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ACYLATION OF DICOBALTHEXACARBONYL COMPLEXES OF 1-ETHYNYLCYCLOHEXENE AND 1-ETHYNYLCYCLOPENTENE BY ACYLIUM SALTS

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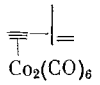
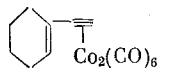
It was previously reported that the dicobalthexacarbonyl (DCHC) complex of isopropenylacetylene (I) reacts with cationoid salts of the type $E^+BF_4^-$ (where E^+ is alkyl, acyl, thioaryl, and nitronium cation) by a two stage mechanism of electrophilic addition to the olefin with independent variations of the electrophile and nucleophile [1, 2]. However, the question of the generality of the discovered reaction remained open, in particular it was unclear to what extent the presence of the bulky fragment of the DCHC complex* will influence the ease of carrying out the Ad_E reaction at the double bond for systems more complex than (I).

In the present work the reactions of certain acylium salts with DCHC complexes of 1-ethynylcyclohexene (II) and 1-ethynylcyclopentene (III) have been studied (preliminary communication [4]).



(I)



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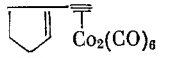

(III)

It was found that the reactions of (II) or (III) with acylium salts of the acetyl tetrafluoroborate (IV) or trans-crotonyl tetrafluoroborate (V) type occur under conditions analogous to those described previously in [1]. The formation of a cationoid intermediate (CI-I) or (CI-II) was evidently the result of addition of the acyl cation at the double bond of (II) or (III). The intermediates were sufficiently stable in solution but were able to be further converted on treatment with water or methanol into the corresponding hydroxy or methoxy adducts (VI)-(XII). The structures of the latter were proved by data of ^1H NMR spectroscopy, the stereochemistry of the products will be considered below. Oxidative decomplexation of (VI)-(VIII) and (X)-(XII) occurred fairly effectively (80-95% yields)† and led to the forma-

*It is known from [3] that DCHC complexes of acetylenes have a tetrahedral structure, see also data from the present work on the stereochemistry of the obtained adducts.

†The assumed conditions proved to be unsuitable for decomplexation of the DCHC complex of the crotonoyloxy adduct (IX) which gave a complex mixture of products under these conditions.

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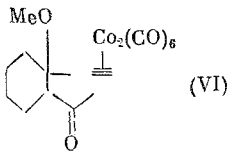
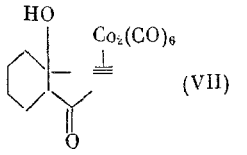
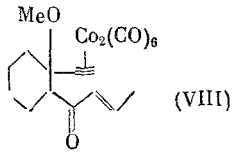
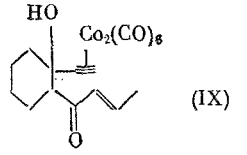
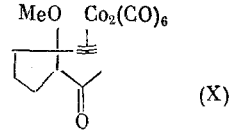
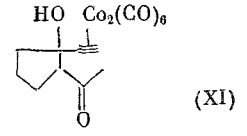
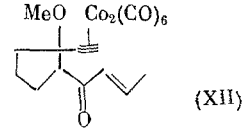
TABLE 1. Structures and Yields of Adducts of DCHC Complexes of 1-Ethynylcyclohexene (VI)-(IX) and 1-Ethynylcyclopentene (X)-(XII)

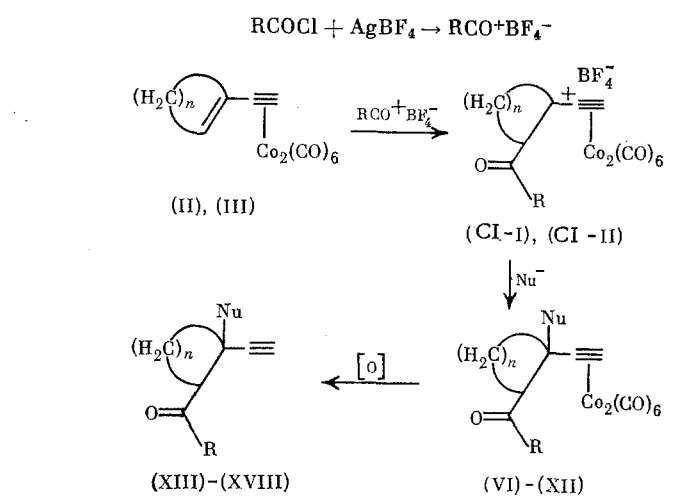
Acyl	Nucleophile	Adduct	Yield, %
$MeCO^+$	MeO^-	 (VI)	60
$MeCO^+$	HO^-	 (VII)	56
$MeCH:CHCO^+$	MeO^-	 (VIII)	63
$MeCH:CHCO^+$	HO^-	 (IX)	50
$MeCO^+$	MeO^-	 (X)	44
$MeCO^+$	HO^-	 (XI)	38
$MeCH:CHCO^+$	MeO^-	 (XII)	50

tion of adducts (XIII)-(XVIII) which were the addition products of the corresponding acyl cations and nucleophiles (OH^-, MeO^-) at the double bond of the initial 1-ethynylcycloalkenes.

The structures and yields of products (VI)-(XII) are given in Table 1.

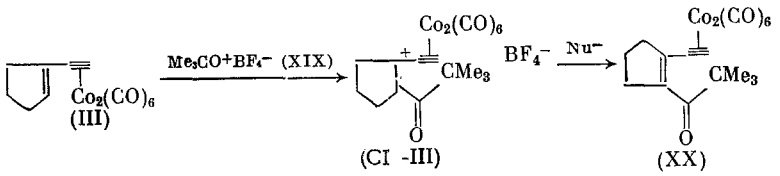
The interaction of complexes (II) and (III) with pivaloyl fluoroborate (XIX), a reagent which readily added to (I) [1], proceeded appreciably less effectively. In this case in spite of significant variations of the conditions of carrying out the reaction (CH_2Cl_2 or liquid SO_2, order of mixing reagents, temperature from −78 to 0°C, time from 20 min to 6 h), the main bulk of the reaction product was the initial substrate. Judging by data of ^1H NMR the reaction medium seemingly contained an insignificant amount (4-20%) of unsaturated ketone (XX). Evidently the presence in substrates of the bulky DCHC group hindered not only the stage of electrophilic attack when using the sterically hindered pivaloyl cation but also made impossible the subsequent approach of a nucleophile to the carbene ion center in CI-III by virtue of which the latter on treatment with nucleophiles was subjected to deprotonation.

Scheme 1



$n = 3$(III), (CI -II), (X)—(XII), (XVI)—(XVIII); $n = 4$(II), (CI -I), (VI)—(IX), (XIII)—(XV).

Scheme 2



The data presented above show that, when applied to an enyne of the type of the ethynylcycloalkenes, the acylation of DCHC complexes by a scheme of discrete addition of electrophile and nucleophile may be carried out but only with the use of sterically unhindered reactants.

Analysis of the decomplexation products (XIII)-(XVIII) by GLC and also the data of their ^{1}H NMR spectra clearly showed that in all cases a mixture of two stereoisomers was formed in various ratios but with one predominating. The stereochemistry of the reaction was studied in the case of forming acetyl-hydroxy adduct (VII) in the reaction of complex (II) with acetyl tetrafluoroborate (IV).

In this example both resulting isomers (VIIa) and (VIIb) were successfully isolated in a homogeneous state by chromatography on SiO_2. A monocrystal of the main isomer (VIIa) with a melting point of 89°C was obtained by recrystallization from pentane which permitted its structure to be established by x-ray crystallographic analysis.

The constitution of the molecule of (VIIa) is shown in Fig. 1, the major bond lengths, bond, and torsion angles are given in Tables 2-4. The molecule of (VIIa) consists of a $Co_2(CO)_6$ fragment and an organic ligand, the acetylenic bond of which C^7—C^8 is coordinated with both Co atoms according to a η^2 type. The structure of the coordination unit $Co_2(CO)_6$ (μ_2-acetylene) in (VIIa) was mainly the same as in complexes $Co_2(CO)_6$ (RC≡CR) (XXI) (R = t-Bu [5], Ph [6]) and $Co_2(CO)_4(PMe_3)$(HC≡CH) (XXII) [7]. The length of the Co—Co bond in (VIIa) was in agreement with those found in (XXI) and (XXII) (2.460-2.464 Å).

As usual in π-acetylenic complexes the acetylenic fragment in (VIIa) is nonlinear (C^7—H[C^7] and C^8—C^9 bonds are bent "backwards," i.e., away from the $Co_2(CO)_6$ fragment) and the C^7—C^8 bond [1.319(5) Å] is significantly longer than a normal triple bond (1.205 Å [8]) although a little shorter than the coordinated acetylenic bonds in (XXI) and (XXII) (1.33-1.36 Å).

Each of the Co atoms has one carbonyl group (C^2O^2 and C^4O^4) in the cis position in relation to the acetylenic ligand (relative to the Co—Co bond). These particular CO groups form the shortest Co—CO bonds [mean 1.787(4) Å against 1.812(5) Å for the remainder].

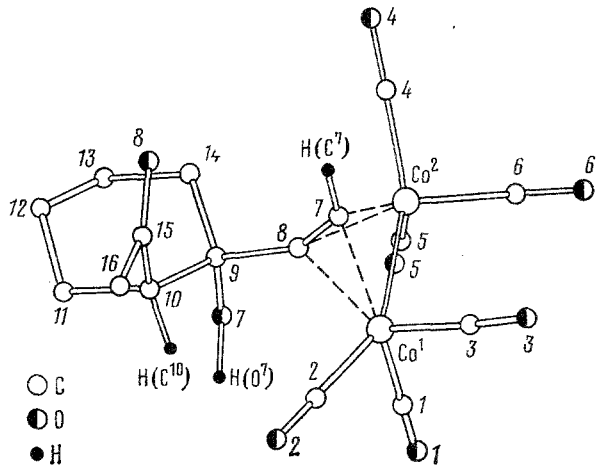


Fig. 1. Structure of the DCHC complex of 1-ethynyl-1-α-hydroxy-2-*α*-acetylcyclohexane (VIIa) (hydrogen atoms of the methyl and methylene groups are not shown).

TABLE 2. Bond Lengths d

Bond	*d*, Å	Bond	*d*, Å	Bond	*d*, Å
Co^1-Co^2	2,462(1)	C^1-O^1	1,128(6)	$C^{12}-C^{13}$	1,505(7)
Co^1-C^1	1,806(5)	C^2-O^2	1,131(5)	$C^{13}-C^{14}$	1,517(6)
Co^1-C^2	1,791(4)	C^3-O^3	1,139(6)	$C^{14}-C^9$	1,533(5)
Co^1-C^3	1,807(4)	C^4-O^4	1,133(6)	C^9-O^7	1,426(4)
Co^1-C^7	1,946(4)	C^5-O^5	1,125(7)	$C^{10}-C^{15}$	1,514(5)
Co^1-C^8	1,985(3)	C^6-O^6	1,137(6)	$C^{15}-O^8$	1,202(4)
Co^2-C^4	1,783(5)	C^7-C^8	1,319(5)	$C^{15}-C^{16}$	1,499(8)
Co^2-C^5	1,828(5)	C^8-C^9	1,497(4)	$O^7-H[O^7]$	0,76(4)
Co^2-C^6	1,806(5)	C^9-C^{10}	1,548(5)	$C^7-H[C^7]$	0,91(4)
Co^2-C^7	1,956(4)	$C^{10}-C^{11}$	1,545(5)	$C^{10}-H[C^{10}]$	0,94(3)
Co^2-C^8	1,975(3)	$C^{11}-C^{12}$	1,525(6)		

TABLE 3. Bond Angles ω

Angle	ω, deg	Angle	ω, deg	Angle	ω, deg
$Co^2Co^1C^1$	95,7(1)	$C^4Co^2C^8$	104,2(2)	$Co^2C^8C^9$	132,7(2)
$Co^2Co^1C^2$	152,2(1)	$C^5Co^2C^6$	105,4(2)	$C^7C^8C^9$	145,4(3)
$Co^2Co^1C^3$	98,7(1)	$C^5Co^2C^7$	136,0(2)	$C^8C^9C^{10}$	110,6(3)
$Co^2Co^1C^7$	51,1(1)	$C^5Co^2C^8$	97,2(2)	$C^8C^9C^{14}$	110,8(3)
$Co^2Co^1C^8$	51,4(1)	$C^6Co^2C^7$	111,3(2)	$C^8C^9O^7$	110,1(3)
$C^1Co^1C^2$	99,2(2)	$C^6Co^2C^8$	144,4(2)	$C^{10}C^9C^{14}$	111,3(3)
$C^1Co^1C^3$	108,2(2)	$C^7Co^2C^8$	39,2(1)	$C^{10}C^9O^7$	108,9(3)
$C^1Co^1C^7$	140,8(2)	$Co^1C^1O^1$	179,6(4)	$C^{14}C^9O^7$	104,9(3)
$C^1Co^1C^8$	106,0(2)	$Co^1C^2O^2$	179,2(4)	$C^9C^{10}C^{11}$	110,6(3)
$C^2Co^1C^3$	98,7(2)	$Co^1C^3O^3$	175,8(4)	$C^9C^{10}C^{15}$	115,9(3)
$C^2Co^1C^7$	104,9(2)	$Co^2C^4O^4$	176,8(4)	$C^9C^{10}H(C^{10})$	106(2)
$C^2Co^1C^8$	101,7(2)	$Co^2C^5O^5$	177,5(5)	$C^{11}C^{10}C^{15}$	108,2(3)
$C^3Co^1C^7$	98,2(2)	$Co^2C^6O^6$	178,7(5)	$C^{11}C^{10}H(C^{10})$	107(2)
$C^3Co^1C^8$	136,3(2)	$Co^1C^7Co^2$	78,2(1)	$C^{15}C^{10}H(C^{10})$	109(2)
$C^7Co^1C^8$	39,2(1)	$Co^1C^7C^8$	72,0(2)	$C^{10}C^{11}C^{12}$	112,2(4)
$Co^1Co^2C^4$	146,8(2)	$Co^2C^7C^8$	71,2(2)	$C^{11}C^{12}C^{13}$	111,2(4)
$Co^1Co^2C^5$	103,1(2)	$Co^1C^7H(C^7)$	135(2)	$C^{12}C^{13}C^{14}$	112,2(4)
$Co^1Co^2C^6$	95,8(2)	$Co^2C^7H(C^7)$	128(2)	$C^{13}C^{14}C^9$	112,1(3)
$Co^1Co^2C^7$	50,7(1)	$C^8C^7H(C^7)$	145(2)	$C^{10}C^{15}O^8$	122,8(3)
$Co^1Co^2C^8$	51,8(1)	$Co^1C^8Co^2$	76,9(1)	$C^{10}C^{15}C^{16}$	116,9(4)
$C^4Co^2C^5$	102,6(2)	$Co^1C^8C^7$	68,8(2)	$O^8C^{15}C^{16}$	120,1(4)
$C^4Co^2C^6$	97,4(2)	$Co^2C^8C^7$	69,6(2)	$C^9O^7H(O^7)$	110(3)
$C^4Co^2C^7$	96,0(2)	$Co^1C^8C^9$	134,3(2)		

In complexes (XXI) and (XXII) the $Co(CO)_3$ grouping is in a shielded conformation (relative to the Co—Co bond) and each coordination unit has a local plane of symmetry m passing through the Co atom, the middle of the C≡C bond and the two CO groups in the cis position to the acetylenic ligand. In complex (VIIa) this symmetry is destroyed as a result of the awkward substituent at the C^8 atom. The $Co_2(CO)_6$ fragment is twisted relative to the Co—Co

TABLE 4. Torsion Angles τ

Angle	τ, deg	Angle	τ, deg
$C^2Co^1Co^2C^4$	34,4(6)	$C^7C^8C^9C^{10}$	−52,1(5)
$C^1Co^1Co^2C^5$	17,0(3)	$C^7C^8C^9C^{14}$	71,9(6)
$C^3Co^1Co^2C^6$	19,2(3)	$O^7C^9C^{10}C^{11}$	−62,5(4)
$C^{14}C^9C^{10}C^{11}$	52,7(4)	$O^7C^9C^{14}C^{13}$	64,0(4)
$C^9C^{10}C^{11}C^{12}$	−53,9(4)	$C^8C^9C^{10}C^{11}$	176,4(5)
$C^{10}C^{11}C^{12}C^{13}$	55,3(4)	$C^8C^9C^{14}C^{13}$	−177,2(5)
$C^{11}C^{12}C^{13}C^{14}$	−55,5(4)	$C^{15}C^{10}C^9C^{14}$	−70,8(4)
$C^{13}C^{14}C^9C^{10}$	−53,7(4)	$C^{15}C^{10}C^{11}C^{12}$	73,9(5)
$C^{12}C^{13}C^{14}C^9$	55,2(4)		

bond (see Table 4) and the Co—C^8 distance is on average 0.03 Å greater than Co—C^7. A similar nonequivalence of the Co—C (acetylene) distances was also observed in the $[(CO)_9Co_3C{-}C{\equiv}CH]\cdot Co_2(CO)_6$ complex [9] with the awkward (cluster) substituent on the acetylenic fragment.

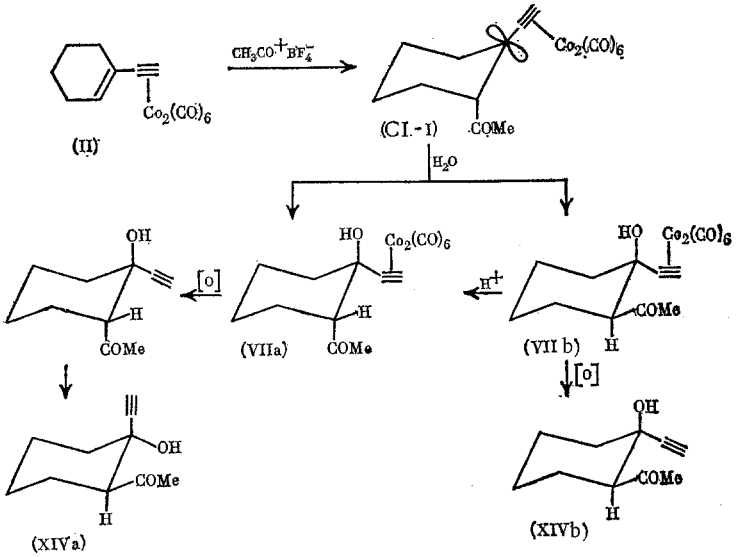
The cyclohexane ring has a clearly marked chair conformation with axial disposition of the hydroxyl and acetyl substituents and equatorial disposition for the ethynyl substituent and the H(C^{10}) atom (see Table 4). The C^{10}, C^{11}, C^{13}, and C^{14} atoms are (with a precision of 0.001 Å) in one plane from which the other atoms are distant C^9 0.65 Å, C^{12} 0.65 Å, C^8 0.57 Å, O^7 2.01 Å, C^{15} 1.41 Å, and H(C^{10}) 0.56 Å.

The molecules, linked in a screw axis [1/4 y 3/4], are united by hydrogen bonds O^7 — $H(O^7)\ldots O^8$ (1/2 − x, 1/2 + y, 3/2 − z) at distances $O^7\ldots O^8$ — 2.837(4) Å, $H(O^7)\ldots O^8$ — 2.08(4) Å, angles $O^7H(O^7)O^8$ 174(4)°, $H(O^7)O^8C^{15}$ 121(1)° in an infinite chain along the direction of the b axis. There are only Van der Waals interactions between the chains.

The x-ray structural analysis data therefore showed that the main isomer (VIIa) is the product of trans diaxial addition of acetyl and hydroxyl groups. The ^{1}H NMR spectrum (250 MHz) showed clearly that in solution (VIIa) has the same conformation [the signal of the equatorial H(C^{10}) is displayed as a triplet with spin—spin interaction constant (SSIC) J = 5 Hz] as in the crystalline state.

It follows from these data that stereoisomer (VIIb) must be the product of cis addition of acetyl and hydroxyl groups. The ^{1}H NMR data for (VIIb) indicate an axial orientation for H(C^{10}) [the signal for H(C^{10}) is displayed as a doublet of doublets with SSIC J_1 = 9, J_2 = 6 Hz] from which it follows that (VIIb) has the conformation expressed in Scheme 3.

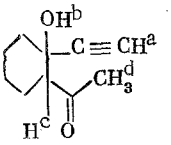
Scheme 3



The ^{1}H NMR spectral data for stereoisomers (VII) and (XIV) are given in Table 5 and the ^{13}C NMR data for stereoisomers (XIV) in Table 6.

A more careful study of the stereochemistry of the formation of isomers (VII) showed that their ratio depended on the time interval Δt between treatment of the reaction complex with

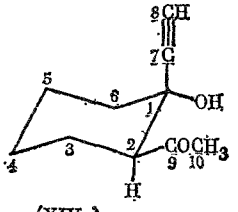
TABLE 5. Data of ^{1}H NMR Spectra of Stereoisomers (VIIa) and (VIIb) (upper portion of table) and of Their Decomplexation Products (XIVa) and (XIVb) [250 MHz, deuterobenzene for (VIIa) and (XIIb), deuterochloroform for (XIVa) and (XIVb), internal standard TMS]



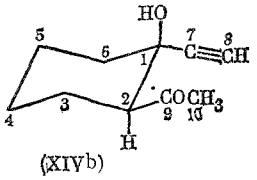
Main isomer				
compound	H^a	H^b	H^c	H^d
(VIIa)	5,57 s	2,61 m	2,44 t (J=5Hz) eq	1,72 s
(XIVa)	2,53 s	4,51 br. s	2,36 d.d (J_1=13, J_2=3,5 Hz) ax	2,23 s

Minor isomer				
compound	H^a	H^b	H^c	H^d
(VIIb)	5,70 s	5,00 br. s	2,51 d.d (J_1=9, J_2=6 Hz) ax	2,00 s
(XIVb)	2,39 s	4,62 br. s	2,79 d.d (J_1=14, J_2=3,5 Hz) ax	2,27 s

TABLE 6. Chemical Shifts of Carbon Atoms (δ from TMS) in ^{13}C NMR Spectra of Stereoisomers (XIVa) and (XIVb) and Multiplicity of Signals on Drawing Spectra under Conditions of "Off" Resonance (62.89 MHz, deuterochloroform)



(XIVa)



(XIVb)

Number of C atom	ppm	Multiplicity	Number of C atom	ppm	Multiplicity
1	29,58	s	1	29,63	s
2	59,74	d	2	57,13	d
3, 4, 5	26,50	t	3, 4, 5	24,80	t
	25,22	t		24,36	t
	22,98	t		20,18	t
6	39,98	t	6	38,14	t
7	70,01	s	7	66,25	s
8	74,15	d	8	70,48	d
9	211,8	s	9	214,2	s
10	29,14	q	10	30,68	q

the nucleophile (water) and the subsequent neutralization of the mixture with base. Thus on changing Δt from 20 sec to 90 min the ratio (VIIa)—(VIIb) changed from 2:1 to 10:1 [GLC data of the mixture of decomplexation products (XIVa) + (XIVb)].

From this it follows that the kinetically controlled result of the reaction of the cationoid intermediate CI-I with nucleophile (HO^-) is the stereo nonspecific addition of the latter with some predominance of anti attack. Of the resulting isomers (VIIa) and (VIIb) the latter is evidently the less stable (because of the strong gauche interaction of the acetyl group and the bulky DCHC-ethyl fragment) and in the presence of acid (HBF_4) it may be isomerized into the more stable (VIIa) as a result of the usual epimerization at the carbon atom α to the carbonyl group.

The stereo nonspecificity of forming adducts (VIIa) and (VIIb) is evidently due to the fact that CI-I resulting at the acylation stage has the structure of the classical sp^3 hybridized carbene ion (see Scheme 3).

Study of the ^1H NMR spectra of the decomplexation products (XIVa) and (XIVb) showed (Table 5) that the $H(C^{10})$ proton had an axial orientation in both isomers with signals in the form of a doublet of doublets with SSIC $J_1 = 13$, $J_2 = 3.5$ Hz for (XIVa) and $J_1 = 14$, $J_2 = 3.5$ Hz for (XIVb). The complete stereochemistry of the process including the decomplexation stage is depicted in Scheme 3.

EXPERIMENTAL

The ^1H NMR spectra were taken in deuterobenzene with TMS as internal standard (DCHC complexes) and in CCl_4 with TMS as internal standard (decomplexed accuts) on Varian DA-60 IL (60 MHz), Tesla BS-467 (60 MHz), Tesla BS-497 (100 MHz), and Bruker WM-250 (250 MHz) instruments. The ^{13}C NMR spectra were taken on a Bruker WM-250 (62.89 MHz) instrument. All chemical shifts are given in the δ scale from TMS. GLC analysis was carried out on a LKhM-8MD-5 chromatograph on capillary columns of diameter 0.2 mm and length 30 m, liquid phase was SE-30 or PEG-40000. TLC analysis was carrie d out on Silufol UV-254 plates. Preparative chromatography was effected on plates with binder-free layers of silica gel 40/100 and on columns of silica gel 100/160. Reactions were carried out in a current of dry argon in absolute solvents prepared by the standard procedure of [10].

The initial 1-ethynylcycohexene and 1-ethynylcyclopentene were obtained by the procedures of [11, 12] by dehydration of the corresponding alcohols [13]. Dicobaltoctacarbonyl, required for the synthesis of the DCHC complexes, was obtained by the procedure of [14]. Silver fluoroborate was obtained by the interaction of AgF and BF_3 in dichloroethane [15]. The preparation of the DCHC complexes of the initial enynes was carried out by a modified procedure of [16]. A typical procedure is given below.

DCHC Complex of 1-Ethynylcyclohexene (II). A solution of 1-ethynylcyclohexene (1.06 g: 10 mmole) in benzene (10 ml) was poured into a solution of $Co_2(CO)_8$ (3.48 g: 10 mmole) in benzene (10 ml), the mixture was stirred for 2 h at ~20°C, and filtered through a layer of Al_2O_3. After removal of benzene on a rotary evaporator,* the residue was dissolved in hexane, and filtered once again through a layer of Al_2O_3 until removal of contaminants (check by TLC, eluent was hexane, R_f 0.74). After removal of hexane, compound (II) (3.53 g: 90%) was obtained. Data of PMR spectrum: 5.92 m (1 H), 5.84 s (1 H), 1.97 m (8 H).

Signals observed in the PMR spectrum of the DCHC complex of 1-ethynylcyclopentene (III) were 5.80 m (2 H), 2.08 m (6 H).

All acylation reactions were carried out according to the typical procedure given below. The spectral characteristics of the obtained complex adducts and their decomplexation products are shown in Table 7.

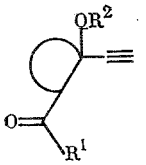
DCHC Complex of 1-Ethynyl-1-hydroxy-2-acetylcyclohexane (VII). Solutions of the DCHC complex (4.7 g: 12 mmole) in CH_2Cl_2 (30 ml) and of AcCl (2.83 g: 36 mmole) in CH_2Cl_2 (10 ml) were poured sequentially into a solution of $AgBF_4$ (7.02 g: 36 mmole) in nitromethane (10 ml) and CH_2Cl_2 (20 ml) stirred at −78°C. After 10 min a 10% solution (30 ml) of water in acetone cooled to −78°C was poured into the mixture, after 20 sec the mixture was treated with a saturated solution (40 ml) of $NaHCO_3$, and with ether. The ether extract was filtered through Al_2O_3 and dried over anhydrous $MgSO_4$. After removal of ether a dark red oil was obtained which was chromatographed on a column (hexane–ether, 4:1) and the trans isomer (VIIa) (R_f 0.24) (2.55 g: 47%) and the cis isomer (VIIb) (R_f 0.44) (0.48 g: 9%) were isolated.†

DCHC Complex of 1-Ethynyl-1-methoxy-1-crotonoylcyclopentane (XII). Solutions of the DCHC complex (III) (0.38 g: 1 mmole) in CH_2Cl_2 (10 ml) and of trans crotonoyl chloride (0.31 g 3 mmole) in CH_2Cl_2 (5 ml) were poured sequentially into a solution of $AgBF_4$ (0.59 g: 3 mmole)

*DCHC complexes are thermally labile, it is therefore recommended not to heat the bath above 30°C when removing solvent. DCHC complexes must be stored at reduced temperature dissolved in readily removable solvents (ether, pentane, etc.).

†GLC analysis of test samples of the reaction mixture (afrer decomplexation) showed that the ratio (VIIa):(VIIb) was equal to 2.11:1. The change in ratio of isomers observed after separation (5.22:1) is seemingly explained by losses on isolation.

TABLE 7. Data of PMR Spectra of DCHC Complexes of the Obtained Adducts (VI)-(XII) (upper portion of graph) and of Their Decomplexation Products (XIII)-(XVIII) of Type



Compound	Ethynyl H	R^1	R^2
(VI) *	5,60 s	1,83 s	2,98 s
(XIII)	2,57 s	2,16 s	3,34 s
(XV) †	2,50 s	7,00 m 1,96 d	3,30 s
(IX)	5,62 s	6,13 s 2,00 d	–
(X)	5,46	1,74 s	2,86 s
(XVI)	2,58 s	2,20 s	3,26 s
(XI)	5,54 s	2,34 s	5,14 m
(XVII)	2,49 s	2,27 s	4,30 m
(XII)	5,56 s	6,72 m 1,48 d	2,93 s
(XVIII)	2,58 s	6,60 m 1,93 d	3,24 s

*Signals were observed for protons of the cyclic fragments in the 1.60-1.20 ppm region in the spectra of adducts (VI)-(XVIII).
†The corresponding DCHC complex was not characterized.

TABLE 8. Results of Elemental Analysis of Adducts (XIII)-(XVIII)

Compound	Found, %		Calculated, %		Empirical formula
	C	H	C	H	
(XIII)	73,13	9,00	73,30	8,95	$C_{11}H_{16}O_2$
(XIV)	72,44	8,54	72,26	8,49	$C_{10}H_{14}O_2$
(XV)	75,13	9,01	75,62	8,80	$C_{13}H_{18}O_2$
(XVI)	72,23	8,26	72,26	8,49	$C_{10}H_{14}O_2$
(XVII)	70,39	8,10	71,03	7,95	$C_9H_{12}O_2$
(XVIII)	74,48	8,47	74,97	8,39	$C_{12}H_{16}O_2$

in CH_2Cl_2 (5 ml) stirred at −78°C. After 20 min methanol (0.8 g: 25 mmole) cooled to −78°C was poured into the mixture and after 30 min the mixture was treated with a saturated aqueous solution (20 ml) of $NaHCO_3$ and with ether. The ether extract was filtered through Al_2O_3 and dried over anhydrous $MgSO_4$. The dark red oil obtained after removal of ether was chromatographed on a preparative plate (silica gel 40/100, eluent was benzene) and (XII) (0.24 g: 50%) was obtained as a mixture of two diastereoisomers (ratio of isomers according to GLC of the decomplexed mixture was equal to 4:1) (R_f 0.27).

Oxidative decomplexation of products (VI)-(XII) was effected according to the modified procedure of [17]. A typical procedure is given below. Data of elemental analysis of the decomplexed products (XIII)-(XVIII) are given in Table 8.

1-Ethynyl-1-methoxy-2-crotonoylcyclohexane (XV). $Fe_2(NO_3)_3 \cdot 9H_2O$ (4.93 g 12.2 mmole) was added during 1 h to a solution of DCHC complex (VIII) (0.3 g: 0.61 mmole) in ethanol (5 ml) stirred at 0°C. The mixture was heated to ~20°C, stirred a further 2 h, diluted with water (50 ml), and extracted with ether. The ether extract was dried over anhydrous $MgSO_4$. Pure (XV) (0.11 g: 88%) was obtained after removal of the ether.

TABLE 9. Atomic Coordinates ($\cdot 10^4$, $\cdot 10^5$ for Co)*

Atom	x	y	z
Co^1	6154(4)	23780(4)	88499(3)
Co^2	−8937(4)	11241(4)	78486(3)
O^1	−654(3)	4612(3)	8301(3)
O^2	3072(3)	3278(3)	9528(2)
O^3	164(3)	1584(4)	10550(2)
O^4	−1332(4)	−1130(3)	6913(3)
O^5	−2261(4)	2823(4)	6532(3)
O^6	−2356(3)	702(4)	9140(3)
O^7	701(3)	3044(2)	6607(2)
O^8	2956(2)	−26(2)	7482(2)
C^1	−163(4)	3755(4)	8515(3)
C^2	2121(4)	2931(4)	9260(2)
C^3	327(3)	1933(4)	9900(3)
C^4	−1192(4)	−242(4)	7262(3)
C^5	−1757(4)	2180(5)	7045(3)
C^6	−1800(4)	857(4)	8634(4)
C^7	818(3)	814(3)	8386(2)
C^8	730(3)	1581(3)	7731(2)
C^9	1201(3)	1934(3)	6948(2)
C^{10}	2596(3)	2038(3)	7220(2)
C^{11}	3088(4)	2323(4)	6400(3)
C^{12}	2650(4)	1443(5)	5643(3)
C^{13}	1291(4)	1367(4)	5385(3)
C^{14}	778(4)	1066(4)	6174(2)
C^{15}	3270(3)	971(3)	7684(2)
C^{16}	4426(6)	1201(6)	8374(5)

*The anisotropic temperature factors ($\cdot 10$, $\cdot 10^2$ for Co) of atoms may be obtained from the authors.

TABLE 10. Coordinates ($\cdot 10^3$) for H Atoms

Atom	x	y	z
$H(O^7)$	604(3)	145(3)	188(2)
$H(C^7)$	883(3)	−13(3)	137(2)
$H(C^{10})$	276(2)	269(2)	760(2)
$H(C^{11})$	399(4)	233(3)	659(2)
$H'(C^{11})$	274(3)	313(4)	621(2)
$H(C^{12})$	299(3)	70(3)	585(2)
$H'(C^{12})$	295(4)	167(4)	514(3)
$H(C^{13})$	106(3)	75(3)	497(3)
$H'(C^{13})$	92(3)	215(3)	514(2)
$H(C^{14})$	104(3)	26(3)	636(2)
$H'(C^{14})$	−4(3)	110(3)	605(2)
$H(C^{16})$	488(5)	55(5)	848(4)
$H'(C^{16})$	471(5)	191(5)	839(4)
$H''(C^{16})$	421(6)	141(7)	893(5)

X-Ray Structural Analysis of the DCHC Complex of the Main Isomer of 1-Ethynyl-1-hydroxy-2-acetylcyclohexane (VIIa). The experiment was carried out on an automatic four circle Hilger–Watts Y-290 diffractometer (Mo K_α radiation, graphite monochromator) at ~20°C and was calculated on an Eclipse S/200 computer using the INEXTL program from [18].

Crystals of (VIIa) were monoclinic, a = 11.412(2), b = 11,325(1), c = 15,476(2), A, β = 104,35(1)°, V = 1937,7(8) A^3, d_{calc} = 1.55 g/cm^3, Z = 4, space group $P2_1/n$.

The intensities of 2701 independent reflections with $I \geq 2\sigma$, $\theta \leq 30°$ were measured by $\theta/2\theta$ scanning. The structure was interpreted by the heavy atom method and refined (nonhydrogen atoms in anisotropic approximation, all H atoms were made apparent by a difference synthesis in isotropic approximation, weighting scheme $w^{-1} = \sigma_F^2 + (0.01|F_o|)^2$ to R = 0.041, R_w = 0.037. The positional parameters of atoms are given in Tables 9 and 10.

CONCLUSIONS

1. A scheme has been established for the two-stage addition of acyl cation and nucleophile at the double bond of the dicobalthexacarbonyl complexes of 1-ethynylcyclohexene and 1-ethynylcyclopentene.

2. The stereochemistry of the addition of electrophile and nucleophile pointed to a stereononspecific course for the reaction comprising a stage of forming an sp^2 hybridized carbene ion.

3. The structure of the main isomer of the hydroxy-acetylation reaction of the dicobalt-hexacarbonyl complex of 1-ethynylcyclohexene was established by x-ray analysis.

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