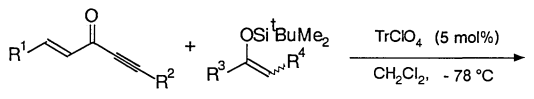
Regioselective Condensation of Ethynyl Vinyl Ketone or 2-Propynyl Ether Derivatives with Silyl Enol Ethers Catalyzed by Trityl Perchlorate

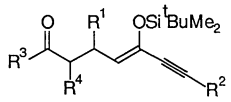
Teruaki MUKAIYAMA,* Shigekazu MATSUI, Koichi HOMMA, and Shū KOBAYASHI
Department of Applied Chemistry, Faculty of Science, Science University of Tokyo, Kagurazaka, Shinjuku-ku, Tokyo 162
(Received April 9, 1990)

In the presence of a catalytic amount of trityl perchlorate, ethynyl vinyl ketone derivatives regioselectively react with silyl enol ethers to afford the corresponding Michael adducts in high yields. 2-Propynyl ether derivatives also react with silyl enol ethers in the presence of a catalytic amount of trityl perchlorate, to give the corresponding adducts in high yields. In the case of the reaction with 2-propynyl ether derivatives, regioselectivities were apparently different between two silylated nucleophiles, silyl enol ethers of ketones and ketene silyl acetals.

In the previous paper, we have reported that, in the presence of a catalytic amount of trityl perchlorate, α,β-acetylenic ketones (ethynyl ketones) regio- and stereoselectively react with various kinds of silyl enol ethers to afford the corresponding aldol adducts (1,2-addition products) in high yields.[1] This regioselectivity is contrastive with that of the reaction between α,β-unsaturated ketones (α,β-olefinic ketones) and silyl enol ethers, which is also catalyzed by a catalytic amount of trityl salt to afford the corresponding Michael adducts (1,4-addition products) exclusively.[2] In this paper, we would like to describe the reaction of other acetylenic compounds, such as ethynyl vinyl ketone or 2-propynyl ether derivatives, with silyl enol ethers, in which interesting regioselectivities are observed.



1 2



3 (1)

1a: R^1=Ph, R^2=Me
1b: R^1=Me, R^2=Ph
2a: R^3=Ph, R^4=H
2b: R^3=Me, R^4=H
2c: R^3=Ph, R^4=Me
2d: R^3=MeO, R^4=Me_2
3a: R^1=Ph, R^2=Me, R^3=Ph, R^4=H
3b: R^1=Ph, R^2=Me, R^3=Me, R^4=H
3c: R^1=Ph, R^2=Me, R^3=Ph, R^4=Me
3d: R^1=Ph, R^2=Me, R^3=MeO, R^4=Me
3e: R^1=Me, R^2=Ph, R^3=Ph, R^4=H
3f: R^1=Me, R^2=Ph, R^3=Ph, R^4=Me

In the first place, ethynyl vinyl ketone **1a** was chosen as a model, and the reaction of **1a** with silyl enol ether of acetophenone **2a** was carried out in the presence of a catalytic amount of trityl perchlorate (5 mol%). The reaction was found to proceed smoothly at −78 °C to afford the corresponding Michael-type addition product **3a** in 94% yield.

Several examples of this reaction are shown in Table 1. In every case, the Michael adducts are obtained in high yields without accompanying any other regioisomers. As far as we know, this is a first example of regioselective addition of enolate components to ethynyl vinyl ketones.

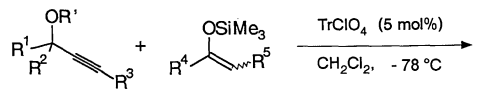
Next, the reaction of 2-propynyl ethers was investigated.[3] Concerning similar type of reaction, it was reported from this laboratory that, in the presence of a catalytic amount of trityl perchlorate, allyl ethers smoothly react with silyl enol ethers,[4] allylsilane or silyl cyanide[5] to give the corresponding γ,δ-unsaturated carbonyl compounds, 1,5-dienes or γ,δ-unsaturated nitriles (with the elimination of alkoxides), respectively, although the regioselectivities were generally moderate. When 2-propynyl ether **4a** was treated with silyl enol ether of acetophenone **5a** in the presence of a catalytic amount of trityl perchlorate

Table 1. The Reaction of Ethynyl Vinyl Ketones

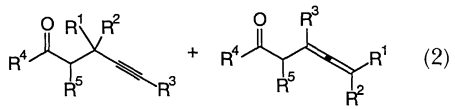
Entry	Ethynyl vinyl ketone	Silyl enol ether	Product	Yield/%
1	**1a**	**2a**	**3a**	94
2	**1a**	**2b**	**3b**	96
3	**1a**	**2c**	**3c**	quant.
4	**1a**	**2d**	**3d**	84
5	**1b**	**2a**	**3e**	quant.
6	**1b**	**2c**	**3f**	88

Table 2. The Reaction of 2-Propynyl Ethers

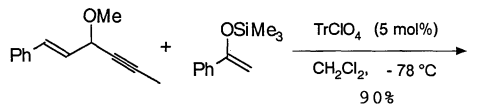
2-Propynyl ether	Silyl enol ether	Product	Yield/%	6/7
4a	**5a**	**6a**	90	100/ 0
4a	**5b**	**6b**	62	100/ 0
4a	**5c**	**6c**+**7c**	97	56/44
4a	**5d**	**6d**+**7d**	90	44/56
4b	**5a**	**6e**+**7e**	88	93/ 7
4b	**5d**	**6f** +**7f**	quant.	19/81
4c	**5a**	**6g**+**7g**	96	90/10
4c	**5d**	**6h**+**7h**	quant.	28/72



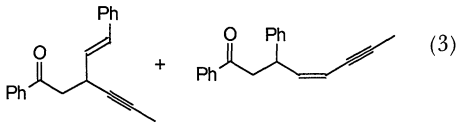
4 **5**



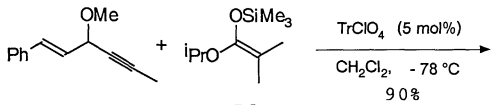
6 **7** (2)



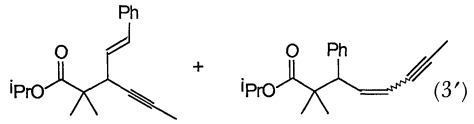
8 **5a**



9 (56:44) **10** (3)



8 **5d**



11 (91:9) **12** (*Z*:*E*=4:1) (3′)

4a: R¹=Ph, R²=H, R³=Me, R′=Me
4b: R¹=R²=$(CH_2)_5$, R³=Ph, R′=Ac
4c: R¹=Ph$(CH_2)_2$, R²=Me, R³=Ph
5a: R⁴=Ph, R⁵=H
5b: R⁴=Me, R⁵=H
5c: R⁴=MeO, R⁵=Me_2
5d: R⁴=*i*-PrO, R⁵=Me_2
6a: R¹=Ph, R²=H, R³=Me, R⁴=Ph, R⁵=H
6b: R¹=Ph, R²=H, R³=Me, R⁴=Me, R⁵=H
6c: R¹=Ph, R²=H, R³=Me, R⁴=MeO, R⁵=Me_2
6d: R¹=Ph, R²=H, R³=Me, R⁴=*i*-PrO, R⁵=Me_2
6e: R¹=R²=$(CH_2)_5$, R³=Ph, R⁴=Ph, R⁵=H
6f: R¹=R²=$(CH_2)_5$, R³=Ph, R⁴=*i*-PrO, R⁵=Me_2
6g: R¹=Ph$(CH_2)_2$, R²=Me, R³=Ph, R⁴=Ph, R⁵=H
6h: R¹=Ph$(CH_2)_2$, R²=Me, R³=Ph, R⁴=*i*-PrO, R⁵=Me_2
7c: R¹=Ph, R²=H, R³=Me, R⁴=MeO, R⁵=Me_2
7d: R¹=Ph, R²=H, R³=Me, R⁴=*i*-PrO, R⁵=Me_2
7e: R¹=R²=$(CH_2)_5$, R³=Ph, R⁴=Ph, R⁵=H
7f: R¹=Ph$(CH_2)_2$, R²=Me, R³=Ph, R⁴=*i*-PrO, R⁵=Me_2
7g: R¹=Ph$(CH_2)_2$, R²=Me, R³=Ph, R⁴=Ph, R⁵=H
7h: R¹=Ph$(CH_2)_2$, R²=Me, R³=Ph, R⁴=*i*-PrO, R⁵=Me_2

(5 mol%), the reaction regioselectively proceeded at −78 °C to produce the corresponding acetylenic ketone **6a** in 90% yield. No other regioisomers were obtained in this reaction. In contrast, the reaction of **4a** with ketene silyl acetal derived from methyl isobutyrate **5c** proceeded smoothly at −78 °C to give a mixture of regioisomers **6c** and **7c** (97% yield, **6c**/**7c**=56/44).

Several examples of the reaction between 2-propynyl ethers and silyl enol ethers of ketones or ketene silyl acetals are demonstrated in Table 2. In the case of silyl enol ethers derived from ketones, the corresponding acetylenic ketones **6** were obtained with high regioselectivities. On the other hand, allenic ester **7** was predominantly produced by using ketene silyl acetals as nucleophiles. It is noted that the regioselectivities depend on the kinds of silyl nucleophiles, silyl enol ethers derived from ketones and ketene silyl acetals, probably due to the hard and soft character of them.

Thirdly, the reaction of allyl 2-propynyl ether **8** was investigated. In this case, silyl enol ether of acetophenone **5a** reacted with **8** to give a mixture of acetylenic ketone **9** and conjugated enyne **10**, whereas ketene silyl acetal derived from isopropyl isobutyrate **5d** regioselectively reacted with **8** to produce acetylenic ester **11** in high yield. It is noted again that regioselectivities of the reaction of a silyl enol ether derived from a ketone and a ketene silyl acetal with the same ether **8** are markedly different.

Thus, trityl perchlorate effectively catalyzed the reaction of some acetylenic compounds such as ethynyl vinyl ketone or 2-propynyl ether derivatives with silyl enol ethers to afford the corresponding adducts regioselectively in high yields. Marked difference in the regioselectivities between two silyl

nucleophiles, silyl enol ethers of ketones and ketene silyl acetals, is a quite interesting problem in terms of the hard and soft character of the silyl enolates in the trityl salt-mediated reaction, and we are currently investigating further development of this reaction including synthetic utilities as well as theoretical approach.

Experimental

IR spectra were recorded on JASCO IRA-2 infrared spectrophotometer. ^{1}H NMR spectra were recorded on a Hitachi R-24B, R-1100, JEOL JNM-GSX-400 spectrometer and ^{13}C NMR on Bruker AM 500, JEOL JNM-GSX-400 spectrometer. Gas chromatographic analyses were conducted on a Shimizu GC-9A instrument (OV-101). Law and High resolution mass spectra were recorded on HITACHI M80, 80 A mass spectrometer. Column chromatography was performed on silica gel 60 (Merck) or Wakogel B5F.

Trityl perchlorate was prepared by the method of Dauben et al.[6] and purified by that of Kochetkov et al.[7] Ethynyl vinyl ketone and 2-propynyl ether derivatives were synthesized according to standard procedures.

1-Phenyl-1-hexen-4-yne-3-one (1a). IR(neat) 2200, 1630 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=2.05 (s, 3H), 6.55 (d, 1H, J=16.0 Hz), 7.20—7.55 (m, 5H), 7.60 (d, 1H, J=16.0 Hz). Found: m/z 170.0730. Calcd for $C_{12}H_{10}O$: M, 170.0730.

6-Phenyl-2-hexen-5-yne-4-one (1b). IR(neat) 2200, 1645, 1620 cm^{-1}; ^{1}H NMR (CCl_4) δ=1.97 (d, 3H, J=6.0 Hz), 6.20 (d, 1H, J=15.0 Hz), 6.85—7.70 (m, 6H). Found: m/z 170.0726. Calcd for $C_{12}H_{10}O$: M, 170.0731.

1-Methoxy-1-phenyl-2-butyne (4a). IR(neat) 2200 cm^{-1}; ^{1}H NMR (CCl_4) δ=1.90 (d, 3H, J=1.8 Hz), 3.30 (s, 3H), 4.95 (d, 1H, J=1.8 Hz), 7.15—7.45 (m, 5H). Found: m/z 160.0888. Calcd for $C_{11}H_{12}O$: M, 160.0888.

1-Acetoxy-1-(phenylethynyl)cyclohexane (4b). IR(neat) 2269 cm^{-1}; ^{1}H NMR (CCl_4) δ=1.40—2.40 (m, 10H), 2.05 (s, 3H), 7.15—7.50 (m, 5H). Found: m/z 242.1293. Calcd for $C_{16}H_{18}O_2$: M, 242.1305.

1-Phenyl-3-acetoxy-3-methyl-5-phenyl-1-pentyne (4c). IR (neat) 2240, 1750 cm^{-1}; ^{1}H NMR (CCl_4) δ=1.80 (s, 3H), 2.00 (s, 3H), 2.10—2.35 (m, 2H), 2.60—3.00 (m, 2H), 7.10—7.50 (m, 10H). Found: m/z 292.1488. Calcd for $C_{20}H_{20}O_2$: M, 292.1462.

1-Phenyl-3-methoxy-1-hexene-4-yne (8). IR(neat) 2250, 1605 cm^{-1}; ^{1}H NMR (CCl_4) δ=1.95 (d, 3H, J=2.0 Hz), 3.30 (s, 3H), 4.55 (m, 1H), 6.10 (dd, 1H, J=14.0, 6.0 Hz), 6.65 (d, 1H, J=14.0 Hz), 7.20 (m, 5H). Found: m/z 186.1046. Calcd for $C_{13}H_{14}O$: M, 186.1049.

The Reaction of Ethynyl Vinyl Ketone Derivatives with Silyl Enol Ethers. A typical experimental procedure is described for the reaction of 1-phenyl-1-hexene-4-yne-3-one (**1a**) with *t*-butyldimethylsilyl enol ether of acetophenone (**2a**); to a dichloromethane solution of trityl perchlorate (5 mol%, 1 ml) was added a mixture of **1a** (0.4 mmol) and **2a** (0.44 mmol) in dichloromethane (2 ml) at −78 °C. After stirring at this temperature for an appropriate time (1—2 h), the reaction was quenched with aqueous sodium hydrogen carbonate. The aqueous layer was extracted with dichloromethane and the combined organic layer was dried. Then the solvent was removed under reduced pressure and the residue was purified by silica gel chromatography to afford the corresponding adduct, 5-*t*-butyldimethylsiloxy-1,3-diphenyl-4-octen-6-yn-1-one (**3a**, 94%); IR(neat) 2220, 1670 cm^{-1}; ^{1}H NMR (CCl_4) δ=0.00 (s, 6H), 0.83 (s, 9H), 1.83 (s, 3H), 2.97 (dd, 1H, J=15.5, 7.5 Hz), 3.27 (dd, 1H, J=15.5, 6.5 Hz), 4.00—4.40 (m, 1H), 5.20 (d, 1H, J=11.0 Hz), 6.97—7.28 (m, 3H), 7.00 (m, 5H), 7.60—7.95 (m, 2H). Found: m/z 404.2159. Calcd for $C_{26}H_{32}O_2Si$: M, 404.2169.

6-*t*-Butyldimethylsiloxy-4-phenyl-5-nonen-7-yne-2-one (3b). IR(neat) 2220, 1680 cm^{-1}; ^{1}H NMR (CCl_4) δ=0.03 (s, 6H), 0.85 (s, 9H), 1.88 (s, 3H), 1.96 (s, 3H), 2.5—2.7 (m, 2H), 3.75—4.20 (m, 1H), 5.03 (d, 1H, J=12.0 Hz), 7.00 (m, 5H).

4-*t*-Butyldimethylsiloxy-6,8-diphenyl-7-methyl-4-octanen-2-yne-8-one (3c). IR(neat) 2220, 1680 cm^{-1}; ^{1}H NMR ($CDCl_3$) (major isomer) δ=0.14 (s, 3H), 0.16 (s, 3H), 0.91 (s, 9H), 1.26 (d, 3H, J=6.9 Hz), 1.91 (s, 3H), 3.90 (dq, 1H, J=9.3, 6.9 Hz), 4.21 (dd, 1H, J=10.8, 9.3 Hz), 5.34 (d, 1H, J=10.8 Hz), 7.02—7.07 (m, 1H), 7.14—7.22 (m, 4H), 7.36—7.40 (m, 2H), 7.45—7.50 (m, 1H), 7.82—7.85 (m, 2H); (minor isomer) δ=−0.14 (s, 3H), 0.01 (s, 3H), 0.79 (s, 9H), 1.04 (d, 3H, J=6.9 Hz), 2.01 (s, 3H), 3.82—3.92 (m, 1H), 4.03 (dd, 1H, J=10.3, 9.0 Hz), 5.39 (d, 1H, J=10.3 Hz), 7.50—7.56 (m, 1H), 7.95—7.98 (m, 2H); ^{13}C NMR ($CDCl_3$) (major isomer) δ=75.7, 89.8, 203.2. Found: m/z 418.2324. Calcd for $C_{27}H_{34}O_2Si$: M, 418.2326. Diastereomer ratio =88/12, determined by ^{1}H NMR. Relative configuration assignment was not made.

Methyl 5-*t*-Butyldimethylsiloxy-2,2-dimethyl-3-phenyl-4-octen-6-ynoate (3d). IR(neat) 2220, 1740 cm^{-1}; ^{1}H NMR (CCl_4) δ=0.07 (s, 6H), 0.84 (s, 9H), 0.97 (s, 6H), 1.81 (s, 3H), 3.31 (s, 3H), 3.60 (d, 1H, J=12.0 Hz), 5.30 (d, 1H, J=12.0 Hz), 6.84 (m, 5H). Found: m/z 386.2271. Calcd for $C_{23}H_{34}O_3Si$: M, 386.2275.

5-*t*-Butyldimethylsiloxy-1,7-diphenyl-3-methyl-4-hepten-7-yne-1-one (3e). IR(neat) 2220, 1730 cm^{-1}; ^{1}H NMR (CCl_4) δ=0.06 (s, 6H), 0.87 (s, 9H), 1.01 (d, 3H, J=7.0 Hz), 2.7—2.9 (m, 2H), 2.95—3.40 (m, 1H), 5.06 (d, 1H, J=12.0 Hz), 7.11 (m, 5H), 7.0—7.25 (m, 3H), 7.69—7.95 (m, 2H). Found: m/z 404.2165. Calcd for $C_{26}H_{32}O_2Si$: M, 404.2169.

5-*t*-Butyldimethylsiloxy-2,3-dimethyl-1,7-diphenyl-4-hepten-6-yne-1-one (3f). IR(neat) 2190, 1670 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=0.24 (s, 6H), 0.97 (s, 9H), 1.05 (d, 3H, J=6.8 Hz), 1.21 (d, 3H, J=6.8 Hz), 3.12—3.22 (m, 1H), 3.41 (quint, 1H, J=6.8 Hz), 5.18 (d, 1H, J=10.8 Hz), 7.28—7.63 (m, 8H), 7.95—8.00 (m, 2H); ^{13}C NMR ($CDCl_3$) δ=85.1, 92.4, 204.0. Found: m/z 418.2319. Calcd for $C_{27}H_{34}O_2Si$: M, 418.2325. Only one diastereomer was observed. Relative configuration assignment was not made.

The Reaction of 2-Propynyl Ether Derivatives with Silyl Enol Ethers. A typical experimental procedure is described for the reaction of a 1-methoxy-1-phenyl-2-butyne (**4a**) with 1-phenyl-1-trimethylsiloxyethene (**5a**); to a dichloromethane solution of trityl perchlorate (5 mol%, 1 ml) was added a mixture of **4** (0.4 mmol) and **5** (0.44 mmol) in dichloromethane (2 ml) at −78 °C. After stirring at this temperature for an appropriate time (2—3 h), the reaction was quenched with aqueous sodium hydrogen carbonate. After the same work up procedure, the desired acetylenic ketone, 1,3-diphenyl-4-hexyn-1-one (**6a**) was obtained (90%); IR (neat) 1685 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=1.79 (d, 3H, J=2.4 Hz), 3.27 (dd, 1H, J=16.8, 6.1 Hz), 3.52 (dd, 1H, J=16.8, 8.1 Hz), 4.30—4.42 (m, 1H), 7.15—7.60 (m, 8H), 7.90—8.00 (m, 2H); ^{13}C NMR ($CDCl_3$) δ=78.7, 80.2, 197.3. Found: m/z 248.1196. Calcd for $C_{18}H_{16}O$: M, 248.1200.

In the reactions of **4a** with **5c**, **4b** with **5a**, **5d**, **4c** with **5a**, **5d**, and **8** with **5a**, **5d**, the products were a mixture of regioisomers. The regioisomer ratios were determined by GC, ^{1}H NMR and/or ^{13}C NMR. In the reaction of **4a** with **5d**, the regioisomers were separated by TLC (silica gel).

4-Phenyl-5-heptyne-2-one (6b). IR(neat) 1715 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=1.82 (d, 3H, J=2.4 Hz), 2.13 (s, 3H), 2.75 (dd, 1H, J=16.2, 6.1 Hz), 2.91 (dd, 1H, J=16.2, 8.3 Hz), 4.05—4.20 (m, 1H), 7.15—7.43 (m, 5H). ^{13}C NMR ($CDCl_3$) δ=78.7, 79.8, 206.3. Found: m/z 186.1028. Calcd for $C_{13}H_{14}O$: M, 186.1043.

Methyl 2,2-Dimethyl-3-phenyl-4-hexynoate (6c) and Methyl 5-Phenyl-2,2,3-trimethyl-3,4-pentadienoate (7c). IR($CHCl_3$) 1720 cm^{-1}. Found: m/z 230.1303. Calcd for $C_{15}H_{18}O_2$: M, 230.1305. **6c** ^{1}H NMR ($CDCl_3$) δ=1.09 (s, 3H), 1.30 (s, 3H), 1.86 (d, 3H, J=2.4 Hz), 3.64 (s, 3H), 4.07 (q, 1H, J=2.4 Hz), 7.15—7.40 (m, 5H); ^{13}C NMR ($CDCl_3$) δ=78.1, 79.7, 177.0. **7c** ^{1}H NMR ($CDCl_3$) δ=1.36 (s, 3H), 1.39 (s, 3H), 1.79 (d, 3H, J=2.8 Hz) 3.71 (s, 3H), 6.19 (q, 1H, J=2.8 Hz); ^{13}C NMR ($CDCl_3$) δ=176.7, 202.8.

Isopropyl 2,2-Dimethyl-3-phenyl-4-hexynoate (6d). IR(neat) 1720 cm^1; ^{1}H NMR ($CDCl_3$) δ=1.07 (s, 3H), 1.16 (d, 3H, J=6.2 Hz), 1.24 (d, 3H, J=6.2 Hz), 1.25 (s, 3H), 1.84 (d, 3H, J=2.5 Hz), 4.07 (q, 1H, J=2.5 Hz), 4.97 (hept., 1H, J=6.2 Hz), 7.10—7.35 (m, 5H). Found: m/z 258.1621. Calcd for $C_{17}H_{22}O_2$: M, 258.1618.

Isopropyl 5-Phenyl-3,4-pentadienoate (7b). IR($CHCl_3$) 1715 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=1.26 (d, 3H, J=6.2 Hz), 1.28 (d, 3H, J=6.2 Hz), 1.34 (s, 3H), 1.35 (s, 3H), 1.79 (d, 3H, J=2.8 Hz), 5.04 (hept., 1H, J=6.2 Hz), 6.17 (q, 1H, J=2.8 Hz), 7.25—7.35 (m, 5H); ^{13}C NMR ($CDCl_3$) δ=175.6, 203.0. Found: m/z 258.1634. Calcd for $C_{17}H_{22}O_2$: M, 258.1618.

1-Phenyl-2-[1-(2-phenylethynyl)]cyclohexyl-1-ethanone(6e) and 4-Cyclohexylidene-1,4-diphenyl-3-butene-1-one (7e). IR(neat) 2210, 1685, 1665 cm^{-1}; Found: m/z 302.1661. Calcd for $C_{22}H_{22}O$: M, 302.1653. **6e** ^{1}H NMR ($CDCl_3$) δ=1.21 (tq, 1H, J=12.6, 3.3 Hz), 1.48 (dt, 2H, J=12.6, 3.3 Hz), 1.60—1.83 (m, 5H), 2.02 (bd, 2H, J=12.6 Hz), 3.13 (s, 2H), 7.10—7.15 (m, 2H), 7.16—7.22 (m, 3H), 7.40—7.44 (m, 2H), 7.50—7.53 (m, 1H), 8.00—8.04 (m, 2H); ^{13}C NMR ($CDCl_3$) δ=84.5, 94.0, 198.4. **7e** ^{1}H NMR ($CDCl_3$) δ=4.00 (s, 2H), 7.97—8.00 (m, 2H); ^{13}C NMR ($CDCl_3$) δ=198.1, 199.8.

Isopropyl 2-methyl-2-[1-(2-phenylethynyl)]cyclohexylpropanoate(6f) and Isopropyl 4-cyclohexylidene-2,2-dimethyl-3-phenyl-3-butenoate (7f). IR(neat) 1720 cm^{-1}; Found: m/z 312.2090. Calcd for $C_{21}H_{28}O_2$: M, 312.2087. **6f** ^{1}H NMR ($CDCl_3$) δ=1.24 (d, 6H, J=6.3 Hz), 1.34 (s, 6H), 5.01 (hept, 1H, J=6.3 Hz); ^{13}C NMR ($CDCl_3$) δ=85.4, 93.0, 175.5. **7f** ^{1}H NMR ($CDCl_3$) δ=1.11 (d, 6H, J=6.3 Hz), 1.39 (s, 6H), 1.50—1.75 (m, 6H), 2.15—2.30 (m, 4H), 4.96 (hept., 1H, J=6.3 Hz), 7.12—7.43 (m, 5H); ^{13}C NMR ($CDCl_3$) δ=177.0, 198.8.

1,4-Diphenyl-2-methyl-2-(2-phenethyl)-3-butyn-1-one (6g) and 5-Methyl-1,3,7-triphenyl-3,4-heptadien-1-one (7g). IR (neat) 2230, 2180, 1690, 1675 cm^{-1}; Found: m/z 352.1820. Calcd for $C_{26}H_{24}O$: M, 352.1825. **6g** ^{1}H NMR ($CDCl_3$) δ=1.52 (s, 3H), 1.80—2.30 (m, 2H), 2.90 (m, 2H), 3.09 (d, 1H, J=14.7 Hz), 3.37 (d, 1H, J=14.7 Hz), 7.05—7.30 (m, 10H), 7.35—7.59 (m, 3H), 7.99—8.04 (m, 2H); ^{13}C NMR ($CDCl_3$) δ=83.1, 94.7, 198.3. **7g** ^{1}H NMR ($CDCl_3$) δ=1.57 (s, 3H), 1.80—2.30 (m, 2H), 2.61 (t, 2H, J=8.0 Hz), 3.88 (d, 1H, J=15.1 Hz), 3.96 (d, 1H, J=15.1 Hz), 7.92—7.96 (m, 2H); ^{13}C NMR ($CDCl_3$) δ=197.9, 203.2.

Isopropyl 3-(2-Phenetyl)-2,2,3-trimethyl-4-hexynoate(6h) and Isopropyl 3,7-Diphenyl-2,2,5-trimethyl-3,4-heptadienoate (7h). IR(neat) 1720 cm^{-1}; Found: m/z 362.2227. Calcd for $C_{25}H_{30}O_2$: M, 362.2227. **6h** ^{1}H NMR ($CDCl_3$) δ=1.21 (d, 3H, J=6.3 Hz), 1.22 (d, 3H, J=6.3 Hz), 1.36 (s, 6H), 1.41 (s, 3H), 1.75 (dt, 1H, J=12.8, 4.5 Hz), 2.04 (dt, 1H, J= 12.8, 4.5 Hz), 2.98 (dt, 1H, J=12.8, 4.5 Hz); ^{13}C NMR ($CDCl_3$) δ=83.7, 93.7, 175.3. **7h** ^{1}H NMR ($CDCl_3$) δ=1.10 (d, 3H, J=6.3 Hz), 1.11 (d, 3H, J=6.3 Hz), 1.37 (s, 6H), 1.84 (s, 3H), 2.32—2.44 (m, 2H), 2.72—2.89 (m, 2H), 4.92—5.06 (m, 1H), 7.12—7.45 (m, 10H); ^{13}C NMR ($CDCl_3$) δ=176.8, 201.6.

1-Phenyl-3-[(*E*)-styryl]-4-hexyn-1-one (9). IR(neat) 2220, 1680 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=1.83 (d, 3H, J=2.4 Hz), 3.20 (dd, 1H, J=16.8, 7.1 Hz), 3.37 (dd, 1H, J=16.8, 6.9 Hz), 3.92—3.98 (m, 1H), 6.23 (dd, 1H, J=15.7, 6.2 Hz), 6.73 (dd, 1H, J=15.7, 0.5 Hz), 7.17—7.24 (m, 1H), 7.26—7.30 (m, 2H); 7.33—7.37 (m, 2H), 7.43—7.49 (m, 2H), 7.53—7.58 (m, 1H), 7.90—8.00 (m, 2H); ^{13}C NMR ($CDCl_3$) δ=76.2, 91.3, 198.0. Found: m/z 274.1360. Calcd for $C_{20}H_{18}O$: M, 274.1356.

(*Z*)-1,3-Diphenyl-4-octen-6-yne-1-one (10). IR(neat) 2210, 1680 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=1.90 (d, 3H, J=2.4 Hz), 3.37 (dd, 1H, J=16.1, 7.2 Hz), 3.50 (dd, 1H, J=16.1, 7.2 Hz), 4.66 (dt, 1H, J=10.0, 7.2 Hz), 5.47 (dq, 1H, J=10.0, 2.4 Hz), 5.97 (t, 1H, J=10.0 Hz), 7.16—7.25 (m, 1H), 7.27—7.32 (m, 4H), 7.42—7.46 (m, 2H,), 7.51—7.56 (m, 1H), 7.93—7.97 (m, 2H); ^{13}C NMR ($CDCl_3$) δ=79.0, 79.4, 197.4. Found: m/z 274.1365. Calcd for $C_{20}H_{18}O$: M, 274.1357.

Isopropyl 2,2-dimethyl-3-[(*E*)-styryl]-4-hexynoate (11) and (*Z*)-and (*E*)-Isopropyl 2,2-dimethyl-3-phenyl-4-octen-6-ynoate (12*Z*,*E*). IR(neat) 1720 cm^{-1}; Found: m/z 284.1766. Calcd for $C_{19}H_{24}O_2$: M, 284.1775. **11** ^{1}H NMR ($CDCl_3$) δ=1.19 (s, 3H), 1.22 (d, 3H, J=6.3 Hz), 1.24 (d, 3H, J=6.3 Hz), 1.29 (s, 3H), 1.86 (d, 3H, J=2.4 Hz), 3.56—3.62 (m, 1H), 5.02 (hept, 1H, J=6.3 Hz), 6.07 (dd, 1H, J=15.6, 7.30 Hz), 6.62 (d,1 H, J=15.6 Hz), 7.15—7.40 (m, 5H); ^{13}C NMR ($CDCl_3$) δ=80.5, 176.0. **12Z** ^{1}H NMR ($CDCl_3$) δ=1.97 (d, 3H, J=2.4 Hz), 4.19 (d, 1H, J=10.6 Hz), 5.55 (dq, 1H, J=10.6, 2.4 Hz), 6.29 (t, 1H, J=10.6 Hz); ^{13}C NMR ($CDCl_3$) δ=76.3, 96.1, 176.3. **12E** ^{1}H NMR ($CDCl_3$) δ=1.91 (d, 3H, J=2.3 Hz), 5.48 (ddq, 1H, J=15.7, 2.3, 0.8 Hz), 6.41 (dd, 1H, J=15.7, 9.6 Hz); ^{13}C NMR ($CDCl_3$) δ=85.5, 91.0, 176.2.

References

1) S. Kobayashi, S. Matsui, and T. Mukaiyama, *Chem. Lett.*, **1988**, 1491.

2) S. Kobayashi, M. Murakami, and T. Mukaiyama, *Chem. Lett.*, **1985**, 953; T. Mukaiyama, M. Tamura, and S. Kobayashi, *ibid.*, **1986**, 1017; 1817.

3) M. Hayashi, A. Inubushi, and T. Mukaiyama, *Bull. Chem. Soc. Jpn.*, **61**, 4037 (1988).

4) T. Mukaiyama, H. Nagaoka, M. Ohshima, and M. Murakami, *Chem. Lett.*, **1986**, 1009.

5) M. Murakami, K. Kato, and T. Mukaiyama, *Chem. Lett.*, **1987**, 1167.

6) H. J. Dauben, Jr., L. R. Honnen, and K. M. Harman, *J. Org. Chem.*, **25**, 1442 (1960).

7) N. K. Kochetkov, V. I. Betaneli, M. V. Ovchinnikov, and L. V. Backinowsky, *Tetrahedron*, **37**, *Suppl.* No. 9, 149 (1981).