Tetrahedron Letters 52 (2011) 1090–1092

Contents lists available at ScienceDirect

Tetrahedron Letters

journal homepage: www.elsevier.com/locate/tetlet

Intermolecular Morita–Baylis–Hillman reactions using dicobalthexacarbonyl complexed acetylenic acetals

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ARTICLE INFO

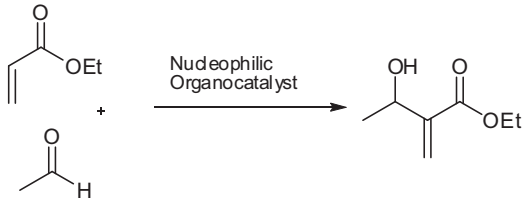
Article history:
Received 30 June 2010
Revised 16 December 2010
Accepted 20 December 2010
Available online 30 December 2010

Key words:
Nicholas reaction
C–C bond formation
Lewis acid
Morita–Baylis–Hillman

ABSTRACT

An intermolecular Morita–Baylis–Hillman (MBH) reaction using dicobalthexacarbonyl complexed acetylenic acetals as the electrophile is reported. Employing BF_3–OEt_2 as the Lewis acid with a sulfide as the Lewis base MBH adducts were obtained.

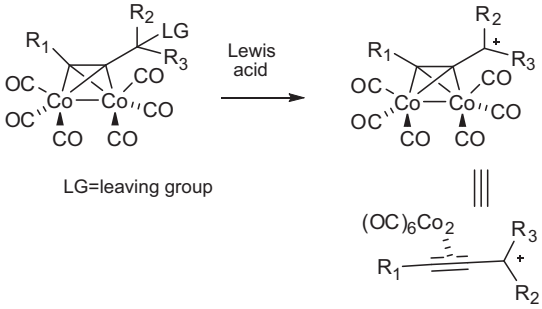
The Morita–Baylis–Hillman (MBH) reaction is a carbon–carbon bond forming reaction that exhibits atom economy with generation of functional groups.[1] In the reaction, an activated alkene is coupled with a carbon electrophile using a nucleophilic catalyst (Eq. (1)).[2] Tertiary amines, trialkylphosphines, sulfides, and Lewis acids[3] have been used to mediate the reaction. The intermolecular reaction has been developed to accommodate a number of sp^2-hybridized electrophiles including alpha-keto esters, aldehydes, 1,2-diketones, arenes, and vinyl sulfones.[2] Activated alkenes used in the MBH reaction include acrylates, vinyl ketones, sulfones, nitriles, sulfoxides, phosphonates, acrolein, thioacrylates, and allenic esters.[2]



(1)

Nucleophilic Catalyst: DABCO, r.t., 7d, 76% (Baylis-Hillman)[1a]
Cy_3P, 130 °C, 2h, 23% (Morita)[1b]

Dicobalthexacarbonyl complexed acetylenic acetals have not been reported as electrophilic partners in the MBH reaction and we herein report their successful application in the carbon–carbon bond forming process. The use of transition metal complexed reagents as electrophiles in the MBH reaction is not common,[4] and dicobalthexacarbonyl complexed acetylenic acetals appeared to be ideal candidates for the electrophilic partner in the Morita–Baylis–Hillman reaction due to their known reactivity under acidic reaction conditions. Reaction of dicobalthexacarbonyl complexed alkynes bearing an appropriate leaving group at the propargylic position undergo reaction with Lewis acids to generate stabilized cationic intermediates known as Nicholas cations (Eq. (2)), which have been shown to react with a variety of nucleophiles including hydrides, amines, azides, fluorides, mercaptans, enols, and alkenes.[5]



(2)

Commonly used Lewis acids in the MBH reaction include $TiCl_4$ and BF_3–OEt_2.[3] In conjunction with sulfides as the nucleophilic catalyst, $TiCl_4$ has also been used. However, chlorinated side products are readily generated.[3b,c] In both MBH and Nicholas reactions, BF_3–OEt_2 has been used as a Lewis acid. The Goodman group used BF_3–OEt_2 in conjunction with tetrahydrothiophene to promote an

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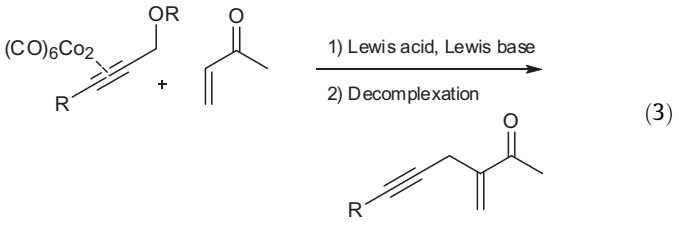
doi:10.1016/j.tetlet.2010.12.096

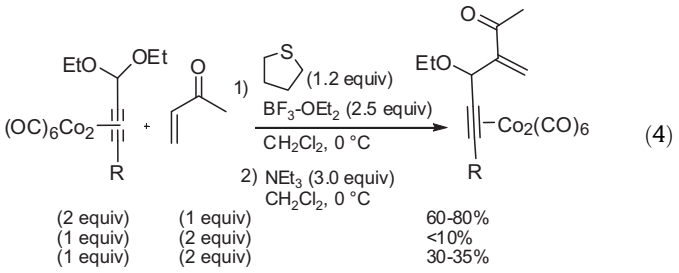
intermolecular MBH reaction between aldehydes and activated alkenes.[3d] Kataoka et al. developed a Lewis-Acid mediated MBH reaction using a sulfide as the mediator.[3e]

Our initial plan was to develop an intermolecular MBH reaction between an enone and a dicobalthexacarbonyl complexed alkyne bearing a leaving group at the propargylic position. We chose BF_3–OEt_2 as the Lewis acid since it is common to both the MBH and the Nicholas reaction.[3d–f,6] Initial optimization studies using Nicholas cations of dicobalthexacarbonyl complexed propargyl ethers and different Lewis acids such as $TiCl_4$ or BF_3–OEt_2 were met with limited success (Eq. (3)).



(3)

Acetals have previously been utilized in both MBH reactions and reactions of dicobalthexacarbonyl complexed alkynes therefore they were selected as the electrophilic partner. Increased activation of the propargylic carbon by the use of an acetal in place of an ether successfully led to MBH coupling products (Eq. (4)).[3f]

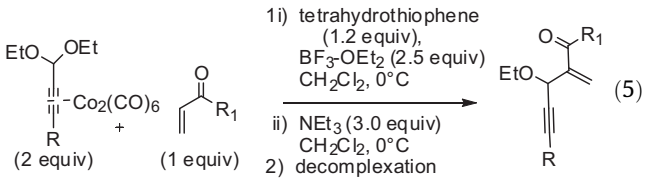


(4)

Reactions performed with tetrahydrothiophene as the nucleophile and BF_3–OEt_2 were the most promising. In the optimization process, it was found that a 2:1 excess of the dicobalthexacarbonyl complexed acetylenic acetal to the activated alkene achieved highest yields (Eq. (4)). With an equal ratio of the dicobalthexacarbonyl complexed acetylenic acetal to activated alkene or if an excess of activated alkene was used, the yields decreased. A series of intermolecular MBH adducts was synthesized (Table 1, Eq. (5)) using commercially available propargylic acetals or propargylic acetals synthesized under Sonogashira coupling conditions.[7] Use of propiolaldehyde diethyl acetals resulted in low isolated yields of anticipated coupling product in addition to significant starting material decomposition under the Lewis acidic conditions.

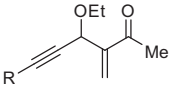
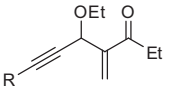
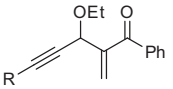
Other Lewis acids such as $BaCl_2$, SmI_2, $AlCl_3$, $AgNO_3$, and $SnCl_4$ were screened and resulted in little or no formation of the desired MBH product. Reaction of the uncomplexed 2-butynal-diethylacetal with pent-1-ene-3-one under the same reaction conditions yielded only 50% of the MBH adduct **6**. The reaction produced more byproducts thus reinforcing the effectiveness of the complexed alkyne. Uncomplexed 2-octynal underwent reaction with pent-1-ene-3-one under the same reaction conditions to give alkyne **13** in 75% yield as the free alcohol rather than the propargylic ether. These conditions give rise to the coupling product in much shorter reaction time than the corresponding base-catalyzed process.[8]

Initial carbon–carbon bond formation leaves the cobalt complex coordinated to the alkyne. Oxidation using either *N*-methylmorpholine-*N*-oxide (NMO) or ceric ammonium nitrate (CAN) liberates the free alkyne. While the metal can be decomplexed directly in the initial reaction flask, yields were higher when filtration of the reaction through Celite® to remove some of the cobalt residues was conducted after the Lewis acid-mediated MBH reaction but prior to decomplexation.[9]

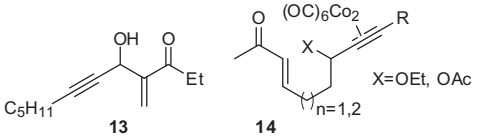


(5)

Table 1

Entry	R	MBH product		% yield (2 steps)
1	Me		**1**	54[a]
2	Et		**2**	61[b]
3	Pr		**3**	54[b]
4	Ph		**4**	65[b]
5	4-NO_2-Ph		**5**	61[b]
6	Me		**6**	71[a]
7	Et		**7**	66[b]
8	Pr		**8**	61[b]
9	Ph		**9**	58[b]
10	Me		**10**	56[b]
11	Et		**11**	47[b]
12	Pr		**12**	54[b]

[a] Decomplexation with NMO.
[b] Decomplexation with CAN.



Alternative activated alkenes including 4-nitrophenyl vinyl ketone and thioacrylic acid-*S*-ethyl ester did not work under Lewis acidic conditions. In addition, beta-substituted activated alkenes such as 3-penten-2-one and cyclohexenone were inert to the reaction conditions. Attempts to develop an intramolecular reaction using enone **14** were not successful. With either an acetate or alkoxy leaving group, there was either no reaction or decomposition of starting material under Lewis acidic or phosphine-mediated conditions.

In summary, an intermolecular MBH reaction with activated alkenes has been developed using the dicobalthexacarbonyl complexed acetylenic acetal as the electrophile. The use of cationic intermediates stabilized by an adjacent dicobalthexacarbonyl complexed alkyne represents an alternative class of electrophiles in the MBH reaction.

Acknowledgments

This work was funded by the National Science Foundation and the MDS Research Foundation (Tallahassee, FL).

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9. *4-Ethoxy-3-methylene-hept-5-yn-2-one*, **1**. To a stirred solution of dicobalthexacarbonyl complexed 2-butyn-1-al diethyl acetal (0.493 g, 1.15 mmol) in 2 mL of CH_2Cl_2 at 0 °C were added tetrahydrothiophene (0.062 mL, 0.696 mmol) and methyl vinyl ketone (0.048 mL, 0.57 mmol). After stirring for 10 min, *freshly distilled* BF_3–OEt_2 (0.184 mL, 1.45 mmol) was added over 5 min and the reaction was followed by TLC. Upon consumption of the enone starting material, the reaction was quenched with NEt_3 (0.243 mL, 1.75 mmol). After warming to room temperature, the mixture was washed successively with aqueous HCl (1 M) and saturated $NaHCO_3$ (aq). The mixture was dried over Na_2SO_4 and the solvent was evaporated.
   Without column chromatography, the mixture was subjected to cobalt decomplexation conditions. To the reaction mixture dissolved in 3 mL of CH_2Cl_2, NMO·H_2O was added slowly until the red color characteristic of dicobalthexacarbonyl complexes no longer appeared by TLC. The mixture was filtered through a plug of silica gel and concentrated by evaporation. Column chromatography on silica gel provided enone **1** as a yellow oil (0.052 g, 54% yield over 2 steps). ^{1}H NMR 300 MHz ($CDCl_3$) δ 6.32 (br s, 1H, C=CH*H*), 6.20 (br s, 1H, C=CH*H*), 5.06 (br s, 1H, CH_3CH_2OCH), 3.76 (ABq, J_{AB} = 9.0, J = 6.2, 1H, $CH_3CHHOCH$), 3.49 (ABq, J_{AB} = 9.0, J = 6.2, 1H, $CH_3CHHOCH$), 2.38 (s, 3H, CH_3CO), 1.87 (d, J = 2.4, 3H, $CH_3C{\equiv}C$), 1.21 (t, J = 6.6, 3H, CH_3CH_2OCH); ^{13}C ($CDCl_3$) δ 201.2, 151.1, 130.6, 87.2, 80.8, 70.9, 68.9, 30.6, 19.4, 7.9. IR (cm^{-1}): 3434, 2976, 2229, 1651, 1079. MS [CI, *m*/*z* (rel intensity)]: 167 (M^++1), 151, 137, 121, 97.
   4-Ethoxy-3-methylene-oct-5-yne-2-one, **2**. ^{1}H NMR 300 MHz ($CDCl_3$) δ 6.33 (br s, 1H, C=CH*H*), 6.20 (br s, 1H, C=CH*H*), 5.09 (br s, 1H, CH_3CH_2OCH), 3.75 (ABq, J_{AB} = 9.0, J = 6.1, 1H, $CH_3CHHOCH$), 3.50 (ABq, J_{AB} = 9.0, J = 6.1, 1H, $CH_3CHHOCH$), 2.25 (qd, J = 7.2, 1.8, 2H, $CH_3CH_2C{\equiv}C$), 1.21 (t, J = 6.6, 3H, CH_3CH_2OCH), 1.15 (t, J = 7.2, 3H, $CH_3CH_2C{\equiv}C$). ^{13}C NMR 75 MHz ($CDCl_3$) δ 201.97, 150.96, 130.76, 93.39, 80.84, 70.81, 68.88, 30.73, 19.38, 18.03, 10.81. IR (cm^{-1}): 3583, 2977, 2229, 1682, 1081(cm^{-1}) MS [CI (rel intensity)]: 181 (M^++1), 135, 85.
   4-Ethoxy-3-methylene-non-5-yn-2-one, **3**. ^{1}H NMR 300 MHz ($CDCl_3$) δ 6.32 (br s, 1H, C=CH*H*), 6.19 (br s, 1H, C=CH*H*), 5.09 (br s, 1H, CH_3CH_2OCH), 3.79 (ABq, J_{AB} = 9.0, J = 7.0, 1H, $CH_3CHHOCH$), 3.53 (ABq, J_{AB} = 9.0, J = 7.0, 1H, $CH_3CHHOCH$), 2.41 (s, 3H, CH_3CO), 2.22 (td, J = 7.2, 1.8, 2H, $CH_3CH_2CH_2C{\equiv}C$), 1.55 (qt, J = 7.2, 7.2, 2H, $CH_3CH_2CH_2C{\equiv}C$), 1.22 (t, J = 7.2, 3H, CH_3CH_3OCH), 0.99 (t, J = 7.2, 3H, $CH_3CH_2CH_2C{\equiv}C$). ^{13}C NMR 75 MHz ($CDCl_3$) δ 201.97, 151.19, 130.58, 91.88, 81.66, 70.90, 68.86, 30.69, 26.33, 25.11, 19.36, 17.70. IR (cm^{-1}): 3502, 2969, 2228, 1688, 1080. MS [CI, *m*/*z* (rel intensity)]: 195 (M^++1), 149.
   4-Ethoxy-3-methylene-6-phenyl-hex-5-yn-2-one, **4**. To a stirred solution of dicobalthexacarbonyl complexed phenylpropargyl aldehyde diethyl acetal (0.929 g, 1.90 mmol) in 3 mL of CH_2Cl_2 at 0 °C were added tetrahydrothiophene (0.064 mL, 0.760 mmol) and methyl vinyl ketone (0.053 mL, 0.630 mmol). After stirring for 10 min, *freshly distilled* BF_3–OEt_2 (0.253 mL, 2.01 mmol) was added over 5 min and the reaction was followed by TLC. Upon consumption of the enone starting material, the reaction was quenched with NEt_3 (0.348 mL, 2.50 mmol). After warming to room temperature, the mixture was washed successively with aqueous HCl (1 M) and saturated $NaHCO_3$ (aq). The mixture was dried over Na_2SO_4 and the solvent was evaporated.
   A ^{1}H NMR spectrum was recorded of the reaction mixture. The NMR sample was prepared by filtration of the mixture through charcoal and Celite®. Without column chromatography, the mixture was subjected to cobalt decomplexation conditions. To the reaction mixture dissolved in 2 mL of THF and 1 mL of acetone, ceric ammonium nitrate was added slowly until the red color characteristic of dicobalthexacarbonyl complexes no longer appeared by TLC. The mixture was filtered through a plug of silica gel and concentrated by evaporation. Column chromatography on silica gel provided enone **4** as a yellow oil (0.094 g, 65% over 2 steps). ^{1}H NMR 300 MHz ($CDCl_3$) δ 7.46 (m, 2H, aromatic), 7.32 (m, 3H, aromatic), 6.48 (br s, 1H, C=CH*H*), 6.30 (br s, 1H, C=CH*H*), 5.35 (br s, 1H, CH_3CH_2OCH), 3.85 (ABq, J_{AB} = 8.8, J = 6.8, 1H, $CH_3CHHOCH$), 3.60 (ABq, J_{AB} = 8.8, J = 6.8, $CH_3CHHOCH$), 2.41 (s, 3H, CH_3CO), 1.26 (t, J = 6.8, 3H, CH_3CH_2OCH); ^{13}C NMR 75 MHz ($CDCl_3$) δ 201.7, 150.7, 136.1, 132.8, 132.6, 131.1, 126.9, 91.1, 90.7, 71.1, 69.3, 26.9, 19.4. IR (cm^{-1}): 3445, 2977, 2198, 1682, 1080, 758. MS [FAB, *m*/*z* (rel intensity)]: 251 (M^++1), 241, 221.
   4-Ethoxy-3methylene-6-(4-nitro-phenyl)-hex-5-yn-2-one, **5**. ^{1}H NMR 300 MHz ($CDCl_3$) δ 8.18 (m, 2H, aromatic), 7.59 (m, 2H, aromatic), 6.44 (br s, 1H, C=CH*H*), 6.32 (br s, 1H, C=CH*H*), 5.37 (br s, 1H, CH_3CH_2OCH), 3.85 (ABq, J_{AB} = 9.0, J = 6.8, 1H, $CH_3CHHOCH$), 3.60 (ABq, J_{AB} = 9.0, J = 6.8, $CH_3CHHOCH$), 2.44 (s, 3H, CH_3CO), 1.28 (t, J = 7.2, 3H, CH_3CH_2OCH).
   5-Ethoxy-4-methylene-oct-6-yn-3-one, **6**. ^{1}H NMR 300 MHz ($CDCl_3$) δ 6.28 (br s, 1H, C=CH*H*), 6.18 (br s, 1H, C=CH*H*), 5.07 (br s, 1H, CH_3CH_2OCH), 3.75 (ABq, J_{AB} = 9.0, J = 7.2, 1H, $CH_3CHHOCH$), 3.49 (ABq, J_{AB} = 9.0, J = 7.2, 1H, $CH_3CHHOCH$), 2.79 (ABq, J_{AB} = 13.0, J = 3.0, 1H, CH_3CHHCO), 2.73 (ABq, J_{AB} = 13.0, J = 3.0, 1H, CH_3CHHCO), 1.87 (d, J = 2.7, 3H, $CH_3C{\equiv}C$), 1.20 (t, J = 7.2, 3H, CH_3CH_2OCH), 1.11 (t, J = 7.2, 3H, CH_3CH_2CO). ^{13}C NMR 75 MHz ($CDCl_3$) δ 201.97, 150.97, 130.76, 87.05, 81.50, 70.77, 68.90, 30.65, 30.63, 19.3, 8.08. IR (cm^{-1}): 3446, 2977, 2228, 1681, 1081. MS [EI, *m*/*z* (rel intensity)]: 179, 165, 151, 123, 97.
   5-Ethoxy-4-methylene-non-6-yn-3-one, **7**. ^{1}H NMR 300 MHz ($CDCl_3$) δ 6.28 (br s, 1H, C=CH*H*), 6.16 (br s, 1H, C=CH*H*), 5.11 (br s, 1H, CH_3CH_2OCH), 3.75 (ABq, J_{AB} = 9.0, J = 6.8, 1H, $CH_3CHHOCH$), 3.50 (ABq, J_{AB} = 9.0, J = 6.8, 1H, $CH_3CHHOCH$), 2.97 (ABq, J_{AB} = 13.0, J = 6.8, 1H, CH_3CHHCO), 2.73 (ABq, J_{AB} = 13.0, J = 6.8, 1H, CH_3CHHCO), 2.27 (qd, J = 7.8, 2.4, 2H, $CH_3CH_2C{\equiv}C$), 1.21 (t, J = 6.6, 3H, CH_3CH_2OCH), 1.15 (t, J = 6.6, 3H, $CH_3CH_2C{\equiv}C$), 1.12 (t, J = 8.0, 3H, CH_3CH_2CO). ^{13}C NMR 75 MHz ($CDCl_3$) δ 205.03, 150.74, 129.35, 93.32, 81.48, 71.17, 68.82, 36.02, 19.39, 18.10, 16.76, 12.39. IR (cm^{-1}): 3582, 2977, 2229, 1688, 1083. MS [CI, *m*/*z* (rel intensity)]: 195 (M^++1), 149, 111.
   5-Ethoxy-4-methylene-dec-6-yn-3-one, **8**. ^{1}H NMR 300 MHz ($CDCl_3$) δ 6.29 (br s, 1H, C=CH*H*), 6.18 (br s, 1H, C=CH*H*), 5.13 (br s, 1H, CH_3CH_2OCH), 3.77 (ABq, J_{AB} = 9.1, J = 6.8, 1H, $CH_3CHHOCH$), 3.50 (ABq, J_{AB} = 9.1, J = 6.8, 1H, $CH_3CHHOCH$), 2.78 (ABq, J_{AB} = 13.0, J = 6.8, 1H, CH_3CHHCO), 2.72 (ABq, J_{AB} = 13.0, J = 6.8, 1H, CH_3CHHCO).
   5-Ethoxy-4-methylene-7-phenyl-hept-6-yn-3-one, **9**. ^{1}H NMR 300 MHz ($CDCl_3$) δ 7.46 (m, 2H, aromatic), 7.32 (m, 3H, aromatic), 6.38 (br s, 1H, C=CH*H*), 6.25 (br s, 1H, C=CH*H*), 5.37, (br s, 1H, CH_3CH_2OCH), 3.86 (ABq, J_{AB} = 8.9, J = 6.8, 1H, $CH_3CHHOCH$), 3.62 (ABq, J_{AB} = 8.9, J = 6.8, 1H, $CH_3CHHOCH$), 2.83 (ABq, J_{AB} = 17.2, J = 7.8, 1H, CH_3CHHCO), 2.75 (ABq, J_{AB} = 17.2, J = 7.8, 1H, CH_3CHHCO), 1.26 (t, J = 6.8, 3H, CH_3CH_2OCH), 1.15 (t, J = 7.8, 3H, CH_3CH_2CO). ^{13}C NMR 75 MHz ($CDCl_3$) δ 204.90, 150.07, 135.95, 132.77, 132.58, 129.71, 126.88, 91.16, 90.71, 71.70, 69.45, 35.91, 19.14, 12.69, 5.59. IR (cm^{-1}): 3584, 2976, 2223, 1681, 1089, 758. MS [EI, *m*/*z* (rel intensity): 241 (M^++1)], 213, 198, 185, 157, 139, 111.
   3-Ethoxy-2-methylene-1-phenyl-hex-4-yn-1-one, **10**. ^{1}H NMR 300 MHz ($CDCl_3$) δ 7.84 (m, 2H, aromatic), 7.56 (m, 1H, aromatic), 7.47 (m, 2H, aromatic), 6.35 (br s, 1H, C=CH*H*), 5.73 (br s, 1H, C=CH*H*), 5.29 (br s, 1H, CH_3CH_2OCH), 3.82 (ABq, J_{AB} = 9.0, J = 6.4, 1H, $CH_3CHHOCH$), 3.55 (ABq, J_{AB} = 9.0, J = 6.4, 1H, $CH_3CHHOCH$), 1.89 (d, J = 2.4, 3H, $CH_3C{\equiv}C$), 1.20 (t, J = 7.2, 3H, CH_3CH_2OCH). ^{13}C NMR 75 MHz ($CDCl_3$) δ 200.32, 150.31, 144.82, 136.87, 133.96, 132.54, 129.46, 88.22, 81.52, 72.42, 69.11, 19.33, 7.97. IR (cm^{-1}): 3390, 2928, 2357, 1652, 1078, 757. MS [CI, *m*/*z* (rel intensity)]: 229 (M^++1), 183, 105.
   3-Ethoxy-2-methylene-1-phenyl-hept-4-yn-1-one, **11**. ^{1}H NMR 300 MHz ($CDCl_3$) δ 7.83 (m, 2H, aromatic), 7.56 (m, 2H, aromatic), 7.47 (m, 2H, aromatic), 6.32 (br s, 1H, C=CH*H*), 5.73 (br s, 1H, C=CH*H*), 5.27 (br s, 1H, CH_3CH_2OCH), 3.80 (ABq, J_{AB} = 9.0, J = 6.8, 1H, $CH_3CHHOCH$), 3.57 (ABq, J_{AB} = 9.0, J = 6.8, 1H, $CH_3CHHOCH$), 2.26 (qd, J = 7.8, 2.4, 2H, $CH_3CH_2C{\equiv}C$), 1.23 (t, J = 7.2, 3H, CH_3CH_2OCH), 1.18 (t, J = 7.2, 3H, $CH_3CH_2C{\equiv}C$). ^{13}C NMR 75 MHz ($CDCl_3$) δ 200.56, 150.36, 141.81, 136.89, 133.99, 132.55, 129.19, 94.10, 81.50, 72.00, 69.09, 19.41, 18.17, 16.84. IR (cm^{-1}): 2977, 2224, 1682, 1084, 757. MS [FAB, *m*/*z* (rel intensity)]: 265. (M^++Na], 242.0.
   3-Ethoxy-2-methylene-1-phenyl-oct-4-yn-1-one, **12**. ^{1}H NMR 300 MHz ($CDCl_3$) δ 7.86 (m, 2H, aromatic), 7.56 (m, 1H, aromatic), 7.45 (m, 2H, aromatic), 6.33 (br s, 1H, C=CH*H*), 5.71 (br s, 1H, C=CH*H*), 5.31 (br s, 1H, CH_3CH_2OCH), 3.81 (ABq, J_{AB} = 9.0, J = 6.0, 1H, $CH_3CHHOCH$), 3.57 (ABq, J_{AB} = 9.0, J = 6.0, 1H, $CH_3CHHOCH$), 2.25 (td, J = 7.2, 1.8, 3H, $CH_3CH_2CH_2C{\equiv}C$), 1.55 (tq, J = 7.2, 7.2, 2H, $CH_3CH_2CH_2C{\equiv}C$), 1.24 (t, J = 7.2, CH_3CH_2OCH), 0.99 (t, J = 7.2, $CH_3CH_2CH_2C{\equiv}C$). IR (cm^{-1}): 3582, 2965, 2203, 1665, 1087, 756. MS [CI, *m*/*z* (rel intensity)]: 255 (M^++1), 227, 105, 77.