HYDRATION OF ALLENYLACETYLENIC ALCOHOLS — NEW ROUTE TO 6-METHYL-2,3-DIHYDRO-4-PYRANONES*

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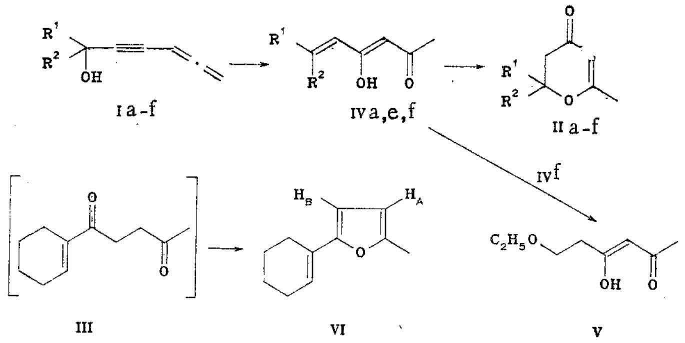
The mercuric sulfate-catalyzed acidic hydration of allenylacetylenic alcohols leads to 6-methyl-2,3-dihydro-4-pyranones — products of cyclization of unsaturated β-diketones. In the case of 1-(3,4-pentadien-1-ynyl)cyclohexanol 2-(1-cyclohexenyl)-5-methylfuran is formed in addition to the corresponding dihydropyranone.

We have previously shown that the preparation of 2,2,6-trimethyl-2,3-dihydro-4-pyranone by the acidic hydration of 2-methyl-5,6-heptadien-3-yn-2-ol [2], which is catalyzed by mercuric sulfate, has certain advantages over other methods of synthesis [3, 4]. In the present communication this reaction was extended to various allenylacetylenic alcohols in order to develop a general method for the preparation of 6-methyl-2,3-dihydro-4-pyranones.

We showed that heating of alcohols I in an aqueous alcohol medium containing mercuric sulfate and sulfuric acid leads to 6-methyl-2,3-dihydro-4-pyranones II as the final products. In the case of carbinol Id, in addition to pyranone IId we isolated 2-(1-cyclohexenyl)-5-methylfuran (VI), the PMR spectrum of which contains characteristic signals of aromatic protons with J_{ab} = 3.3 Hz [5].

The hydration of tertiary alcohol Ia was also accomplished in the absence of sulfuric acid; column chromatography of the reaction medium yielded 6-methyl-5-hepten-2,4-dione (IVa), which underwent cyclization to pyranone IIa [3] when sulfuric acid and mercuric sulfate were added.



I, II, IV a $R^1=R^2=CH_3$; b $R^1=CH_3$, $R^2=C_2H_5$; c $R^1=CH_3$, $R^2=C_4H_9$; d $R^1—R^2=(CH_2)_5$; e $R^1=C_3H_7$, $R^2=H$; f $R^1=R^2=H$

Unsaturated β-diketones IVe,f are also intermediates in the hydration of primary (If) and secondary (Ie) alcohols. It is interesting that the disubstituted double bond in diketone IVe has a trans configuration (J_{gem} = 15 Hz). In the case of alcohol If, in addition to diketone IVf and pyranone IIf, we isolated ethoxy diketone V, which is evidently formed as a result of the addition of ethanol to the double bond of vinyl diketone IVf [6]. It was demonstrated by a separate experiment that diketone V is not converted to dihydropyranone IIf under the reaction conditions.

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Judging from the PMR spectra, unsaturated diketones IVa,e,f exist virtually completely (≈95%) in the enol form in CCl_4 [3]. In the case of ethoxy diketone V the amount of the ketone form (δ_{CH_2} 3.58, δ_{CH_3CO} 2.15 ppm) is 14%.

The observed regioselectivity of the hydration of allenylacetylenic alcohols Ia-c,e,f, which leads through intermediate β-diketones IV to dihydropyranones II, can be explained by assuming that, in analogy with vinylacetylenic alcohols [7], a Meyer–Schuster rearrangement with subsequent hydration of the allenyl vinyl ketones to β-diketones IV occurs in this case. Our attempts to isolate intermediate monocarbonyl compounds were unsuccessful, and this does not provide a basis for excluding alternative schemes for the formation of β-diketones. The formation of furan derivative VI in the hydration of alcohol Id constitutes evidence for the intermediate formation of, in addition to a β-diketone, γ-diketone III as the most likely precursor of VI [8].

EXPERIMENTAL

The PMR spectra of solutions of the compounds in CCl_4 were obtained with a Perkin-Elmer R-12B spectrometer (60 MHz). The IR spectra were recorded with a UR-20 spectrometer. Analysis by gas–liquid chromatography (GLC) was carried out with an LKhM-8MD chromatograph (model 5) with a catharometer and a 2 m by 3 mm column packed with 5% SE-30 on Chromaton N-AW DMCS (0.20-0.25 mm) with helium as the carrier gas (60 ml/min). The retention times were reduced relative to acetone (the column temperature is given in parentheses). Analysis by thin-layer chromatography (TLC) was carried out on Silufol UV-254 plates with detection by means of iodine vapors. Column chromatography was accomplished on KSK silica gel (90-180 μ). The starting allenylacetylenic alcohols were obtained by the methods in [9, 10].

5-Methyl-8,9-decadien-6-yn-5-ol (Ic). The reaction of 15.7 g (0.125 mole) of 3-methyl-1-heptyn-3-ol with 7.5 g (0.1 mole) of propargyl chloride by a procedure similar to that in [9, 10] gave 6.0 g (36%) of carbinol Ic with bp 81-82°C (1 mm) and n_D^{20} 1.5380. IR spectrum (thin layer): 860, 1950, 1970 ($CH{=}C{=}CH_2$); 2230 ($C{\equiv}C$); 3380 cm^{-1} (OH). PMR spectrum, δ: 0.88 (3H, t, CH_3), 1.20-1.60 [m, $(CH_2)_3$], 1.37 (m, $CH_3C{-}O$), 2.60 (OH), and 4.80-5.50 ppm (3H, m, $CH{=}C{=}CH_2$). Found: C 80.4 H 9.8%. $C_{11}H_{16}O$. Calculated: C 80.5; H 9.7%.

Hydration of Carbinol Ia. A) A solution of 6.1 g (0.05 mole) of carbinol Ia in 6 ml of ethanol was added to a mixture of 14 ml of ethanol, 4 ml of water, 0.6 ml of concentrated sulfuric acid, and 0.6 g of mercuric sulfate, and the mixture was heated at 75°C for 1.5 h. A 0.6-g (0.002 mole) sample of mercuric sulfate and 2 ml of water were then added, and heating was continued at the same temperature for another hour. The mixture was cooled, 30 ml of water was added, and the mixture was extracted with ether. The aqueous layer was saturated with potassium carbonate and extracted again with ether. The combined ether extract was dried with magnesium sulfate and distilled to give 4.1 g (57%) of dihydropyranone IIa with bp 56-57°C (1 mm) and n_D^{20} 1.4837. PMR spectrum, δ: 1.27 [6H, s, $(CH_3)_2$], 1.80 (3H, s, CH_3), 2.18 (2H, s, CH_2), and 5.07 ppm (1H, s, $-CH{=}$).

B) A mixture of 1.2 g of carbinol Ia, 2 ml of ethanol, 0.4 g of mercuric sulfate, and 1 ml of H_2O was heated at 70-73°C for 1.5 h, after which it was worked up as in the preceding experiment, and the reaction product was chromatographed with a column by elution with benzene to give, successively, 150 mg of diketone IVa [R_f 0.64 [here and subsequently, elution with benzene–acetone (15:1)]. IR spectrum (CCl_4): 1590 (chelate), 1650 (C=C), and 1715 cm^{-1} (C=O, w) [3]. PMR spectrum, δ: 1.87 (3H, d, J = 1.2 Hz, $CH_3C{=}C$), 1.97 (3H, s, $CH_3C{=}O$), 2.15 (3H, d, J = 1.2 Hz, $CH_3C{=}C$), 5.30 (1H, s, CH=, chelate), 5.60 (1H, m, $J_1 = J_2 =$ 1.2 Hz, C=CH bond of the diketo form), and 14.5 ppm (OH) [3]], 60 mg of carbinol Ia (R_f 0.38), and 250 mg of pyranone II (R_f 0.33). Cyclization to pyranone IIa (according to TLC) occurred when 50 mg of diketone IVa was heated in the presence of catalytic amounts of H_2SO_4 and $HgSO_4$ at 70°C for 30 min.

2,6-Dimethyl-2-ethyl-2,3-dihydro-4-pyranone (IIb). A 4-g (0.03 mole) sample of carbinol Ib was added to a mixture of 8 ml of ethanol, 5.5 ml of water, 1.2 g of mercuric sulfate, and 0.4 ml of concentrated H_2SO_4, and the mixture was heated at 65-70°C for 1.5 h. The usual workup (hydration of alcohol Ia, method A) gave 1.8 g (39%) of pyranone IIb with bp 72-74°C (1 mm) and n_D^{20} 1.4862. IR spectrum (thin layer): 1610 (C=O); 1675 (C=O); 1150, 1250 cm^{-1} (C–O–C). PMR spectrum, δ: 0.95 (3H, t, J = 7.0 Hz, β-CH_3), 1.33 (3H, s, 2-CH_3), 1.85 (2H, q, 2-CH_2), 1.95 (3H, d, J = 1.0 Hz, 6-CH_3), 2.32 (2H, m, 3-H), and 5.17 ppm (1H, broad s, 5-H). Found: C 79.3; H 8.9%. $C_8H_{12}O_2$. Calculated: C 79.4; H 8.8%.

2,6-Dimethyl-2-butyl-2,3-dihydro-4-pyranone (IIc). A 1.6-g (0.01 mole) sample of carbinol Ic was heated with a mixture of 0.12 g of mercuric sulfate, 0.12 ml of H_2SO_4, 1 ml of water, and 5 ml of ethanol at 65°C for 6 h. The usual workup gave 0.7 g (38%) of pyranone IIc [11] with bp 89-91°C (2 mm), n_D^{20} 1.4802, and retention time 11.7 min (125°C). IR spectrum (thin layer): 1620 (C=C); 1670 (C=O); 1160, 1250 cm^{-1} (C—O—C). PMR spectrum, δ: 0.87 (3H, t, ω-CH_3), 1.10-1.70 [6H, m, $(CH_2)_3$], 1.28 (3H, s, 2-CH_3), 1.88 (3H, s, 6-CH_3), 2.27 (2H, m, 3-H), and 5.12 ppm (1H, broad s, 3-H).

Hydration of Carbinol Id. A 16.2-g (0.1 mole) sample of carbinol Id was added to a mixture of 4.2 g of mercuric sulfate, 1.2 ml of concentrated H_2SO_4, 10 ml of H_2O, and 50 ml of ethanol, and the mixture was heated at 65-68°C for 2 h. It was then worked up in the usual way and distilled to give 2.4 g (15%) of 2-(1-cyclohexenyl)-5-methylfuran [VI, bp 68-70°C (1 mm) and n_D^{20} 1.5225. IR spectrum (thin layer): 1020, 1455, 1380, 1495 (furan); 1665 cm^{-1} (C=C). PMR spectrum, δ: 1.68 (4H, m, CH_2CH_2), 2.18 (4H, m, $CH_2C{=}C$), 2.28 (3H, d, J = 1.0 Hz, CH_3), 5.87 (1H, m, J_{ab} = 3.3, J_2 = 1.0 Hz, H_a), 5.92 (1H, d, J = 3.3 Hz, H_b), and 6.18 ppm (1H, m, CH=). Found: C 81.6; H 8.7%. $C_{11}H_{14}O$. Calculated: C 81.5; H 8.6%], 5.9 g of a mixture of VI and IId, and 4.2 g (24%) of 2,2-pentamethylene-6-methyl-2,3-dihydro-4-pyranone [IId, bp 106-108°C (1 mm), n_D^{20} 1.4590, and retention time 6.9 min (150°C). IR spectrum (thin layer): 1610 (C=C); 1680 (C=O); 1170, 1250 cm^{-1} (C—O—C). PMR spectrum, δ: 1.50 (10H, m, pentamethylene), 1.93 (3H, d, J = 0.8 Hz, CH_3), 2.25 (2H, s, 3-CH), and 5.15 ppm (1H, broad s, 5-H). Found: C 67.8; H 8.8%. $C_{11}H_{16}O_2$. Calculated: C 67.7; H 8.8%].

Hydration of Carbinol If. A) A mixture of 7.5 ml of ethanol, 0.6 g of mercuric sulfate, 0.3 ml of concentrated H_2SO_4, 3.6 ml of water, and 3 g (0.032 mole) of alcohol If was heated at 60-65°C for 40 min, after which it was worked up in the usual way to give 0.3 g of diketone IVf [bp 54-57°C (2 mm) [12] and retention time 0.75 min (100°C). IR spectrum (thin layer): 900, 980, 3100 ($CH{=}CH_2$); 1590, 1610, 1640, 1650 cm^{-1} (chelate). PMR spectrum, δ: 2.07 (3H, s, CH_3), 5.45 (1H, s, chelate CH=), 5.60 (1H, m, β-H_{trans}), and 6.13 ppm (2H, m, α-H and β-H_{cis})] and 0.8 g of a mixture of carbinol If and pyranone IIf.

B) The reaction was carried out as in the preceding experiment, and the mixture was worked up in the usual way after 4.5 h to give 1.4 g of a mixture of ethoxy diketone V and pyranone IIf with bp 68-78°C (1 mm). Chromatography of 900 mg of this mixture with a column [elution with benzene—acetone (10:1)] gave, successively, 300 mg of 6-ethoxy-2,4-hexanedione [V, R_f 0.54, benzene—acetone (10:1), and retention time 5.7 min (110°C). IR spectrum (thin layer): 1610 (chelate), 1705 (C=O), and 1120 cm^{-1} (C—O—C). PMR spectrum, δ: 1.12 (t, J = 7.0 Hz, ethyl CH_3), 1.97 (s, enol $CH_3C{=}O$), 2.15 (s, ketone $CH_3C{=}O$), 2.42 (t, J = 6.5 Hz, $CH_2C{=}$), 3.41 (t, J = 7.0 Hz, ethyl CH_2), 3.58 (t, J = 6.5 Hz, OCH_2), 3.58 (s, $O{=}CCH_2C{=}O$), and 5.48 ppm (s, CH=). Found: C 60.6; H 8.8%. $C_8H_{14}O_3$. Calculated: C 60.7; H 8.8%] and 170 mg of dihydropyranone IIf [R_f 0.28, benzene—acetone (10:1), and retention time 5.9 min (110°C). IR spectrum (CCl_4): 1610 (C=C); 1110, 1230, 1260 cm^{-1} (C—O—C) [13]. PMR spectrum, δ: 1.91 (3H, broad s, CH_3), 2.35 (2H, t, J = 6.5 Hz, $CH_2C{=}O$), 4.40 (2H, t, J = 6.5 Hz, CH_2O), and 5.07 ppm (1H, broad s, CH=)].

Hydration of Carbinol Ie. A 1.36-g (0.01 mole) sample of carbinol Ie was heated with a mixture of 0.15 g of mercuric sulfate, 0.12 ml of concentrated H_2SO_4, 1 ml of H_2O, and 4 ml of ethanol at 63-65°C for 5 h. After the usual workup, the residue was chromatographed with a column by elution with benzene to give, successively, 150 mg of 5E-nonene-2,4-dione [IVe, R_f 0.64, benzene—acetone (15:1). IR spectrum (CCl_4): 960, 1650 (C=C); 1590, 1610 (chelate); 1720 cm^{-1} (C=O, w). PMR spectrum, δ: 0.87 (3H, t, 9-H), 1.20 (2H, m, 8-H), 2.10 (2H, m, $J_1 = J_2 = 6.0$, $J_3 = 1.0$ Hz, $CH_2C{=}$), 5.30 (1H, s, chelate CH=), 5.70 (1H, m, $J_1 = 15$, $J_2 = 1.0$ Hz, =CHC=O), and 6.70 ppm (1H, m, $J_1 = 15$, $J_2 = 6.0$ Hz, CH=). Found: C 70.0; H 9.0%. $C_9H_{14}O_2$. Calculated: C 70.1; H 9.0%] and 200 mg of 2-propyl-6-methyl-2,3-dihydro-4-pyranone [IIe, R_f 0.33, benzene—acetone (15:1). IR spectrum (CCl_4): 1615 (C=C); 1670 (C=O); 1120, 1260 cm^{-1} (C—O—C). PMR spectrum, δ: 0.90 (3H, distorted t, γ-CH_3), 1.20-1.70 (4H, m, α- and β-CH_2), 1.92 (3H, s, 6-CH_3), 2.25 (2H, d, J = 6.5 Hz, 3-H), 5.17 (1H, broad s, 5-H), and 5.70 ppm (1H, m, 2-H). Found: C 70.2; H 8.9%. $C_9H_{14}O_2$. Calculated: C 70.1; H 9.0%].

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CHROMATOGRAPHIC MASS-SPECTROMETRIC CHARACTERISTICS OF SUBSTITUTED 4-ACYL-1,3,4-OXADIAZOLINES

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4-Acyl-1,3,4-oxadiazolines were characterized by their mass spectra and retention indexes. It was shown that the spectra of ionic series of compounds of a given class in conjunction with homologous increments of the retention indexes make it possible to carry out their group identification, in particular, to distinguish acyloxadiazolines from the isomeric diacyl- and isobaric monoacylhydrazones, which have similar regularities in electron-impact fragmentation, and that the complete analysis of their mass spectra makes it possible to unambiguously establish the position and character of the hydrocarbon radicals in the molecules.

The reaction of ketone acylhydrazones with carboxylic acid anhydrides in pyridine is a general method for the synthesis of 2-substituted 4-acyl-1,3,4-oxadiazolines. A series of compounds of this class have been synthesized and characterized by this method [1].

Proof of the structures of these compounds by spectral methods is complicated by difficulties in establishing the positions of alkyl radicals R^4 and R^3. In the PMR spectra the signals of the former are shifted only slightly to weak field as compared with the signals of the protons of the latter. In order to develop independent proof for the structures of acyloxadiazolines and methods for their chromatographic mass-spectrometric identification based on the use of statistically treated spectra of ionic series [2] and homologous increments of the retention indexes [3], in the present research we studied the mass spectra of 26 compounds of this class in the case of ionization by electron impact. The following three series of acyloxadiazolines were investigated: 1) compounds with alkyl radicals R^1-R^4 (I-XVI); 2) 5,5-pentamethylene-substituted compounds (XVII-XX); 3) phenyl-substituted acyloxadiazolines with phenyl radicals in the acyl residue (XXI, XXII) and in the 2 position of the ring (XXIII-XXVI).

The regularities in the fragmentation of acyloxadiazolines under electron impact have not been previously investigated. The mass spectra of precursors of oxadiazolines, viz., acylhydrazones containing chiefly aryl groups (see the literature cited in [4]), have been studied in relatively great detail. Of the aliphatic acylhydrazones, the methylformylhydrazones of various carbonyl compounds have been characterized in greatest detail [5].

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