SYNTHESIS OF 4,5-DIHYDROFURAN DERIVATIVES BY THE REACTION OF ACETYLACETONE WITH CONJUGATED ALKENES*

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The reaction of the acetylacetonyl radical (generated from acetylacetone by the action of manganese acetate) with vinylacetylene, 2-vinylfuran, and butadiene was studied. The reaction proceeds nonregioselectively with vinylacetylene: 3-acetyl-2-methyl-5-ethynyl- and 3-acetyl-2-methyl-5-(4'-acetyl-5'-methyl-2'-furyl)-4,5-dihydrofurans in a ratio of 1 : 2.2 were isolated. The principal products in the reaction with 2-vinylfuran and butadiene were 3-acetyl-2-methyl-5-(2'-furyl)- and 3-acetyl-2-methyl-5-vinyl-4,5-dihydrofurans.

The reactivities of α-oxo- and α,α-dioxoalkyl radicals generated from monocarbonyl and β-dicarbonyl compounds by the action of manganese(III) acetate have been studied in detail in the last decade [2-12]. 1-Alkenes [3-5], 1-alkynes [6, 7], alkyl vinyl ethers [8], 1,6-dienes [9], and aromatic hydrocarbons [6, 10] have been investigated as substrates. Regularities in the formation of saturated and unsaturated, linear, and cyclic products have been detected [3, 5, 11], the kinetics of the process have been studied [12], and preparative methods for the synthesis of γ-lactones [2], α-alkylated alkanals [4], 1,4-diketones [8], and substituted dihydrofurans [10] have been proposed.

In order to develop methods for the synthesis of functional highly unsaturated compounds it seemed of interest to investigate the reaction of the acetylacetonyl radical with compounds that contain multiple bonds in the case of vinylacetylene, 2-vinylfuran, and butadiene.

The reaction of vinylacetylene with acetylacetone proceeds nonregioselectively, and the attack by the acetylacetonyl radical is directed both at the vinyl group and at the ethynyl group. The resulting radicals are oxidized by copper(II) acetate to the corresponding carbonium ions A and B. Cyclization of propargyl carbonium ion A leads to 4,5-dihydrofuran I. Cyclization of dienyl (allylvinyl) carbonium ion B leads to the intermediate formation of a furan derivative, the secondary reaction of which with acetylacetone leads to 4,5-dihydrofuran II. Reaction products I and II were isolated in a ratio of 1 : 2.2 by means of column chromatography.

The products of the reaction of butadiene and 2-vinylfuran with acetylacetone are 4,5-dihydrofurans III and IV, which are formed by cyclization, respectively, of allyl and furylmethyl carbonium ions A. The latter confirms the proposed scheme for the formation of 4,5-dihydrofuran II, since 2-vinylfuran is an analog of the

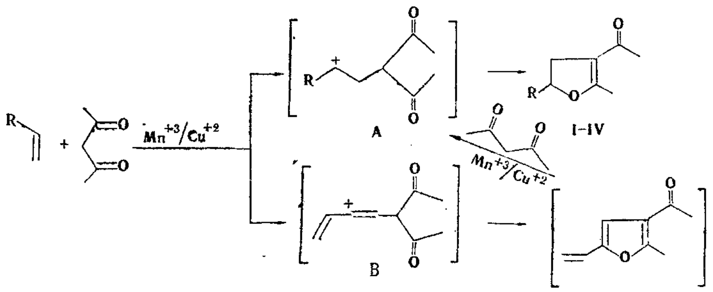

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TABLE 1. Constants of 4,5-Dihydrofurans I-IV

Compound	bp, °C (mm)	n_D^{20}	TLC, R_f	GLC, °C; conditions (ml/min); t_{ret} (min)	Found, %		Empirical formula	Calc., %		Yield, %
					C	H		C	H	
I	—	—	0,41[a]	120; 35; 28,8	72,4	7,0	$C_9H_{10}O_2$	72,0	6,7	8
II	—	—	0,29[a]	—	67,6	7,0	$C_{14}H_{16}O_4$	67,7	6,5	11
III	69—70 (1)	1,4930	0,46[b]	135; 40; 14,7	71,3	7,7	$C_9H_{12}O_2$	71,1	7,9	46
IV	111—112 (1)	1,5358	0,39[b]	—	68,4	6,5	$C_{11}H_{12}O_3$	68,8	6,5	26

[a] Benzene—acetone (10 : 1). [b] Ether.

proposed intermediate furan derivative.

Compounds I-IV have UV, PMR, and IR spectra of the same type. An absorption band of a cyclic β-alkoxyene chromophore is observed in the UV spectra at 275-280 nm (ε 9000-10,000). Long-range spin—spin coupling (1.6 Hz) between the methylene group of the dihydrofuran ring and the methyl group attached to the double bond appears in the PMR spectra. In II and IV the protons of the methylene group of the dihydrofuran ring, which contains a furan substituent in the 5 position, are magnetically equivalent, whereas the analogous protons for products I and III are nonequivalent, and this leads to substantial complication of the spectrum. In addition, the chemical shifts of the methyl groups of the dihydrofuran ring ($2-CH_3$ and $3-CH_3CO$) in the PMR spectrum of II in d_6-DMSO coincide. The use of d-pyridine as the solvent makes it possible to record the signals of both methyl groups with a difference of 1.4 Hz in the chemical shifts. Splitting of the frequency of the vibration of the conjugated double bond at 1600-1620 cm^{-1} is observed in the IR spectra of I-IV.

The data obtained in this research show that cyclization is the only pathway of stabilization of carbonium ions A and B, which are more stable than alkyl carbonium ions owing to conjugation with multiple bonds. The fact of cyclization of the benzyl carbonium ion described in [10, 11] fits into the established regularity.

EXPERIMENTAL

The PMR spectra of the compounds were recorded with a Perkin-Elmer R12B spectrometer (60 MHz). The IR spectra of thin layers of the pure substances were obtained with a UR-10 spectrometer. The UV spectra of solutions of the compounds in ethanol were obtained with a Specord UV-vis spectrophoromeier. The mass spectra were recorded with an MKh-1303 mass spectrometer with an ionizing-electron energy of 30 eV. Analysis by gas—liquid chromatography was accomplished with a Tsvet-104 chromatograph with a catharometer and a column (2 m by 3 mm) packed with 15% Apiezon L/Chromaton N-AW-DMCS (0.200-0.250 mm); the carrier gas was helium. Analysis by thin-layer chromatography (TLC) was carried out on Silufol UV-254 plates with detection by iodine vapors.

β-(2-Furyl)acrylic acid was obtained from furfural and malonic acid by the method in [13]. 2-Vinylfuran was obtained by pyrolysis of β-(2-furyl)acrylic acid by the method in [14].

The constants and spectral characteristics of 4,5-dihydrofurans I-IV are presented in Tables 1 and 2.

3-Acetyl-2-methyl-5-ethynyl- and 3-Acetyl-2-methyl-5-(3-acetyl-2-methyl-5-furyl)-4,5-dihydrofurans (I, II). A 5.4-g (0.02-mole) sample of $Mn(OAc)_3 \cdot 2H_2O$, and 2.0 g (0.02 mole) of acetylacetone were added to a solution of 4.4 g (0.02 mole) of $Cu(OAc)_2 \cdot 2H_2O$ in 15 ml of acetic acid, and 4.3 g (0.04 mole) of vinylacetylene was bubbled into the mixture (the flask was equipped with a dry-ice condenser) at 75°C in a nitrogen atmosphere until the brown coloration vanished (25-30 min). The mixture was cooled to room temperature, and the precipitated $Mn(OAc)_2$ was removed by filtration. The filtrate was diluted with 10 ml of water, and the aqueous mixture was salted out with NaCl and extracted with ether. The ether extract was washed with a saturated solution of Na_2CO_3 and water and dried with Na_2SO_4. The ether was removed by evaporation in vacuo (15 mm) on a water bath at 45°C (under the indicated conditions the unchanged acetylacetone was also removed) to give 960 mg of a crude mixture containing, according to TLC data, two principal reaction products. The individual compounds were isolated by means of column chromatography with a column with an inner diameter of 2.0 cm filled with 50.0 g of Woelm Silica Gel (70-90 μm); the products were eluted with benzene—acetone (10 : 1) (the overall volume was 275 ml) at a mobile phase flow rate of 1 ml/min. This procedure gave 123 mg of I and 275 mg of II. Products I and II underwent appreciable resinification when they were heated above 70°C and also upon prolonged storage.

TABLE 2. Spectral Characteristics of 4,5-Dihydrofurans I-IV

Compound	IR spectrum, cm^{-1}	UV spectrum, λ_{max} nm (log ε)	PMR spectrum, ppm	Mass spectrum, M^+
I	3280 m, 3000 w, 2960 w, 2930 w, 2880 w, 2130 w, 1670 s, 1615, 1600 split, s, 1420 m, 1380 s, 1365 s, 1225 s, 1140 m, 1070 m, 1045 m, 1005 m, 980 m, 950 m, 938 s, 845 w	275 (4,04)	(CCl_4): 2,15 (3H, s, 3-CH_3CO), 2,22 (3H, t, 2-CH_3), 2,60 (1H, d, ethynyl H, 3,15 (2H, center of an AB system, each line a dq, CH_AH_B), 5,16 (1H, d.d.d. 5-H), $J_{H_A-H_B}$ = =14,0, $J_{2\text{-}CH_3-H_{A(B)}}$ =1,6, $J_{5\text{-}H-H_A}$ =8,4, $J_{5\text{-}H-H_B}$ = =10,2, $J_{5\text{-}H\text{-ethynyl-}H}$ =2,2 Hz	150
II	3120 w, 3000 w, 2960 m, 2930 s, 2855 m, 1700 m, 1675 s, 1620, 1605 split s, 1566 s, 1420 s, 1370 s, 1320 m, 1225 s, 1138 m, 1065 m, 1020 m, 1000 m, 945 m, 930 s, 885 m, 840 w	275 (3,97) 208 (4,08)	(ДМСО-d_6): 2,20 (6H, s, superimposition of 2-CH_3 and 3-CH_3CO signals), 2.40 (3H, s, 4-CH_3CO), 2,56 (3H, s, 5-CH_3), 3,26 (2H, dq CH_2), 5,65 (1H, t, 5-H), 6,88 (1H, s, furan ring H, $J_{2\text{-}CH_3-CH_2}$=1,6, $J_{CH_2-5\text{-}H}$= =9,6 Hz	248
III	3090 w, 3020 w, 2995 w, 2930 m, 2870 w, 1668 s, 1645 m, 1615, 1600 split, s, 1425 m, 1380 s, 1360 m, 1315 w, 1225 s, 1132 m, 1065 m, 990 m, 942 m, 932 s, 850 m	280 (3,96)	(CCl_4): 2,06 (3H, s, 3-CH_3CO), 2,15 (3H, t, 2-CH_3), 2,85 (2H, center of an AB system, each line a dq, CH_AH_B, 4,98 (1H, dddt Hx), $J_{2\text{-}CH_3-H_{A(B)}}$ =1,6, J_{AB}= =13,8, J_{AX}=10,0, J_{BX}= =8,2 Hz; vinyl group 5,16 (1H, $H_{A'}$), 5,24 (1H, $H_{B'}$), 5,85 (1H, $H_{C'}$), $J_{B'C'}$ =16,6, $J_{A'C'}$ =9,7, $J_{A'B'}$ = =2,0, $J_{C'X}$ =6,0, $J_{A'(B')-X}$ = =1,0 Hz	152
IV	3150 m, 3125 m, 3000 m, 2965 s, 2935 s, 2830 s 1678 s, 1625, 1610 split m, 1510 m, 1465 s, 1380 s, 1330 m, 1270 m, 1230 s, 1155 s, 1140 s, 1072 s, 1040 m, 1020 s, 980 s, 970 s, 945 s, 935 s, 880 s, 825 m, 745 s	278 (3,92) 215 (3,86)	(CCl_4): 2,10 (3H, s, 3-CH_3CO), 2,15 (3H, t, 2-CH_3), 3,13 (2H, dq, CH_2), 5,45 (1H, t, 5-H), 6,30 (2H, d, furan ring 3-H and 4-H), 7.35, (1H, t, 5-H), $J_{2\text{-}CH_3-CH_2}$ = =1,6, $J_{CH_2-5\text{-}H}$ =9,6, $J_{5\text{-}H-4(3)\text{-}H}$=1,4 Hz	—

3-Acetyl-2-methyl-5-vinyl-4,5-dihydrofuran (III). Similarly, the reaction of 3.0 g (13 mmole) of $Cu(OAc)_2 \cdot 2H_2O$ in 140 ml of acetic acid, 53.6 g (0.20 mole) of $Mn(OAc)_3 \cdot 2H_2O$, 20.0 g (0.20 mole) of acetylacetone, and 21.6 g (0.40 mole) of butadiene gave, after distillation of the crude mixture, 7.0 g of III.

3-Acetyl-2-methyl-5-(2-furyl)-4,5-dihydrofuran (IV). Similarly, the reaction of 1.7 g (8 mmole) of $Cu(OAc)_2 \cdot 2H_2O$ in 70 ml of acetic acid, 32.2 g (0.12 mole) of $Mn(OAc)_3 \cdot 2H_2O$, 12.0 g (0.12 mole) of acetylacetone, and 11.3 g (0.12 mole) of 2-vinylfuran gave, after distillation, 5.0 g of IV.

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