SIMPLE SYNTHESIS OF SUBSTITUTED 3-OXABICYCLO[3.1.0]HEXAN-2-ONES AND THEIR REARRANGEMENT IN THE PRESENCE OF LITHIUM IODIDE

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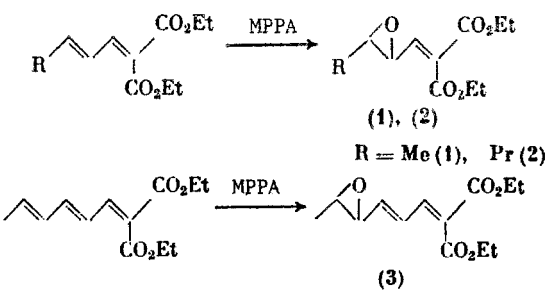
2-Alkenylidenemalonic ester monoepoxides react with organolithium and organomagnesium compounds to give 1-ethoxycarbonyl-4-alkyl-6-alkenyl(alkyl, aryl, alkynyl)-3-oxabicyclo[3.1.0]hexan-2-ones in high yields. The latter, when an alkenyl fragment is present, undergo rearrangement in the presence of LiI to substituted 1-ethoxycarbonyl-3-oxabicyclo[3.3.0]-6-octen-2-ones or 3-(1,3-butadienyl)-4-butanolides.

Keywords: *2-alkenylidenemalonic ester monoepoxides, 1-ethoxycarbonyl-4-alkyl-6-alkenyl-3-oxabicyclo[3.1.0]hexan-2-ones, 1-ethoxycarbonyl-3-oxabicyclo[3.3.0]-6-octen-2-ones, 3-(1,3-butadienyl)-4-butanolides, organolithium compounds, organomagnesium compounds, lithium iodide, synthesis, rearrangement.*

The conjugate addition of nucleophilic reagents to γ-halogen-containing α,β-unsaturated carbonyl substrates and subsequent cyclization of the resulting enolates is an effective method for the synthesis of various cyclopropanes containing functional groups. Halo derivatives of alkyl crotonates [1-3], diethyl alkylidenemalonates [4-6], and unsaturated acylphosphoranes [7] can be used as substrates in reactions of this type. In the present research we studied the possibility of the utilization of 2-alkenylidenemalonic ester monoepoxides for the synthesis of cyclopropanes.

Oxiranes **1-3** can be readily obtained by treatment of diethyl *trans*-2-butenylidenemalonate, diethyl *trans*-2-hexenylidenemalonate, and diethyl *trans,trans*-2,4-hexadienylidenemalonate with monoperphthalic acid (MPPA) in Et_2O at 20°C [8].

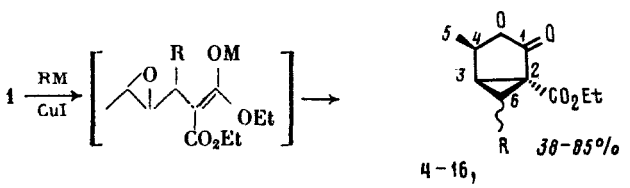


(1), (2)

R = Me (1), Pr (2)

(3)

We have found that the reaction of epoxide **1** with various organolithium and organomagnesium reagents (Et_2O, −78°C → 20°C, 3 h) in the presence of 5 mole % CuI leads to lactones **4-16** containing a cyclopropane fragment (Table 1).



4-16,

R=Me (**4**), Pr (**5**), CH_2=CH (**6**), 1,3-Butadien-2-yl (**7**), CH_2=C(Bu) (**8**), *Z*-*i*-BuCH=CH (**9**), *E*-BuCH=CH (**10**), Pr_2C=CH (**11**), 1-Cyclohexenyl (**12**), *E*-PhCH=CH (**13**), Ph (**14**), PrC≡C (**15**), PhC≡C (**16**);
M=Li, MgCl, MgBr, MgI.

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TABLE 1. Reactions of Epoxide **1** with Organolithium and Organomagnesium Compounds (RM) (Et_2O, −78°C → 20°C, 3 h, $[RM]_0:[1]_0$ = 1.05:1)

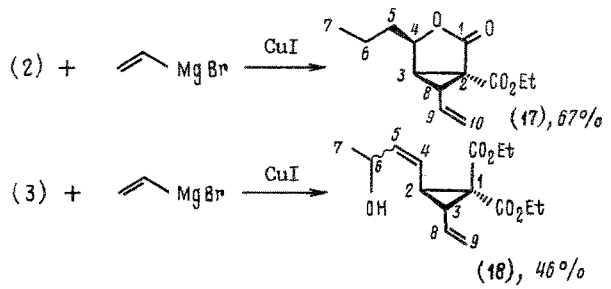
RM	Reaction product	Yield,* %	trans:cis †
MeMgI	4	65	>95 : 5
PrMgBr	5	85	60 : 40
CH_2=CHMgBr	6	70	76 : 24
CH_2=CHC(MgCl)=CH_2	7	72	>95 : 5
CH_2=C(Bu)Li	8	54	>95 : 5
Z-*i*-BuCH=CHLi	9	75	>95 : 5
E-BuCH=CHLi	10	84	>95 : 5
Pr_2C=CHLi	11	71	>95 : 5
(1-Cyclohexenyl)Li	12	66	92 : 8
E-PhCH=CHMgBr	13	64	90 : 10
PhMgBr	14	69	>95 : 5
PrC≡CLi	15	38	75 : 25
PhC≡CLi	16	66	82 : 18

*The yields of the isolated products are presented.

†According to NMR spectroscopic data.

According to the PMR spectroscopic data, substituent R in the lactone ring of products **4-16** has primarily a *trans* orientation [9]. The constants of spin—spin coupling of the H^3 and H^6 protons in isomerically pure cyclopropanes **4**, **7-11**, and **14** range from 4.5 to 5.6 Hz; in the case of **6** and **16** $J_{H^3\text{-}H^6}$ = 4.5 and 8 Hz, respectively, for the major and minor components. Let us note that in the spectrum of product **14** the signals of the protons of the CO_2Et group [δ (ppm) 3.93 m and 0.8 t] are located at anomalously strong field, evidently as a consequence of the shielding effect of the phenyl substituent. It follows from the data in Table 1 that the maximum stereoselectivity of the formation of the *trans*-cyclopropanes is observed when alkenyl derivatives of lithium, as well as MeMgI, PhMgBr, and 1,3-butadien-2-yl magnesium chloride, are used (the corresponding *cis* isomers are not recorded in the ^1H and ^{13}C NMR spectra).

As compared with substrate **1**, epoxide **2** reacts more selectively. Thus its reaction with vinylmagnesium bromide leads to lactone **17** in the form of virtually one stereoisomer. The reaction of CH_2=CHMgBr with epoxide **3** is accompanied by allylic rearrangement in the step involving cyclization of the magnesium enolate and gives *trans*-dialkenylcyclopropane **18** (a mixture of *E* and *Z* isomers with respect to the disubstituted double bond, *E*/*Z* = 20:80).* When other organomagnesium or organolithium compounds (MeMgI, Z-iso-BuCH=CHLi, PhMgBr, PhC≡CLi) are used, cyclopropanes of the **18** type cannot be synthesized in greater than 10-15% yields because of the formation of a complex mixture of products.



We found that bicyclic lactones **6-12**, which contain an alkenyl fragment, undergo rearrangement with opening of the cyclopropane ring when they are refluxed in DMF in the presence of three equivalents of LiI (0.5-2 h) [10] (Table 2).

Cyclopropanes **6-8**, which have a terminal double bond, undergo rearrangement to give cyclopentenes **19-21** [11, 12]. Compounds **20** and **21** are formed in a mixture with decarbethoxylation products **22** and **23**. Replacement of LiI by NaI and Bu_4NI in the reaction with the participation of substrate **6** leads to a decrease in the yield of cyclopentene **19** from 61% to 39% and 23%, respectively. A still more significant decrease (to 10-15%) in the yield of product **19** is observed on passing from DMF to hexamethylphosphoric triamide (HMPT) and DMSO.

Cyclopropanes **9-12**, which contain an internal double bond, react to give conjugated dienes **24-27** [11]. According to the ^1H and ^{13}C NMR spectroscopic data [9], the disubstituted C^6—C^7 bonds in products **24-26** and the C^8=C^9 bonds in products

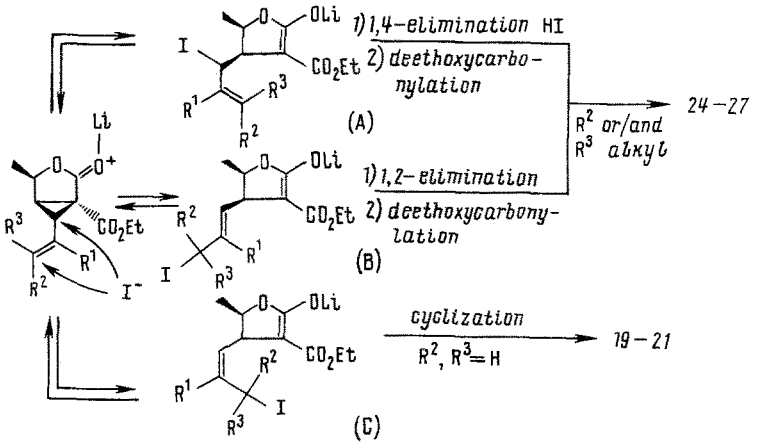
*In the ^{13}C NMR spectrum of **18** a single signal corresponds to both carbonyl C atoms; the pair of signals (Δδ = 1.03 ppm) corresponds to the allyl C^6 atom.

24 and **25** have a trans configuration ($J_{H^6-H^7}$ and $J_{H^8-H^9}$ = 14-16 Hz). Compounds **26** and **27** are mixtures of *E* and *Z* isomers with respect to the trisubstituted $C^8=C^9$ and $C^6=C^7$ bonds, respectively.

It should be noted that complete retention of the relative configuration of the C^3 and C^4 atoms is observed during the reaction.*

β-Styryl derivative **13** and 1,1-diethoxycarbonyl-2-vinylcyclopropane do not undergo rearrangement under the investigated conditions.

The key step in the rearrangement of alkenylcyclopropanes **6-12** to cyclopentenes **19-21** or 1,3-dienes **24-27** is evidently orbital nucleophilic opening of the cyclopropane ring by the I^- anion to give enolates A (1,5-addition) or B and C (1,7-addition), which is facilitated by coordination of the Li^+ cation at the carbonyl oxygen atom [14-16].



Upon cyclization, derivatives A and B give only the starting cyclopropane,† while enolate C is capable of irreversible cyclization to a cyclopentene. The 1,4- and/or 1,2-elimination of HI in enolates A and B when the corresponding CH fragments are present leads to a diene system. Let us note that a necessary condition for the occurrence of the reaction is a rigid bicyclic structure of compounds **6-12**.

Thus the reactions described in this paper open up a simple and effective pathway to the synthesis of various γ-lactones containing a cyclopropane, cyclopentene, or 1,3-diene fragment.

EXPERIMENTAL

The ^1H and ^{13}C NMR spectra of solutions of the compounds in $CDCl_3$ were recorded with a Bruker AM-300 spectrometer with tetramethylsilane (TMS) as the internal standard. The IR spectra of thin layers of the substances were obtained with a UR-20 spectrometer. The mass spectra were recorded with an MKh-1300 spectrometer at an input-cylinder temperature of 100°C and electron-ionization energies of 70 and 12 eV.

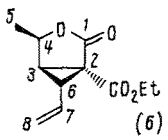
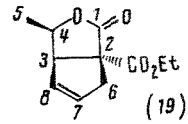
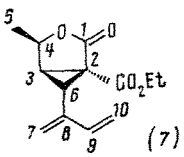
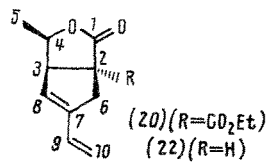
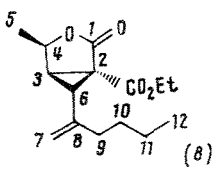
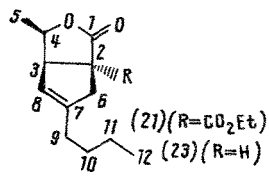
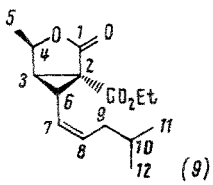
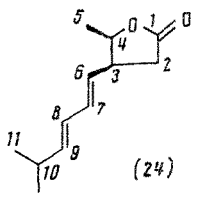
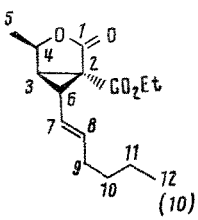
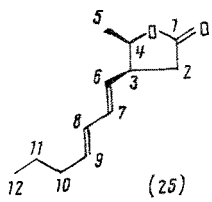
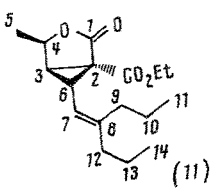
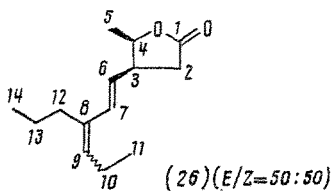
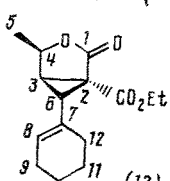
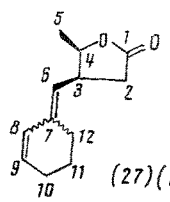
The starting organolithium and organomagnesium compounds were obtained by known methods. All of the experiments were carried out in a dry Ar atmosphere using absolute solvents.

Reactions of Monoepoxides 1-3 with Organolithium and Organomagnesium Compounds. A 1-ml (2.1 mmoles) sample of a 2.1 M ether solution of MeMgI was added with stirring and cooling to −78°C to a solution of 0.456 g (2 mmoles) of epoxide **1** in 15 ml of Et_2O containing 0.019 g (0.1 mmole) of CuI, after which the mixture was stirred for 15 min at −78°C, heated for 3 h to 20°C, and hydrolyzed by the addition of 10 ml of 8% HCl solution. The ether layer was separated, and the aqueous layer was extracted with Et_2O (3 × 5 ml). The combined ether extracts were dried with $MgSO_4$ and concentrated. Column chromatography [silica gel L 40/100, hexane:Et_2O (2:1)] gave 0.257 g (65%) of 1-ethoxycarbonyl-4,6-dimethyl-3-oxabicyclo[3.1.0]-hexan-2-one (**4**) in the form of a colorless oil. PMR spectrum (δ, ppm; J, Hz): 1.35 t (3H, Me, J = 7.2), 1.35 d (3H, Me, J = 5), 1.38 d (3H, Me, J = 5), 1.8 dq (1H, CH, $J_1 = J_2 = 5$), 2.55 dd (1H, CH, $J_1 = J_2 = 5$), 4.32 q (2H, CH_2O, J =

*An analysis of molecular models of compounds **19-21** and **24-27** by the MM2 method [13] gives the following dihedral angles $H^3-C^3-C^4-H^4$ and constants of spin–spin coupling of the H^3 and H^4 protons for syn and anti orientations of the substitutents attached to the C^3 and C^4 atoms relative to the lactone ring: 37-38°, 7.4-7.6 Hz (syn); 85-86°, 1.9-2.0 Hz (anti). The observed $J_{H^3-H^4}$ values correspond to a syn configuration.

†The cyclization of enolate A to a cyclopentene is an unfavorable 5-endo-trigonal process [17].

TABLE 2. Rearrangement of Alkenylcyclopropanes **6-12** in the Presence of Li (3 equivalents) in DMF at 150°C

Substrate	Reaction time	Rearrangment product	Yield, %[a]
 (6)	40 min	 (19)	**61**
 (7)	2 h	 (20)(R=CO_2Et) (22)(R=H)	65 b
 (8)	2 h	 (21)(R=CO_2Et) (23)(R=H)	84 c
 (9)	1.5 h	 (24)	**62**
 (10)	1.5 h	 (25)	**57**
 (11)	30 min	 (26)(E/Z=50:50)	**71**
 (12)	1 h	 (27)(E/Z=85:15)	**57**

[a]The yields of the isolated products are presented.
[b]Overall yield of **20** and **22**: **20**:**22** = 74:26.
[c]Overall yield of **21** and **23**: **21**:**23** = 63:37.

7.2), 4.8 dq (1H, CHO, $J_1 = J_2 = 5$). ^{13}C NMR spectrum (δ, ppm): 170.67 (C^1), 36.46 s (C^2), 35.98 d (C^3), 73.96 (C^4), 17.50 q (C^5), 26.33 d (C^6), 11.92 q (Me), 14.30 q, 61.82 t, 165.67 s (CO_2Et). IR spectrum (ν, cm^{-1}): 1780, 1720. Mass spectrum (*m/z*): 198 M^+.

1-Ethoxycarbonyl-4-methyl-6-propyl-3-oxabicyclo[3.1.0]hexan-2-one (5). PMR spectrum (δ, ppm; *J*, Hz): 0.88 t (3H, Me, $J = 7$); 1.06-1.63 m (10H, Me + CH_2); 2.21-3.08 m (2H, CH); 4.03 q, 4.1 q (2H, CH_2O, $J = 7$); 4.63 dq , 4.71 dq (1H, CHO, $J_1 = J_2 = 4$). ^{13}C NMR spectrum (δ, ppm): 171.64 s, 174.21 s (C^1); 36.81 s, 37.10 s (C^2); 36.03 d, 36.23 d (C^3); 73.89 d, 74.28 d (C^4); 16.71 q, 17.49 q (C^5); 31.70 d, 32.90 d (C^6); 13.64 q, 14.17 q, 61.82 t, 161.50 s, 167.63 s (CO_2Et); 21.67 t, 22.58 t, 27.41 t, 28.53 t (CH_2); 11.13 q, 22.58 q (Me). IR spectrum (ν, cm^{-1}): 1770, 1710. Mass spectrum (*m/z*): 226 M^+.

1-Ethoxycarbonyl-4-methyl-6-vinyl-3-oxabicyclo[3.1.0]hexan-2-one (6). PMR spectrum (δ, ppm; *J*, Hz): 0.88 t (3H, Me, $J = 7$), 1.06-1.63 m (10H, Me + CH_2), 2.21-3.08 m ($J = 7$ and 4.5), 2.63 dd (1H, CH, $J_1 = J_2 = 4.5$), 4.12 q (2H, CH_2O, $J = 7$), 4.66 dq (1H, CHO, $J = 4.5$ and 6), 4.96-6.0 m (3H, CH=CH_2) (trans isomer). ^{13}C NMR spectrum (δ, ppm): 168.92 s, 169.59 s (C^1); 37.53 s, 37.65 s (C^2); 35.12 d, 36.88 d (C^3); 73.83 d, 74.48 d (C^4); 16.64 q, 17.30 q (C^5); 34.20 d (C^6); 129.83 d, 130.36 d (C^7); 120.11 t, 121.15 t (C^8); 14.23 q, 61.88 t, 164.69 s, 166.65 s (CO_2Et). IR spectrum (ν, cm^{-1}): 3080, 1770, 1710, 1640, 980, 910. Mass spectrum (*m/z*): 210 M^+.

1-Ethoxycarbonyl-4-methyl-6-(1,3-butadien-2-yl)-3-oxabicyclo[3.1.0]hexan-2-one (7). PMR spectrum (δ, ppm; *J*, Hz): 1.21 t (3H, Me, $J = 7.2$), 1.42 d (3H, Me, $J = 6.1$), 2.44 d (1H, CHC=, $J = 5.1$), 3.06 dd (1H, CH, $J_1 = J_2 = 5.1$), 4.14 q (2H, CH_2O, $J = 7.2$), 4.87 dq (1H, CHO, $J = 5.1$ and 6.1), 5.1-5.6 m (4H, CH_2=), 6.4 dd (1H, CH=, $J = 18$ and 11). ^{13}NMR spectrum (δ, ppm): 169.48 s (C^1); 36.87 s (C^2); 32.00 d (C^3); 73.68 d (C^4); 17.41 q (C^5); 32.00 d (C^6); 119.53 t (C^7); 137.80 s (C^8); 136.56 d (C^9); 115.64 t (C^{10}); 14.11 q, 61.41 t, 163.53 s (CO_2Et). IR spectrum (ν, cm^{-1}): 3100, 1770, 1725, 1605, 940, 930, 905. Mass spectrum (*m/z*): 136 M^+.

1-Ethoxycarbonyl-4-methyl-6-(1-hexen-2-yl)-3-oxabicyclo[3.1.0]-hexan-2-one (8). PMR spectrum (δ, ppm; *J*, Hz): 0.91 t (3H, Me, $J = 7.1$); 1.25 t (3H, Me, $J = 7.1$); 1.38 d (3H, Me, $J = 6.2$); 1.2-1.5 m (4H, CH_2); 2.09 t (2H, CH_2C=, $J = 7.4$); 2.26 d (1H, CHC=, $J = 5.6$); 2.95 dd (1H, CH, $J = 5.6$ and 4.6); 4.2 q (2H, CH_2O, $J = 7.1$), 4.82 dq (1H, CHO, $J = 4.6$ and 6.2); 4.9 s, 5.02 s (2H, CH_2=). ^{13}C NMR spectrum (δ, ppm): 169.99 (C^1); 38.39 s (C^2); 36.22 d (C^3); 73.95 d (C^4); 17.36 q (C^5); 34.89 d (C^6); 113.94 t (C^7); 140.87 s (C^8); 31.98 t (C^9); 29.83 t (C^{10}); 22.39 t (C^{11}); 13.84 q (C^{12}); 14.16 q, 61.69 t, 163.95 s (CO_2Et). IR spectrum (ν, cm^{-1}): 3100, 1780, 1730, 1650, 920. Mass spectrum (*m/z*): 266 M^+.

1-Ethoxycarbonyl-4-methyl-6-(Z-4-methyl-1-pentenyl)-3-oxabicyclo[3.1.0]hexan-2-one (9). PMR spectrum (δ, ppm; *J*, Hz): 0.87 d (6H, Me, $J = 6.3$), 1.26 t (3H, Me, $J = 7.3$), 1.35 d (3H, Me, $J = 6.1$), 1.62 m (1H, CH), 2.02 dd (2H, CH_2C=, $J_1 = J_2 = 7.2$), 2.47 dd (1H, CHC=, $J = 8.9$ and 5.1), 2.73 dd (1H, CH, $J_1 = J_2 = 5.1$), 4.22 q (2H, CH_2O, $J = 7.3$), 4.74 dq (1H, CHO, $J = 5.1$ and 6.1), 5.24 dd (1H, CH=, $J = 10.8$ and 8.9), 5.64 dt (1H, CH=, $J = 10.8$ and 7.5). ^{13}C NMR spectrum (δ, ppm): 169.75 s (C^1); 37.49 s (C^2); 35.60 d (C^3); 73.74 d (C^4); 17.45 q (C^5); 29.53 d (C^6); 121.96 d, 134.85 d (C^7, C^8); 36.79 t (C^9); 28.34 d (C^{10}); 22.11 q, 22.21 q (C^{11}, C^{12}). IR spectrum (ν, cm^{-1}): 3080, 1770, 1720, 1650. Mass spectrum (*m/z*): 266 M^+.

1-Ethoxycarbonyl-4-methyl-6-(E-1-hexenyl)-3-oxabicyclo[3.1.0]hexan-2-one (10). PMR spectrum (δ, ppm; *J*, Hz): 0.88 t (3H, Me, $J = 6.1$), 1.31 t (3H, Me, $J = 7.3$), 1.38 d (3H, Me, $J = 6.3$), 1.3-1.7 m (4H, CH_2), 2.0 m (2H, CH_2C=), 2.35 dd (1H, CHC=, $J = 8.7$ and 5.2), 2.75 dd (1H, CH, $J_1 = J_2 = 5.2$), 4.26 q (2H, CH_2O, $J = 7.3$), 4.75 dq (1H, CHO, $J = 5.2$ and 6.3), 5.33 dd (1H, CH=, $J = 15.5$ and 8.7), 5.84 dt (1H, CH=, $J = 15.5$ and 6.6). ^{13}C NMR spectrum (δ, ppm): 169.85 s (C^1); 37.53 s (C^2); 34.99 d (C^3); 73.83 d (C^4); 17.36 q (C^5); 34.14 d (C^6); 121.81 d, 137.28 (C^7, C^8); 32.18 t (C^9); 31.07 t (C^{10}); 22.06 t (C^{11}); 13.84 q (C^{12}); 14.23 q, 61.69 t, 164.76 s (CO_2Et). IR spectrum (ν, cm^{-1}): 1780, 1720, 1640, 970. Mass spectrum (*m/z*): 266 M^+.

1-Ethoxycarbonyl-4-methyl-6-(2-propyl-1-pentenyl)-3-oxabicyclo[3.1.0]hexan-2-one (11). PMR spectrum (δ, ppm; *J*, Hz): 0.87 t, 0.93 t (6H, Me, $J = 7.2$), 1.3 t (3H, Me, $J = 7.1$), 1.38 d (3H, Me, $J = 6.3$), 1.3-1.5 m (4H, CH_2), 1.9-2.2 m (4H, CH_2C=), 2.51 dd (1H, CHC=, $J = 8.9$ and 5.2), 2.76 dd (1H, CH, $J_1 = J_2 = 5.2$), 4.25 q (2H, CH_2O, $J = 7.1$), 4.78 dq (1H, CHO, $J = 5.2$ and 6.3), 5.0 d (1H, CH=, $J = 8.9$). ^{13}C NMR spectrum (δ, ppm): 170.01 s (C^1); 37.81 s (C^2); 35.58 d (C^3); 73.87 d (C^4); 17.47 q (C^5); 30.57 d (C^6); 116.60 d (C^7); 147.29 s (C^8); 38.98 t (C^9); 20.98 t, 21.42 t (C^{10}, C^{13}); 13.69 q, 14.01 q (C^{11}, C^{14}); 32.83 t (C^{12}); 14.24 q, 61.64 t, 164.76 s (CO_2Et). IR spectrum (ν, cm^{-1}): 1780, 1730, 1650, 860. Mass spectrum (*m/z*): 294 M^+.

1-Ethoxycarbonyl-4-methyl-6-(1-cyclohexenyl)-3-oxabicyclo[3.1.0]hexan-2-one (12). PMR spectrum (δ, ppm; *J*, Hz): 1.3 t (3H, Me, $J = 7.1$); 1.36 d (3H, Me, $J = 6.2$); 1.55 m (4H, ring CH_2); 1.8-2.3 m (5H, CHC= + CH_2C=); 2.67 m, 2.95 m (1H, CH); 4.17 q (2H, CH_2O, $J = 7.1$); 4.8 m (1H, CHO); 5.63 m, 5.83 m (1H, CH=). ^{13}C NMR spectrum (δ,

ppm): 170.30 s (C^1); 37.66 s (C^2); 36.56 d (C^3); 73.89 d (C^4); 17.36 q (C^5); 31.20 d (C^6); 128.92 s (C^7); 127.29 d (C^8); 25.13 t (C^9); 21.93 t, 22.52 t (C^{10}, C^{11}); 28.79 t (C^{12}); 14.23 q, 61.49 t, 164.04 s (CO_2Et) (trans isomer). IR spectrum (ν, cm^{-1}): 3100, 1760, 1725, 880. Mass spectrum (*m/z*): 264 M^+.

1-Ethoxycarbonyl-4-methyl-6-(E-β-styryl)-3-oxabicyclo[3.1.0]hexan-2-one (13). PMR spectrum (δ, ppm; *J*, Hz): 1.29 t (3H, Me, J = 7.3), 1.4 d (3H, Me, J = 6.4), 2.53 dd (1H, CHC=, J = 8.8 and 5), 2.9 dd (1H, CH, $J_1 = J_2 = 5$), 4.25 q (2H, CH_2O, J = 7.3), 4.8 dq (1H, CHO, J = 5 and 6.4), 6.05 dd (1H, CH=, J = 16 and 8.8), 6.65 d (1H, CH=, J = 16), 7.31 m (5H, arom.) (*trans* isomer). IR spectrum (ν, cm^{-1}): 3090, 3070, 3040, 1775, 1720, 1605, 1500, 980, 770, 750, 715. Mass spectrum (*m/z*): 286 M^+.

1-Ethoxycarbonyl-4-methyl-6-phenyl-3-oxabicyclo[3.1.0]hexan-2-one (14). PMR spectrum (δ, ppm; *J*, Hz): 0.8 t (3H, Me, J = 7.2), 1.45 d (3H, Me, J = 6.3), 2.95 d (1H, CHPh, J = 5.5), 3.3 dd (1H, CH, $J_1 = J_2 = 5.5$), 3.93 m (2H, CH_2O), 4.94 dq (1H, CHO, J = 5.5 and 6.3), 7.3 m (5H, arom.). ^{13}C NMR spectrum (δ, ppm): 169.85 s (C^1); 39.17 s (C^2); 32.12 d, 34.30 d (C^3, C^6); 74.06 d (C^4); 17.45 q (C^5); 128.08 d, 128.35 d, 128.79 d, 132.09 s (Ph), 13.71 q, 61.50 t, 163.47 s (CO_2Et). IR spectrum (ν, cm^{-1}): 3115, 3075, 3045, 1780, 1725, 1610, 1510, 790, 755, 715. Mass spectrum (*m/z*): 260 M^+.

1-Ethoxycarbonyl-4-methyl-6-(1-pentynyl)-3-oxabicyclo[3.1.0]hexan-2-one (15). PMR spectrum (δ, ppm; *J*, Hz): 0.9 t (3H, Me, J = 6.3), 1.26 t (3H, Me, J = 7.2), 1.33 d (3H, Me, J = 6.2), 1.1-1.6 m (2H, CH_2), 2.0 m (3H, CHC= + CH_2C=), 2.6 m (1H, CH), 4.16 q (2H, CH_2O, J = 7.2), 4.63 m (1H, CHO). ^{13}C NMR spectrum (δ, ppm): 168.77 s (C^1); 37.82 s, 38.30 s (C^2); 35.49 d, 35.92 d (C^3); 73.96 d, 74.12 d (C^4); 15.12 q, 17.45 q (C^5); 19.88 d (C^6); 72.65 s, 84.20 s (C≡C); 20.70 t, 21.78 t, 21.94 t, 13.38 q (Ph); 14.14 q, 14.30 q, 62.04 t, 163.46 s (CO_2Et). IR spectrum (ν, cm^{-1}): 2300, 1780, 1720. Mass spectrum (*m/z*): 250 M^+.

1-Ethoxycarbonyl-4-methyl-6-phenylethynyl-3-oxabicyclo[3.1.0]hexan-2-one (16). PMR spectrum (δ, ppm; *J*, Hz): 1.29 t, 1.33 t (3H, Me, J = 7); 1.44 d, 1.67 d (3H, Me, J = 6.5); 2.42 d, 2.45 d (1H, CHC=, J = 8 and 4.9); 2.75 dd, 3.04 dd (1H, CH, J = 8 and 4.9, $J_1 = J_2 = 4.9$); 4.29 q, 4.31 q (2H, CH_2O, J = 7); 4.81 dq, 4.88 dq (1H, CHO, J = 4.9 and 6.5); 7.33 m (5H, arom.). ^{13}C NMR spectrum (δ, ppm): 168.45 s (C^1); 37.93 s, 38.74 s (C^2); 35.87 d, 36.30 d (C^3); 73.96 d, 74.12 d (C^4); 15.28 q, 17.45 q (C^5); 19.94 d, 20.64 d (C^6); 81.87 s, 82.03 s, 83.38 s (C≡C); 122.07 s, 128.30 d, 128.68 d, 131.66 d (Ph); 14.09 q, 14.25 q, 62.15 t, 62.36 t, 163.25 s, 165.73 s (CO_2Et). IR spectrum (ν, cm^{-1}): 3090, 3075, 2270, 1780, 1725, 1600, 1580, 1500, 775, 750, 710. Mass spectrum (*m/z*): 284 M^+.

1-Ethoxycarbonyl-4-propyl-6-vinyl-3-oxabicyclo[3.1.0]hexan-2-one (17). PMR spectrum (δ, ppm; *J*, Hz): 0.97 t (3H, Me, J = 7.3), 1.31 t (3H, Me, J = 7.1), 1.53 m (4H, CH_2), 2.37 dd (1H, CHC=, J = 8.2 and 4.8), 2.79 dd (1H, CH, $J_1 = J_2 = 4.8$), 4.26 q (2H, CH_2O, J = 7.1), 4.62 dt (1H, CHO, J = 4.8 and 7.5), 5.0-5.8 m (3H, CH= + CH_2=). IR spectrum (ν, cm^{-1}): 3095, 1780, 1725, 1640. Mass spectrum (*m/z*): 238 M^+.

1,1-Diethoxycarbonyl-2-(3-hydroxy-1-butenyl)-3-vinylcyclopropane (18). PMR spectrum (δ, ppm; *J*, Hz): 1.22 t (6H, Me, J = 7), 1.28 d (3H, Me, J = 6.3), 2.55 m (2H, CHC=), 3.05 broad s (1H, OH), 4.1 q (4H, CH_2O, J = 7), 4.0-4.3 m (1H, CHOH), 4.9-6.0 m (5H, CH= + CH_2=). ^{13}C NMR spectrum (δ, ppm): 42.97 s (C^1); 34.03 d, 35.49 d (C^2, C^3); 123.68 d (C^4); 138.70 d (C^5); 68.24 d, 69.27 d (C^6); 21.56, 23.30 q (C^7); 132.09 d (C^8); 118.66 t (C^9); 14.20 q, 61.66 t, 167.15 s (CO_2Et). IR spectrum (ν, cm^{-1}): 3500, 3095, 1730, 1645, 985, 930. Mass spectrum (*m/z*): 282 M^+.

Rearrangement of Alkenylcyclopropanes 6-12 in the Presence of LiI. A solution of 0.42 g (2 mmoles) of cyclopropane **6** and 0.804 g (6 mmoles) of LiI in 10 ml of DMF was stirred at 150°C, during which the progress of the reaction was monitored by TLC. After 40 min, the reaction mixture was cooled to 20°C, 20 ml of H_2O was added, and the aqueous mixture was extracted with Et_2O (3 × 10 ml). The ether layer was dried with $MgSO_4$, concentrated, and subjected to column chromatography [silica gel L 40-100, hexane—Et_2O (1:1)] to give 0.256 g (61%) of 1-ethoxycarbonyl-4-methyl-3-oxabicyclo[3.3.0]-6-octen-2-one (**19**) in the form of a colorless oil. PMR spectrum (δ, ppm; *J*, Hz): 1.3 t (3H, Me, J = 7.2), 1.43 d (3H, Me, J = 6.5), 3.05 ddd (1H, ring CH_2, J = 17.4, 4.3, and 2.5), 3.14 ddd (1H, ring CH_2, J = 17.4, 4.6, and 2.5), 3.73 m (1H, CH), 4.25 q (2H, CH_2O, J = 7.2), 4.94 dq (1H, CHO, $J_1 = J_2 = 6.5$), 5.6 m (1H, CH=), 5.88 m (1H, CH=). ^{13}C NMR spectrum (δ, ppm): 175.85 s (C^1); 61.75 s (C^2); 56.86 d (C^3); 78.46 d (C^4); 16.78 q (C^5); 40.41 t (C^6); 125.26 d (C^7); 132.84 d (C^8); 14.01 q, 62.21 t, 169.00 s (CO_2Et). IR spectrum (ν, cm^{-1}): 3080, 1770, 1735, 1620. Mass spectrum (*m/z*): 210 M^+.

1-Ethoxycarbonyl-4-methyl-7-vinyl-3-oxabicyclo[3.3.0]-6-octen-2-one (20). PMR spectrum (δ, ppm; *J*, Hz): 1.3 t (3H, Me, J = 6.9), 1.45 d (3H, Me, J = 6.4), 3.15 d (1H, ring CH_2, J = 16.7), 3.25 d (1H, ring CH_2, J = 16.7), 3.77 (1H, CH), 4.26 q (2H, CH_2O, J = 6.9), 4.93 dq (1H, CHO, $J_1 = J_2 = 6.4$), 5.25 m (2H, CH_2=), 5.51 broad s (1H, CH=), 6.48 dd (1H, CH=, J = 17.4 and 10.7). ^{13}C NMR spectrum (δ, ppm): 175.64 s (C^1); 61.47 s (C^2); 56.63 d (C^3); 78.17 d (C^4); 16.79 q (C^5); 38.61 t (C^6); 144.29 s (C^7); 131.69 d (C^8); 123.30 d (C^9); 117.76 t (C^{10}); 14.09 q, 62.29 t, 168.95 s (CO_2Et). IR spectrum (ν, cm^{-1}): 3085, 3040, 1770, 1740, 1650, 990, 910. Mass spectrum (*m/z*): 236 M^+.

1-Ethoxycarbonyl-4-methyl-7-butyl-3-oxabicyclo[3.3.0]-6-octen-2-one (21). PMR spectrum (δ, ppm; J, Hz): 0.9 t (3H, Me, J = 7), 1.30 t (3H, Me, J = 7.1), 1.42 d (3H, Me, J = 6.3), 1.3-1.5 m (4H, CH_2), 2.1 t (2H, $CH_2C=$, J = 7.2), 2.88 d (1H, ring CH_2, J = 16.9), 3.09 d (1H, ring CH_2, J = 16.9), 3.67 m (1H, CH), 4.25 q (2H, CH_2O, J = 7.1), 4.88 dq (1H, CHO, $J_1 = J_2$ = 6.3), 5.19 broad s (1H, CH=). ^{13}C NMR spectrum (δ, ppm): 176.02 s (C^1); 65.54 s (C^2); 56.62 d (C^3); 78.24 d (C^4); 16.70 q (C^5); 42.48 t (C^6); 147.77 s (C^7); 117.70 d (C^8); 30.69 t (C^9); 29.63 t (C^{10}); 22.38 t (C^{11}); 13.78 q (C^{12}); 14.09 q, 62.05 t, 169.24 s (CO_2Et). IR spectrum (ν, cm^{-1}): 1770, 1740, 1640. Mass spectrum (m/z): 266 M^+.

4-Methyl-7-vinyl-3-oxabicyclo[3.3.0]-6-octen-2-one (22). PMR spectrum (δ, ppm; J, Hz): 1.41 d (3H, Me, J = 6.4), 2.76 dd (1H, ring CH_2, J = 16.2 and 8.7), 2.97 d (1H, ring CH_2, J = 16.2), 3.29 dd (1H, CH, $J_1 = J_2$ = 8.7), 3.62 m (1H, CHC=), 4.74 dq (1H, CHO, $J_1 = J_2$ = 6.4), 5.21 m (2H, CH_2=), 5.60 broad s (1H, CH=), 6.54 dd (1H, CH=, J = 17.3 and 10.7). IR spectrum (ν, cm^{-1}): 3085, 3040, 1770, 1640, 1595, 990, 910. Mass spectrum (m/z): 164 M^+.

3-(5-Methyl-1,3-hexadienyl)-4-pentanolide (24). PMR spectrum (δ, ppm; J, Hz): 1.05 d (6H, Me, J = 6.8), 1.27 d (3H, Me, J = 6.6), 2.35 m (1H, CH), 2.47 dd (1H, ring CH_2, J = 17.4 and 7.4), 2.67 dd (1H, ring CH_2, J = 17.4 and 8.1), 3.19 m (1H, CH), 4.7 dq (1H, CHO, J = 7.2 and 6.6), 5.45 dd (1H, CH=, J = 14.6 and 8.8), 5.68 dd (1H, CH=, J = 15 and 6.7), 6.0 dd (1H, CH=, J = 15.0 and 10.2), 6.1 dd (1H, CH=, J = 14.6 and 10.2). ^{13}C NMR spectrum (δ, ppm): 176.20 s (C^1); 34.57 t (C^2); 42.69 d (C^3); 79.62 d (C^4); 16.53 q (C^5); 134.02 d (C^6); 126.27 d, 126.29 d (C^7, C^8); 142.82 d (C^9); 31.12 d (C^{10}); 22.24 q (C^{11}). IR spectrum (ν, cm^{-1}): 3040, 1775, 1655, 960. Mass spectrum (m/z): 194 M^+.

3-(1,3-Heptadienyl)-4-pentanolide (25). PMR spectrum (δ, ppm; J, Hz): 0.91 t (3H, Me, J = 7.4), 1.27 d (3H, Me, J = 6.6), 1.42 tq (2H, CH_2, $J_1 = J_2$ = 7.4), 2.06 dt (2H, $CH_2C=$, J = 7.4 and 7.2), 2.45 dd (1H, ring CH_2, J = 17.4 and 7.4), 2.67 dd (1H, ring CH_2, J = 17.4 and 8.1), 3.2 m (1H, CH), 4.7 dq (1H, CHO, J = 7.2 and 6.6), 5.44 dd (1H, CH=, J = 14.1 and 8.9), 5.7 dt (1H, CH=, J = 14.5 and 7.2), 6.02 dd (1H, CH=, J = 14.5 and 10.2), 6.1 dd (1H, CH=, J = 14.1 and 10.2). ^{13}C NMR spectrum (δ, ppm): 176.18 s (C^1); 34.53 t (C^2); 42.63 d (C^3); 79.57 d (C^4); 16.54 q (C^5); 135.71 d (C^6); 125.99 d (C^7); 129.25 d (C^8); 133.82 (C^9); 34.53 t (C^{10}); 22.39 t (C^{11}); 13.71 q (C^{12}). IR spectrum (ν, cm^{-1}): 1775, 1660, 960. Mass spectrum (m/z): 194 M^+.

3-(3-Propyl-1,3-hexadienyl)-4-pentanolide (26). PMR spectrum (δ, ppm; J, Hz): 0.9 t, 0.93 t, 0.99 t, 1.0 t (6H, Me, J = 7.4); 1.26 d, 1.28 d (3H, Me, J = 6.6); 1.43 m (2H, CH_2); 2.08-2.24 m (4H, $CH_2C=$); 2.4 dd, 2.45 dd (1H, ring CH_2, J = 17.4 and 6.9); 2.7 dd, 2.72 dd (1H, ring CH_2, J = 17.4 and 8.1); 3.22 m (1H, CH); 4.71 dq, 4.73 dq (1H, CHO, $J_1 = J_2$ = 6.6); 5.37 t, 5.44 t (1H, CH=, J = 7.3, 7.2); 5.42 dd, 5.54 dd (1H, CH=, J = 15.7 and 8.8, 15.7 and 9); 6.01 d, 6.4 d (1H, CH=, J = 15.7). ^{13}C NMR spectrum (δ, ppm): 176.24 s, 176.36 s (C^1); 34.85 t (C^2); 43.05 d, 43.46 d (C^3); 79.12 d, 79.78 d (C^4); 16.58 q (C^5); 135.61 d, 137.20 d (C^6); 129.60 d, 132.85 d (C^7); 134.47 s, 136.69 s (C^8); 121.50 d, 124.28 d (C^9); 21.94 t, 22.23 t (C^{10}); 13.97 q, 14.13 q, 14.23 q, 14.44 q (C^{11}, C^{14}); 28.78 t, 36.09 t (C^{12}); 20.78 t, 21.51 t (C^{13}). IR spectrum (ν, cm^{-1}): 1775, 1650, 960, 860. Mass spectrum (m/z): 222 M^+.

3-[(2-Cyclohexenylidene)methyl]-4-pentanolide (27). PMR spectrum (δ, ppm; J, Hz): 1.25 d (3H, Me, J = 6.6); 1.7 m (2H, ring CH_2); 2.15 m, 2.3 m (4H, $CH_2C=$), 2.38 dd (1H, ring CH_2, J = 17.3 and 7.2); 2.7 dd (1H, ring CH_2, J = 17.3 and 8.1); 3.49 m, 3.57 m (1H, CH); 4.72 dq (1H, CHO, $J_1 = J_2$ = 6.6); 4.99 d, 5.12 d (1H, CH=, J = 9.4, 9.9); 5.83 dt, 5.95 dt (1H, ring CH=, J = 8.5 and 4.1, 10.2 and 4.1); 6.06 d, 6.3 d (1H, ring CH=, J = 8.5, 10.2). ^{13}C NMR spectrum (δ, ppm): 176.37 s, 176.45 s (C^1); 35.36 t, 35.46 t (C^2); 36.76 d, 37.42 d (C^3); 79.50 d, 79.71 d (C^4); 16.33 q, 16.34 q (C^5); 120.02 d, 121.88 d (C^6); 137.43 s, 138.34 s (C^7); 123.38 d, 129.89 d, 130.21 d, 132.60 d (C^8, C^9); 25.49 t, 26.14 t (C^{10}); 22.29 t, 23.00 t (C^{11}); 25.62 t, 32.32 t (C^{12}). Mass spectrum (m/z): 192 M^+.

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