TMS. The IR spectra were obtained on a UR-20 spectrometer in a thin layer. The obtained compounds were purified by distillation in vacuo or by column chromatography on SiO_2. The purity of the products was analyzed on a Chrom-4 gas-liquid chromatograph [flame-ionization detector, Chromaton-N-AW-DMCS (0.200-0.250 mm) impregnated with 5% SE-30 liquid phase, column length 2000 mm, carrier gas He (40 ml/min), and vaporizer temperature 300°C].

5-Methyl-5-acyl-1,3-dioxane (I) was obtained by the method of [4], and the bp, n_D^{20}, and PMR and IR spectra agreed with the data of [4].

5-Methyl-5-(α-hydroxyethyl)-1,3-dioxane (II, $C_7H_{14}O_3$). In an Ar atmosphere, 9 g (70 mmoles) of dioxane I in 20 ml of ether was added to a suspension of 2.75 g (72 mmoles) of $LiAlH_4$ in 300 ml of absolute ether cooled to 0°C. The course of the reaction was followed by thin-layer chromatography (R_f 0.29, in a hexane–ethyl acetate system, 1:1). After 30 min, the reaction mixture was treated with 150 ml of a saturated NH_4Cl solution. The organic layer was separated and dried with $MgSO_4$, and the solvent was evaporated. The residue was distilled in vacuo. We obtained 7.6 g (85%) of compound II with bp 81-82°C (1 mm). IR spectrum: 3470, 1180, 1050, and 940 cm^{-1}. PMR spectrum: 0.83 (3H, singlet, CH_3), 1.14 (3H, doublet, CH_3CH), 3.09 (1H, singlet, OH), 3.45 and 4.08 (4H, two multiplets, CH_2), 3.71 (1H, singlet, CHOH), 4.79 ppm (2H, quartet, OCH_2O).

5-Methyl-5-vinyl-1,3-dioxane (III, $C_7H_{12}O_2$). To a solution of 3 g (20 mmoles) of dioxane II in 100 ml of absolute cyclohexane was added 1 drop of concentrated H_2SO_4. The reaction mixture was boiled with a Dean–Stark attachment for 15 h and washed with a 5% $NaHCO_3$ solution to pH 7, and the organic layer was separated, dried with $MgSO_4$, and evaporated. The residue was purified by column chromatography on SiO_2 (500 × 30-mm column, hexane–ethyl acetate eluent, 1:1, and R_f 0.6). We obtained 1.9 g (63%) of dioxane III. IR spectrum: 1180, 1050, and 950 cm^{-1}. PMR spectrum: 0.73 (3H, doublet, CH_3), 3.08-3.94 (6H, multiplet, CH_2), 4.56 (2H, multiplet, C = CH_2), 4.92 ppm (1H, triplet, C = CH).

5-Methyl-5-(α-methyl-α-hydroxyethyl)-1,3-dioxane (IV, $C_8H_{16}O_3$). To a suspension of 1.5 g (62 mmoles) of Mg chips in 100 ml of absolute ether was added dropwise with stirring 7.75 g (55 mmoles) of CH_3I in 20 ml of ether at a rate such that boiling of the ether was maintained. After completion of addition of CH_3I, the mixture was heated for 30 min more until complete dissolution of Mg, the solution was cooled to 20°C, and a solution of 3.6 g (28 mmoles) of I in 10 ml of absolute ether was added. The course of the reaction was followed by thin-layer chromatography (R_f 0.37 and hexane–ethyl acetate eluent, 1:1). After 30 min, 20 g of ice was added to the reaction mixture, which was neutralized with a saturated NH_4Cl solution until complete dissolution of the precipitate. The organic layer was separated, dried with $MgSO_4$, and evaporated, and the residue was chromatographed on SiO_2 (600 × 25-mm column, hexane–ethyl acetate eluent, 1:1, and R_f 0.26). We obtained 3.5 g (95%) of compound IV. IR spectrum: 3490, 1190, 1050, and 950 cm^{-1}. PMR spectrum: 1.12 (3H, singlet, CH_3), 1.19 (6H, singlet, CH_3), 2.16 (1H, singlet, OH), 3.63 and 4.03 (4H, two doublets, CH_2), 4.79 ppm (2H, quartet, OCH_2O).

5-Methyl-5-isopropenyl-1,3-dioxane (V, $C_8H_{14}O_2$). To a solution of 2.5 g (16 mmoles) of dioxane IV in 70 ml of absolute cyclohexane was added 1 drop of concentrated H_2SO_4. The reaction mixture was boiled with a Dean–Stark attachment for 3 h, cooled, washed with 50 ml of a 5% $NaHCO_3$ solution, dried with $MgSO_4$, and evaporated, and the residue was purified by chromatography on SiO_2 (hexane–ethyl acetate eluent, 1:1, and R_f 0.71). We obtained 1.8 g (75%) of compound V. IR spectrum: 3090, 2975, 1645, 1180, 1055, and 950 cm^{-1}. PMR spectrum: 1.18 (3H, singlet, CH_3), 1.74 (3H, singlet, CH_3), 3.75 (4H, quartet, CH_2), 4.76 (2H, multiplet, OCH_2O), 4.9 ppm (2H, singlet, C=CH_2).

5-Methyl-5-[α-(methyloxycarbonylbutylidene)ethyl]-1,3-dioxane (VI, $C_{13}H_{22}O_4$). In an Ar atmosphere, 30 ml of a 0.5 N sodium hexamethyldisilazide solution was added to a suspension of 3 g (8.4 mmoles) of (4-carboxybutyl)triphenylphosphonium bromide in 6 ml of benzene with intensive stirring, the whole was heated for 30 min at 70°C, 0.18 g (1.4 mmoles) of dioxane I in 1 ml of benzene was added, and the heating was continued for 3 h. Completion of the reaction was followed by thin-layer chromatography according to the disappearance of starting ketone I. The reaction mixture was cooled and decomposed with 30 ml of a saturated NH_4Cl solution. The organic layer, containing impurities, was separated. The aqueous layer was acidified with 1 N HCl to pH 6, extracted with ether (50 ml) and chloroform (3 × 50 ml), the extract was dried with $MgSO_4$, and the solvent was evaporated. The residue was treated with an ether solution of diazomethane, the solvent was evaporated, and the residue was purified by chromatography on SiO_2 (500 × 20-mm column, hexane–ethyl acetate eluent, 1:1, and R_f 0.63). We obtained 0.1 g (53%) of dioxane VI. IR spectrum: 1740, 1180, 1050, and 950 cm^{-1}. PMR spectrum: 0.96 (3H, singlet, CH_3), 1.15 (3H, doublet, CH_3–C = CH_2), 1.35-2.56 (6H, multiplet, CH_2), 3.67 (3H, singlet, CH_3CO), 4.4 (2H, quartet, CH_2), 4.9 ppm (3H, multiplet, OCH_2O and C = CH).

3,3-Bis(hydroxymethyl)-2-butanone (VII). To a solution of 3.6 g (28 mmoles) of dioxane I in 50 ml of a 10:1 methanol–water mixture was added 0.1 ml of concentrated H_2SO_4. The reaction mixture was heated with distillation at 40-42°C for 15 h. Then the solvent was driven off, and the residue was chromatographed on SiO_2 (600 × 30-mm column, hexane–ethyl acetate eluent, 1:1, and R_f 0.13). We obtained 0.8 g (24%) of compound VII. IR spectrum: 1740 and 3290 cm^{-1}. PMR spectrum: 1.0 (3H, singlet, CH_3), 2.25 (3H, singlet, CH_3CO), 3.64-3.99 ppm (6H, multiplet, CH_2, OH).

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LUMINESCENCE-SPECTRAL AND ACID-BASE CHARACTERISTICS OF 3-ARYL-7-DIETHYLAMINOCOUMARINS

N. S. Patalakha, D. S. Yufit, M. A. Kirpichenok, N. A. Gordeeva, Yu. T. Struchkov, and I. I. Grandberg

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The absorption and fluorescence spectra and the acid-base characteristics of 7-diethylaminocoumarins containing an aromatic substituent at position 3 and H, Cl, CH_3, CF_3, and $N(CH_2CH_2)_2O$ at position 4 were studied. For the para-substituted derivatives a linear correlation was obtained between the pK_a values and the Hammett σ_p constants. On the basis of the obtained data, and also of an x-ray crystallographic investigation of 3-phenyl-4-methyl-7-diethylaminocoumarin it was concluded that there is weak π–π conjugation between the 3-aryl groups and the coumarin fragment.

Earlier we reported the synthesis of a series of 3-aryl-7-diethylaminocumarins by means of photochemical substitution reactions [1, 2]. It is known that the 3-aryl derivatives of 7-aminocoumarins exhibit strong fluorescence and can be used as laser dyes [3].

In the present work we studied the luminescence-spectral and acid-base characteristics of 3-arylcoumarins (I-XIV) in order to investigate the following questions: The effectiveness of π–π conjugation between the aryl substituent and the aminocoumarin fragment; the spectral changes in the ground (S_0) and excited (S_1) states which occur with change in the electronic nature of the substituents in the phenyl ring; the effect of the substituent R at position 4 on the above-mentioned characteristics of 3-aryl-7-aminocoumarins.

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