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REGIOSELECTIVE ADDITION OF C-ELECTROPHILES AND C-NUCLEOPHILES TO A DOUBLE BOND OF VINYLACETYLENE — AN EXAMPLE OF A TWO-STAGE Ad_E REACTION WITH FORMATION OF TWO NEW CARBON–CARBON BONDS

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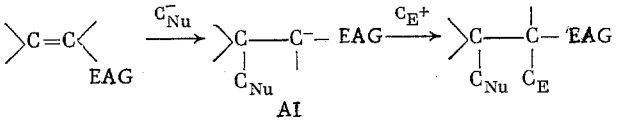
UDC 542.955:541.571.3:547.316.4

The development of methods of chemistry of carbanions made it possible to carry out Ad_N reactions at multiple bonds as sequences of time-separated addition of nucleophile and electrophile. In a modern directed synthesis, this scheme is widely used, since it ensures the possibility of producing two new C–C bonds, and varying the structure of the attached C-nucleophiles (C_{Nu}) and C-electrophiles (C_E) [1]



where EAG is an electron-acceptor group.

For the synthesis, an analogous (but with a reversed sequence of stages) scheme of carrying out the Ad_E reaction at the multiple bonds is just as promising, but in such a

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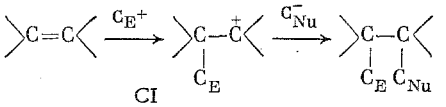
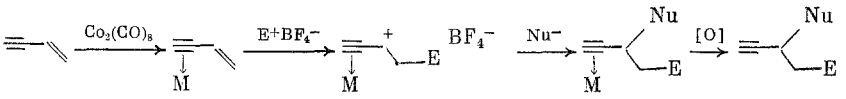
general form it could not so far be accomplished, because of the difficulties due to the lower stability of the cationoid intermediates (CI) compared with that of the anionoid intermediates (AI)



CI

It has already been found that the two-stage ADE reaction can proceed at the double bond of conjugated enynes, if a dicobalthexacarbonyl (DCHC) complex is first obtained at the triple bond, which is able to stabilize the α-carbenium center in the CI-1 [2-7] (cf. [8])



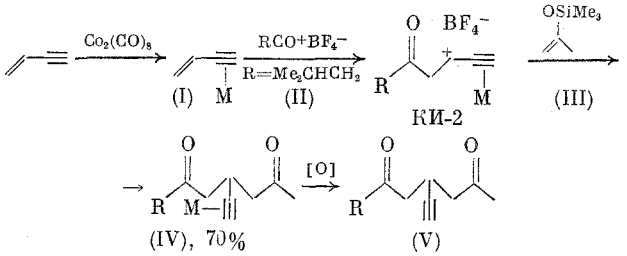
CI -1

Here and below M = $Co_2(CO)_6$.

Thus, we only studied variations in the nature of the electrophiles (E = RS^+, NO_2^+, CE^+ – acyl or alkyl cations) and enynes, while water or methanol was always used as the nucleophile.

The aim of the present investigation was to clarify the possible use in the above sequence of stages of π-donors as nucleophiles, such as trimethylsilyl enol ethers (TMSE) and trimethylallylsilane (TMAS).* As a model, we chose the DCHC complex of vinylacetylene (I), for which we have already described a series of reactions of sequential addition of the electrophile RCO^+BF_4 and nucleophile MeO^- [6, 7]. It was found that the cationoid intermediate (CI-2) obtained during the addition of isovaleroyl tetrafluoroborate (II) (obtained by the reaction of Me_2CHCH_2COF with BF_3) to (I), fairly readily enters into a reaction with acetone trimethylsilyl enol ether (III) to give the DCHC complex of 4-ethynyl-8-methylnonane-2,6-dione (IV) as the main product. In the first experiments, the formation of a side product (VII) was also observed, probably as the result of a reaction of CI-2 with 6-methylheptane-2,4-dione (VI), obtained by acylation of (III) by excess of (II).† To suppress the formation of (VI), it is advisable to "quench" excess of (II) before introducing nucleophile (III). Cyclohexene was added to the solution of CI-2 obtained at the acylation stage, in an amount equivalent to the initial excess of (II) (the reaction of cyclohexene with the acylium salt proceeds instantly at –78°C), and then (III) was introduced. Under these conditions, no (VII) was formed, and dione (IV) was obtained in a 70% yield. The oxidative decomplexation of the latter by means of $(NH_4)_2Ce(NO_2)_6$ gave 4-ethynyl-8-methylnonane-2,6-dione (V) in a 97% yield.

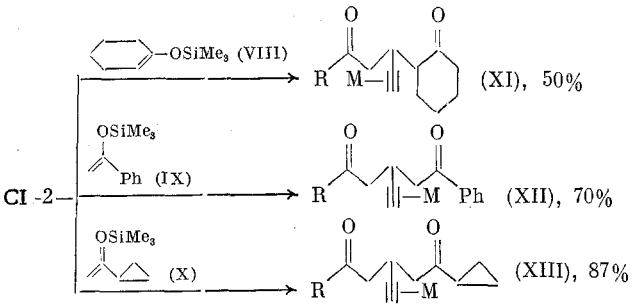
Under similar conditions CI-2 reacts with cyclohexanone (VIII), acetophenone (IX), and methyl cyclopropyl ketone (X) trimethylsilyl enol ethers to give diketones (XI), (XII), and (XIII), respectively.



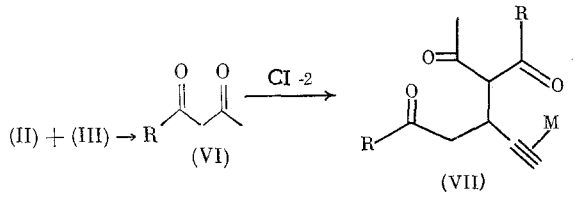
(I) (II) КИ-2 (III) (IV), 70% (V)

*It is known that DCHC complexes of the simplest propargyl cations (for example, CI-1, E = H) can alkylate different types of π-donors [9], but the applicability of these reactions for our systems (CI-1, E ≠ H) is not obvious (see below).

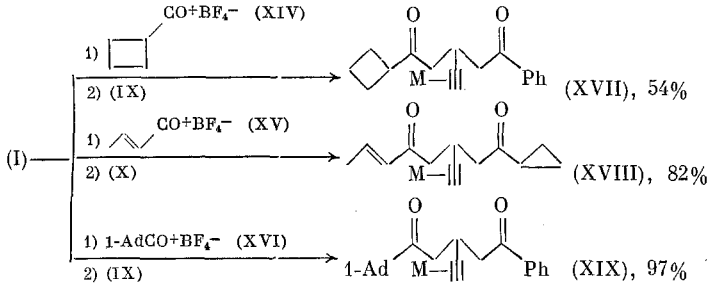
†An excess of up to 3 equivalents of the acylating reagent (II) was used for complete conversion of (I) into CI-2. Product (VII) was not isolated in an analytically pure state, and its structure was accepted from PMR data and mass spectra (M^+ 564).



The side reaction is

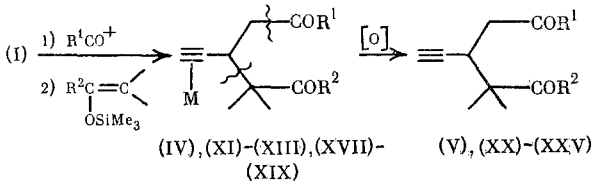


The reaction of sequential addition of other acylium salts [cyclobutanoyl-, crotonoyl-, and 1-adamantoyl tetrafluoroborates (XIV), (XV), and (XVI), respectively and TMSE (IX) and (X) to (I) proceeds exactly in the same way



In all cases adducts (XI)-(XIII) and also (XVII)-(XIX) are readily purified from impurities by the TLC method, and after oxidative decomplexation give the corresponding 1,5-diketones (XX)-(XXV) in yields of 85-97%.

The results show that for the DCHC complex of vinylacetylene (I), a general two-stage AdE reaction, in which the stages of the addition of a C-electrophile (the acylium cation) and C-nucleophile (the double bond in TMSE) are separated in time and are independent of one another, can in fact be realized. The result of this successive process is the formation "in one flask" of two new C—C bonds with the introduction of of COR (the electrophile) and C—COR^1 (nucleophile) residues and the obtaining of very different 3-ethynyl derivatives of 1,5-diketones by an assembly scheme from simple precursors



The structure of all the adducts have been confirmed by analytical and spectral data (see the Experimental section, Tables 1 and 2).

On some of the examples, we also studied the possible use of carbenium ion type reagents, as electrophiles for the sequential AdE reaction. The addition of tert-butyl tetrafluoroborate

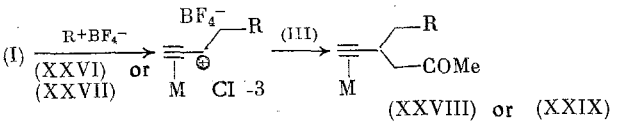
TABLE 1. Data of Mass and PMR Spectra of DCHC Complexes and Their Decomplexation Products*

Compound	M_x^+/M^+†	PMR spectrum	
		frequency, MHz, solvent	δ, ppm
4-Ethynyl-8-methylnonane-2,6-dione (IV)/(V)	312	60, CCl_4	5,97 s (1H), 3,80 m (1H), 2,65 m (4H), 2,25m (2H), 2,17 s (3H), 0,97 d (6H)
	194	60, CCl_4	3,20 m (1H), 2,58 two d (4H), 2,24 d (2H), 2,12 s (3H), 1,97 d (1H), 0,94 d (6H)
3-(2-Oxocyclohexyl)-7-methyloct-1-yn-5-one (XI)/(XX)	352	60, C_6D_6	5,95 s (1H), 3,70 m (1H), 2,73 d (2H), 2,25 m (2H), 1,85m (6H), 0,92 d (6H)
	234	250, C_6D_6	3,39 m (1H), 2,62 d (2H), 2,45 m (1H), 2,40 m (2H), 2,31 d (2H), 2,07 d (1H), 1,80 m (6H), 0,92 d (6H)
1-Phenyl-3-ethynyl-7-methyloctane-1,5-dione (XII)/(XXI)	374	60, CCl_4	7,73 m (5H), 6,00 s (1H), 4,00 m (2H), 3,20m (2H), 2,72 m (2H), 2,28 m (2H), 0,94 d (6H)
	256	60, CCl_4	7,75 m(5H), 3,40 m (2H), 3,27m (2H), 2,68d (2H), 2,27 m (2H), 1,98d (1H), 0,90d (6H)
1-Phenyl-3-ethynyl-5-cyclobutylpentane-1,5-dione (XVII)/(XXIII)	372	60, CCl_4	7,66 m(5H), 5,98 s (1H), 4,00 m (1H), 3,23 m (3H), 2,68d (2H), 2,05 m (6H)
	254	250, $CDCl_3$	7,66m (5H), 3,55 m (1H), 3,23 m (3H), 2,70d (2H), 2,07d (1H), 2,05 m(6H)
1-Cyclopropyl-3-ethynyloct-6-ene-1,5-dione (XVIII)/(XXIV)	322	60, CCl_4	6,69m (2H), 5,98s (1H), 3,92 m (1H), 2,68 two d (4H), 1,92 d (3H), 1,90 m (1H), 1,00 m(4H)
	204	60, CCl_4	6,36m (2H), 3,45 m (1H), 2,75 two d (4H), 1,91 d (1H), 1,90 d (3H), 1,90 m(1H), 0,95m (4H)

*In the table, only the names of the decomplexated products are given; upper part of each row — spectral data for the DCHC complex; lower part — for the decomplexation product.

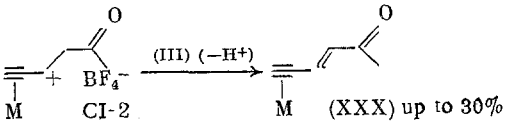
†As the mass spectrometric characteristic of the DCHC complexes, the characteristic mass number M_x^+ is used, which corresponds to the $(RC{\equiv}CH)Co_2$ fragment with a mass of $M^+ - 168$ (i.e., 6 CO groups).

(XXVI) and 1-adamantyl tetrafluoroborate (XXVII) to (I), followed by treatment of the cationoid intermediate CI-3 with acetone TMSE (III), gives ketones (XXVIII) and (XXIX) (yield 94 and 80%, respectively)

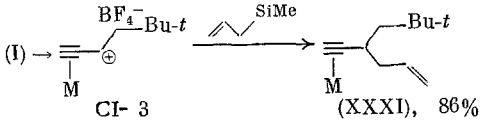


R = *t*-Bu (XXVI), (XXVIII), 1-Ad (XXVII), (XXIX).

Another π-donor for the reactions with electrophiles, TMAS, was found to be a less active nucleophile (compared with TMSE), and it could not be introduced into the reaction with β-ketocarbenium intermediates of the CI-2 type, obtained in acylation of (I). At a temperature of −78 to −60°C, there was no reaction of CI-2 with TMAS (control by TLC), while when the temperature was increased to −50 to 0°C, the main result of the reaction was deprotonation of CI-2 with the formation of the corresponding α,β-unsaturated ketone (XXX)

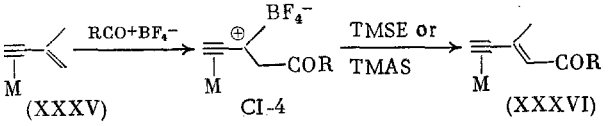


The CI-3 intermediates do not contain a β-carbonyl group and therefore are less prone to the elimination of a proton. It is clear that for this reason, CI-3 can be introduced into a reaction with TMAS, as was shown on the example of the reaction of CI-3 (R = t-Bu) with TMAS



The oxidative decomplexation of adducts (XXVIII), (XXIX), and (XXXI) proceeds to give yields of 89-98%, and leads to (XXXII-XXXIV), respectively. Two new C—C bonds can thus also be formed in the AdE reaction of the DCHC complex of vinylacetylene, using alkyl cations as electrophiles, and TMSE or TMAS as nucleophiles.

It is known that the DCHC complex of isopropenylacetylene (XXXV) also readily converts into intermediates of the CI-4 type [2, 3], which are much less active than CI-2 or CI-3 in reactions with π-donors. Thus, in all the cases studied (−78 to +20°C, 6 h), it was impossible to carry out the reaction of β-ketocarbenium intermediate CI-4 with TMSE and TMAS, and the result of the reaction was the formation of an α,β-unsaturated ketone (XXXVI)



Only in the case of the alkylated intermediate CI-5 was a reaction with (III) observed, but the yield of the desired products (XXXVII) was inappreciable

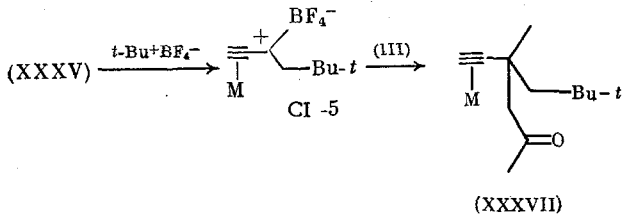


TABLE 2. Data of Elemental Analyses of 1,5-Diketones Obtained

Compound	Found, %		Empirical formula	Calculated, %	
	C	H		C	H
(V)	74,21	9,55	$C_{12}H_{18}O_2$	74,19	9,34
(XX)	76,71	9,57	$C_{15}H_{22}O_2$	76,88	9,46
(XXI)	80,60	7,93	$C_{17}H_{20}O_2$	79,65	7,86
(XXIII)	79,99	7,35	$C_{17}H_{18}O_2$	80,28	7,13
(XXIV)	76,01	8,22	$C_{13}H_{16}O_2$	76,44	7,90

The intermediates CI-4 and CI-5 belong to the type of tertiary carbenium ions. It is possible that, in particular, the increased stability of these ions, and also the hindrance to the nucleophilic attack at the tertiary center, are the reason for their lower activity in reaction with π-donors.

Thus, using the DCHC complex of vinylacetylene (I) as an example, an AdE reaction at the double bond, in which the nature of the C-electrophile and C-nucleophile can be varied within wide limits, was carried out for the first time. This reaction can be used for the simultaneous production of two new C–C bonds and also for converting vinylacetylene into polyfunctional compounds which can be useful in synthesis.

EXPERIMENTAL

The PMR spectra were run in $CDCl_3$ or CCl_4 on Tesla BS-467 (60 MHz) and Bruker WM-250 (250 MHz) spectrometers. The chemical shifts are given on the δ scale with reference to TMS. The mass spectra were taken in a Varian MAT-CH-6 mass spectrometer. The GLC analysis was carried out on an LKhM-80-I chromatograph on 4 mm × 1 m and 4 mm × 2 m steel packed columns (5% KhE-60 on Chezasorb AW-HMDS and 5% DC-550 on Chromaton AW-HMDS, respectively). The TLC analysis was carried out on Silufol UV-254 plates. The preparative TLC was carried out on glass plates 280 × 290 mm in size, with nonstationary layer of 40/100 silica gel.

The reactions were carried out in a current of dry Ar in absolute solvents. The solvents were made absolute by standard methods [10]. All the acylation reactions were carried out by standard methods, and only typical examples are given below. Cerium(IV) ammonium nitrate was used for the decomplexation of the DCHC complexes obtained [11].

DCHC Complex of Vinylacetylene (I). A solution of 1.04 g of vinylacetylene (20 mmoles) in 10 ml of benzene was added at ~20°C to a stirred solution of 6.84 g of $Co_2(CO)_8$ (20 mmoles) in 50 ml of benzene. At the cessation of the liberation of CO and disappearance of $Co_2(CO)_8$ (TLC, hexane), the mixture was filtered in a pentane solution through Al_2O_3 up to the disappearance of impurities (TLC, hexane). After the separation of pentane, 4.74 g (70%) of (I) was obtained, which, according to PMR data, was identical with the sample described in [8].

DCHC Complex of 1-Cyclopropyl-3-ethynyl-7-methyloctane-1,5-dione (XIII). A 90-ml portion of a gaseous BF_3 (3.6 mmoles) was introduced at −78°C by means of a syringe to a stirred solution of 0.38 g of isovaleroyl fluoride (3.6 mmoles) in 20 ml of CH_2Cl_2, and a solution of 0.4 g of (I) (1.18 mmoles) in a mixture of 5 ml of CH_2Cl_2 and 5 ml of $MeNO_2$ was added. The mixture was allowed to stand for 5-10 min at −78°C, and a solution of 0.2 g of cyclohexene (2.42 mmoles) in 2 ml of CH_2Cl_2 was added, and after another 10 min was followed by a solution of 0.94 g of methyl cyclopropyl ketone TMSE (X) (6 mmoles) in 5 ml of CH_2Cl_2. After 20 min, the mixture was treated with saturated $NaHCO_3$ solution, and extracted by ether. The extract was filtered through a layer of Al_2O_3 and dried over anhydrous $MgSO_4$. After removal of solvents, the remaining dark-red oil was partitioned by preparative TLC (benzene). Yield, 0.52 g (87%) of diketone (XIII) (R_f = 0.32, Silufol, benzene). PMR spectrum (CCl_4, 60 MHz): 5.98 s (1H, ≡CH), 3.38 m (1H, H at C^3), 2.75 two d (4H, H at C^2 and C^4), 2.25 m (2H, H at C^6), 1.93 m (1 H) and 0.98 m (4H, H of cyclopropyl fragment), 0.98 m (6H, 2-CH_3). M_X^+ 338.

1-Cyclopropyl-3-ethynyl-7-methyloctane-1,5-dione (XXII). PMR spectrum (CCl_4, 60 MHz): 3.22 m (1H, H at C^3), 2.63 two d (4 H, H at C^2 and C^4), 2.23 d (2H, H and C^6), 1.94 d (1H, ≡CH), 1.94 m (1H), and 0.93 m (4H, H of cyclopropyl fragment), 0.93 d (6H, 2-CH_3). Mass spectrum (m/z): M^+ 220. Found: 76.20; H 9.42%. $C_{14}H_{20}O_2$. Calculated: C 76.33; H 9.15%.

DCHC Complex of 1-(1-Adamantyl)-3-ethynyl-5-phenylpentane-1,5-dione (XIX). A solution of 0.3 g of silver tetrafluoroborate (1.5 mmoles) in 2 ml of dichloroethane was added at −78°C to a stirred solution of 0.34 g of (I) (1 mmole) in a mixture of 15 ml of CH_2Cl_2 and 5 ml of $MeNO_2$. Then, a solution of 0.3 g of 1-adamantoyl chloride (1.5 mmoles) in 10 ml of CH_2Cl_2 was added, followed after 10 min by 0.082 g of cyclohexene (1 mmole), and after another 10 min, by a solution of 0.96 g of acetophenone TMSE (IX) (5 mmoles) in 5 ml of CH_2Cl_2. After 20 min, the mixture was treated with a saturated solution of $NaHCO_3$, and extracted by ether. The extract was filtered through a layer of Al_2O_3, and dried over anhydrous $MgSO_4$. After removal of solvents, the remaining dark-red oil was chromatographed on a column (silica gel 100/160, benzene). Yield, 0.6 g (97%) of diketone (XIX) (R_f = 0.65, Silufol, benzene). PMR spectrum: 7.66 d (5H, C_6H_5), 5.97 s (1H, ≡CH), 3.95 m (1H, H at C^3), 3.17 m (2H, H at C^4), 2.82 d (2H, H at C^2), 1.88 m (15H, H of Ad fragment). Mass spectrum (m/z): M_X^+ 452.

1-(1-Adamantyl)-3-ethynyl-5-phenylpentane-1,5-dione (XXV). PMR spectrum (CCl_4, 60 MHz): 7.64 m (5H, C_6H_5), 3.42 m (1H, H at C^3), 3.14 m (2H, H at C^4), 2.74 d (2H, H at C^2), 1.75 m (16H, ≡CH of Ad fragment). M^+ 334. Found: C 82.20; H 8.15%. $C_{23}H_{26}O_2$. Calculated: C 82.60; H 7.84%.

DCHC Complex of 4-Ethynyl-6,6-dimethylheptan-2-one (XXVIII). A solution of 0.31 g of silver tetrafluoroborate (1.6 mmoles) in 2 ml of dichloroethane was added at −50°C to a mixture of 0.43 g of (I) (1.2 mmoles) and 0.14 g of t-BuCl (1.5 mmoles) in 20 ml of a 1:4 mixture of CH_2Cl_2 and $MeNO_2$. After 15 min 0.65 g of acetone TMSE (III) (5 mmoles) was added to the mixture, which was then warmed to 20°C, treated with a saturated solution of $NaHCO_3$, and extracted by ether. After removal of solvents, the residue was partitioned by preparative TLC (benzene). Yield, 0.51 g (94%) of (XXVIII) (R_f 0.45, Silufol, petroleum ether–benzene, 12:7). PMR spectrum (CCl_4, 60 MHz): 5.97 s (1H, ≡CH), 3.50 m (1H, H at C^4), 2.63 m (2H, H at C^3), 2.10 s (3H, H at C^1), 1.30 d (2H, H, at C^5), 1.02 s (9H, 3-CH_3). Mass spectrum (m/z): M_X^+ − 2.84.

4-Ethynyl-6,6-dimethylheptan-2-one (XXXII). PMR spectrum (CCl_4, 60 MHz): 2.75 m (1H, H at C^4), 2.40 m (2H, at C^3), 2.02 s (3H, H at C^1), 1.85 d (1H, ≡CH), 1.22 d (2H, H at C^5), 0.92 s (9H, 3-CH_3). M^+ 166. Found: C 79.25; H 10.59%. $C_{11}H_{18}O$. Calculated: C 79.47; H 10.91%.

DCHC Complex of 4-Ethynyl-3,6,6-trimethylheptan-2-one (XXXVII). This complex was obtained under conditions similar to those used in the preceding experiment, from 0.42 g of DCHC complex of isorpopenylacetylene (XXXV) (1.2 mmoles). Yield, 0.155 g (28%) of (XXXVII) (R_f 0.3, Silufol, benzene). PMR spectrum (CCl_4, 60 MHz): 6.12 s (1H, ≡CH), 2.58 s (2H, H at C^3), 2.07 s (3H, H at C^1), 1.70 m, (2H at C^5), 1.37 s (9H, 3-CH_3), 1.10 s (3H, CH_3 at C^4). M_X^+ 298.

DCHC Complex of 4-Ethynyl-5-(1-adamantyl)pentan-2-one (XXIX). A solution of 0.33 g of silver tetrafluoroborate (1.7 mmoles) in 2 ml of dichloroethane was added at −60°C to a mixture of 0.34 g of (I) (1 mmole) and 0.27 g of 1-bromoadamantane (1.25 mmoles) in 20 ml of a mixture of CH_2Cl_2 and $MeNO_2$ (4:1). After 15 min, 0.52 g of acetone TMSE (III) (4 mmoles) was added to the mixture, and after 30 min, the mixture was warmed to 0°C, treated with a saturated solution of $NaHCO_3$, and extracted by ether. The extract was filtered through an Al_2O_3 layer and dried over anhydrous $MgSO_4$. After the removal of solvents, the residue was partitioned by preparative TLC (benzene–heptane, 1:1). Yield, 0.43 g (80%) of (XXIX) (R_f 0.35, Silufol, benzene–heptane, 1:1). PMR spectrum (CCl_4, 60 MHz): 5.93 s (1H, ≡CH), 3.50 m (1H, H at C^4), 2.67 m (2H, H at C^3), 2.10 s (3H, H at C^1)1.80 m (15 H, H of Ad fragment), 1.31 m (2H, H at C^5), M_X^+ 362.

4-Ethynyl-5-(1-adamantyl)pentan-2-one (XXXIII). PMR spectrum (CCl_4, 60 MHz): 2.83 m (1H, H at C^4), 2.52 m (2H H at C^3), 2.08 s (3H, H at C^1), 1.93 d (1H, ≡CH), 1.65 m (15H, H of Ad fragment) 1.23 d (H at C^5). M^+ 2.44.

DCHC Complex of 4-Ethynyl-6,6-dimethylhept-1-ene (XXXI). A solution of 0.39 g of silver tetrafluoroborate (2.0 mmoles) in 2 ml of dichloroethane was added at −20°C to a mixture of 0.42 g of (I) (1.25 mmoles) and 0.14 g of t-BuCl (1.5 mmoles) in 20 ml of a mixture of CH_2Cl_2 and $MeNO_2$ (1-4), and after 15 min, 0.8 g of TMAS (7 mmoles) was introduced to the mixture. After 1 h, the mixture was warmed to ~20°C, treated with a saturated solution of $NaHCO_3$, and extracted by ether. The ether layer was filtered through Al_2O_3 and dried over anhydrous $MgSO_4$. After the removal of solvents, the residue was partitioned by preparative TLC (petroleum ether). Yield, 0.47 g (86%) of (XXXI) (R_f 0.74, Silufol, petroleum ether), M_X^+ 268.

4-Ethynyl-6,6-dimethylhept-1-ene (XXXIV). PMR spectrum ($CDCl_3$, 250 MHz): 5.87 m (1H, H at C^2), 5.10 m (2H, H at C^1), 2.42 m (1H, H at C^4), 2.22 (2H, H at C^3), 2.08 d (1H, ≡CH), 1.42 m (2H, H at C^5), 0.97 s (9H, 3-CH_3). Found: C 88.00; H 11.97%. $C_{11}H_{18}$. Calculated: C 87.93, H 12.07%.

CONCLUSIONS

The two-stage reaction of electrophilic addition to a double bond of a C-electrophile and C-nucleophile, whose nature can be independently varied, was carried out for the first time on a dicobalthexacarbonyl complex of vinylacetylene used as an example. The reaction resulted in the formation of two carbon–carbon bonds. This opens up new possibilities for synthesizing polyfunctional compounds from vinylacetylene.

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