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REACTIONS OF [2 + 2 + 1]-CYCLOADDITION WITH THE PARTICIPATION OF CYCLOPROPENES AND DICOBALT HEXACARBONYL COMPLEXES OF ACETYLENES

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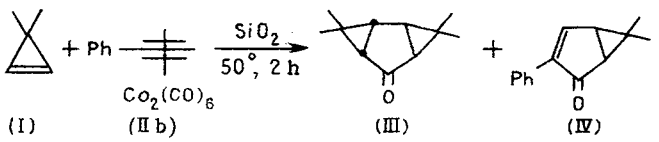
The reaction of dicobalt hexacarbonyl complexes of acetylene and its phenyl and dimethyl derivatives with the methyl ester of 1-methyl-2-(trimethylsilyl)-1-cyclopropene-3-carboxylic acid with adsorption on a silica gel or NaX zeolite surface leads to the formation of a mixture of bicyclo[3.1.0]hex-2-en-4-one and tricyclo[4.1.0.$0^{2,4}$]heptan-5-one derivatives, whereby the yields and the composition of products are dependent on the type of the adsorbent. It has been found that under the reaction conditions partial isomerization of the bicyclo-[3.1.0]hex-2-en-4-one derivatives into substituted phenols occurs. Action of anhydrous KF and crown-ether in acetonitrile on the bicyclo[3.1.0]hex-2-en-4-one derivatives in acetonitrile leads to protodesilylation.

Alkenes are capable of reacting with dicobalt hexacarbonyl complexes (DCHCC) of acetylenes according to a [2 + 2 + 1]-cycloaddition scheme thus forming derivatives of cyclopenten-2-one (the Khand-Pauson reaction) [1]. The intramolecular variant of this reaction for the synthesis of several natural polycyclic compounds and their analogs [2] is particularly widely used. The intermolecular variant has less synthetic application because of the low activity and low regioselectivity of the cyclization of most alkenes under these reaction conditions [1-3]. However, a strained methylenecyclopropane readily undergoes the Khand-Pauson intermolecular reaction, and the process is characterized by high regioselectivity [4].

In the present work, we studied for the first time the possibility of the participation in this reaction of still another class of strained cycloolefins – cyclopropenes which are very active in cycloaddition reactions, including those catalyzed by transition metal compounds [5]. As the subjects of the investigation we chose 3,3-dimethylcyclopropene (I) as the most available and stable representative of cyclopropenes, and DCHCC of a series of acetylenes with different numbers of substituents at the triple bond – acetylene (IIa), phenylacetylene (IIb), and 2-butyne (IIc).

The reaction of (I) with DCHCC of phenylacetylene (IIb) was carried out under conditions previously developed by us for the reaction of (IIb) with methylenecyclopropane [4] (heating in a sealed ampul in the presence of chromatographic adsorbents). Under these conditions, a rapid conversion of (I) was observed, but the cycloaddition product according to Khand-Pauson (IV) formed in a yield of ~2% only, while the main reaction product was (III) – a cyclodimerization product of the initial (I) with inclusion of the CO molecule.



(I) (IIb) (III) (IV)

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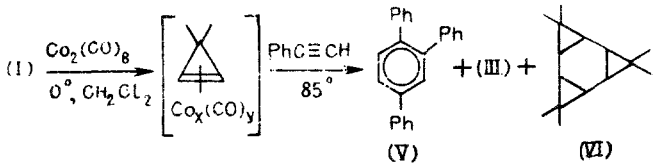
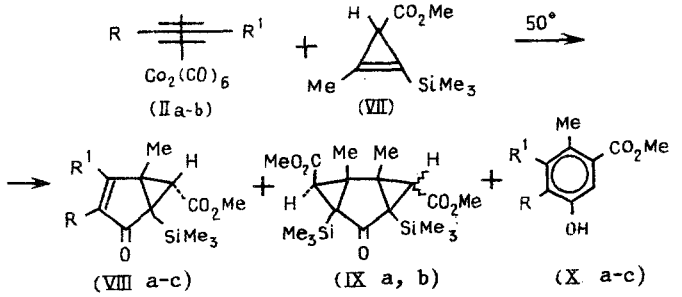
The change in the reaction conditions (temperature, duration, ratio of the reagents, type of adsorbent, thermolysis in hexane) did not lead to increase in the yield of (IV). Compound (III) was previously obtained in 54% yield from (I) and CO in the presence of catalytic amounts of $Ni(CO)_4$ under the pressure of 40 atm [4] while in our case the formation of (III) requires stoichiometric amounts of (IIb) as a source of CO, whereby the yield of (III) is 46% per (I) used.

An attempt to carry out the transformation of (I) into (III) directly by the action of $Co_2(CO)_8$ did not give positive results, although an exothermal reaction was observed already at 0°C and the formation of a new Co complex was recorded (TLC data). However, the latter could not be isolated because of its lability, while its decomposition product did not include the ketone (III). On treatment with phenylacetylene of the in situ obtained complex of (I) with $Co_2(CO)_8$, the main product was a cyclotrimer of phenylacetylene – 1,2,4-triphenylbenzene (V) [yield 52%, with the yield of (III) being 17%, of the cyclotrimer of (I) (VI) 3% and with the complete absence of (IV)].

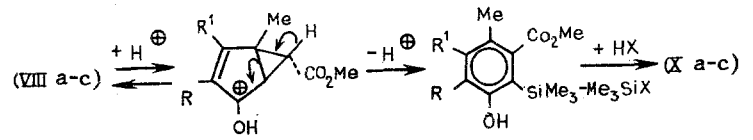


It follows from the results obtained that to effect the cycloaddition according to Khand-Pauson, it is necessary to block to the utmost the possible cyclooligoisomerization of the initial cycloolefin, for example, by the total substitution of the double bond in cyclopropene, as happens in the readily accessible derivatives of 1,2-disubstituted of cyclopropene-3-carboxylic acids. In particular, the methyl ester of 1-methyl-2-(trimethylsilyl)cyclopropene-3-carboxylic acid (VII) actually reacts readily with complexes (IIa-c) deposited on various adsorbents, in a sealed ampul at 50-60°C, or during thermolysis in a nonpolar solvent (hexane). The reaction of (VII) with (IIa-c) thereby leads to the formation of a mixture of products, the ratio and yields of which are dependent on the reaction conditions (Table 1).



R = R¹ = H (a); R = Ph, R¹ = H (b); R = R¹ = Me (c).

In all cases the formation according to Khand-Pauson was observed of [2 + 2 + 1]-cycloaddition products, which are derivatives of bicyclo[3.1.0]hexane (VIII) together with tricyclic ketones (IX) and phenols (X). We believe that the latter are formed under the acid catalysis conditions from adducts (VIII) with a subsequent protodesilylation.



It was shown by special experiments that phenols (Xa-c) were not formed during the thermolysis of the individual adducts (VIIIa-c) on adsorbents. Hence, the isomerization of (VIII) into (X) does not proceed by the action of the acidic adsorbent, but more likely by the action of traces of $HCo(CO)_4$ formed under these conditions, which is a compound with fairly strong acid properties ($pK_a HCoCO)_4 \approx pK_a HCl$ [7].

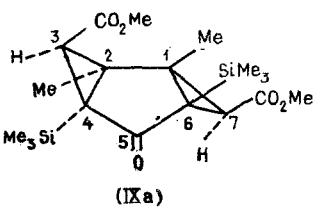
TABLE 1. Products of Reaction of (VII) with (IIa-c)[a]

Initial DCHCC	Reaction conditions[b]	Yield, %		
		(VIII)	(IX)[c]	(X)
(IIa)	SiO_2	37	4,5	30
	NaX zeolite	17	62	29
	Hexane	2	67	17
(IIb)	SiO_2	86	3	12
	NaX zeolite	8	62	–
	Hexane	2	65	4
(IIc)	SiO_2	58	14	9
	NaX zeolite	26	42	10
	Hexane	11	66	11

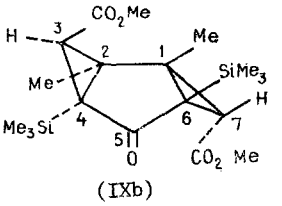
[a]The chemical and steric structures of all the compounds obtained were determined from the ^1H and ^{13}C NMR spectral data, monitoring the nuclear Overhauser effect and they conform with results of IR and mass spectra and chemical analysis (see the experimental part).
[b]For the reactions on SiO_2 or NaX zeolite: 50°C, 13 h, (VII):(IIa-c) = 2:1. ((VII) + (IIa-c)):adsorbent = 1:10 (by weight). For reactions in hexane: 50°C, 15 h, (VII):(IIa-c) = 2:1, 4 ml of hexane per 1 mmole of (VII).
[c]The yield of (IX) was calculated based on the initial cyclopropene (VII).

Table 1 shows that the preferential path of the reaction carried out on the surface of silica gel is the Khand-Pauson reaction, while the hydrolysis in hexane gives mainly cyclodimers (IX). The two processes proceed on the NaX zeolite to a commensurable extent. The structure of adducts (VIII) indicates that the Khand-Pauson reaction with the participation of cyclopropenes is characterized by a high regio- and stereoselectivity. It is known that the more bulky substituents in the alkyne occupy the α position to the carbonyl group as the result of the reaction [1]. This pattern also holds for the reactions that we have studied. On the other hand, the addition of asymmetric alkenes is usually characterized by a low regioselectivity [3]. In the present case, the asymmetric (VII) adds to (IIa-c) regio- and stereospecifically, so that the trimethylsilyl substituent turns out to be in the α position to the carbonyl group, while the methoxycarbonyl group has an endo-orientation.

The cyclocodimerization of (VII) with formation of (IX) also proceeds strictly regiospecifically: The trimethylsilyl substituents orient themselves into the α position to the carbonyl group. Thus, one molecule of (VII) reacts stereospecifically, giving an endo-oriented methoxycarbonyl group, and the other nonstereospecifically, leading to the formation of epimers with an exo- and endo-orientation of the methoxycarbonyl group in an approximately equal ratio.



(IXa)

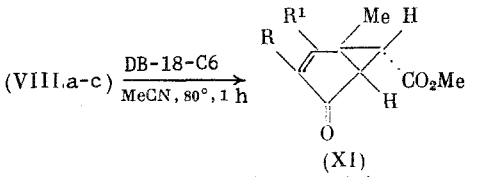


(IXb)

Further investigations are required to establish the reasons for this course of the reaction.

To obtain additional confirmation of the structure of adducts (VIIIa-c), we studied the possibility of the removing the trimethylsilyl group from these adducts. It was found that the protodesilylation proceeds easily by the action of anhydrous KF in acetonitrile in the presence of a crown-ether (see scheme on top of following page).

Thus, cyclopropenes, especially those which are 1,2-substituted can be used in the Khand-Pauson reaction.



(XI)

74% (a), 92% (b), 70% (c)

EXPERIMENTAL

The PMR spectra were recorded on Bruker WM-250 (250, 13 MHz) spectrometers, the ^{13}C NMR spectra on a Bruker AM-300 spectrometer (75.46 MHz) for solutions in acetone-d_6, the mass spectra – on a Varian MAT CH-6 mass spectrometer, and the IR spectra on Specord M-80 and Perkin-Elmer 577 spectrophotometers.

Silica gel Silpearl (Chemapol) and NaX- 2,6 zeolite were used for carrying out the reactions. The preparation of 3,3-dimethylcyclopropene (I) [8], the methyl ester of 1-methyl-2-(trimethylsilyl)cyclopropene-3-carboxylic acid (VII) [9] and also DCHCC of acetylenes (IIa-c) [4] was carried out by known methods.

Reaction of 3,3-Dimethylcyclopropene (I) with DCHCC of Phenylacetylene (IIb). A 20-g portion of silica gel was added to a solution of 1.18 g (3.0 mmoles) of (IIb) in pentane. The solvent was evaporated in vacuo, and the residue was cooled to −78°C and rapidly transferred into an ampul containing 0.52 ml (6.1 mmoles) of (I), cooled to −78°C. The ampul was sealed and after vigorous shaking was held for 2 h at 50°C, then was cooled by liquid nitrogen, opened, and the contents were rapidly transferred to another ampul cooled to −78°C containing 0.52 ml (6.1 mmoles) of (I), which was heated for a further 2 h at 50°C. The adsorbent was washed on the filter with 100 ml of ether, and the solvent was evaporated in vacuo. After the separation by means of column chromatography on silica gel (eluent – petroleum ether) of unreacted (IIb) [0.70 g, conversion of (IIb) 41%], the residue was subjected to microdistillation in vacuo (1 torr) to yield 0.46 g (46%) of 3,3,7,7-tetramethyltricyclo[4.1.0.$0^{2,4}$]heptan-5-one (III). PMR spectrum (δ, ppm, J, Hz): 1.61 d.d (2H, H^4, H^6, J = 4.7 and 1.9), 1.31 d.d (2H, H^1, H^2, J = 4.7 and 1.9), 1.13 s (6H, 2 Me), 1.06 s (6H, 2 Me). ^{13}C NMR spectrum (δ, ppm): 208.7 (C=O), 40.9 (C^4, C^6), 32.9 (C^1, C^2), 30.9 (C^3, C^7), 26.4 (Me), 16.2 (Me). IR spectrum (ν, cm^{-1}): 1705 (C=O). Mass spectrum, m/z: 164 (M^+).

From the residue of the microdistillation, 15 mg (2.5%) of 6,6-dimethyl-3-phenylbicyclo[3.1.0]hex-2-en-4-one (IV) was isolated by means of preparative TLC. PMR spectrum (δ, ppm, J, Hz): 7.70-7.63 m, 7.48-7.30 m (2H and 3H, Ph), 7.58 d (1H, H^2, J = 2.8), 2.48 d.d (1H, H^1, J = 2.8 and 4.5), 2.20 d (1H, H^5, J = 4.5), 1.28 s (3H, Me), 1.21 s (3H, Me). IR spectrum (ν, cm^{-1}): 1705 (C=O). Mass spectrum, m/z: 198 (M^+).

Reaction of Phenylacetylene with the Cobalt Carbonyl Complex of 3,3-Dimethylcyclopropene. Compound (I) (1.3 ml, 15 mmoles) was added in few portions at 0°C, with stirring, to a solution of 1.03 g (3.0 mmoles) of $Co_2(CO)_8$ in 15 ml of CH_2Cl_2. The mixture was allowed to warm up to 20°C and was stirred for another 30 min, and then 1.33 ml (12 mmoles) of phenylacetylene was added in two portions, and stirring was continued for 15 min. The reaction mixture was then sealed within an ampul, which was heated for 4 h at 85°C. After cooling, the ampul was opened, the solvent was removed in vacuo, and the residue was treated with a solution of 3.84 g (7 mmoles) of cerium(IV) ammonium nitrate in 10 ml of acetone to decompose the organic cobalt compounds, finally obtaining 2.34 g of a dark-brown oil, which was subjected to microdistillation. From the fraction boiling at 20-70°C (12 mm) (0.12 g), 0.10 g of unreacted phenylacetylene was isolated by preparative TLC (conversion 92%). From the fraction boiling at 20-95°C (0.2 mm), (0.31 g), 3,3,6,6,9,9-hexamethyltetracylco[6.1.0.$0^{2,4}$.$0^{5,7}$]-nonane (VI) (34 mg, yield 3%) and a cyclocodimer (III) (0.21 g, yield 17%) were isolated by preparative TLC. The PMR, IR, and mass-spectral data of (VI) coincide with the previously described data [6].

From the still residue (1.70 g) 0.64 g (52%) of 1,2,4-triphenylbenzene (V) was obtained by means of column chromatography on Al_2O_3 (eluent ether–petroleum ether, 1:2). PMR spectrum (δ, ppm): 6.70-7.90 m. ^{13}C NMR spectrum (δ, ppm): 141.57, 141.19, 141.08, 140.59, 140.38, 131.17, 129.92, 129.49, 128.89, 127.97, 127.48, 127.16, 126.62, 126.18. IR spectrum (ν, cm^{-1}): 3010, 1600, 1475, 740, 700. Mass spectrum, m/z: 306 (M^+).

Reaction of DCHCC of Acetylenes (IIa-c) with the Methyl Ester of 1-Methyl-2-(trimethylsilyl)cyclopropene-3-carboxylic Acid (VII). General Procedure. A. A 1.01-g portion (2.6 mmoles) of (IIb) and 0.96 g (5.2 mmoles) of (VII) in 20 ml of hexane were sealed within an ampul, which was then heated for 15 h at 50°C. The ampul was cooled, opened, the contents were dissolved in ether and the solution was filtered through a layer of silica gel. The filtrate was evaporated in vacuo, and the residue was partitioned by means of preparative TLC (silica gel, C_6H_6) to yield 0.52 g of unreacted (IIb) (conversion 58%), 30 mg (2%) of methyl ester of 1-methyl-4-oxo-5-(trimethylsilyl)-3-phenylbicyclo[3.1.0]-2-hexene-6-carboxylic acid (VIIIb), 0.69 g (65%) of a mixture (~1:1) of cyclocodimers (IXa, b), and 0.12 g (4%) of the methyl ester of 3-hydroxy-6-methyl-4-phenylbenzoic acid (Xb).

B. A 14-g portion of silica gel was added to a solution of 0.68 g (1.8 mmoles) of (IIb) and 0.65 g (3.5 mmoles) of (VII) in pentane. The solvent was evaporated under vacuum, and the residue was sealed within an ampul, which was heated for 13 h at 50°C. The ampul was cooled, opened, the contents were washed on a filter with ether, and the solvent was evaporated under vacuum. The residue (0.85 g) was separated by means of preparative TLC (silica gel, C_6H_6) to yield 70 mg of unreacted (IIb) (conversion 95%), 200 mg (86%) of adduct (VIIIb), 30 mg (3%) of a mixture (~1:1) of cyclocodimers (IXa, b), 120 mg of unreacted cyclopropene (VII) (conversion 82%), and 130 mg (12%) of the substituted benzoic acid (Xb).

Methyl Ester of 1-Methyl-4-oxo-5-(trimethylsilyl)bicyclo[3.1.0]-2-hexene-6-carboxylic Acid (VIIIa). PMR spectrum (δ, ppm, J, Hz): 0.20 s (9H, $SiMe_3$), 1.60 s (3H, Me), 2.06 s (1H, H^6), 3.68 s (3H, OMe), 5.61 d (1H, J = 5.4, H^3), 7.76 d (1H, J = 5.4, H^2). NOE (the nuclear Overhauser effect): In the differential spectrum during preirradiation of $SiMe_3$ group protons, a response is observed corresponding to H^6 and Me. ^{13}C NMR spectrum (δ, ppm, J, Hz): 0.04 q ($^1J_{C-H}$ = 120.0, $SiMe_3$), 11.91 q ($^1J_{C-H}$ = 128.4, Me), 35.17 m (C^5), 40.44 q.d.d ($^2J_{C-H}$ = 6.6, 10.2, and 5.7, C^1), 52.15 q ($^1J_{C-H}$ = 145.7, OMe), 54.06 d ($^1J_{C-H}$ = 155.0, C^5), 128.18 d.d ($^1J_{C-H}$ = 173.6, $^2J_{C-H}$ = 4.7, C^3), 168.42 d.d.q ($^1J_{C-H}$ = 169.4, $^2J_{C-H}$ = 5.5 and 4.7, C^2), 168.71 q ($^3J_{C-Me}$ = 3.8, COOMe), 208.50 d.d.d (J_{C-H} = 14.2, 5.1, and 5.3, C^4). IR spectrum (ν, cm^{-1}): 1735 (C=O of ester); 1700 (C=O of ketone); 1585 (C=C); 1200, 1180 (C–O). Mass spectrum, m/z: 238 (M^+). Found, %: C 60.56; H 7.57. $C_{12}H_{18}O_3Si$. Calculated, %: C 60.47; H 7.61.

Dimethyl ester of 1,2-dimethyl-5-oxo-4,6-di(trimethylsilyl)-trans-tricyclo[4.1.0.$0^{2,4}$]-heptane-3-endo-7-exo-dicarboxylic acid (IXa), mp 116°C (from MeOH–H_2O, 3:1). PMR spectrum (benzene-d_6, δ, ppm): 0.038 s [9H, $(SiMe_3)^4$], 0.52 s [9H, $(SiMe_3)^6$], 1.12 s (3H, Me^2), 1.61 s (3H, Me^1), 1.73 s (1H, H^7), 1.95 s (1H, H^3), 3.25 s [3H, $(COOMe)^3$], 3.33 s [3H, $COOMe)^7$]. NOE: preirradiation of $(SiMe_3)^6$ protons (0.52 ppm), response corresponding to Me^1 (1.61 ppm); preirradiation of $(SiMe_3)^4$ protons (0.038 ppm), response corresponding to Me^2 (1.12 ppm), H^7 (1.73 ppm) and H^3 (1.95 ppm). ^{13}C NMR spectrum (benzene-d_6, δ, ppm, J, Hz): −1.58 q [$^1J_{C-H}$ = 119.0, $(SiMe_3)^4$], 0.53 q [$^1J_{C-H}$ = 119.8, $(SiMe_3)^6$], 10.22 q ($^1J_{C-H}$ = 128.5, Me^1), 16.52 q.d ($^1J_{C-H}$ = 127.4, $^3J_{C-H}$ = 4.0, Me^2), 36.32 m (C^6), 38.03 d.q ($^1J_{C-H}$ = 164.8, $^3J_{C-Me}$ = 3.0, C^7), 39.39 d.q ($^1J_{C-H}$ = 161.3, $^3J_{C-Me}$ = 4.0, C^3), 40.59 m (C^4), 41.89 q.q.d.d ($^2J_{C-Me^2}$ = 4.2, $^3J_{C-Me^1}$ = 2.5, $^2J_{C-H^3}$ = 2.5, $^3J_{C-H^7}$ = 2.0, C^2), 49.39 q.q.d.d ($^2J_{C-Me^1}$ = 4.4, $^3J_{C-Me^2}$ = 2.0, $^2J_{C-H^7}$ = 3.0, $^3J_{C-H^3}$ = 2.0, C^1), 51.44 q [$^1J_{C-H}$ = 146.7 $(COOMe)^7$], 51.68 q [$^1J_{C-H}$ = 147.06 $(COOMe)^3$], 169.64 d.q [$^2J_{C-H^3}$ = 1.7, $^3J_{C-Me^2}$ = 4.2, $(COOMe)^3$], 170.25 d.q [$^2J_{C-H^7}$ = 1.2, $^3J_{C-Me^1}$ = 3.8, $(COOMe)^7$], 211.17 d.d ($^3J_{C-H^7}$ = 4.6, $^3J_{C-H^3}$ = 3.5, C^5). IR spectrum (ν, cm^{-1}): 1738, 1730 (C=O of esters); 1701 (C=O of ketone); 1266, 1244, 1196, 1176 (C–O). Mass spectrum, m/z: 396 (M^+). Found, %: C 57.61; H 8.23. $C_{19}H_{32}O_5Si_2$. Calculated, %: C 57.54; H 8.13.

Dimethyl ester of 1,2-dimethyl-5-oxo-4,6-di(trimethylsilyl)-trans-tricyclo[4.1.0.$0^{2,4}$]-heptane-3-endo-7-endo-dicarboxylic acid (IXb), mp 128°C (from MeOH–H_2O, 3:1). PMR spectrum (benzene-d_6, δ, ppm): 0.21 s (18H, $SiMe_3$), 1.24 s (6H, Me), 1.92 s (2H, H^3, H^7), 3.31 s (6H, OMe). NOE: preirradiation of $SiMe_3$ protons – response corresponding to Me and H. ^{13}C NMR spectrum (benzene-d_6, δ, ppm, J, Hz): −0.77 q ($^1J_{C-H}$ = 119.0, $SiMe_3$), 16.91 q.d ($^1J_{C-H}$ = 127.3, $^3J_{C-H}$ = 4.3, Me), 39.88 d.q ($^1J_{C-H}$ = 160.0, $^3J_{C-Me}$ = 4.2, C^3, C^7), 40.11 m (C^4, C^6), 45.83 q.q.d.d ($^2J_{C-Me}$ = 4.3, $^3J_{C-Me}$ = 3.5, $^2J_{C-H}$ = 2.2, $^3J_{C-H}$ = 2.2, C^1, C^2), 51.52 q ($^1J_{C-H}$ = 146.8, OMe), 170.06 d.q ($^2J_{C-H}$ = 4.0, $^3J_{C-OMe}$ = 3.7, COOMe), 209.43 t ($^3J_{C-H}$ = 4.0, C^5). IR spectrum (ν, cm^{-1}): 1738 (C=O of ester); 1693 (C=O of ketone); 1282, 1260, 1190, 1172 (C–O). Mass spectrum, m/z: 396 (M^+). Found, %: C 57.67; H 8.18. $C_{19}H_{32}O_5Si_2$. Calculated, %: C 57.54; H 8.13.

Methyl Ester of 3-Hydroxy-6-methylbenzoic Acid (Xa). PMR spectrum (δ, ppm, J, Hz): 2.41 d (3H, ^4J = 0.65, Me), 3.80 s (3H, OMe), 6.92 d.d (1H, $^3J_{ortho}$ = 8.5, $^4J_{meta}$ = 2.9, H^4), 7.10 d.q (1H, $^3J_{ortho}$ = 8.5, ^4J = 0.65, H^5), 7.35 d (1H, $^4J_{meta}$ = 2.9, H^2), 8.43 s (1H, OH). Mass spectrum, m/z: 166 (M^+).

Methyl Ester of 1-Methyl-4-oxo-5-(trimethylsilyl)-3-phenylbicyclo[3.1.0]-2-hexene-6-carboxylic Acid (VIIIb). PMR spectrum (δ, ppm): 0.29 s (9H, $SiMe_3$), 1.68 s (3H, Me), 2.27 s (1H, H^6), 3.70 s (3H, OMe), 7.2-7.8 m (5H, Ph), 7.94 s (1H, H^2). NOE: preirradiation of Me^1 protons – response corresponding to $SiMe_3$ and H^6. ^{13}C NMR spectrum (δ, ppm, J, Hz): 0.17 q ($^1J_{C-H}$ = 119.7, $SiMe_3$), 12.10 q ($^1J_{C-H}$ = 128.3, Me), 37.04 q.q ($^3J_{C-Me}$ = 2.3, $^3J_{C-SiMe_3}$ = 2.0, C^5), 37.85 q.d ($^2J_{C-Me}$ = 5.0, $^2J_{C-CH}$ = 2.2, C^1), 52.22 q ($^1J_{C-H}$ = 147.3 OMe), 54.01 d.q ($^1J_{C-H}$ = 169.9, $^3J_{C-Me}$ = 3.3, C^6), 137.36 d.t ($^2J_{C-H}$ = 3.9, $^3J_{C-H(arom)}$ = 3.5, C^3), 162.27 d.q.d ($^1J_{C-H}$ = 167.7, $^3J_{C-Me}$ = 4.4, $^3J_{C-H}$ = 4.1, C^2), 168.68 q ($^3J_{C-OMe}$ = 4.0, COOMe), 206.40 d.d ($^3J_{C-CH}$ = 4.7, $^3J_{C-HC=}$ = 13.0, C^4), 127.95, 128.97, 128.99, 132.51 (Ph). IR spectrum (ν, cm^{-1}): 1735 (C=O of ester), 1694 (C=O of ketone), 1508 (C=C), 1248 (Si–Me), 1198, 1176 (C–O). Mass spectrum, m/z: 314 (M^+). Found, %: C 68.92; H 7.08. $C_{18}H_{22}O_3Si$. Calculated, %: C 68.75; H 7.05.

Methyl ester of 3-hydroxy-6-methyl-4-phenylbenzoic acid (Xb), mp 179°C (from MeOH–H_2O, 3:1). PMR spectrum (δ, ppm, J, Hz): 2.52 d (3H, $^4J_{Me-H^5}$ = 0.7, Me), 3.85 s (3H, OMe), 7.23 q (1H, $^4J_{H-Me}$ = 0.7, H^5), 7.55 s (1H, H^2), 7.30-7.45 m, 7.60-7.65 m (3H and 2H, Ph), 8.45 s (1H, OH). ^{13}C NMR spectrum (δ, ppm, J, Hz): 20.75 q.d ($^1J_{C-H}$ = 127.7, $^3J_{C-H^5}$ = 5.2, Me), 51.96 q ($^1J_{C-H}$ = 147.0, OMe), 118.74 d ($^1J_{C-H}$ = 159.5, C^2), 128.08, 128.85, 130.07, 133.08 (Ph), 129.94 m (C^4), 131.78 q ($^2J_{C-Me}$ = 6.0, C^6), 134.52 d.q ($^1J_{C-H}$ = 157.1, $^3J_{C-Me}$ = 5.3, C^5), 138.59 d.q ($^2J_{C-H}$ = 9.6, $^3J_{C-H}$ = 3.4, C^3), 167.89 q.d ($^3J_{C-H}$ = 4.3, $^3J_{C-H}$ = 4.0, COOMe). IR spectrum (ν, cm^{-1}): 3370 (OH), 1695 (C=O), 1300, 1200 (C–O). Mass spectrum m/z: 242 (M^+). Found: C 74.25; H 6.02%. $C_{15}H_{14}O_3$. Calculated C 74.36; H 5.82%.

Methyl ester of 1,2,3-trimethyl-4-oxo-5-(trimethylsilyl)bicyclo[3.1.0]-2- hexene-6-carboxylic acid (VIIIc), mp 89°C (from hexane). PMR spectrum (δ, ppm, J, Hz): 0.07 s (9H, $SiMe_3$), 1.38 q (3H, $^5J_{Me-Me}$ = 1.0 Me^2), 1.45 s (3H, Me^1), 1.94 q (3H, $^5J_{Me-Me}$ = 1.0, Me^3), 1.81 s (1H, H^6), 3.55 s (3H, OMe). NOE: preirradiation of Me^1 protons (1.45 ppm) – response corresponding to H^6 (1.82 ppm) and $SiMe_3$ (0.07 ppm). ^{13}C NMR spectrum (δ, ppm, J, Hz): 0.18 q ($^1J_{C-H}$ = 120.0 $SiMe_3$), 8.12 q ($^1J_{C-H}$ = 127.5, Me), 10.24 q ($^1J_{C-H}$ = 128.0, Me), 13.65 q ($^1J_{C-H}$ = 127.8, Me), 34.45 m (C^5), 40.16 q.q ($^2J_{C-Me^1}$ = 6.0, $^3J_{C-Me^2}$ = 3.5, C^1), 52.00 q ($^1J_{C-H}$ = 145.0, OMe), 52.81 d.q ($^1J_{C-H}$ = 152.2, $^3J_{C-Me^1}$ = 3.5, C^6), 130.56 q.q.q ($^2J_{C-Me^3}$ = 6.8, $^3J_{C-Me^2}$ = 3.9, $^3J_{C-Me^1}$ = 3.6, C^3), 168.90 q ($^3J_{C-OMe}$ = 3.6, COOMe), 170.65 q.q ($^2J_{C-Me^2}$ = 6.3, $^3J_{C-Me^3}$ = 3.1, C^2), 207.19 q ($^3J_{C-Me^3}$ = 3.5, C^4). IR spectrum (ν, cm^{-1}): 1735 (C=O of ester), 1690 (C=O of ketone), 1250 (Si–Me), 1200, 1180 (C–O). Mass spectrum, m/z: 266 (M^+). Found, %: C 62.96; H 8.53. $C_{14}H_{22}O_3Si$. Calculated, %: C 63.12; H 8.32.

Methyl ester of 3-hydroxy-4,5,6-trimethylbenzoic acid (Xc), mp 158°C (from hexane). PMR spectrum (δ, ppm): 2.19 s (6H, Me^4, Me^6), 2.34 s (3H, Me^5), 3.79 s (3H, OMe), 7.15 s (1H, H^2), 8.18 s (1H, OH). ^{13}C NMR spectrum (δ, ppm, J, Hz): 12.66 q ($^1J_{C-H}$ = 127.2, Me^4), 16.15 q ($^1J_{C-H}$ = 127.0, Me^6), 16.64 q ($^1J_{C-H}$ = 127.0, Me^5), 51.87 q ($^1J_{C-H}$ = 146.8, OMe), 114.07 ($^1J_{C-H}$ = 150.0, C^2), 128.02 q.q ($^2J_{C-Me^4}$ = 6.0, $^3J_{C-Me^5}$ = 3.5, C^4), 128.66 q.q ($^2J_{C-Me^6}$ = 6.6, $^3J_{C-Me^5}$ = 3.2, C^6), 129.73 q.q.q ($^2J_{C-Me^5}$ = 6.0, $^3J_{C-Me}$ = 3.5 and 3.7, C^5), 138.50 d.q ($^2J_{C-H}$ = 5.6, $^3J_{C-Me^6}$ = 4.0, C^1), 153.28 d.q ($^2J_{C-H}$ = 5.7, ($^3J_{C-Me^4}$ = 4.1, C^3), 169.35 q.d ($^3J_{C-OMe}$ = 3.5, $^3J_{C-H}$ = 4.5, COOMe). IR spectrum (ν, cm^{-1}): 3360 (O–H), 1688 (C=O), 1292, 1112 (C–O), 1584, 1440, 1420 (C–C arom.), 1324 (O–H), 1240 (C_{arom}–O). Mass spectrum, m/z: 194 (M^+). Found, %: C 67.72; H 7.42. $C_{11}H_{14}O_3$. Calculated, %: C 68.02; H 7.27.

Protodesilylation Reaction of Adducts (VIIIa-c). A 120-mg portion (2.0 mmoles) of anhydrous KF and 80 mg (0.23 mmole) of dibenzo-18-crown-6 was added to a solution of 212 mg (0.67 mmole) of adduct (VIIIb) in 2 ml of acetonitrile. The mixture was stirred for 48 h at 20°C, and then was filtered off, the solvent was evaporated under vacuum, and the residue was separated by preparative TLC on silica gel in an ether–hexane system. Thus, 17 mg of the initial adduct (VIIIb) (92% conversion) and 138 mg (92%) of the desilylated adduct (XIb) were obtained.

Methyl ester of 1-methyl-4-oxobicyclo[3.1.0]-2-hexene-6-carboxylic acid (XIa), mp 51°C (from hexane). PMR spectrum (δ, ppm, J, Hz): 1.52 s (3H, Me), 2.30 d (1H, $^3J_{H^6-H^5}$ = 3.0, H^6), 2.38 d.d.d (^1H, $^3J_{H^5-H^6}$ = 3.0, $^4J_{H^5-H^2}$ = 1.2, $^4J_{H^5-H^3}$ = 1.2, H^5), 3.67 s (3H, OMe),

5.66 d.d (1H, $^3J_{H^3-H^2}$ = 5.8, $^4J_{H^3-H^5}$ = 1.2, H^3), 7.68 d.d (1H, $^3J_{H^2-H^3}$ = 5.8, $^4J_{H^2-H^5}$ = 1.2, H^2). NOE: preirradiation of Me protons (1.52 ppm) – response corresponding to H^5 (2.38 ppm) and H^6 (2.30 ppm). ^{13}C NMR spectrum (δ, ppm, J, Hz): 10.78 q.t ($^1J_{C-H}$ = 126.7, J = 2.1, Me), 35.56 d.d.q ($^1J_{C-H}$ = 168.5, J = 5.0, $^3J_{C-Me}$ = 3.0, C^5), 36.72 q.d.d ($^2J_{C-Me}$ = 4.5, J = 5.1, J = 2.8, C^1), 49.35 d.d.d.q ($^1J_{C-H}$ = 155.2, J = 2.1 and 2.1, $^3J_{C-Me}$ = 3.0, C^6), 52.31 q ($^1J_{C-H}$ = 145.7, OMe), 129.05 d.d.d ($^1J_{C-H}$ = 174.2, J = 4.1 and 4.1, C^3), 165.61 d.q.d ($^1J_{C-H}$ = 171.0, $^3J_{C-Me}$ = 3.6, $^2J_{C-H^3}$ = 4.0, C^2), 168.26 d.d.q ($^2J_{C-H^6}$ = 5.5, $^3J_{C-H^5}$ = 4.4, $^3J_{C-OMe}$ = 3.5, COOMe), 203.45 d.d.d.d ($^3J_{C-H^3}$ = 13.5, $^2J_{C-H^3}$ = 6.0, $^3J_{C-H^6}$ = 2.8, $^3J_{C-H^5}$ = 2.0, C^4). IR spectrum (ν, cm^{-1}): 1725 (C=O of ester), 1705 (C=O of ketone) 1575 (C=C), 1205, 1180, 1165 (C–O). Mass spectrum, m/z: 166 (M^+). Found C 64.63; H 6.20%. $C_9H_{10}O_3$. Calculated C 65.05; H 6.07%.

Methyl ester of 1-methyl-4-oxo-3-phenylbicyclo[3.1.0]-2-hexene-6-carboxylic acid (XIb), mp 70°C (from hexane). PMR spectrum (δ, ppm, J, Hz): 1.60 s (3H, Me), 2.53 d (1H, ^3J = 3.2, H^6), 2.59 d.d (1H, ^3J = 3.2, ^4J = 1.3, H^5), 3.70 s (3H, OMe), 7.30-7.70 m (5H, Ph), 7.86 d (1H, J = 1.3, H^2). NOE: preirradiation of Me protons (1.56 ppm) – response corresponding to H^6 (2.61 ppm) and H^2 (7.86 ppm). ^{13}C NMR spectrum (δ, ppm, J, Hz): 10.94 q ($^1J_{C-H}$ = 129.0, Me), 34.29 q.d ($^2J_{C-Me}$ = 5.9, J = 2.0, C^1), 36.96 d.m ($^1J_{C-H}$ = 178.0, C^5), 49.31 d.m ($^1J_{C-H}$ = 174.4, C^6), 52.32 q ($^1J_{C-H}$ = 147.3, OMe), 138.10 d.t ($^2J_{C-H}$ = 4.0, $^3J_{C-H(arom)}$ = 3.5, C^3), 159.00 d.d.q ($^1J_{C-H}$ = 171.1, $^3J_{C-H}$ = 3.8 and 3.6, $^3J_{C-Me}$ = 4.0, C^2), 168.12($^3J_{C-OMe}$ = 4.2, COOMe), 201.77 d.d ($^3J_{C-H^2}$ = 12.0, J_{C-H} = 3.8, C^4), 127.86, 129.05, 129.13, 132.30 (Ph). IR spectrum (ν, cm^{-1}): 1730 (C=O of ester), 1698 (C=O of ketone), 1495 (C=C), 1205, 1180, 1163, 1140 (C–O). Mass spectrum, m/z: 242 (M^+). Found, %: C 74.29; H 5.98. $C_{15}H_{14}O_3$. Calculated, %: C 74.36; H 5.82.

Methyl Ester of 1,2,3-Trimethyl-4-oxobicyclo[3.1.0]-2-hexene-6-carboxylic Acid (XIc). PMR spectrum (δ, ppm, J, Hz): 1.48 d (3H, $^4J_{Me^1-H^5}$ = 0.3, Me^1), 1.49 q (3H, $^5J_{Me^3-Me^2}$ = 1.1, Me^3), 2.03 q.d (3H, $^5J_{Me^2-Me^3}$ = 1.1, $^5J_{Me^2-H^5}$ = 0.3, Me^2), 2.17 d (1H, $^3J_{H^6-H^5}$ = 3.2, H^6), 2.28 d.q.q (1H, $^3J_{H^5-H^6}$ = 3.2, $^4J_{H^5-Me^1}$ = 0.3, $^5J_{H^5-Me^2}$ = 0.3, H^5), 3.63 s (3H, OMe). NOE: preirradiation of Me^1 protons (1.48 ppm) – response corresponding to H^6 (2.17 ppm) and H^5 (2.28 ppm); preirradiation of H^5 protons (2.28 ppm) – response corresponding to H^6 (2.17 ppm) and Me^1 (1.48 ppm). ^{13}C NMR spectrum (δ, ppm, J, Hz): 7.80 q ($^1J_{C-H}$ = 126.9, Me^3), 9.52 q.d ($^1J_{C-H}$ = 128.3, $^3J_{Me^1-H^6}$ = 2.9, Me^1), 13.37 q ($^1J_{C-H}$ = 127.5, Me^2); 35.27 d.q ($^1J_{C-H}$ = 157.7, $^3J_{C-Me^1}$ = 3.4, C^5), 36.56 q.m ($^2J_{C-Me^1}$ = 4.7, C^1), 48.11 d.d.q ($^1J_{C-H}$ = 148.7, $^2J_{C-H^5}$ = 2.2, $^3J_{C-Me^1}$ = 3.5, C^6), 52.15 q ($^1J_{C-H}$ = 147.2, OMe), 131.25 q.q.d ($^2J_{C-Me^3}$ = 4.5, $^3J_{C-Me^2}$ = 3.4, $^3J_{C-H^5}$ = 3.4, C^3), 168.39 q.d ($^3J_{C-OMe}$ = 4.0, J_{C-H} = 3.0, COOMe), 168.51 q.q.d.d ($^3J_{C-Me^3}$ = 4.6, $^3J_{C-Me^2}$ = 3.2, C^2), 202.55 q.d ($^3J_{C-Me^3}$ = 3.1, J_{C-H} = 2.7, C^4). IR spectrum (ν, cm^{-1}): 1730 (C=O of ester), 1710 (C=O of ketone), 1650 (C=C). Mass spectrum, m/z: 194 (M^+). Found, %: C 67.97; H 7.08. $C_{11}H_{14}O_3$. Calculated, %: C 68.02; H 7.27.

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