90. J.-P. Montillier and J. Dreux, Compt. Rend., C, 264, 891 (1967).
91. J.-P. Montillier, J. Royer, and J. Dreux, Bull. Soc. Chim. France, No. 5, 1956 (1970).
92. J.-P. Schirmann, J. Dreux, and J. Doris, Bull. Soc. Chim. France, No. 10, 3896 (1967).
93. J.-P. Montillier and J. Dreux, Bull. Soc. Chim. France, No. 10, 3638 (1969).
94. M. Trollier, J. Royer, R. Longeray, and J. Dreux, Tetrahedron, 30, 173 (1974).
95. M. Trollier, R. Longeray, and J. Dreux, Tetrahedron, 30, 163 (1974).
96. J. Kuthan, J. Palesek, and L. Vavraska, Coll. Czech. Chem. Commun., 39, 854 (1974).
97. J. Kuthan, J. Palesek, and J. Valihrach, Coll. Czech. Chem. Commun., 46, 748 (1981).
98. T. Kitazume, K. Chino, and N. Ishikawa, J. Fluor. Chem., 18, 213 (1981).
99. F. Fournier, S. Altenburger-Combrisson, N. K. Cuong, and J. J. Basselier, Tetrahedron, 35, 2633 (1979).
100. A. Christofides, J. A. K. Howard, J. A. Rattue, J. L. Spencer, and F. G. A. Stone, J. Chem. Soc., Dalton Trans., No. 11, 1980 (1980).
101. K. Öfele, A. Wurzinger, and W. Kalbfus, J. Organomet. Chem., 69, 279 (1974).
102. I. I. Kritskaya, Usp. Khim., 41, 2160 (1972).
103. W. J. Powell and G. A. Ozin, Adv. Inorg. Chem. Radiochem., 23, 80 (1980).
104. A. Blackborow and D. Jonng, Metal Vapor Synthesis in Organometallic Chemistry, Springer Verlag, Berlin (1979).
105. R. G. Pearson, Usp. Khim., 40, 1259 (1971).
106. A. D. Garnovskii, Koordinats. Khim., 6, 1779 (1980).

SYNTHESIS OF 4,5-DIHYDROFURAN DERIVATIVES. STEREOCHEMICAL STUDY OF THE REACTIONS OF 1,3-ALKADIENES WITH β-DICARBONYL COMPOUNDS*

G. G. Melikyan, D. A. Mkrtchyan,
V. M. Mkrtchyan, and Sh. O. Badanyan

UDC 547.722.3'315.2'422.3:541.634

4,5-Dihydrofuran derivatives were obtained by the reaction of cis- and trans-1,3-alkadienes with carbonyl compounds in the presence of the manganese(III) acetate/copper(II) acetate oxidizing system. It was observed that in the case of cis-1,3-alkadienes, in contrast to trans-1,3-alkadienes, inversion of the cis double bond, the degree of which depends on the structures of the unsaturated and carbonyl components of the reaction, occurs. It was shown that the reaction of cis-1,3-dodecadiene with diethyl malonate leads to the corresponding 1,4-addition product.

The study of the reactions of unsaturated compounds with α-oxo- and α,α-dioxoalkyl radicals generated by oxidation of carbonyl compounds by manganese(III) acetate has proved to be extremely fruitful in a synthetic respect [2-13]. In particular, the reaction of 1,3-alkadienes with dicarbonyl compounds is a preparative method for the synthesis of 4,5-dihydrofuran derivatives [14-16]. A stepwise mechanism that includes the following steps has been proposed for reactions of this type: 1) the formation of a complex of the dicarbonyl compound with manganese(III) acetate; 2) ligand formation with the 1,3-alkadiene; 3) addition of the carbonyl compound to the 1,3-alkadiene in the coordination sphere of the manganese(III) ion; 4) dissociation of the allyl complex at the Mn—C bond to give an allyl radical and a manganese(II) ion; 5) oxidative cyclization of the allyl radical under the influence of copper(II) acetate [16]. This reaction scheme is hypothetical and should be refined on the basis of research specially designed to ascertain specific aspects of the mechanism. In particular, it seemed of interest to use a sterochemical test: separate subjection to the reaction of the cis and trans isomers of 1,3-alkadienes in order to detect the possible inversion of the C_3—C_4 double bonds during the process.

---

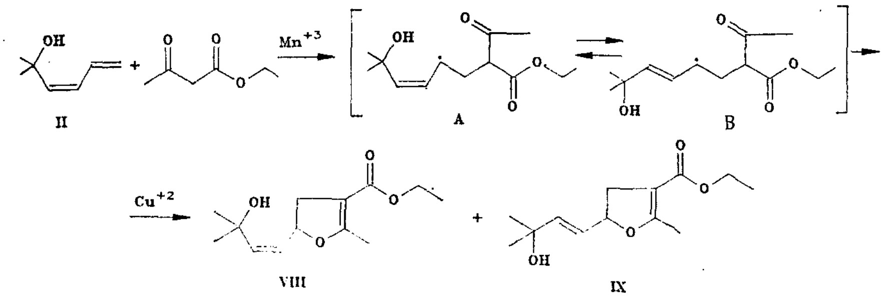
*Communication 119 from the series "Reactions of unsaturated compounds." See [1] for Communication 118.

Institute of Organic Chemistry, Academy of Sciences of the Armenian SSR, Yerevan 375094. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 3, pp. 308-314, March, 1985. Original article submitted May 22, 1984.

We have studied the reaction of cis- and trans-1,3-alkadienes with carbonyl compounds, viz., acetic acid, acetylacetone, acetoacetic ester, and diethyl malonate, in the presence of the manganese(III) acetate/copper(II) acetate oxidative system. We selected cis-1,3-dodecadiene and cis- and trans-5-methyl-1,3-hexadien-5-ols as the unsaturated components.

The reaction products in the case of acetic acid are 5-tetradecen-4-olides IV and V, whereas the products in the case of acetylacetone and acetoacetic ester are 2-methyl-3-acetyl(carbethoxy)-5-(1-alken-1-yl)-4,5-dihydrofurans VI-XI (Table 1).

Compounds IV-XI are formed as a result of oxidation of the carbonyl compounds by manganese(III) acetate, addition of α-oxo- and α,α-dioxoalkyl radicals to the terminal double bond of the 1,3-alkadienes, and subsequent oxidative cyclization of the allyl radical adducts. The reaction scheme in the case of the reaction of cis-5-methyl-1,3-hexadien-5-ol with acetoacetic ester appears to be as follows:

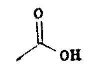
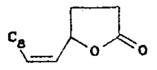
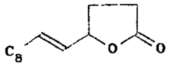
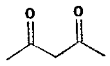
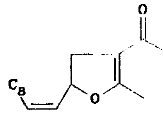
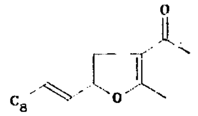
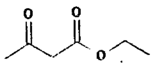
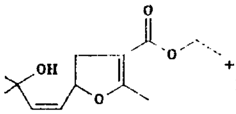
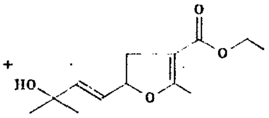
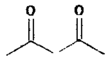
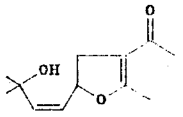
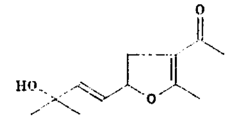
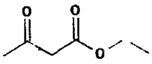
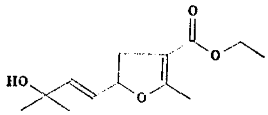
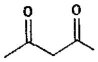
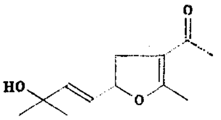


It should be noted that it has previously been shown in the case of 1-alken-3-ynes and 1,3-alkadienes that cyclization is the preferred direction of stabilization of radical adducts that contain multiple bonds in the α position [11, 14-17].

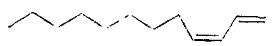
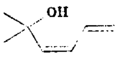
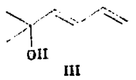
The data on the stereoisomeric compositions of the synthesized compounds presented in Table 1 constitute evidence that partial inversion of the cis-double bond occurs in the case of cis-1,3-alkadienes I and II, whereas trans-1,3-alkadiene III reacts with retention of the configuration of the double bond. The degree of inversion differs, depending on the structures of the unsaturated and carbonyl components of the reaction. Inversion evidently occurs in allyl radical adduct A, which undergoes partial isomerization to radical adduct B via rotation relative to the C_3—C_4 bond of the 1,3-alkadiene. The observed fact of inversion of the double bond constitutes evidence for the formation of intermediate allyl radical adducts in the reactions of 1,3-alkadienes with α-oxo- and α,α-dioxoalkyl radicals. However, the available experimental data do not enable one to establish if the inversion of the double bond of the allyl radical adduct occurs within the coordination sphere of manganese(III) or outside of it [16]. In addition to this, one cannot completely exclude the possibility of inversion taking place in the step involving oxidative cyclization with participation of copper(II) acetate.

The stereochemical assignment of IV-XI was made on the basis of the spin—spin coupling constants (SSCC) of the vinyl protons, which range from 10.8 to 11.8 Hz for the cis isomers and from 15.3 to 15.5 Hz for the trans isomers. In addition, a detailed analysis of the PMR spectra showed that the chemical shift (CS) of the 5-H proton (4-H for IV and V) is extremely sensitive to a change in the geometry of the double bond and can be used for analytical purposes to distinguish the geometrical isomers (Table 2). Thus for trans isomers V, VII, IX, and XI the signal of the 5-H proton is observed at 4.86-5.06 ppm, whereas for cis isomers IV and VI it is observed at 5.21 and 5.36 ppm, respectively, i.e., it is shifted 0.35 ppm to weak field. In the case of cis isomers VIII and X the signals of the 5-H proton are observed at 6.02 ppm, i.e., the weak-field shift is $\sim$1 ppm relative to the signal of the 5-H proton of trans isomers IX and XI. This should be explained by the deshielding effect of the oxygen atom of the hydroxy group. In fact, the construction of molecular models showed that in VIII and X rotation about the C_2—C_3 bond of the side chain is hindered; the conformation in which the oxygen atom of the hydroxy group and the 5-H proton are oriented in direct spatial proximity to one another is the stable conformation. For the same reason, the 2-H proton in cis-dienol II is observed at 7.2 ppm, whereas in trans-dienol III it is observed at 6.22 ppm. As we found out, the CS of the vinyl protons also depend on the geometry of the double bonds (Table 2). In the trans isomers the signals of the vinyl protons are observed at weaker field as compared with the corresponding signals of the cis isomers; the difference in the CS of the 1-H proton in IV and V is 0.05 ppm, as compared with 0.21 ppm in VIII and IX and 0.3 ppm in X and XI. Similarly, for the 2-H proton the differences are 0.12, 0.2, and 0.3

TABLE 1. Structures and Stereoisomeric Compositions of IV- XI

Starting compounds		Reaction products	Stereoisomeric composition,† %	
unsaturated component*	carbonyl component		cis	trans
I	—	—	⩾93	
I		 IV +  V	56	44
I		 VI +  VII	80	20
II	—	—	78	22
II		 VIII +  IX	40	60
II		 X +  XI	30	70
III	—	—	—	100
III		 IX	—	100
III		 XI	—	100

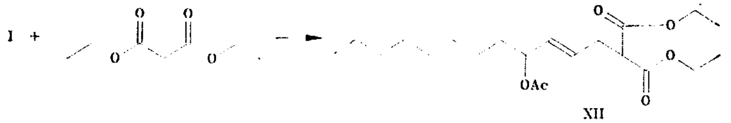
---

*  I  II  III

†The stereoisomeric composition was determined from the PMR spectra of the crude products.

ppm. Let us also note that in cis isomers VIII and X, in contrast to trans isomers IX and XI, the methyl groups of the side chain are magnetically nonequivalent, as a consequence of which, the difference in their PMR spectral CS is 0.04 ppm. The reason for this is the retarded character of the rotation about the C_2—C_3 bond, which was demonstrated with molecular models. The spectra of individual VIII and IX, as well as a mixture of these isomers, are presented in Fig. 1.

The product of the reaction of cis-1,3-dodecadiene (I) with diethyl malonate is ethyl trans-6-acetoxy-2-carbethoxy-4-tetradecenoate (XII) — the product of concerted 1,4 addition of the dicarbethoxymethyl and acetoxy groups to the diene block of I. According to the PMR spectral data, the double bond of product XII has a trans configuration.



XII

TABLE 2. Chemical Shifts of the Characteristic Protons of IV-XI

Proton	cis Isomer				trans Isomer			
	IV*	VI	VIII	X	V*	VII	IX	XI
5-H	5,21	5,36	6,02	6,02	4,86	5,0	4,97	5,06
1-H	5,41	—	5,47	5,48	5,46	—	5,68	5,78
2-H	5,65	—	5,60	5,61	5,77	—	5,80	5,91

*In IV and V the 5-H, 1-H, and 2-H protons have the designations 4-H, 5-H, and 6-H, respectively [18].

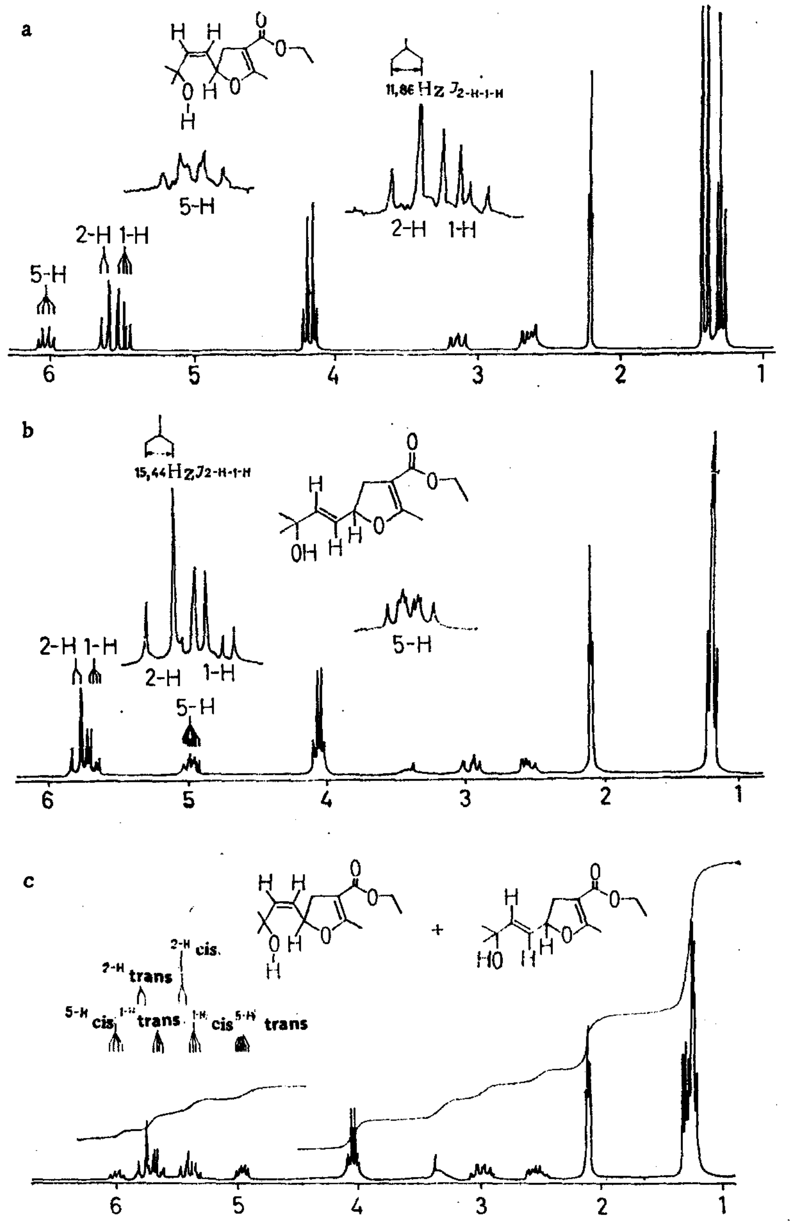
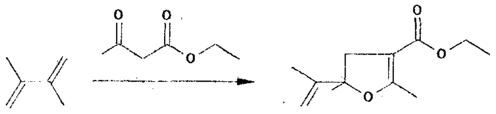


Fig. 1. PMR spectra of cis-VIII (a), trans-IX (b), and a mixture of these isomers (c).

In the 1,3-alkadiene series, 2,3-dimethyl-1,3-butadiene was also subjected to oxidative cyclization with acetoacetic ester. The reaction product is 3-carbethoxy-2,5-dimethyl-5-isopropenyl-4,5-dihydrofuran (XIII).



XIII

EXPERIMENTAL

The PMR spectra were obtained with a Bruker WM-250 spectrometer (250 MHz); the chemical shifts (CS) are the shifts relative to tetramethylsilane (TMS). The IR spectra of thin layers of the pure substances were recorded with a UR-20 spectrometer. The mass spectra were obtained with an MX-1306 spectrometer at an ionizing-electron energy of 70 eV. Analysis by thin-layer chromatography (TLC) was carried out on Silufol UV-254 plates with detection of the spots by means of iodine vapors. Analysis by gas—liquid chromatography (GLC) was carried out with an LKhM-8 MD chromatograph (model 3) with a 2 m by 3 mm steel column packed with 15% Apiezon L/Chromaton N-AW-HMDS (0.125-0.160 mm).

cis-1,3-Dodecadiene (I). This compound was obtained by the reduction of 1-dodecen-3-yne by means of zinc—copper vapor [18]. The stereoisomeric purity was determined from the ^{13}C NMR spectra by comparison of the peak intensities of the signals of the vinyl $C_{(2)}$ and $C_{(3)}$ atoms, which are observed at 133.06 and 129.24 ppm, with the magnitude of the noise of the base line at 135-137 ppm, over which range one should have observed the signals of the corresponding carbon atoms of trans-1,3-dodecadiene [19]. In conformity with this, the stereoisomeric purity of I is $\geqslant$93%.

cis-5-Methyl-1,3-hexadien-5-ol (II). This compound was similarly obtained in 69.2% yield from 5-methyl-1-hexen-3-yn-5-ol and had bp 73°C (20.0 hPa) and n_D^{20} 1.4756. PMR spectrum ($CDCl_3$): 1.38 (6H, s, two CH_3), 2.63 (1H, s, OH), 5.08-5.20 (2H, m, $=CH_2$), 5.51 (1H, d, 4-H, $J_{4\text{-H}-3\text{-H}}$ = 11.8), 5.90 (1H, t, 3-H, $J_{3\text{-H}-2\text{-H}}$ = 11.8), and 7.20 ppm (1H, dt, 2-H, $J_{2\text{-H}-1\text{-H}_{trans}}$ = 16.2). The percentage of trans isomer III was 22%. The ratio of II and III was determined from the PMR spectrum by integration of the signals of the methyl groups at 1.38 ppm for II and at 1.33 ppm for III. IR spectrum: 1585, 1635 (C=C—C=C); 3400 cm^{-1} (broad, O—H). Found: C 74.8; H 10.4%. $C_7H_{12}O$. Calculated: C 75.0; H 10.7%.

trans-5-Methyl-1,3-hexadien-5-ol (III). The compound was obtained in 82% yield by the reduction of 5-methyl-1-hexen-3-yn-5-ol with lithium aluminum hydride [20] and had bp 57°C (17.3 hPa) and n_D^{20} 1.4710. PMR spectrum ($CDCl_3$): 1.33 (6H, s, two CH_3), 2.44 (1H, s, OH), 4.98 (1H, dd, 1-H_{cis}, $J_{1\text{-H}_{cis}-2\text{-H}}$ = 9.5, $J_{1\text{-H}_{cis}-1\text{-H}_{trans}}$ = 1.7), 5.15 (1H, dd, 1-H_{trans}, $J_{1\text{-H}_{trans}-2\text{-H}}$ = 16.5), 5.75 (1H, d, 4-H, $J_{4\text{-H}-3\text{-H}}$ = 14.7), 6.12 (1H, dd, 3-H, $J_{3\text{-H}-2\text{-H}}$ = 10.3), and 6.22 ppm (1H, ddd, 2-H). The stereoisomeric purity was ∿100%. IR spectrum: 1605, 1650 (C=C—C=C); 3380 cm^{-1} (broad, O—H).

cis- and trans-5-Tetradecen-4-olides (IV, V). These compounds were synthesized by the reaction of I with acetic acid in the presence of manganese(III) acetate at 120°C [18].

Typical Experiment (VI-XIII). A 25-mmole sample of $Mn(OAc)_3 \cdot 2H_2O$, 50 mmoles of the carbonyl compound, and 25 mmoles of the 1,3-alkadiene were added to a solution of 1.7 mmoles of $Cu(OAc)_2 \cdot 2H_2O$ in 20 ml of acetic acid, and the mixture was heated in a nitrogen atmosphere at 60°C until the brown coloration had vanished (15 min). The reaction mixture was then cooled to 20°C and filtered. The filtrate was diluted with water and extracted with ether, and the ether extract was washed successively with water, saturated sodium carbonate solution, and water and dried with Na_2SO_4. The ether was evaporated *in vacuo*, and the residue was chromatographed on silica gel (70-90 μm). The substance—sorbent ratio was 1:50 and the eluent was hexane—ether (1:1) for VI-XI, as compared with CCl_4—acetone (8:1) for XII; the process was monitored by TLC.

cis- and trans-3-Acetyl-2-methyl-5-(1-decen-1-yl)-4,5-dihydrofurans (VI, VII). These compounds were obtained in 76.8% yield and had n_D^{20} 1.4920 and R_f 0.83 (ether). PRM spectrum ($CDCl_3$): 0.88 (3H, t, CH_3, $J_{CH_3-CH_2}$ = 6.7), 1.28 (12H, broad s, $6CH_2$), 2.10 (2H, m, $CH_2CH=$), 2.19 (3H, s, CH_3CO), 2.22 (3H, t, 2-CH_3, $J_{2\text{-}CH_3-4\text{-}CH_2}$ = 1.5), 2.67 (1H, ddq, 4-H_A, $J_{H_A-H_B}$ = 14.0, $J_{4\text{-H}_A-5\text{-H}}$ = 8.5), 3.12 (1H, ddq, 4-H_B, $J_{4\text{-H}_B-5\text{-H}}$ = 10.0), 5.0 (1H, dt, 5-H of trans isomer VII), 5.36 (1H, dt, 5-H of cis isomer VI, $J_{5\text{-H}-1\text{-H}}$ = 8.5), and 5.50-5.84 ppm (2H, m, 1-H, 2-H). IR spectrum: 1598, 1620 (C=C); 1670 cm^{-1} (C=O). Found: C 77.1; H 10.7%. $C_{17}H_{28}O_2$. Calculated: C 77.3; H 10.6%.

cis-3-Carbethoxy-2-methyl-5-(3-hydroxy-3-methyl-1-buten-1-yl)-4,5-dihydrofuran (VIII). This compound was obtained in 23.3% yield and had n_D^{20} 1.4915 and R_f 0.40 [ether—hexane (5:1)]. PRM spectrum (CCl_4): 1.27 (3H, t, CH_3, $J_{CH_3-CH_2}$ = 6.75), 1.36 (3H, s, CH_3), 1.40 (3H, s, CH_3), 2.18 (3H, t, 2-CH_3, $J_{2-CH_3-4-CH_2}$ = 1.68), 2.62 (1H, ddq, 4-H_A, $J_{H_A-H_B}$ = 14.40, J_{4-H_A-5-H} = 8.55), 3.12 (1H, dd, q, 4-H_B, J_{4-H_B-5-H} = 10.80), 4.15 (2H, q, OCH_2), 5.47 (1H, dd, 1-H, $J_{1-H-2-H}$ = 11.86, $J_{1-H-5-H}$ = 8.0), 5.60 (1H, d, 2-H), and 6.02 ppm (1H, dt, 5-H). IR spectrum: 1635 (C=C), 1680 (C=O), 3470 cm^{-1} (broad, O—H). Found: C 65.5%; H 8.0%. $C_{13}H_{20}O_4$. Calculated: C 65.0; H 8.3%.

trans-3-Carbethoxy-2-methyl-5-(3-hydroxy-3-methyl-1-buten-1-yl)-4,5-dihydrofuran (IX). This compound was obtained in 36.7% and 57.2% yields (in the reactions of acetoacetic ester with II and III, respectively) and had n_D^{20} 1.4962 and R_f 0.28 [ether—hexane (5:1)]. PMR spectrum (CCl_4): 1.23 (3H, t, CH_3, $J_{CH_3-CH_2}$ = 7.07), 1.24 (6H, s, 2CH_3), 2.12 (3H, t, 2CH_3, $J_{2-CH_3-4-CH_2}$ = 1.56), 2.56 (1H, ddq, 4-H_A, $J_{H_A-H_B}$ = 14.43, J_{4-H_A-5-H} = 8.18), 2.97 (1H, ddq, 4-H_B, J_{4-H_B-5-H} = 10.38), 4.06 (2H, q, OCH_2), 4.97 (1H, ddd, 5-H, $J_{5-H-1-H}$ = 6.62), 5.68 (1H, dd, 1-H, $J_{1-H-2-H}$ = 15.44), and 5.80 ppm (1H, d, 2-H). IR spectrum: 1640 (C=C), 1685 (C=O), and 3460 cm^{-1} (broad), O—H). Found: C 64.6; H 8.2%. $C_{13}H_{20}O_4$. Calculated: C 65.0; H 8.3%.

cis-3-Acetyl-2-methyl-5-(3-hydroxy-3-methyl-1-buten-1-yl)-4,5-dihydrofuran (X). This compound was obtained in 18.3% yield and had R_f 0.37 (ether). PMR spectrum ($CDCl_3$): 1.38 (3H, s, CH_3), 1.42 (3H, s, CH_3), 2.20 (3H, s, CH_3CO), 2.23 (3H, t, 2-CH_3, $J_{2-CH_3-4-CH_2}$ = 1.5), 2.69 (1H, ddq, 4-H_A, $J_{H_A-H_B}$ = 14.0, J_{4-H_A-5-H} = 8.2), 3.18 (1H, ddq, 4-H_B, J_{4-H_B-5-H} = 10.0), 5.48 (1H, dd, 1-H, $J_{1-H-2-H}$ = 11.7, J_{1-H_5-H} = 8.2), 5.61 (1H, dd, 2-H, $J_{2-H-5-H}$ = 1.2), and 6.02 ppm (1H, dtd, 5-H). IR spectrum: 1598 (broad, C=C), 1660 (C=O), and 3430 cm^{-1} broad (O—H). Found: C 68.2; H 8.8%. $C_{12}H_{18}O_3$. Calculated: C 68.6; H 8.6%.

trans-3-Acetyl-2-methyl-5-(3-hydroxy-3-methyl-1-buten-1-yl)-4,5-dihydrofuran (XI). This compound was obtained in 38.1% and 52.6% yields (in reactions of acetylacetone with II and III, respectively) and had R_f 0.22 (ether). PMR spectrum ($CDCl_3$): 1.35 (6H, s, 2CH_3, $\Delta\delta_{CH_3}$ = 0.006 ppm), 2.21 (3H, s, CH_3CO), 2.24 (3H, t, 2-CH_3, $J_{2-CH_3-4-CH_2}$ = 1.5), 2.74 (1H, ddq, 4-H_A, $J_{H_A-H_B}$ = 14.0, J_{4-H_A-5-H} = 8.2), 3.13 (1H, ddq, 4-H_B, J_{4-H_B-5-H} = 10.5), 5.06 (1H dtd, 5-H, $J_{5-H-1-H}$ = 8.2, $J_{5-H-2-H}$ = 0.7), 5.78 (1H, dd, 1-H, $J_{1-H-2-H}$ = 15.5), and 5.91 ppm (1H, dd, 2-H). IR spectrum: 1600 (broad, C=C), 1660 (C=O), and 3370 cm^{-1} (broad, O—H). Found: C 68.5; H 9.0%. $C_{12}H_{18}O_3$. Calculated: C 68.6; H 8.6%.

Ethyl trans-6-Acetoxy-2-carbethoxy-4-tetradecenoate (XII). The reaction was carried out at 80°C for 10 min and gave a product with R_f 0.65 [CCl_4—acetone (4:1)] in 67.2% yield. PMR spectrum (C_6D_6): 0.90 (3H, t, CH_3, $J_{CH_3-CH_2}$ = 6.7), 0.96 (6H, t, 2CH_3, $J_{CH_3-CH_2}$ = 6.7), 1.24 (14H, broad s, 7CH_2), 1.75 (3H, s, CH_3CO), 2.67 (2H, t, 3-CH_2, $J_{3-CH_2-2(4)-H}$ = 7.1), 3.36 (1H, t, 2-H), 3.96 (4H, q. 2CH_2), 5.34 (1H, q, 6-H, $J_{6-H-5-H(7-CH_2)}$ = 6.5), 5.50 (1H, dd, 5-H, $J_{5-H-4-H}$ = 15.5), and 5.70 ppm (1H, dt, 4-H). ^{13}C NMR spectrum (62.89 MHz, $CDCl_3$): 14.0, 21.1, 22.5, 25.0, 29.1, 29.3, 29.4, 29.6, 31.3, 31.8, 34.4 (C_3, C_7—C_{14}, $OCOCH_3$, $COOCH_2CH_3$); 51.7 (C_2); 61.3 ($COOCH_2CH_3$); 74.2 (C_6); 128.7, 131.7 (C_4, C_5); 168.6, 170.1 ppm ($OCOCH_3$, $COOCH_2CH_3$). IR spectrum: 1733 cm^{-1} (COOR). Mass spectrum, m/z: 384.

3-Carbethoxy-2,5-dimethyl-5-isopropenyl-4,5-dihydrofuran (XIII). This compound, with bp 80°C (2.7 hPa) and n_D^{20} 1.4775, was isolated in 65.3% yield by fractional distillation. Analysis by GLC yielded a product at 173°C (carrier-gas flow rate 40 ml/min) with t_{ret} 9.6 min and R_f 0.78 (ether). PMR spectrum (60 MHz, CCl_4): 1.18 (3H, t, CH_3, $J_{CH_3-CH_2}$ = 7.0), 1.38 (3H, s, 5-CH_3), 1.72 (3H, dd, $CH_3C{=}CH_2$, $J_{CH_3-H_{cis}}$ = 1.5, $J_{CH_3-H_{trans}}$ = 0.7), 2.12 (3H, t, 2-CH_3, $J_{2-CH_3-4-CH_2)}$ = 1.5), 2.70 (2H, ABX_3, 4-CH_AH_B, J_{H-H} = 14.0), 4.08 (2H, q, CH_2), 4.74 (1H, dq, H_{cis}, $J_{H_{cis}-H_{trans}}$ = 1.5), and 4.93 ppm (1H, dq, H_{trans}), IR spectrum: 1645 (C=C); 1696 ($COOCH_2CH_3$); 910, 985, 3100 cm^{-1} (=CH_2). Found: C 68.5; H 8.6%. $C_{12}H_{18}O_3$. Calculated: C 68.6; H 8.6%.

LITERATURE CITED

1. A. P. Khrimyan, A. V. Karapetyan, S. K. Vardapetyan, and Sh. O. Badansyan, Arm. Khim. Zh., 37, No. 7, 430 (1984).
2. G. M. Nikishin and É. I. Troyanskii, Zh. Vses. Khim. Ova., No. 2, 169 (1979).
3. D. I. Davies and M. J. Parrott, Free Radicals in Organic Synthesis, Springer-Verlag (1978).
4. E. I. Heiba, R. M. Dessau, and W. J. Koehl, J. Am. Chem. Soc., 90, 5905 (1968).

5. M. G. Vinogradov, S. P. Verenchikov, and G. I. Nikishin, Izv. Akad. Nauk SSSR, Ser. Khim., No. 1, 200 (1971).
6. G. I. Nikishin, M. G. Vinogradov, and G. P. Il'ina, Zh. Org. Khim., 8, 1401 (1972).
7. R. M. Dessau and E. I. Heiba, J. Org. Chem., 39, 3457 (1974).
8. F. I. McQuillin and M. I. Wood, J. Chem. Soc., Perkin Trans., No. 16 1762 (1976).
9. M. G. Vinogradov, T. M. Fedorova, and G. I. Nikishin, Zh. Org. Khim., 12, 1175 (1976).
10. M. G. Vinogradov, P. A. Direi, and G. I. Nikishin, Zh. Org. Khim., 13, 2498 (1977).
11. G. G. Melikyan, D. A. Mkrtchyan, and Sh. O. Badanyan, Khim. Geterotsikl. Soedin., No. 1, 19 (1982).
12. M. G. Vinogradov, M. S. Pogosyan, A. Ya. Shteinshneider, and G. I. Nikishin, Izv. Akad. Nauk SSSR, Ser. Khim., No. 4, 842 (1983).
13. M. G. Vinogradov, V. N. Dolinko, and G. I. Nikishin, Izv. Akad. Nauk SSSR, Ser. Khim., No. 2, 375 (1984).
14. G. G. Melikyan, D. A. Mkrtchyan, and Sh. O. Badanyan, Khim. Geterotsikl. Soedin., No. 7, 884 (1980).
15. M. G. Vinogradov, N. L. Radyukina, M. S. Pogosyan, S. P. Verenchikov, A. Ya. Shteinshneider and G. I. Nikishin, Izv. Akad. Nauk SSSR, Ser. Khim., No. 8, 1949 (1980).
16. M. G. Vinogradov, M. S. Pogosyan, A. Ya. Shteinshneider, and G. I. Nikishin, Izv. Akad. Nauk SSSR, Ser. Khim., No. 9, 2077 (1981).
17. G. G. Melikyan, D. A. Mkrtchyan, and Sh. O. Badanyan, Arm. Khim. Zh., 34, 1011 (1981).
18. G. G. Melikyan, D. A. Mkrtchyan, K. V. Lebedeva, U. Yu. Myaéorg, G. A. Panosyan, and Sh. O. Badanyan, Khim. Prir. Soedin., No. 1, 98 (1984).
19. R. Rossi, A. Carpita, M. G. Quirica, and C. A. Vericini, Tetrahedron, 38, 639 (1982).
20. E. B. Bates, E. R. H. Jones, and M. C. Whiting, J. Chem. Soc., 1854 (1954).

SYNTHESIS AND REARRANGEMENT OF PHENYL ETHERS OF 5,6-DIHYDROPYRANS

U. G. Ibatullin, Kh. F. Sagitdinova,
G. R. Talipova and M. G. Safarov

UDC 547.811'562.04

4-Methyl-5-phenoxy-5,6-dihydropyrans were synthesized by the reaction of 3,4-dibromo-4-methyltetrahydropyran with a number of substituted phenols. The products are converted to the corresponding phenols under the conditions of the Claisen rearrangement.

3,4-Dibromo-4-methyltetrahydropyran (I), which is readily formed in the bromination of a side product in the synthesis of isoprene, viz., 4-methyl-5,6-dihydropyran, is a potentially valuable intermediate for organic synthesis. The first research devoted to this topic was published by Gevorkyan and co-workers [1]. They synthesized a number of amines starting from the dibromide.

We have studied the reaction of I with phenol and its alkyl, nitro, and halo derivatives.

We found that dehydrobromination of the tertiary bromine atom and substitution of the secondary bromine atom to give the corresponding phenyl ethers (II) occur when the dibromide is heated with phenols in methyl ethyl ketone in the presence of potassium carbonate (Table 1):

I

IIa-e

II a R=H, b $R=p\text{-}NO_2$, c R=o-Cl, d R=p-I, e $R=2.6\text{-}CH_3$

Bashkir State University, Ufa 450074. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 3, pp. 315-317, March, 1985. Original article submitted April 10, 1984; revision submitted September 17, 1984.