TWO-STEP Ad_E REACTION OF DICOBALTHEXACARBONYL COMPLEXES OF CONJUGATED ENYNES WITH INDEPENDENT VARIATION IN THE NATURE OF THE ELECTROPHILE AND NUCLEOPHILE

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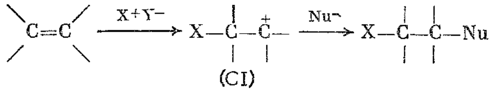
It is generally assumed that Ad_E reactions of most electrophiles $X^{\delta+} - Y^{\delta-}$ with alkenes proceed according to a two-step machanism: the first step is addition of the electrophile X^+ with formation of a cationoid intermediate (CI); and the second step is the reaction of the cationoid intermediate with the nucleophile, with formation of the final adduct [1]. It is also well known that in reactions of alkenes with covalent electrophiles, these two steps have not been successfully observed as independent reactions because the cationoid intermediate formed is rapidly captured by the nucleophilic residue of the reagent Y^- or another nucleophile Nu^- present in the medium [2]. The study of cationoid electrophiles of type X^+Y^- (Y^- is a nonnucleophilic counterion) has shown that, using these reagents, in principle it is possible to realize a discrete Ad_E process according to Scheme 1, but only when the cationoid intermediate obtained has sufficient stability under the reaction conditions [2, 3]:

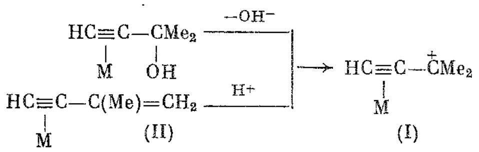
Scheme 1



This condition is satisfied in particular when the electrophiles used as reagents are capable of forming bridge cationoid intermediates with alkenes, such as episulfonium ions. It is precisely owing to the increased stability of the latter Ad_E-reaction of alkenes with cationoid reagents of type ArS^+Y^- that we can carry out the addition of the electrophile ArS^+ and a foreign nucleophile as a sequence of independent steps [4-6].

In continuing these investigations, we have turned to a search for systems in which stabilization of the cationoid intermediate formed as as a result the Ad_E-reaction would be ensured as a result of groups available in the substrate. It is well known that the stability of carbenium ions sharply increases if they are generated in the presence of transition metal complexes [7]. Thus, stable salts of propargyl cations such as (I) may be obtained upon solvolysis of dicolbalt hexacarbonyl (DCHC) complexes of propargyl alcohols, or upon protonation of DCHC complexes of conjugated enynes [8]:

Scheme 2



Here and later on, M = $CO_2(CO)_6$.

Based on these data, we have undertaken the task of determining the possibility of carrying out a more general Ad_E- reaction of DCHC complexes of conjugated enynes with different kinds of cationoid electrophiles of type $X^+BF_4^-$ ($X \neq H$) according to an analogous scheme.

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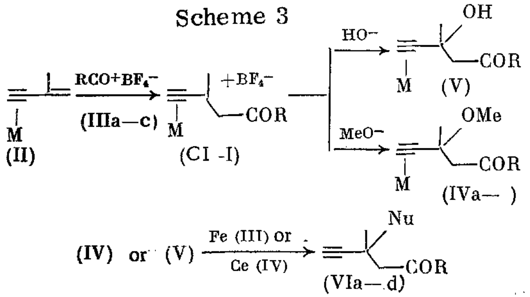
As the model substrate we chose the DCHC complex of isopropenylacetylene (II) [9], and as the cationoid reagents we chose acylium salts of the general formula BCO^+BF_4 (III), which are easily obtained by known methods (reaction of RCOF with BF_3 or the exchange reaction between RCOCl and $AgBF_4$). The reaction of (II) with (III) proceeds rather easily (30-60 min) in CH_2Cl_2 even at −40° C. The reaction complex obtained was then treated with a nucleophile (MeO^-, HO^-), which led to formation of the final adducts (IV) or (V) respectively. The structures of the latter clearly indicated that addition of the electrophile RCO^+ was oriented exclusively at the terminal atom of the double bond (according to Markovnikov's rule), while the nucleophile was added at the tertiary center. Rigorous proof of the structure of the intermediate obtained in the electrophilic attack step requires detailed investigations by NMR spectroscopy. However, the results of "suppressing" this intermediate by nucleophiles allows us to assign the structure of the cationoid complex CI-(I), as indicated on Scheme, 3, with sufficient reliability. We note that a solution of this complex may be stored at −40° C for several hours without changes (judging from the yield of the "suppression" products (IV) or (V)), which indicates the stability of CI-(I) under these conditions.

On the basis of these data, the overall course of the transformations upon acylation of (II) may be represented as the reaction of discrete addition of the acyl cation and the nucleophile (see Scheme 3).

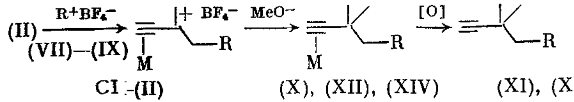
Scheme 3



R = Me (IIIa), (IVa), (VIa); CMe_3 (IIIb), (IVb), (V); MeCH=CH (IIIc), (IVc), (VId).

The reaction of (II) with carbenium ion cationoid reagents also may be accomplished as the kinetically distinguishable process of addition of an electrophile and nucleophile, which was shown when using as the electrophile such stable carbenium salts as $Me_3C^+BF_4^-$ (VII), 1-Ad^+BF_4 (VIII), and the DCHC complex of the propargyl cation (IX) which was used in the form of the stable salt obtained according to [9] (Scheme 4):

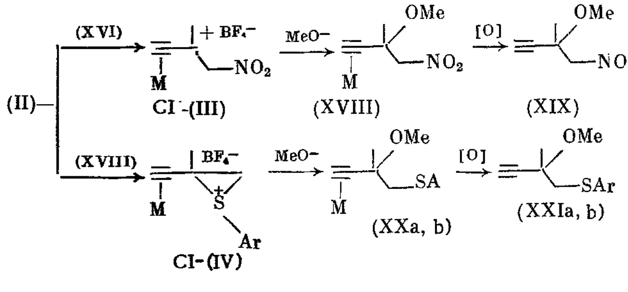
Scheme 4



R = Me_3C (VII), (X), (XI); 1-Ad (VIII), (XII), (XIII); HC≡C—CH_2 (IX), (XIV), (XV).
M

An analogous sequence of steps can be accomplished also in reactions of (II) with heteroatomic cationoid electrophiles such as $NO_2^+BF_4^-$ (XVI) and ArS^+BF_4 (XVII, a, b)*

Scheme 5



In all the listed cases, the reaction proceeds in a sufficiently unambiguous manner. Subsequent decomplexation of the adducts obtained (with iron(III) nitrate [10] or cerium(IV) ammonium nitrate [11]) also as a rule proceeds without complications. A general summary of the characteristics of the adducts is given in Table 1.

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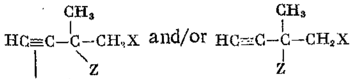
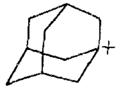
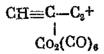
*Reagent XVII is generated in the ArSCl + $AgBF_4$ system. It is technically simpler to obtain CI-(IV) according to the Ad_E-reaction of (II) with ArSCl, with subsequent treatment of the adduct (without its separation) with $AgBF_4$.

TABLE 1. Characteristics of the Adducts of the Reaction of the DCHC Complex of (II) with $X^+BF_4^-$ with the



$HC{\equiv}C{-}C(CH_3)(Z){-}CH_2X\cdot Co_2(CO)_6$ and/or $HC{\equiv}C{-}C(CH_3)(Z){-}CH_2X$

Compound	Electrophile X+	Nucleophile z	Yield, %	Mass spectrum	Found/Calc., %		PMR spectrum*				
					C	H	CH	CH_2	CH_3	X	Z
(IVa) (VIa)	$MeCO^+$	MeO^-	65	–	$\frac{68,51}{68,57}$	$\frac{8,65}{8,57}$	5,57	2,55 m	1,37	1,82 s	2,87
(VIb)	Me_3CCO^+	HO^-	72		$\frac{71,79}{71,39}$	$\frac{9,53}{9,59}$	2,17	2,72 m	1,40	1,17 c	4,83
(VIc)	Me_3CCO^+	MeO^-	64		$\frac{72,42}{72,49}$	$\frac{9,90}{9,95}$	2,32	2,77 m	1,52	1,08 s	3,27
(VId)	$MeCH{=}CHCO^+$	MeO^-	60	166 (10%)			2,28	2,8 m	1,55	1,42, d.d (3H), 6,1 m (1H), 6,62 m (1H)	3,26
(XI)	Me_3C^+	MeO^-	83	154 (2%)			2,35	1,60 s	1,25	1,02 s	3,27
(XIII)		MeO^-	75		$\frac{83,32}{82,71}$	$\frac{10,60}{10,41}$	2,34	1,87 m	1,37	1,95	3,28
(XIV)	 $CH{\equiv}C{-}C_3^+ \cdot Co_2(CO)_6$	MeO^-	78	540 †			6,08	2,95 m	1,51	5,95 s (1H), 2,05 m (2H)	3,21
(XV)							2,48	2,37 m	1,42	1,98 m (3H)	3,34
(XIX)	NO_2^+	HO^-	35		$\frac{46,64}{46,51}$	$\frac{5,93}{5,42}$	2,00	3,87 m	1,14	–	3,28
(XXIa)	$4\text{-}MeC_6H_4^+$	HO^-	63		$\frac{69,66}{69,85}$	$\frac{7,30}{6,85}$	2,29	3,20 m	1,49	2,29 s, 7,30 m (4H)	3,25
(XXIb)	$4\text{-}ClC_6H_4^+$	MeO^-	76		$\frac{60,03}{69,85}$	$\frac{5,43}{5,45}$	2,36	3,14 m	1,46	7,23 m (4H)	3,28
(XXIII)	$Me_2CHCH_2CO^+$	MeO^-	60	182 (2%)	$\frac{72,71}{72,49}$	$\frac{10,26}{9,95}$	2,57	2,76 m	1,52	0,91 d (6H), 2,16 m (1H), 2,42 m (2H)	3,38

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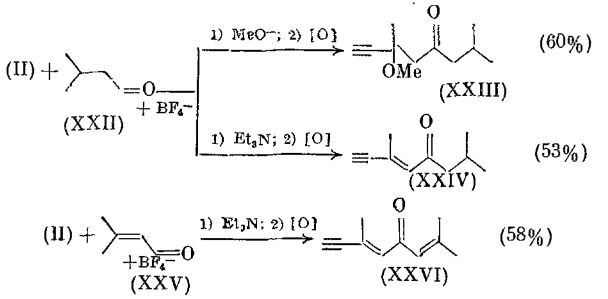
*The PMR spectra are recorded for 10-15% solutions in C_6D_6 (VIa, d), (XIX), CCl_4 (VIb, c), (XI), (XIII), (XIV), (XXIa, b), $CDCl_3$ (XV), (XXIII) with internal standard TMS. The signals of the HC≡, Me^-, and Z groups are singlets.

†We give the mass number of the characteristic ion $[M-6CO]^+$.

The presented results are evidence that, in the case of the Ad_E- reaction of the DCHC complex of isoproprenyl acetylene (II), the scheme of a two-step electrophilic addition could be realized in sufficiently general form, in which the step of addition of the electrophile X^+ and the nucleophile Nu^- are separated in time and are independent. We should especially emphasize that formation of cationoid intermediates CI-(I)–CI-(IV) is successfully detected for quite different electrophiles. This means that the stability of these cationoid intermediates in general does not depend very strongly on the donor or acceptor character of the substitutent X at the carbon atom relative to the carbenium center, and is mainly due to effective participation of the DCHC fragment. Obviously, for this reason we can "stop" at the cationoid intermediate step of the Ad_E- reaction of acylation and nitration of (II), which previously could not be observed in a single case [1, 2, 12].

In the reactions shown in Schemes 3 and 4, the DCHC complex of isopropenylacetylene (II) is a C_5 isoprenoid unit, which forms a new carbon–carbon bond with the required electrophile. Below we present examples of the use of this synthon for obtaining several dehydro derivatives C_5 + C_5 of monoterpenes of regular structure according to a (XXIII), (XXIV), (XXVI) scheme. From the latter reduction of the C ≡ C bond, we may obtain respectively the natural terpenes: the methyl ester of tagetonol [13], tagetone [14], and ocimenone [15].

Scheme 6

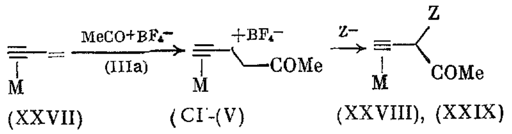


Another aspect of the use of the DCHC-(II) also appears promising, connected with the possibility of its conversion to new difunctionalized isoprenoid C_5 synthons (XIX) and (XXI) (Scheme 5).

The possibility of carrying out the Ad_E- reaction analogous to that considered above for other conjugated enynes was then studied for the case of the DCHC complex of the simplest enyne: vinyl acetylene (XXVII). In this case, we might expect complications connected with the fact that usually the monosubstituted double bond is less active in Ad_E- reactions compared with the 1,1-disubstituted double bond; and the proposed cationoid intermediate of the first step of the Ad reaction with the complex (XXVI) pertains to destruction of the secondary carbenium ions, which are significantly less stable compared with ions of the tertiary type.

However, experiment has shown that in reality, the reaction of DCHC complex of (XXVII) with acetyltetrafluoroborate (IIIa) proceeds analogously to acylation of (II) with formation of a stable intermediate, which upon subsequent treatment with water or methanol gives the corresponding acetyloxy or acetylmethoxy derivatives (XXVIII) and (XXIX) respectively

Scheme 7

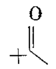
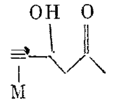
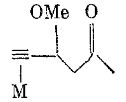
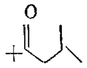
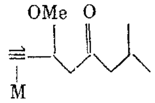
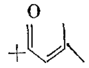
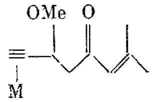
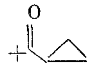
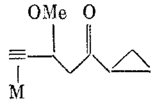
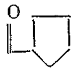
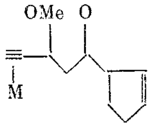
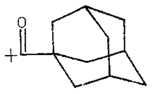
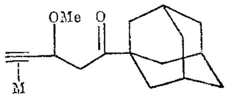
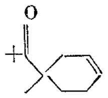
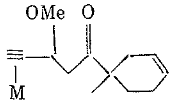
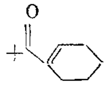
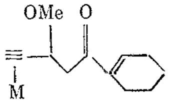
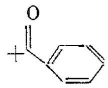
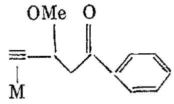


Z = OH (XXVIII), OMe (XXIX).

In the same way (i.e., through a step of formation of an intermediate of the CI-(V) type), the DCHC complex of vinylacetylene (XXVII) reacts with a number of other acylium salts: (XXII), (XXV), (XXXIa-f). The summary of the results of this series of experiments is given in Table 2. As follows from the presented data, the nature of the R group in the acyl cation may be varied within sufficiently broad limits: the presence of sterically hindered groups, an aromatic ring, conjugated and unconjugated double bonds, a cyclopropane ring to a substantial degree do not affect the efficiency of the reaction, which allows us to consider it as a universal method for obtaining adducts of the type (XXVIII) – (XXX), (XXXIIa, g).

Oxidative decomplexation of these adducts in all cases except (XXXIIg) proceeded without complications and in high yields 85-90% gave substituted alkynes of the type $RCOCH_2CH(Nu)C \equiv CH$ (XXXIIIa-h). The latter might prove to be useful intermediates for a whole series of syntheses, especially if we take into account the diverse conversions allowed by the presence of the propargyl ester or alcohol fragment.

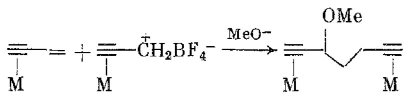
TABLE 2. Products of Acylation of (XXVII) by Acylium Tetrafluoroborates RCO^+BF_4

RCO^+BF_4	RCO^+	Nu	Adduct*		Yield, %
(IIIa)		HO−		(XXVIII)	69
(IIIa)	The same	MeO−		(XXIX)	78
(XXII)		The same		(XXX)	95
(XXV)		»		(XXXIIa)	80
(XXXIa)		»		(XXXIIb)	85
(XXXIb)		»		(XXXIIc)	60
(XXXIc)		»		(XXXIIId)	94
(XXXId)		»		(XXXIIe)	78
(XXXIe)		MeO−		(XXXIIf)	77
(XXXIf)		»		(XXXIIg)	55

*M = $CO_2(CO)_6$.

The reaction of (XXVII) with electrophiles of other types has been studied in less detail. However, in the case **of alklylation of** (XXVII) by the DCHC complex of the propargyl cation (IX), the efficiency of the described **addition scheme has** also been demonstrated as a possible route for obtaining the functionally substituted 1,6-**diyne structures of** type (XXXIV)

Scheme 8

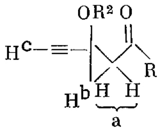


(XXVII) (IX) (XXXIV)

Preliminary data have shown that the reaction of (XXVII) with other electrophiles (Me_3C^+, NO_2^+, ArS^+) proceeds **in the same** way.

Thus, the discrete scheme of Ad_E-reaction has proven to be also suitable for the DCHC complex of the **simplest enyne:** vinyl acetylene (XXVII).

TABLE 3. Data from PMR and Mass Spectroscopy* of DCHC Complexes of the Adducts (XXVIII) – (XXX) (in the upper part of the column) and Decomplexated Adducts (XXXIIa-j) (in the lower part of the columns) (XXXIIIa-j)



Compound	H^{a}	$H^{б}$	H^{c}	R¹	R²	Mx^{+} †
(XXVIII) ‡	2,80 m	4,08 m	6,02 s	2,20 s (3H)	3,43 s	244
(XXIX) ‡	2,77 m	4,75 m	6,05 s	2,15 s (3H)	3,43 s	244
(XXXa)	2,68 m	4,77 m	6,03 s	2,24 m (2H), 0,93 d (6H)	3,44 s	286
(XXXIIIa)	2,65 m	4,32 m	2,35 d	2,25 m (2H), 0,90 d (6H)	3,32 s	168
(XXXIIa)	2,73 m	4,80 m	6,02 s	6,02 s (1H), 2,15 s (3H) 1,88 s (3H)	3,44 s	284
(XXXIIIb)	2,67 m	4,37 m	2,32 d	6,02 s (1H), 2,15 s (3H) 1,88 s (3H)	3,35 s	166
(XXXIIb)	2,93 m	4,80 m	6,05 s	1,92 m (1H), 0,98 m (4H)	3,47 s	270
(XXXIIIc)	2,82 m	4,35 m	2,33 d	1,85 m (1H), 0,92 m (4H)	3,35 s	152
(XXXIIc)	2,79 m	4,80 m	6,05 s	1,70 m (8H)	3,47 m	298
(XXXIIId)	2,73 m	4,37 m	2,32 d	1,68 m (8H)	3,33 s	180
(XXXIId)	2,80 m	4,82 m	6,03 s	1,92 m (15H)	3,47 s	364
(XXXIIIe)	2,73 m	4,42 m	2,32 d	1,87 m (15H)	3,35 s	246
(XXXIIe)	2,67 m	4,82 m	6,03 s	5,62 m (2H), 2,00 m (6H), 1,10 s (3H)	3,45 s	324
(XXXIIId)	2,63 m	4,48 m	2,44 d	5,64 m (2H), 1,96 m (6H), 1,14 s (3H)	3,39 s	206
(XXXIIf)	2,92 m	4,88 m	6,03 s	6,83 m (1H), 2,25 m (4H), 1,63 m (4H)	3,45 s	310
(XXXIII g)	2,92 m	4,42 m	2,32 d	6,85 m (1H), 2,23 m (4H), 1,67 m (4H)	3,35 s	192
(XXXIIg)	3,30 m	5,03 m	6,08 s	7,73 m (5H)	3,58 s	306
(XXXIIIh)	–	–	–	–	–	187

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*For structure of adducts, see Table 2.

†Due to the weak intensity of the amolecular ions for the DCHC complexes, , we give the mass numbers for the characteristic ions Mx^{+} = $[M - 168]^{+}$ (6 CO-groups).

‡Preparative decomplexation of (XXVIII) and (XXIX) was not carried out, since under standard conditions it was accompanied by side reactions.

In conclusion, we should emphasize that the described reactions open up new possibilities for the synthetic use of Ad_E-reactions of enynes. In fact, in most cases, the reactions of conjugated enynes with traditional electrophilic reagents proceeds quite nonselectively, giving mixtures of addition products with respect to both multiple bonds [16]. At the same time, the use of DCHC complexes of enynes as substrates ensures completely regioselective orientation of reactions of this type with respect to the double bond, with independent variations of the electrophilic and nucleophilic addends.

Proof of the structure for all the obtained DCHC complexes of adducts for the Ad_E- reactions and or the corresponding decomplexation products were carried out using data from PMR spectra, mass spectra, and the results of elemental analysis (see Tables 1 and 3).

EXPERIMENTAL

The PMR spectra were taken in deuterated benzene with an external standard, or in CCl_4 with an internal TMS standard on the instruments Varian DA-60 (60 MHz), Tesla BS-467 (60 MHz), Tesla BS-497 (100 MHz), and Bruker WM-250 (250 MHz). All the chemical shifts are given on the δ scale relative to TMS. The mass spectra were taken on the Varian CH-6 spectrometer. GLC was carried out on the chromatographs LKhM-8MD-5 and LKhM-80-1 on glass capillary columns, 0.2 mm × 30 m, liquid phase SE-30 in PÉG-40000 and on steel packed columns, 4 mm × 1 m and 4 mm × 2 m (5% XE-60 on Chezasorb AW-HMDS and 5% DC-550 on Chromaton N-AW-HMDS respectively). TLC was carried out on Silufol UV-254 plates. Preparative TLC was done on 280 × 290 mm glass plates with un unfixed layer of silica gel.

Reactions were carried out under a stream of dry Ar in absolute solvents. The solvents were made absolute by standard techniques. The DCHC complexes of enynes (II) and (XXVII) were obtained according to a modified technique [17]. The Ad_E-reactions of the DCHC complex of isopropenyl acetylene (II) was carried out in a standard fashion; below we give the typical techniques.

4-Methyl-4-methoxylhex-5-yne-2-one (VIa). To a solution of 0.29 g $AgBF_4$ (1.5 millimoles) in three 3 ml of a mixture of CH_2Cl_2 : $C_2H_4Cl_2$ (1:1) at −40° C, we added a solution of 0.35 g (1.0 moles) of previously purified* DCHC complex of isopropenylacetylene.

Then, at −60° C, we introduced 0.1 ml (1.5 millimoles) solution of AcCl in 1 ml CH_2Cl_2 and mixed for thirty minutes, monitoring the presence of the original DCHC (II) using TLC (R_f 0.74; hexane). Then we added 0.2 ml MeOH; and after 10 min we added a mixture of 10 ml ether and 10 ml saturated aqueous solution of $NaHCO_3$. We extracted it with ether, washed the extract with water, and dried it with Na_2SO_4. The residue after evaporation of the solvent (0.42 g) was separated by TLC. The obtained 0.29 g (68%) (IVa) was decomplexated, treated with $Fe(NO_2)_3$ (3 g in 5 ml ethanol) at 0° C for 2 h, decanted into water, and extracted with ether. The extract was washed with water and dried with Na_2SO_4. After evaporation of the ether, the residue of 0.09 g (65%) was purified by distillation, b.p. (bath) 55-60°C (18 mm). For the characteristics of the products (IVa) and (VIa), see Table 1. Analogously, we obtained 2,2,5-trimethyl-5-methoxyhept-6-yne-3-one (VIc) and 6-methyl-6-methoxyoct-7-yne-2-ene-4-one, (VId). In order to obtain 2,2,5-trimethyl-5-oxyhept-6-yne-3-one (VIb), the reaction mixture was treated with a saturated solution of MeOH instead of $NaHCO_3$.

3-Methyl-3-methoxy-4-(1-adamantyl)-1-butyne (XIII). To a solution of 0.29 g $AgBF_4$ (1.5 millimoles) in 6 ml of a mixture of CH_2Cl_2 : $C_2H_4Cl_2$ (1 : 1) at −40°C, we added a solution of 0.35 g (1.0 millimoles) of (II) and then added at −60° C a solution of 0.32 g (1.5 millimoles)-1-bromoadamantane. After 1 h, we introduced 0.5 ml MeOH and mixed for 15 min. Then we treated it with aqueous $NaHCO_3$, extracted it with ether, and dried the extract with Na_2SO_4 and removed the solvent. After purification by TLC, we decomplexated with $Fe(NO_2)_3$. We obtained 0.18 g (75%) of (XIII). After sublimation at 2 torr, we obtained m.p. 94-95°C. For characteristics, see Table 1. Analogously, we obtained 3,5,5-trimethyl-3-methoxy-1-hexyne (XI).

3-Methyl-3-methoxy-1,6-heptadiyne (XV). To a solution of 1.37 g (4 millimoles) DCHC complex of propargyl alcohol (obtained according to the technique in [17]) in 8 ml of a mixture of CH_2Cl_2 : CH_3NO_2 (4 : 1) at −30°C, we introduced by syringe 400 ml BF_3 and mixed for 15 min. We then added 50 ml absolute ether cooled down to −50°C. Crystalline (IX) was precipitated, which was washed again with 50 ml ether and 50 ml pentane. To the (IX) purified in this way, we added at −40° C a solution of 0.35 g (1.0 millimoles) (II) in 10 ml CH_2Cl_2 : CH_3NO_2 (7 : 3) and mixed at −40° C for 15 min. The mixture was decanted into a mixture of 4 ml MeOH and 1 g $NaHCO_3$ cooled down to −40°C. The temperature was raised to 20°C, filtered through a layer of Al_2O_3, and the solvent was evaporated. After separation by the TLC method, we obtained 1.1 g (78%) (XIV). The mass and PMR spectra are given in Table 1.

Decomplexation of (XIV) was carried out by adding a solution of (XIV) in 5 ml acetone to a solution of 2.47 g (4.5 millimoles) $(NH_4)_2Ce(NO_3)_6$ in 10 ml acetone at 20°C. The mixture was shaken until evolution of CO ended. Then 30 ml ether was added, it was filtered through a layer of Al_2O_3, and evaporated. We obtained 0.24 g (78%) (XV). The PMR spectrum (250 MHz) of the (XV) obtained is given in Table 1; the structure of (XV) is also confirmed by recording the spectrum under double-resonance conditions (irradiation of the $C-CH_2{}^{a,b}-CH_2{}^{c,d}-C\equiv C$ protons $H^{a,b}$ leads to simplification of the signal from the $H^{c,d}$ protons).

2-Methyl,-2-methoxy-1-nitrobut-3-yne (XIX). To a suspension of 0.4 g (1.05 millimoles) NO_2BF_4 in liquid SO_2 (20 ml) at −60°C we added 0.26 g (0.74 millimoles) DCHC complex of (II) and mixed for 3.5 h. Without raising the temperature, we removed the SO_2 under vacuum. To the residue we added 10 ml CH_2Cl_2 and introduced a mixture of 10 ml ether and 1 ml aqueous $NaHCO_3$ and extracted with either. The extract was dried with Na_2SO_4 and the solvent was removed. From the residue using TLC (SiO_2, benzene) we obtained 0.15 g (46%) DCHC complex (XIX), which was decomplexated with $Fe(NO_2)_3$. We obtained 0.035 g (35%) (XIX).

2,6-Dimethyl-6-methoxy-oct-7-yne-4-one (XXIII). To a solution of 0.21 g (2.0 millimoles), 3-methylbutyroyl fluoride in CH_2Cl_2 (10 ml), we introduced by syringe 100 ml (4 millimoles) BF_3 at −70°C. Then at −50°C we added a solution of 0.64 g (1.8 millimoles) (II) in $MeNO_2$ (5 ml). The mixture was shaken for 10 min at −50°C (until (II) disappeared, TLC) and decanted into a mixture of 3 ml MeOH and 1 g $NaHCO_3$ in CH_2Cl_2 (20 ml). cooled down to −50°C. It was heated up to 20°C, filtered through a layer of Al_2O_3. The solvent was evaporated and the residue was decomplexated by an excess of $(NH_4)_2Ce(NO_3)_6$ in acetone. The decomplexation products were separated by TLC. We isolated 0.20 g (60%) (XXIII). The characteristics are given in Table 1.

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*The purification was carried out by filtering a solution of (II) in pentane or hexane through a layer of neutral Al_2O_3 with subsequent evaporation of the filtrate.

TABLE 4. Results of Elemental Analysis of the Adducts (XXXIIIa-g)*

Compound	Found, %		Calculated, %		Empirical formula
	C	H	C	H	
(XXXIIIa)	70,38	9,93	71,39	9,58	$C_{10}H_{16}O_2$
(XXXIIIb)	72,23	8,91	72,26	8,49	$C_{10}H_{14}O_2$
(XXXIIIc)	70,12	8,10	71,03	7,95	$C_9H_{12}O_2$
(XXXIIId)	73,21	9,38	73,30	8,95	$C_{11}H_{16}O_2$
(XXXIIIe)	77,57	9,32	78,01	9,00	$C_{16}H_{22}O_2$
(XXXIIIf)	76,04	9,23	75,69	8,80	$C_{13}H_{18}O_2$
(XXXIIIg)	75,16	8,65	74,97	8,39	$C_{12}H_{10}O_2$

*The adduct (XXXIIg) upon decomplexation gave a mixture of products. As a result, there are no PMR spectral and elemental analysis data for (XXXIIIh).

3,7-Dimethyloct-3-ene-1-yne-5-one (XXIV). The reaction complex, obtained analogous to (XXIII) from 0.23 g (2.2 millimoles) 3-methyl-butyroyl fluoride, 4.5 millimoles BF_3, and 0.70 g (2.0 millimoles) (II) was treated at −60° C with 1 ml Et_3N in 1 ml CH_2Cl_2 for 20 min. Further treatment is analogous to that described for (XXIII). We obtained 0.16 g (53%) (XXIV). The mass spectrum is M^+ 150 (60%). The PMR spectrum is: (250 MHz, $CDCl_3$, TMS): 0.93 d (6H, $CH(C\underline{H}_3)_2$) 2.15 m (1H, $C\underline{H}(CH_3)_2$), 2.26 d (3H, $=C-CH_3$, J = 2.5 Hz), 2.34 d (CH_2CO), 3.21 s (1H, =CJ), 6.49 s (1H, =CHCO).

3,7-Dimethylocta-3,6-diene-1-yne-5-one (XXVI) was obtained analogously to the method described for (XXIII) from 0.36 g (3.5 millimoles) β-methyl crotonoyl fluoride, 7 millimoles BF_3, 0.88 g (2.5 millimoles) (II), and 0.5 ml Et_3N. We obtained 0.23 g (58%) (XXVI). Mass spectrum $[M+H]^+$ 149 (70%); PMR spectrum (250 MHz, $CDCl_3$, TMS): 1.92 d (3H, $=CCH_3$), 2.18 d (3H, $=CCH_3$), 2.29 d (3H, $=C-C(C\underline{H}_3)C=$), 3.19 s (1H, $\underline{H}C\equiv$ 6.07 m (1H, $\underline{H}C=C(CH_3)_2$), 6.37 m (1H, $\underline{H}C=C(CH_3)C\equiv$).

Acylation of the DHCH complex of vinylacetylene (XXVII) by acylium tetrafluoroborates (IIIa), (XXII), (XXV), (XXXIa-f) was carried out according to a standard technique, described below for the reaction with cyclopropanoyl tetrafluoroborate (XXXIa).

1-Cyclopropyl-4-methoxyhex-5-yne-2-one (XXXIIIc). To a solution (mixed at −78°C) of 0.32 g (3.6 millimoles) fluoroanhydride of cyclopropane carboxylic acid in CH_2Cl_2 (10 ml), by syringe we introduced 90 ml (3.6 millimoles) BF_3. We then added a solution of 0.41 g (1.2 millimoles) DCHC complex of (XXVII) in a mixture of $CH_2Cl_2 : CH_3NO_2$ (1 : 1, 10 ml). After 10 min we introduced methanol (2 ml); and after 10 min, the mixture was treated with aqueous $NaHCO_3$ (20 ml).

After extraction with ether, the organic phase was washed with water, filtered through a layer of Al_2O_3 and dried with Na_2SO_4. The solvent was then evaporated. The residue was separated using TLC (SiO_2 benzene). We obtained 0.45 g (85%) pure (according to TLC and PMR) product (XXXIIb). By oxidative decomplexation (Ce(IV)) we obtained (XXXIIIc) (80%). The analytical and spectral characteristic of (XXXIIb), (XXXIIIc), and also other acylation products of (XXVII) are given in Tables 3 and 4.

Bis-DCHC-complex of 3-methoxy-1,6-heptadiyne (XXXIV) is obtained by a method analogous to that described for (XIV), from 0.513 g (1.5 millimoles) DCHC complex of propargyl alcohol, 0.49 g (3.0 millimoles) $HBF_4 \cdot Et_2O$, and 0.33 g (0.98 millimoles) (XXVII) without intermediate separation of (IX). By TLC separation of the reaction products, we obtained 0.45 g (65%) (XXXIII). Found: Co 33.89%. $C_{19}H_8O_{13}Co_4$. Calculated: Co 33.97%. Mass spectrum: 666 (20%) $[M-CO]^+$; 606 (40%) $[M-3CO]^+$; 578 (100%) $[M-4CO]^+$. PMR spectrum (CCl_4, TMS): 6.05 s (1H, HC≡), 5.98 s (1H, HC≡), 4.35 t (1H, $\underline{H}COCH_3$), 3.52 s (3H, OCH_3), 3.12 m (2H, $CHC\underline{H}_2CH_2$), 2.J2 t (2H, $CH_2C\underline{H}_2C=C$).

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CONCLUSIONS

1. Reactions of dicoboalt hexacarbonyl complexes of conjugated enynes with cationoid reagents of the type acyl-, alkyl-, nitronium, and arylsulfene-tetrafluoroborates leads to formation of cationoid intermediates which are stable in solution. These cationoid intermediates may then react with nucleophiles of the water or methanol type with formation of covalent adducts.

2. The observed two-step Ad_E-reaction is a suitable route for synthetic use of enynes, which is shown for the case of the syntheses of a number of monoterpenoids.

LITERATURE CITED

1. G. H. Schmid and D. Garratt, in: The Chemistry of Double Bonded Functional Groups (S. Patai, ed.), New York (1977).
2. W. A. Smit, Zh. Vses. Khim. O-va im. D. I. Mendeleeva, 22, 300 (1977).
3. W. A. Smit, A. V. Semenovsky, O. Y. Lubinskaya, T. N. Chernova, M. Z. Krimer, and V. F. Kucherov, Tetrahedron Lett., 33, 3101 (1971).
4. M. Z. Krimer, W. A. Smit, and A. A. Shamshurin, Dokl. Akad. Nauk SSSR, 208, 864 (1973).
5. W. A. Smit, N. S. Zefirov, J. V. Bodrikov, and M. Z. Krimer, Acc. Chem. Res., 12, 282 (1979).
6. M. A. Ibragimov and W. A. Smit, Tetrahedron Lett., 24, 961 (1983).
7. H. Alper, ed., Transition Metal Organometallics in Organic Synthesis, Academic Press, New York (1976), Vol. 1; (1978), Vol. 2.
8. K. N. Nicholas and R. Pettit, J. Organomet. Chem., 44, C21 (1972).
9. R. E. Connor and K. N. Nicholas, J. Organomet. Chem., 125, C45 (1977).
10. K. N. Nicholas and R. Pettit, Tetrahedron Lett., 3475 (1971).
11. D. Seyterth, M. O. Nestle, and A. T. Wehman, J. Am. Chem. Soc., 94, 7417 (1975).
12. A. V. Nikulin, Dissertation, Moscow (1981).
13. O. P. Vig, B. Ram, and V. Vig, J. Indian Chem. Soc., 50, 408 (1973).
14. D. R. Adams, R. C. Cookson, and S. N. Batnagar, J. Chem. Soc., Perkin Trans. 1, 1741 (1975).
15. C. F. Garbers and F. Scott, Tetrahedron Lett., 1625 (1976).
16. Sh. O. Badanyan, G. G. Melikyan, G. R. Mkhitaryan, and K. A. Atanesyan, Arm. Khim. Zh., 34, 926 (1981).
17. H. W. Sternberg, H. Greenfield, R. A. Friedel, G. Wotiz, R. Markby, and J. Wender, J. Am. Chem. Soc., 78, 120 (1956).