4. Y. Takahashi, H. Hagiwara, H. Uda, and H. Kosugi, Heterocycles, 15, 225 (1981).
5. P. Brownbridge, P. G. Hung, and S. Warren, Tetrahedron Lett., No. 32, 3391 (1983).
6. W. J. Evers, H. H. Heinsohn, M. H. Vock, and C. Giacino, US Patent No. 4,041,186; Chem. Abstr., 87, 152,002 (1977).
7. T. Hasegawa, Jpn. Patent No. 58,121,286; Chem. Abstr., 99, 158,228 (1983).
8. P. Prownbridge, E. Egert, P. G. Hunt, O. Kennard, and S. Warren, J. Chem. Soc., Perkin Trans. 1, No. 10, 2751 (1981).
9. O. G. Kulinkovich, I. G. Tishchenko, and Yu. N. Romashin, Khim. Geterotsikl. Soedin., No. 2, 163 (1988).
10. H. Minato and T. Nagasaki, J. Chem. Soc., No. 4, 377 (1966).
11. P. A. Grieco, C. S. Pogonowski, and S. Burke, J. Org. Chem., 40, 542 (1975).
12. K. Isobe, M. Fuse, H. Kosugi, H. Hagiwara, and H. Uda, Chem. Lett., No. 7, 785 (1979).
13. P. Bakuzis and M. L. F. Bakuzis, J. Org. Chem., 46, 235 (1981).
14. H. Ishibashi, S. Akai, H.-D. Choi, H. Nakagawa, and Y. Tamura, Tetrahedron Lett., No. 36, 3877 (1983).

SYNTHESIS OF DERIVATIVES OF 4,5-DIHYDROFURAN, FURAN, AND HEXAHYDROBENZOFURAN FROM CONJUGATED ALKENYNES*

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The regiochemistry of the reaction of 1,2- and 1-substituted derivatives of 1-buten-3-yne and its 4- and 2,4-substituted derivatives of the isoprenoid type with acetoacetic ester and acetylacetone in the presence of the manganese(III) acetate—copper(II) acetate oxidative system was studied. Derivatives of 4,5-dihydrofuran, furan, and hexahydrobenzofuran were obtained.

The radical reactions of conjugated systems with β-dicarbonyl compounds initiated by manganese acetate have recently been the subject of detailed investigation [2-6]. It was shown that in the case of 1-alken-3-ynes the regiochemistry of the process basically depends on the structure of the substrate. 1-Buten-3-yne reacts nonregioselectively with α,α-dioxoalkyl radicals with the commensurable participation of both the double bond and the triple bond [2, 3], while in the case of 2-, 4-, and 2,4-substituted 1-buten-3-ynes the reaction proceeds selectively at the double bond [3, 5, 6].

In the present research we studied the regiochemistry of the reaction of conjugated alkenynes with acetoacetic ester and acetylacetone in the presence of manganese(III) acetate using 1,2- and 1-substituted derivatives of 1-buten-3-yne, as well as its 4- and 2,4-substituted derivatives of the isoprenoid type, as the substrates.

Cyclohexenylacetylene was selected as a 1,2-disubstituted derivative of 1-buten-3-yne. Its reaction with acetoacetic ester under the conditions used in the analogous reactions of 1-alken-3-ynes [60-70°C, substrate:Mn(III):addend:Cu(II) molar ratio 1:1:2:0.07] led only to resinification products, evidently as a consequence of rapid polymerization of the vinyl radical-adducts formed in the addition of an α-carbethoxyacetonyl radical to the triple bond of the substrate [3]. The role of copper(II) acetate in this reaction consists in the oxidation

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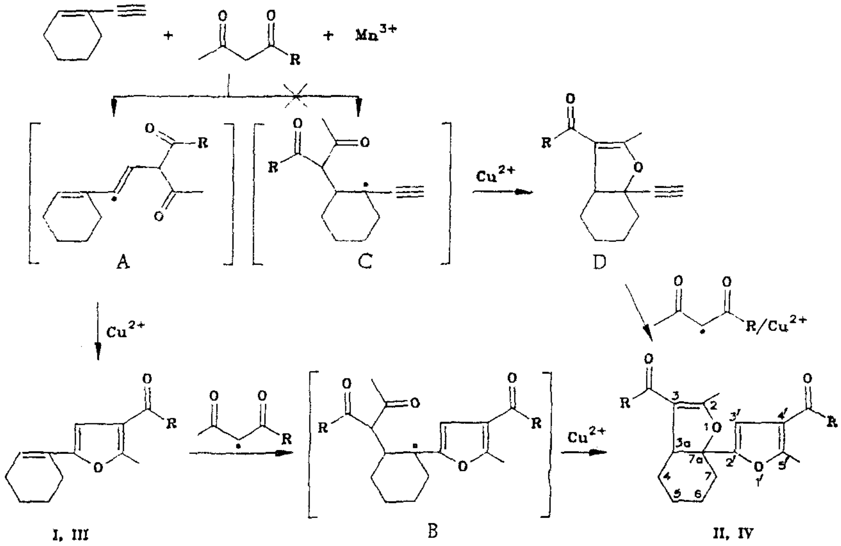
of the intermediate radical-adducts [7]; one therefore might have expected that an increase in the copper(II) acetate concentration in the reaction mixture would prevent the polymerization process significantly owing to the efficient reaction of copper(II) acetate with the vinyl radical-adducts. In fact, by varying the reaction conditions (the molar reagent ratio and the temperature) it was found that, judging from the yields of products, carrying out the process in the presence of an equimolar amount of copper(II) acetate at 30°C should be considered to be the optimal procedure. Compounds I and II are formed under these conditions in the reaction of cyclohexenylacetylene with acetoacetic ester. Compound I is the result of attack by the α-carbethoxyacetonyl radical at the triple bond of the substrate with subsequent oxidative cyclization of radical-adduct A under the influence of copper(II) acetate. Compound II may be formed via two alternative pathways. The first pathway includes the addition of the addend to the double bond of reaction product I and subsequent oxidative cyclization of α-furylalkyl radical-adduct B. The second pathway consists in attack by the α-carbethoxyacetonyl radical at the double bond of the substrate, in cyclization of propargyl radical-adduct C to acetylenic dihydrofuran D, and in rereaction of the latter with the addend at the triple bond.



I, II $R=OC_2H_5$; III, IV $R=CH_3$

The second pathway for the formation of II is unlikely, since if D were formed in the reaction, then, as a consequence of the significantly lower reactivity of an isolated triple bond as compared with conjugated systems, it would of necessity be detected in the reaction products, as in the analogous reaction of vinyl- and isopropenylacetylene [3]. The formation of I is unexpected, since in the case of vinyl- and isopropenylacetylene compounds with a similar structure could not be isolated previously, and their formation was postulated as intermediates in the reaction [2, 3]. The presence of an alkyl substituent attached to the terminal carbon atom of the vinyl group, because of the combination of steric and electronic factors, evidently decreases the reactivity of I as compared with analogs — 3-carbethoxy(acetyl)-2-methyl-5-vinylfurans [2, 3]. The validity of this assumption is confirmed by kinetic data on the relative reactivities of styrene and trans-β-methylstyrene [8].

To prove that II is formed as a result of the secondary reaction of I the latter, after isolation in the individual state by means of column chromatography, was resubjected to reaction with acetoacetic ester. In fact, II was formed in high yield as a result of the reaction. The next stage in the study of this reaction was carrying out the reaction of cyclohexenylacetylene with acetoacetic ester in a substrate—Mn(III)—addend—Cu(II) molar ratio of 1:3:6:3. In this case II was the only product obtained and was obtained in high yield. The experimental data make it possible to assert that the reaction of cyclohexenylacetylene with acetoacetic ester proceeds regioselectively at the triple bond, despite the fact that structure II formally constitutes evidence for nonregioselective occurrence of the process.

In the PMR spectrum of II the signal of the 7-CH_2 group is shifted to a weak field relative to the signals of the remaining methylene groups of the cyclohexane ring (4-CH_2, 5-CH_2, 6-CH_2) because of the deshielding effect of the aromatic ring. The observed fact of the mag-

TABLE 1. Physicochemical Characteristics of I-IV, VI, VIII, and X

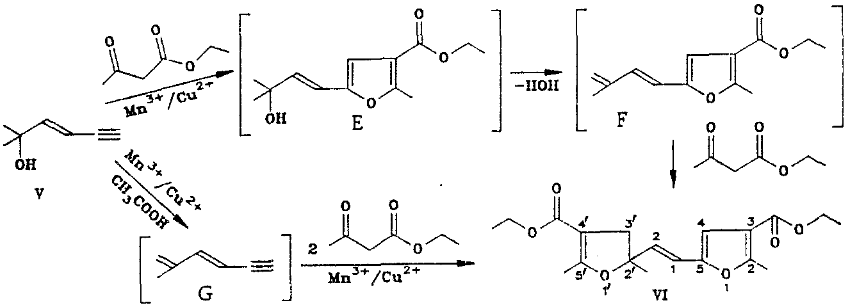
Compound	n_D^{20} (mp, °C)	R_f*	Found, %		Empirical formula	Calculated, %		Yield, %**
			C	H		C	H	
I	1,5268	0,65	71,9	8,0	$C_{14}H_{18}O_3$	71,8	7,7	19
II	(40—41)	0,33	66,3	7,3	$C_{20}H_{26}O_6$	66,3	7,2	23; (77); [60]
III	(54—55)	0,77	76,9	8,2	$C_{13}H_{16}O_2$	76,4	7,8	24
IV	(89—90)	0,36	71,3	7,6	$C_{18}H_{22}O_4$	71,5	7,3	20; (70); [63]
VI	1,5155	0,66	65,2	6,3	$C_{19}H_{24}O_6$	65,5	6,9	36
VIII	1,5120	0,59	70,5	8,9	$C_{18}H_{26}O_4$	70,6	8,5	48
X	1,4935	0,63	71,0	8,5	$C_{19}H_{28}O_4$	71,2	8,7	50

*The eluent was hexane—ether [2:1 (for I, II), 1:3 (for III, IV, VIII, X), and 1:2 (for VI)].

**The yield for a molar reagent ratio of 1:3:6:3 is presented in brackets; the yield from I is presented in parentheses for II, as is the yield from III for IV.

netic nonequivalence of the methylene protons of the carbethoxy group in the 3 position of the dihydrofuran ring is exceptionally interesting. Instead of the expected quartet, the signal of the CH_2 group appears in the form of an ABX_3 system in which the geminal spin-spin coupling constant (SSCC) of the methylene protons is 10.9 Hz. The reason for this is evidently the retarded character of rotation relative to the $C_{(3)}—COOCH_2CH_3$ bond, which is revealed by constructing molecular models. For comparison, one should note that in the case of 4'—$COOCH_2CH_3$ rotation relative to the C—C bond that connects this group to the furan ring is unhindered.

Acetylacetone was also used as the carbonyl component in the reaction with cyclohexenylacetylene; the chemical mechanism of the process is retained completely in comparison with the above examined reaction of acetoacetic ester. Compounds III and IV are formed at a substrate—Mn(III)—addend—Cu(II) molar ratio of 1:1:2:1. Compound IV is the only product when a molar reagent ratio of 1:3:6:3 is used. In this case it was also shown that III reacts with acetylacetone to give IV in high yield.



The reaction of a 1-substituted derivative of 1-buten-3-yne — E-5-hydroxy-5-methyl-3-hexen-1-yne (V) — with acetoacetic ester gave, instead of the expected furan derivative E, an unexpected result — VI. The latter may be formed either from intermediate E in the case of its dehydration to diene F and subsequent reaction with the addend through the isopropenyl group or as a consequence of dehydration of the starting V with the formation of 2-methyl-1, 3-hexadien-5-yne (G) and subsequent reaction of the latter with acetoacetic ester through the acetylenic and isopropenyl groups.

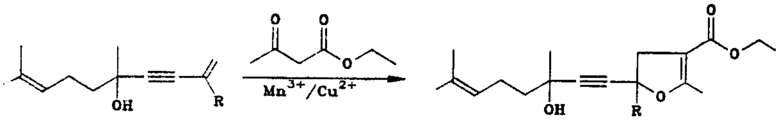
The fact of obtaining VI was unexpected, since a similar dehydration reaction was not observed in the reaction of related systems such as 5-hydroxy-5-methyl-1-hexen-3-yne [5], 5-hydroxy-2,5-dimethyl-1-hexen-3-yne [6], and cis- and trans-5-hydroxy-5-methyl-1,3-hexadiene [4] with acetoacetic ester.

The E configuration of the double bond in VI was established on the basis of data from the PMR spectrum, in which the SSCC of the vinyl protons is 15.8 Hz. It should be noted that the vinyl protons appear in the form of an AB system with a difference in the chemical shifts of 0.03 ppm; the weak-field signal was assigned to the 1-H proton adjacent to an aromatic ring.

TABLE 2. Spectral Characteristics of I-IV, VI, VIII, and X

Compound	IR spectrum, cm^{-1}	PMR spectrum, ppm (J, Hz)	Mass spectrum, M^+
I	3142 (C—H furan ring), 1717 ($COOC_2H_5$), 1608, 1555 (C=C furan ring)	(60 MHz, CCl_4): 1,25 (3H, t, 3-$COOCH_2CH_3$, $J_{CH_3-CH_2}=7{,}3$); 1,45—1,85 (4H, m, 2CH_2); 1,90—2,30 (4H, m, 2CH_2); 2,47 (3H, s, 2-CH_3); 4,16 (2H, q, 3-$COOCH_2CH_3$); 6,15 (1H, m 2′-H); 6,23 (1H, s, 4-H)	234
II	3150 (C—H furan ring), 1715, 1690 (2$COOC_2H_5$), 1645 (C=C dihydrofuran ring), 1615, 1582 (C=C furan ring)	(360 MHz $CDCl_3$): 1,293 (3H, t 3-$COOCH_2CH_3$, $J_{CH_3-CH_2}=7{,}4$); 1,341 (3H, t, 4′-$COOCH_2CH_3$, $J_{CH_3-CH_2}=7{,}4$); 1,18—1,95 (6H, m, 4-CH_2, 5-CH_2, 6-CH_2); 2,051 (2H, t, 7-CH_2, $J_{7\text{-}CH_2-6\text{-}CH_2}=6{,}5$); 2,207 (3H, d, 2-$CH_3$, $J_{2\text{-}CH_3-3a\text{-}H}=1{,}4$); 2,567 (3H, s, 5′-$CH_3$); 3,415 (1H, t,q, , 3a-H. $J_{3a\text{-}H-4\text{-}CH_2}=6{,}1$); 4,182 (2H, center of ABX_3 system 3-$COOCH_AH_BCH_3$, $J_{H_A-H_B}=10{,}9$, $J_{CH_3-H_A(H_B)}=7{,}1$); 4,276 (2H, q, 4′-$COOCH_2CH_3$); 6,54 (1H, s 3′-H)	362
III	3150 (C—H furan ring), 1682 (C=O, 1589, 1555 (C=C furan ring)	(60 MHz CD_3OD): 1,40—1,80 (4H, m, 2-CH_2); 1,90—2,30 (4H, m, 2-CH_2); 2,31 (3H, s, 3-$COCH_3$); 2,47 (3H, s, 2-CH_3); 6,21 (1H, m, 2′-H); 6,38 (1H, s, 4-H)	204
IV	3118 (C—H furan ring), 1688 (C=O), 1630, 1605 (C=C), 1577 (C=C furan ring)	(60 MHz CCl_4): 1,18—2,05 (8H, m, 4-CH_2, 5-CH_2, 6-CH_2, 7-CH_2); 2,13 (3H, s 3-$COCH_3$); 2,18 (3H, d, 2-CH_3, $J_{2\text{-}CH_3-3a\text{-}H}=1{,}2$); 2,29 (3H, s, 4′-$COCH_3$); 2,52 (3H, s, 5′-$CH_3$); 3,37 (1H, m, 3a-H); 6,55 (1H, s, 3′-H)	302
VI	3138 (C—H furan ring), 1725, 1705 (2$COOC_2H_5$), 1648 (C=C dihydrofuran ring), 1605, 1555 (C=C furan ring)	(400 MHz, $CDCl_3$): 1,251 (3H, t, 4′-$COOCH_2CH_3$, $J_{CH_3-CH_2}=7{,}20$); 1,319 (3H, t, 3-$COOCH_2CH_3$, $J_{CH_3-CH_2}=7{,}24$); 1,508 (3H, s, 2′-CH_3); 2,208 (3H, split s , 5′-CH_3); 2,554 (3H, s, 2-CH_3); 2,838 (2H, center of ABX_3-system, 3′-CH_AH_B, $J_{5'\text{-}CH_3-3'\text{-}H_A(H_B)}\simeq 1{,}2$); 4,136 (2H, q, 4′-$COOCH_2CH_3$); 4,253 (2H, q, 3-$COOCH_2CH_3$); 6,459 (1H, s, 4-H); 6,214 (1H, d, 2-H_B, $J_{2\text{-}H_B-1\text{-}H_A}=15{,}76$); 6,247 (1H, d, 1-$H_A$)	—
VIII	3470 br (O—H), 2250 (C≡C), 1700 ($COOC_2H_5$), 1652 (C=C dihydrofuran ring)	(250 MHz $CDCl_3$): 1,25 (3H, t, 3-$COOCH_2CH_3$, $J_{CH_3-CH_2}=7{,}2$); 1,46 (3H, s, 3′-CH_3); 1,61 (3H, d, 7′-CH_3, $J_{7'\text{-}CH_3-6'\text{-}H}=1{,}0$); 1,67 (3H, d, CH_3, $J_{CH_3-6'\text{-}H}=1{,}5$); 2,17 (3H, t, 2-$CH_3$, $J_{2\text{-}CH_3-4\text{-}H_A(H_B)}=1{,}5$); 2,05—2,35 (4H, m, 4′-$CH_2$, 5′-$CH_2$); 2,50 (1H, s, OH); 3,03 (2H, center of $ABXY_3$ system 4-CH_AH_B, $J_{H_A-H_B}=14{,}4$, $J_{4\text{-}H_A-5\text{-}H}=8{,}3$, $J_{4\text{-}H_B-5\text{-}H}=10{,}6$); 4,14 (2H, q, 3-$COOCH_2CH_3$); 5,13 (1H, split t, 6′-H, $J_{6'\text{-}H-5'\text{-}CH_2}\simeq 5{,}1$); 5,18 (1H, dd, 5-H)	—
X	3460 br (O—H), 2245 (C≡C), 1705 ($COOC_2H_5$), 1655 (C=C dihydrofuran ring)	(250 MHz $CDCl_3$): 1,26 (3H, t, 3-$COOCH_2CH_3$, $J_{CH_3-CH_2}=7{,}2$); 1,46 (3H, s, 3′-CH_3); 1,59 (3H, s, 5-CH_3); 1,62 (3H, d, 7′-CH_3, $J_{7'\text{-}CH_3-6'\text{-}H}=1{,}0$); 1,67 (3H, d CH_3, $J_{CH_3-6'\text{-}H}= =1{,}5$); 2,16 (3H, t, 2-$CH_3$, $J_{2\text{-}CH_3-4\text{-}H_A(H_B)}=1{,}5$); 2,05—2,40 (4H, m, 4′-$CH_2$, 5′-$CH_2$); 2,37 (1H, (1H, s, OH); 3,00 (2H, center of, ABX_3-system., 4-CH_AH_B, $J_{H_A-H_B}=14{,}5$); 4,14 (2H, q, 3-$COOCH_2CH_3$); 5,15 (1H, t, sext, 6′-H, $J_{6'\text{-}H-5'\text{-}CH_2}=7{,}2$)	—

4-Substituted derivatives of 1-buten-3-yne that contain a hydroxydimethyl group react with β-dicarbonyl compounds regioselectively at the double bond owing to effective protection of the triple bond by a bulky sutstituent [5, 6]. It seemed of interest to carry out a similar reaction with 4- and 2,4-substituted derivatives of 1-buten-3-yne that contain an unsaturated substituent of the isoprenoid type in the 4 position to ascertain the possibility of a competitive reaction through the enyne fragment and the trisubstituted double bond and also to synthesize derivatives of 4,5-dihydrofuran of the isoprenoid series. Dienynols VII and IX were selected as the model compounds. Their reaction with acetoacetic ester was carried out at a substrate:Mn(III):addend:Cu(II) molar ratio of 1:1:2:0.07 at 60°C. The reaction proceeds selectively at the double bond of the enyne fragment and leads to 4,5-dihydrofuran derivatives VIII and X.



VII, IX

VIII, X

VII, VIII R=H; IX, X R=CH$_3$

No substances whose structure would constitute evidence for occurrence of the reaction at the trisubstituted double bond could be detected, evidently as a consequence of the higher reactivities of conjugated systems as compared with an isolated double bond [9]. For comparison, it should be noted that in the case of 3,7-dimethyl-1,6-octadiene the reaction with acetoacetic ester proceeds selectively at the trisubstituted double bond with the formation of the corresponding 4,5-dihydrofuran derivative [10].

In the PMR spectra of VIII and X the assignments of the methyl groups of the isoprenoid fragment, which appear at 1.61 and 1.67 ppm, were made on the basis of data for the individual geometrical isomers of methyl farnesoates [11], as well as on the basis of the SSCC of the methyl groups and the 6'-H proton, which are 1.5 and 1.0 Hz, respectively, for the cis- and trans-methyl groups [12].

EXPERIMENTAL

The PMR spectra were obtained with Bruker AM-400 (400 MHz), Bruker WM-360 (360 MHz), and Perkin–Elmer R-12 (60 MHz) spectrometers. Chemical shifts are given relative to TMS. The IR spectra of solution in CCl_4 were recorded with a UR-20 spectrometer. The mass spectra were measured with an MKh-1320 spectrometer at an ionizing-electron energy of 70 eV. Analysis by TLC was carried out on Silufol UV-254 plates with detection by means of a saturated $KMnO_4$.

Compound V was obtained by a reverse Favorskii reaction from 2,7-dihydroxy-2,7-dimethyl-3-octen-5-yne [13]. Compounds VII and IX were synthesized by condensation of vinylacetylene and isopropenylacetylene with 6-methyl-5-hepten-2-one [14].

3-Carbethoxy-2-methyl-5-(1-cyclohexenyl)furan (I) and 3-Carbethoxy-2-methyl-7a-(4'-carbethoxy-5'-methyl-2'-furyl)hexahydrobenzofuran (II). A 25-mmole sample of $Mn(OAc)_3 \cdot 2H_2O$, 50 mmole of acetoacetic ester, and 25 mmole of cyclohexenylacetylene were added to a solution of 25 mmole of $Cu(OAc)_2 \cdot 2H_2O$ in 75 ml of glacial acetic acid, and the mixture was heated in an argon atmosphere at 30°C until the brown coloration vanished (3 h). The reaction mixture was then cooled to 20°C and filtered, and the filtrate was diluted with water. The aqueous mixture was extracted with ether, and the ether extract was washed successively with water, saturated sodium carbonate solution, and water and dried with $MgSO_4$. The ether was evaporated in vacuo, and individual reaction products I and II were isolated by means of column chromatography on silica gel (40-100 μm) at a sample:sorbent ratio of 1:50 by elution with hexane–ether (2:1) with monitoring by TLC.

3-Carbethoxy-2-methyl-7a-(4'-carbethoxy-5'-methyl-2'-furyl)hexahydrobenzofuran (II). A. Compound II was similarly obtained from 0.64 mmole of $Cu(OAc)_2 \cdot 2H_2O$, 0.64 mmole of $Mn(OAc)_3 \cdot 2H_2O$, 1.28 mmole of acetoacetic ester, and 0.64 mmole of I in 10 ml of acetic acid; the product was eluted with hexane–ether (2:1).

B. Compound II was similarly obtained from 37.5 mmole of $Cu(OAc)_2 \cdot 2H_2O$, 37.5 mmole of $Mn(OAc)_3 \cdot 2H_2O$, 75 mmole of acetoacetic ester, and 12.5 mmole of cyclohexenylacetylene in 90 ml of acetic acid; the product was eluted with hexane–ether (1:1).

3-Acetyl-2-methyl-5-(1-cyclohexenyl)furan(III) and 3-Acetyl-2-methyl-7a-(4-acetyl-5-methyl-2-furyl)hexahydrobenzofuran (IV). Compounds III and IV were similarly obtained from 25 mmole of $Cu(OAc)_2 \cdot 2H_2O$, 25 mmole of $Mn(OAc)_3 \cdot 2H_2O$, 50 mmole of acetylacetone, and 25 mmole of cyclohexenylacetylene in 75 ml of acetic acid; the products were eluted with hexane—ether (3:1).

3-Acetyl-2-methyl-7a-(4-acetyl-5-methyl-2-furyl)hexahydrobenzofuran (IV). A. Compound IV was similarly obtained from 0.98 mmole of $Cu(OAc)_2 \cdot 2H_2O$, 0.98 mmole of $Mn(OAc)_3 \cdot 2H_2O$, 1.96 mmole of acetylacetone, and 0.98 mmole of III in 15 ml of acetic acid (75% conversion of the starting compound); the product was eluted with hexane—ether (3:1).

B. Compound IV was similarly obtained from 37.5 mmole of $Cu(OAc)_2 \cdot 2H_2O$, 37.5 mmole of $Mn(OAc)_3 \cdot 2H_2O$, 75 mmole of acetylacetone, and 12.5 mmole of cyclohexenylacetylene in 90 ml of acetic acid (2 h); the product was eluted with hexane—ether (1:1).

(E)-3-Carbethoxy-2-methyl-5-[1-ethenyl-2-(4-carbethoxy-2,5-dimethyl-2,3-dihydro-2-furyl)]furan (VI). Compound VI was similarly obtained from 9.6 mmole of $Cu(OAc)_2 \cdot 2H_2O$, 9.6 mmole of $Mn(OAc)_3 \cdot 2H_2O$, 19.2 mmole of acetoacetic ester, and 8 mmole of V in 40 ml of acetic acid; the product was eluted with hexane—ether (3:1).

3-Carbethoxy-2-methyl-5-(3-hydroxy-3,7-dimethyl-6-octen-ynyl)4,5-dihydrofuran (VIII). This compound was similarly obtained from 0.7 mmole of $Cu(OAc)_2 \cdot 2H_2O$, 10 mmole of $Mn(OAc)_3 \cdot 2H_2O$, 20 mmole of acetoacetic ester, and 10 mmole of VII in 50 ml of acetic acid at 60°C (20 min); the product was eluted with hexane—ether (3:1).

3-Carbethoxy-2,5-dimethyl-5-(3-hydroxy-3,7-dimethyl-6-octen-1-ynyl)-4,5-dihydrofuran (X). Compound X was similarly obtained from 0.7 mmole of $Cu(OAc)_2 \cdot 2H_2O$, 10 mmole of $Mn(OAc)_3 \cdot 2H_2O$, 20 mmole of acetoacetic ester, and 10 mmole of IX in 50 ml of acetic acid at 60°C (20 min); the product was eluted with hexane—ether (3:1).

LITERATURE CITED

1. G. G. Melikyan, É. V. Babayan, A. A. Tosunyan, and Sh. O. Badanyan, Arm. Khim. Zh., 40, 452 (1987).
2. G. G. Melikyan, D. A. Mkrtchyan, and Sh. O. Badanyan, Khim. Geterotsikl. Soedin., No. 7, 884 (1980).
3. G. G. Melikyan, D. A. Mkrtchyan, and Sh. O. Badanyan, Khim. Geterotsikl. Soedin., No. 1, 19 (1982).
4. G. G. Melikyan, D. A. Mkrtchyan, V. M. Mkrtchyan, and Sh. O. Badanyan, Khim. Geterotsikl. Soedin., No. 3, 308 (1985).
5. G. G. Melikyan, D. A. Mkrtchyan, and Sh. O. Badanyan, Arm. Khim. Zh., 34, 1011 (1981).
6. G. G. Melikyan, A. B. Sargsyan, and Sh. O. Badanyan, Arm. Khim. Zh., 39, 228 (1986).
7. G. I. Nikishin and É. I. Troyanskii, Zh. Vses. Khim. Obva., No. 2, 169 (1979).
8. E. I. Heiba, R. M. Dessau, and W. J. Koehl, J. Am. Chem. Soc., 90, 5905 (1968).
9. J. K. Kochi (ed.), Free Radicals, Wiley, New York—London—Sydney—Toronto (1973), p. 92.
10. F. J. McQuillin and M. Wood, J. Chem. Soc., Perkin Trans. 1, No. 16, 1762 (1976).
11. J. W. K. Burrel, R. F. Garwood, L. M. Jackman, E. Oskay, and B. C. L. Weedon, J. Chem Soc., C, No. 23, 2144 (1966).
12. J. Emsley, J. Feeney, and L. Sutcliff, High-Resolution NMR Spectroscopy, Pergemon, Elmford, New York (1966), Ch. 10.
13. L. A. Akopyan, S. G. Grigoryan, G. A. Chukhadzhyan, and S. G. Matsoyan, Zh. Org. Khim., 9, 2004 (1973).
14. S. A. Vartanyan, G. A. Chukhadzhyan, and V. N. Zhamagortsyan, Izv. Akad Nauk Arm. SSR, Khim. Nauki, 12, 107 (1959).