with water (25 mL), dried (Na_2SO_4), and evaporated leaving **7** as a yellow oil (0.110 g, 97%): ^1H NMR ($CDCl_3$) δ 1.17 (d, J = 7 Hz, 6 H), 2.24 (s, 3 H), 3.09 (septet, 1 H), 4.75 (b s, 1 H), 6.61–7.19 (m, 3 H). Compound **5** (0.250 g) underwent hydrolysis to give **2** (0.185 g, 96%) and **7** (0.069 g, 92%). Hydrolysis of compound **6** (0.250 g) gave **2** (0.205 g, 95%) and **7** (0.048 g, 87%).

Method B: Tri-*o*-thymotide (1) by the Action of $POCl_3$ on 2 at 100 °C for 2 h. A mixture of **2** (19.4 g, 0.10 mol) and freshly distilled $POCl_3$ (10.0 mL, 0.1 mol) was heated in oil bath at ~100 °C with stirring for 2 h. The cooled viscous mixture was added slowly, with stirring, to cold water (200 mL) over 30 min. The aqueous mixture was extracted with ethyl acetate (200 mL). The organic layer was separated and washed with $NaHCO_3$ (5%, 100 mL) and water (100 mL), dried (Na_2SO_4), and evaporated to give a yellow solid. Recrystallization from boiling ethanol yielded the ethanol complex of **1** (14.8 g, 84%) as colorless crystals (mp 175–180 °C). The ethanol complex of **1** was recrystallized by extraction with methanol (500 mL) in a Soxhlet apparatus (approximately 10 g is extracted per 10 h). The cooled methanol extracts were filtered to give solvent-free **1**, mp 217–8 °C dec.[20] The yield of solvent-free **1** is 80%.

Method C: Tri-*o*-thymotide (1) by the Action of $POCl_3$ on 2 at 50 °C for 48 h. A higher yield of **1** (93%, ethanol complex) was obtained when the reaction mixture using the above conditions was heated at 50 °C for 48 h. The yield of solvent-free **1** was 89%.

The R_f values of the following compounds, **17–20**, were determined in 10% ethyl acetate–hexane.

Tri-3-ethyl-6-methylsalicylide (17): R_f = 0.19; yield 27% (method A), 64% (method B); mp 228–9 °C (benzene); IR (KBr) 1743 (C=O), 1764 cm^{-1} (C=O): MS 486 (M^+, $C_{30}H_{30}O_6$), 324, 162, 134; ^1H NMR ($CDCl_3$) δ 1.22 (t, J = 7.5 Hz, 9 H), 2.59 (s, 9 H), 2.65 (q, J = 7 Hz, 6 H), 6.70 (d, J = 8 Hz, 3 H), 7.22 (d, J = 8 Hz, 3 H). Anal. Calcd: C, 74.06; H, 6.22. Found: C, 73.95; H, 6.36.

Tri-3-(2-propyl)salicylide (18): R_f = 0.30; yield 31% (method A), 76% (method B); mp 285–6 °C (ethanol); IR (KBr) 1733 cm^{-1} (C=O): MS 486 (M^+, $C_{30}H_{30}O_6$), 324, 162, 134; ^1H NMR ($CDCl_3$) δ 1.16, 1.27 (2 d, J = 8 Hz, 18 H), 3.29 (septet, J = 7 Hz, 3 H), 7.34 (t, J = 7 Hz, 3 H), 7.57 (d, J = 7 Hz, 3 H), 8.28 (d, J = 7 Hz, 3 H). Anal. Calcd: C, 74.06; H, 6.22. Found: C, 74.15; H, 6.20.

Tri-3-(1-propyl)salicylide (19): R_f = 0.29; yield 22% (method A), 55% (method B); mp 204–6 °C (ethyl acetate): IR (KBr) 1743 (C=O), 1759 cm^{-1} (C=O): MS 486 (M^+, $C_{30}H_{30}O_6$), 324, 162, 134; ^1H NMR ($CDCl_3$) δ 0.93 (t, J = 8 Hz, 9 H), 1.65 (sextet, J = 8 Hz, 6 H), 2.61 (t, J = 8 Hz, 6 H), 7.28 (t, J = 7 Hz, 3 H), 7.49 (d, J = 7 Hz, 3 H), 8.27 (d, J = 8 Hz, 3 H). Anal. Calcd: C, 74.06; H, 6.22. Found: C, 73.81; H, 6.18.

Tri-3-methyl-6-(2-propyl)salicylide (20): R_f = 0.26; yield 29% (method A), 65% (method B); mp 259–260 °C (*n*-hexane) [lit.[26] mp 247 °C]; IR (KBr) 1761 cm^{-1} (C=O); MS 528 (M^+, $C_{33}H_{36}O_6$), 352, 176; ^1H NMR ($CDCl_3$) δ 1.29 (t, J = 8 Hz, 18 H), 2.23 (s, 9 H), 3.18 (septet, J = 7 Hz, 3 H), 7.25 (d, J = 8 Hz, 3 H), 7.39 (d, J = 8 Hz, 3 H). Anal. Calcd: C, 74.98; H, 6.86. Found: C, 74.86; H, 6.69.

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Registry No. 1, 4399-52-4; 1·0.5EtOH, 55217-06-6; 2, 548-51-6; 3, 50397-25-6; 4, 134153-43-8; 5, 134153-44-9; 6, 134153-45-0; 7, 89-83-8; 13, 20717-15-1; 14, 7053-88-5; 15, 22890-52-4; 16, 4389-53-1; 17, 134153-46-1; 18, 134153-47-2; 19, 134153-48-3; 20, 2281-45-0.

Selenium-Mediated Conversion of Alkynes into α-Dicarbonyl Compounds

Marcello Tiecco,* Lorenzo Testaferri, Marco Tingoli, Donatella Chianelli, and Donatella Bartoli

Istituto di Chimica Organica, Facoltà di Farmacia, Università di Perugia, 06100 Perugia, Italy

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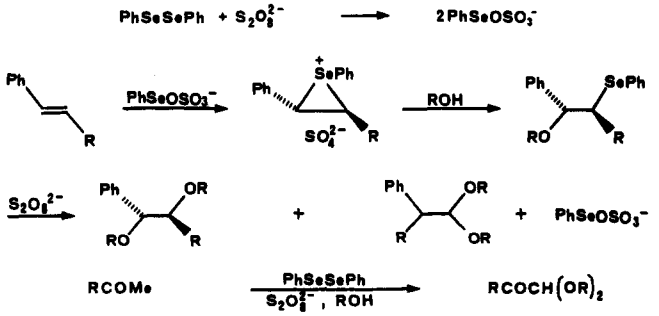
The reaction of terminal and internal alkynes with diphenyl diselenide and ammonium peroxydisulfate in methanol proceeds smoothly to give α-keto acetals and α-keto ketals, respectively. This one-pot procedure is suggested to proceed through the initial formation of phenylselenenyl sulfate, a strong electrophilic reagent which effects the methoxyselenenylation of the alkynes. The addition products thus formed suffer methoxydeselenenylation giving the observed products and regenerating the phenylselenenylating agent. In some cases the reaction can be carried out using only catalytic amounts of diphenyl diselenide. The same reaction carried out in the presence of water or of ethylene glycol gives the unprotected or the diprotected α-dicarbonyl compounds, respectively.

We have recently introduced the use of ammonium peroxydisulfate to convert diphenyl diselenide into a strongly electrophilic phenylselenenylating agent. We suggested that from this very simple reaction phenylselenenyl sulfate is produced (Scheme I). Since the sulfate is a strong electron-withdrawing group, phenylselenenyl sulfate behaves as a phenylselenium cation synthetic equivalent which easily adds to unsaturated compounds. Moreover, the sulfate anion is a very weak nucleophile and therefore it does not interfere with other nucleophiles that can be added to the reaction mixture or that can be present in the molecule of the unsaturated compounds used as substrates. This simple method, which presents several advantages over the other previously described procedures,[1] has been successfully used to effect the methoxy-,[2] hydroxy-,[2] and amidoselenenylation[3] of alkenes. Similarly, several selenium-induced ring-closure reactions have also been carried out. Thus, starting from alkenes containing

Scheme I



(1) Tiecco, M.; Testaferri, L.; Tingoli, M.; Chianelli, D.; Bartoli, D. *Tetrahedron Lett.* **1989**, *30*, 1417.

(2) Tiecco, M.; Testaferri, L.; Tingoli, M.; Bartoli, D. *Tetrahedron* **1989**, *45*, 6819.

(3) Tiecco, M.; Testaferri, L.; Tingoli, M.; Chianelli, D.; Bartoli, D. *Tetrahedron* **1988**, *44*, 2261.

0022-3263/91/1956-4529$02.50/0

Table I. Conversion of Alkynes 1 into α-Keto Acetals 2 or α-Dicarbonyl Compounds 3[a] (eq 2)

substrate	reaction time (h)	product	yield[b] (%)
1a, PhC≡CH	1	**2a**, $PhCOCH(OMe)_2$	87[c] (75)[d]
1b, $PhCH_2C{\equiv}CH$	2	**2b**, $PhCH_2COCH(OMe)_2$	56[c]
1c, $C_4H_9C{\equiv}CH$	2	**2c**, $C_4H_9COCH(OMe)_2$	51[c]
1d, $C_6H_{13}C{\equiv}CH$	2	**2d**, $C_6H_{13}COCH(OMe)_2$	67[c] (42)[d]
1e, $HOOCCH_2CH_2C{\equiv}CH$	2	**2e**, $MeOOCCH_2CH_2COCH(OMe)_2$	88 (80)[d]
1f, $C_3H_7C{\equiv}CC_3H_7$	1.5	**2f**, $C_3H_7COC(OMe)_2C_3H_7$	51[c]
1g, PhC≡CPh	1.5	**2g**, $PhCOC(OMe)_2Ph$	84[e]
1h, $PhC{\equiv}CC_6H_4CMe_3$-*m*	2	**2h**, $PhCOC(OMe)_2C_6H_4CMe_3$-*m* + $PhC(OMe)_2COC_6H_4CMe_3$-*m*	78[e,f]
1i, $PhC{\equiv}CC_6H_4Br$-*o*	2	**2i**, $PhCOC(OMe)_2C_6H_4Br$-*o*	70[e]
1j, $PhC{\equiv}CC_6H_4F$-*p*	2	**2j**, $PhCOC(OMe)_2C_6H_4F$-*p* + $PhC(OMe)_2COC_6H_4F$-*p*	71[e,f]

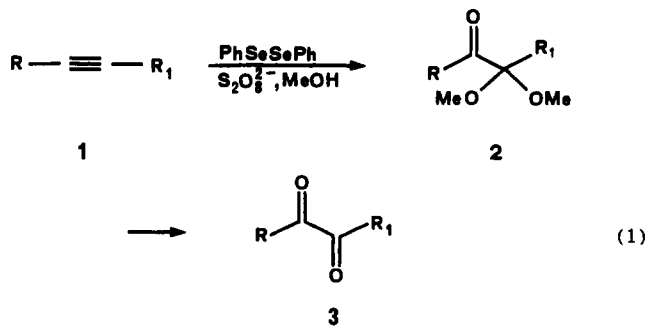
[a] The reactions were run in refluxing methanol. [b] Based on the quantity of the alkyne employed and calculated on the isolated products after column chromatography. [c] Small amounts of other products were also isolated (see text). [d] Reaction carried out with 10% PhSeSePh for 6–12 h. $PhCO_2Me$ (10%) and $C_6H_{13}CO_2Me$ (21%) were also isolated from the reactions of **1a** and **1d**, respectively. [e] 5–10% of ArCOCOAr′ was also present. [f] Calculated from the ArCOCOAr′ obtained after treatment with water and *p*-toluenesulfonic acid.

different types of internal nucleophiles, the phenylselenoetherification, phenylselenolactonization, and phenylselenoamination processes have all been realized with excellent results.[4]

In the course of our investigations on the alkoxyselenenylation of alkenes,[2] it was also observed that the use of an excess of ammonium peroxydisulfate gave rise to the deselenenylation of the addition products to afford dialkoxyalkanes, regenerating the phenylselenium electrophilic species. It was thus possible to effect the conversion of alkenes into dialkoxyalkanes using only catalytic amounts of diphenyl diselenide[5] (Scheme I). This interesting procedure has been recently used to obtain the conversion of several types of methyl ketones into α-keto acetals[6] (Scheme I).

Thus, in a very simple way, using an excess of ammonium peroxydisulfate and catalytic amounts of diphenyl diselenide, it is possible to effect in one pot the entire process consisting in the production of the phenylselenenylating agent, the alkoxyselenenylation of the unsaturated compounds, and the alkoxydeselenenylation of the addition products.

We now report that under similar experimental conditions, both terminal and internal alkynes, **1**, can be conveniently converted into α-keto acetal and α-keto ketals, **2**, respectively (eq 1). However, the catalytic procedure



(1)

described for alkenes and methyl ketones could be used with good results only for some terminal alkynes. In all the other cases, clean reactions required stoichiometric amounts of diphenyl diselenide. This compound was almost quantitatively recovered at the end of the reactions. In few cases it was observed that the same reactions, carried out in acetonitrile and water or ethylene glycol, gave the unprotected or the diprotected α-dicarbonyl compounds, respectively.

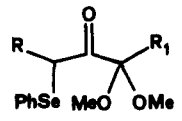
Results and Discussion

The experimental procedure to convert alkynes into the monoprotected α-dicarbonyl compounds is very simple and consists of heating the mixture of the alkyne **1** (2 mmol), the diphenyl diselenide (2 mmol), and ammonium peroxydisulfate (4 mmol) in methanol (20 mL) for 1.5–2 h. After the usual workup, recovered PhSeSePh (80–90%) and compounds **2** can be obtained in pure form by column chromatography. In the case of the unsymmetrical diarylacetylenes **1h** and **1j** the reaction products were a mixture of the two isomers, $ArCOC(OMe)_2Ar'$ and $ArC(OMe)_2COAr'$, which could not be separated by column chromatography. Therefore they were converted into the corresponding α-dicarbonyl compounds, ArCOCOAr′, **3h** and **3j** (eq 2) by heating the solution of the crude reaction products in tetrahydrofuran containing water and *p*-toluenesulfonic acid for 20 h. In the case of the bromo derivative **1i** a single product was surprisingly obtained. On the basis of spectral data this compound was identified as the $PhCOC(OMe)_2C_6H_4Br$-*o* (**2i**). This was easily converted into the $PhCOCOC_6H_4Br$-*o* (**3i**) under the conditions described for **3h** and **3j**. The results obtained with the various alkynes employed in the present investigation are collected in Table I. Satisfactory to good reaction yields were obtained in every case, indicating that this method can be of general application.

A careful investigation of these reactions was carried out in order to isolate and identify other reaction products. It was thus observed that, with the exception of compound **1e**, all the alkynes containing a methylene group α to the triple bond gave rise to compounds derived from the further functionalization of the major reaction products **2**. These compounds, which were present in low yield (5–10%), were identified as the β-(phenylseleno)-α-keto acetals or ketals **4**. The formation of these products was previously observed in the case of the α-keto acetals obtained from alkyl methyl ketones under similar reaction conditions.[6] In the case of the 3-phenylpropyne (**1b**), the reaction proceeded further to afford the products of complete functionalization of the methylene group **5b** (5%) and **6b** (8%).

Compound **6b** was the only reaction product obtained (62%) when **1b** was heated in methanol with PhSeSePh and an excess of $(NH_4)_2S_2O_8$ (8 mmol) for 12 h, and the crude reaction mixture was then treated with water and *p*-toluenesulfonic acid in tetrahydrofuran. Another interesting product type was isolated from the reactions of phenylacetylene (**1a**) and 1-octyne (**1d**). This was identified as the tetramethoxy derivative **7a** (6%) or **7d** (8%).

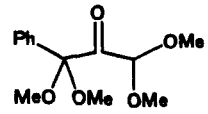
(4) Tiecco, M.; Testaferri, L.; Tingoli, M.; Bartoli, D.; Balducci, R. *J. Org. Chem.* **1990**, *55*, 429.
(5) Tiecco, M.; Testaferri, L.; Tingoli, M. *Free Radicals in Synthesis and Biology*; Minisci, F., Ed.; Kluwer Academic: Dordrecht, 1989; p 253.
(6) Tiecco, M.; Testaferri, L.; Tingoli, M.; Bartoli, D. *J. Org. Chem.* **1990**, *55*, 4523.



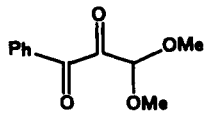
4b: R = Ph, R_1 = H

4c: R = C_3H_7, R_1 = H

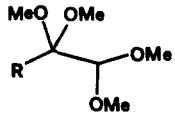
4d: R = C_5H_{11}, R_1 = H



5b

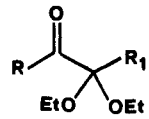


6b



7a: R = Ph

7d: R = C_6H_{13}

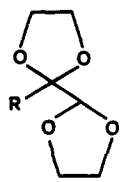


8a: R = Ph, R_1 = H

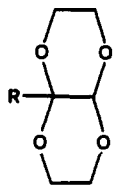
8g: R = R_1 = Ph

These compounds, when treated with ammonium peroxydisulfate in refluxing methanol, were easily converted into the corresponding α-keto acetals **2a** and **2d**.

All the reactions described so far were run in methanol. The same reactions can be effected in other solvents as well. Thus, when **1a** was treated with diphenyl diselenide and ammonium peroxydisulfate in ethanol, the α-keto acetal $PhCOCH(OEt)_2$ (**8a**) was obtained in 72% yield. Under the same conditions the diphenylacetylene (**1g**) gave $PhCOC(OEt)_2Ph$ (**8g**) in 26% yield, the major reaction product being PhCOCOPh (**3g**, 64%). When the reactions of these two alkynes were carried out in water, using acetonitrile as a cosolvent, the unprotected α-dicarbonyl compounds **3a** and **3g** were isolated in 65% and 75% yield, respectively. Finally some experiments were carried out in acetonitrile containing ethylene glycol. From the terminal alkynes **1a** and **1d** an almost equimolar mixture of the two types of diprotected α-dicarbonyl compounds (**9** and **10**) was obtained in 75 and 65% yield, respectively. In both cases the two products could be separated by column chromatography, and structural assignments were made on the basis of their proton and carbon-13 NMR and mass spectra.[7] On the contrary, in the case of the symmetrical internal alkynes **1f** and **1g**, the products obtained were the monoprotected **11f** (35%) and **11g** (55%) and the diprotected α-dicarbonyl compounds **12f** (38%) and **12g** (28%).



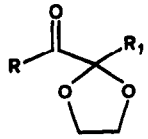
9a,d



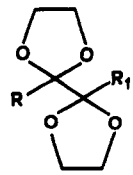
10a,d

a: R = Ph

d: R = C_6H_{13}



11f,g



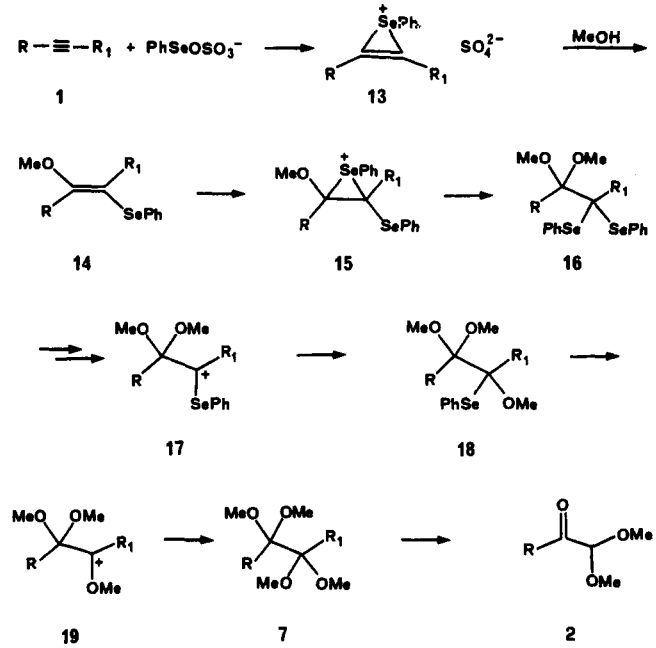
12f,g

f: R = R_1 = Ph

g: R = R_1 = C_3H_7

Finally, some control experiments were also carried out with alkynes and ammonium peroxydisulfate in methanol in the absence of diphenyl diselenide. It was observed that under these conditions the starting alkynes were consumed to give complex reaction mixtures. Compounds deriving from oxidative fragmentation of the triple bond were observed in every case. Thus, in order to have a clean conversion of the acetylenic compounds **1** into the α-keto acetals **2**, the use of diphenyl diselenide is essential. The results of these experiments can also explain why the diphenyl diselenide must be used in stoichiometric amounts in the present case even if it is almost quantitatively recovered at the end of the reaction. Under these conditions ammonium peroxydisulfate is rapidly consumed in the reactions with PhSeSePh or with other selenium-containing compounds,[6] thus minimizing its undesired reactions with the starting alkynes.

Scheme II



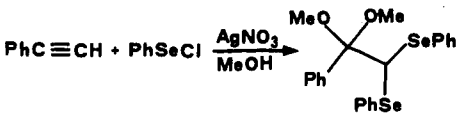
1 **13** **14** **15** **16** **17** **18** **19** **7** **2**

Several steps are needed to explain the selenium-promoted formation of α-dicarbonyl compounds from various alkynes. First of all, as indicated in Scheme I, the reaction of diphenyl diselenide with ammonium peroxydisulfate forms the strongly electrophilic phenylselenenyl sulfate. We suggest that this species reacts with the alkynes **1** to give the products of methoxyselenenylation **14** and **16** through the selenirenium **13** and seleniranium **15** intermediates, respectively (Scheme II). In the case of terminal alkynes (R_1 = H), compounds **16** are identical with those that are proposed, under similar reaction conditions, in the conversion of methyl ketones into α-keto acetals.[6] It is therefore suggested that the formation of compounds **2** from **16** occurs as previously reported.[6] Compounds **16** may deselenenylate to afford the selenium-stabilized carbocations **17**, which react with methanol to give **18**. Further deselenenylation should give the methoxy-stabilized carbocations **19** and, ultimately, the tetramethoxy derivatives **7**. Owing to their sterically crowded structure, these compounds are easily deprotected to afford the α-keto acetals or α-keto ketals **2**. This process can occur during the workup also. In some cases small amounts of these tetramethoxy derivatives may also be isolated. When the reactions are run in the presence of ethylene glycol the deprotection step is less important. It partially takes place in the case of internal alkynes, and it does not occur at all with terminal alkynes and the diprotected α-dicarbonyl compounds **9** and **10** are isolated.

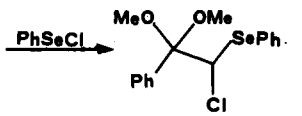
In order to find some evidence to support the proposed reaction sequence described in Scheme II, parallel ex-

(7) Fuchs, B. *Tetrahedron Lett.* **1970**, 1747.

periments were carried out. In an attempt to isolate some of the products formed in the early stages of the reaction, experiments were performed at room temperature and with an excess of phenylacetylene **1a**. Monitoring the progress of the reactions by TLC and GLC demonstrated that the major product in these cases was the tetramethoxy derivative **7a**. Under these conditions, compounds **14a** and **16a** are evidently too reactive to be detected. Some experiments were then carried out using phenylselenenyl chloride, thus avoiding the presence of peroxydisulfate ions in the reaction mixture. From a reaction of **1a** with PhSeCl and silver nitrate in methanol at room temperature, a second compound (10%) was isolated together with the tetramethoxy derivative **7a** (48%). This was identified as the chloro seleno ketal (**20**), probably arising from the chlorodeselenenylation[8] of **16a** (eq 2). Under slightly



1a **16a**

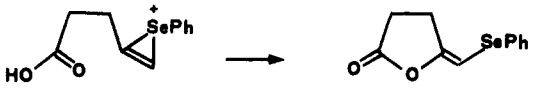


(2)

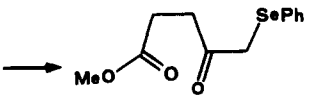
20

different conditions, together with **7a** (40%), diphenylseleno ketal (**16a**) could be isolated (25%). Both **20** and **16a**, when treated with ammonium peroxydisulfate in methanol, were quantitatively converted into **2a**. These results suggest that **16** is a likely intermediate in the reactions of alkynes with diphenyl diselenide and ammonium peroxydisulfate also.

Finally, the reaction of 4-pentynoic acid (**1e**), which forms the methyl ester **2e**, deserves some comment. This conversion very likely occurs in a different way since an internal nucleophile is present in this alkyne. A closer investigation of this reaction was carried out by generating the phenylselenenyl sulfate from the reaction of PhSeSePh and $(NH_4)_2S_2O_8$ in hot methanol[4] and adding **1e** to the resulting mixture after cooling at room temperature. Two new products, identified as **22** and **23** (eq 3), could be



21 **22**



(3)

23

isolated in low yield by stopping the reaction after few minutes. The formation of **22** indicates that the selenirenium intermediate **21**, derived from **1e**, can easily suffer intramolecular capture by the carboxy group even in the presence of a nucleophilic solvent like methanol. Thus the selenirenium ion **21** behaves in a way similar to that of the corresponding seleniranium ions obtained from alkenoic acids under identical reaction conditions.[4] The phenylseleno derivative of methyl levulinate **23** is then formed by a ring-opening transesterification reaction effected by methanol. Indeed, it has already been reported that 4-pentynoic acid reacts with *N*-(phenylseleno)phthalimide, or with PhSeCl in the presence of bases, in CH_2Cl_2, to afford **22**, and that this is easily converted into **23** when treated with methanol.[9] Compound **23** is very likely the intermediate from which the α-keto acetal **2e** originates. In the previously described conversion of methyl ketones into α-keto acetals[6] it was demonstrated that the first step was the formation of phenylseleno ketones like **23**. As a matter of fact, methyl levulinate, under reaction conditions identical with those employed in the present work for 4-pentynoic acid (**1e**), gives the same reaction product **2e**.

In conclusion, the results described in this paper indicate that monoprotected, diprotected, or unprotected α-dicarbonyl compounds can be obtained from alkynes by taking advantage of the peculiar behavior of organoselenium compounds. This simple procedure can have some synthetic importance since α-dicarbonyl compounds have interesting properties[6,10] and find several practical[6] and synthetic[6,11] applications. Several methods are reported in the literature for the synthesis of these products starting from different compounds.[12-24] Particular attention has been devoted to the conversion of alkynes into α-dicarbonyl compounds. These reactions were carried out with several types of oxidizing agents;[25-35] in most cases,

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however, the overoxidation to afford carboxylic acids could not be avoided. In this respect the presently described one-pot procedure presents several advantages over the other previously described methods. Moreover, the results described in this paper make an additional contribution to the knowledge of the chemical behavior of organoselenium compounds.

Experimental Section

Compounds **1a,c–g** were commercially available and were used without further purification. Compounds **1b**[36] and **1h–j**[37] were prepared as described in the literature. ^1H and ^{13}C NMR spectra were recorded at 90 or 200 MHz and at 50.32 MHz, respectively, in $CDCl_3$. GC and GC–MS analyses were carried out with a 15.5-m dimethylsilicone capillary column.

The presence of six natural isotopes of selenium leads to highly characteristic groups of peaks for selenium-containing fragments. The values reported below refer only to the prominent peaks; for the ions containing selenium only, the peak arising from the selenium-80 isotope is given. Melting points were determined on a Kofler melting point apparatus and are uncorrected. Silica gel 60 (70–230 mesh) was used for column chromatography. Thin-layer chromatography (TLC) was performed on Merck silica gel 60 F-254.

Conversion of Alkynes into α-Keto Acetals or α-Dicarbonyl Compounds. General Procedure. A mixture of the alkyne **1** (2 mmol), diphenyl diselenide (2 mmol), and ammonium peroxydisulfate (4 mmol) in the appropriate solvent (MeOH, EtOH, CH_3CN/H_2O (5:1)) (20 mL) was stirred and refluxed. The progress of the reaction was monitored by TLC, GLC, and NMR. The reaction mixture was poured into water and extracted with ether. The organic layer was washed with water, dried (Na_2SO_4), and evaporated. The products were obtained in pure form after column chromatography on silica gel with mixtures of petroleum ether and ether (from 98:2 to 80:20) as eluants. The conversion of α-keto acetals **2** into α-dicarbonyl compounds **3** was performed by refluxing the crude product with catalytic *p*-toluenesulfonic acid in THF/H_2O (5:1) (15 mL) for 20 h. The reaction mixture was poured into water and extracted with ether. The organic layer was washed with water, dried (Na_2SO_4), and evaporated. The residue was chromatographed as above. Reaction times and yields are reported in the table and in the Results and Discussion. Physical and spectral data of compounds **2a**,[6] **2c**,[6] **2e**,[6], **22**,[9] **23**,[9] and **11f**[38] are identical with those reported in the literature. Compounds **8a**, **2g**, and **3g** are identical with commercially available samples.

Physical and spectral data of the other reaction products are reported below.

1,1,2,2-Tetramethoxy-1-phenylethane (7a): mp 33–34 °C (lit.[19] mp 32–33 °C); ^1H NMR δ 7.6–7.4 (m, 2 H), 7.4–7.2 (m, 3 H), 4.4 (s, 1 H), 3.45 (s, 6 H), 3.35 (s, 6 H); ^{13}C NMR δ 137.6, 128.4, 128.0, 127.5, 107.1, 102.5, 57.2, 49.6; MS *m/e* (rel intensity) 195 (7), 151 (100), 121 (34), 105 (40), 77 (41), 75 (62).

1,1-Dimethoxy-3-phenyl-2-propanone (2b): oil; ^1H NMR δ 7.35–7.1 (m, 5 H), 4.55 (s, 1 H), 3.85 (s, 2 H), 3.45 (s, 6 H); ^{13}C NMR δ 202.5, 133.6, 129.7, 128.5, 126.9, 103.8, 54.7, 44.1; MS *m/e* (rel intensity) 193 (1), 103 (5), 91 (22), 75 (100). Anal. Calcd for $C_{11}H_{14}O_3$: C, 68.03; H, 7.27. Found: C, 68.40; H, 7.05.

1,1-Dimethoxy-3-phenyl-3-(phenylseleno)-2-propanone (4b): oil; ^1H NMR δ 7.6–7.05 (m, 10 H), 5.4 (s, 1 H), 4.65 (s, 1 H), 3.3 (s, 3 H), 3.25 (s, 3 H); ^{13}C NMR δ 199.2, 135.85, 129.2, 128.9, 128.6, 128.4, 127.6, 102.2, 54.3, 54.2, 50.6; MS *m/e* (rel intensity) 287 (1), 232 (1), 167 (3), 157 (2), 121 (4), 75 (100). Anal. Calcd for $C_{17}H_{18}O_3Se$: C, 58.46; H, 5.19. Found: C, 58.58; H, 5.31.

1,1,3,3-Tetramethoxy-1-phenyl-2-propanone (5b): oil; ^1H NMR δ 7.6–7.3 (m, 5 H), 5.0 (s, 1 H), 3.35 (s, 6 H), 3.2 (s, 6 H); ^{13}C NMR δ 197.8, 134.9, 129.1, 128.3, 127.3, 103.4, 97.1, 53.8, 50.3; MS *m/e* (rel intensity) 223 (1), 151 (100), 105 (47), 91 (19), 77 (38), 75 (90). Anal. Calcd for $C_{13}H_{18}O_5$: C, 61.41; H, 7.14. Found: C, 61.03; H, 7.28.

3,3-Dimethoxy-1-phenyl-1,2-propanedione (6b): oil; ^1H NMR δ 8.0–7.8 (m, 2 H), 7.6–7.3 (m, 3 H), 5.35 (s, 1 H), 3.55 (s, 6 H); ^{13}C NMR δ 196.4, 193.6, 134.7, 129.8, 128.9, 100.9, 55.3; MS *m/e* (rel intensity) 177 (1), 149 (1), 121 (3), 105 (28), 77 (32), 75 (100). Anal. Calcd for $C_{11}H_{12}O_4$: C, 63.46; H, 5.81. Found: C, 63.61; H, 5.97.

1,1-Dimethoxy-3-(phenylseleno)-2-hexanone (4c): oil; ^1H NMR δ 7.55–7.35 (m, 2 H), 7.35–7.15 (m, 3 H), 5.05 (s, 1 H), 4.05 (t, 1 H, *J* = 7.5 Hz), 3.4 (s, 3 H), 3.35 (s, 3 H), 2.0–1.1 (m, 4 H), 0.9 (t, 3 H, *J* = 7.5 Hz); ^{13}C NMR δ 199.7, 136.1, 129.1, 128.8, 101.4, 54.4, 54.1, 45.6, 31.9, 21.1, 13.7; MS *m/e* (rel intensity) 316 (1), 232 (1), 157 (4), 121 (6), 91 (2), 75 (100), 47 (11). Anal. Calcd for $C_{14}H_{20}O_3Se$: C, 53.34; H, 6.39. Found: C, 53.21; H, 6.48.

1,1-Dimethoxy-2-octanone (2d): oil;[39] ^1H NMR δ 4.45 (s, 1 H), 3.45 (s, 6 H), 2.55 (t, 2 H, *J* = 7.5 Hz), 1.75–1.15 (m, 8 H), 0.9 (t, 3 H, *J* = 7.5 Hz); ^{13}C NMR δ 205.7, 104.3, 54.7, 37.3, 31.5, 28.8, 22.9, 22.4, 13.9; MS *m/e* (rel intensity) 157 (1), 113 (1), 87 (1), 75 (100), 55 (4).

1,1-Dimethoxy-3-(phenylseleno)-2-octanone (4d): oil; ^1H NMR δ 7.55–7.35 (m, 2 H), 7.35–7.2 (m, 3 H), 5.0 (s, 1 H), 4.0 (t, 1 H, *J* = 7.5 Hz), 3.4 (s, 3 H), 3.35 (s, 3 H), 1.9–1.6 (m, 2 H), 1.6–1.1 (m, 6 H), 0.85 (t, 3 H, *J* = 7.5 Hz); ^{13}C NMR δ 199.5, 135.9, 128.9, 128.6, 101.2, 54.2, 53.8, 45.7, 31.2, 29.5, 27.3, 22.2, 13.7; MS *m/e* (rel intensity) 344 (1), 232 (1), 187 (2), 157 (4), 121 (5), 75 (100), 55 (8). Anal. Calcd for $C_{16}H_{24}O_3Se$: C, 55.98, H, 7.05. Found: C, 56.07; H, 6.95.

1,1,2,2-Tetramethoxyoctane (7d): oil; ^1H NMR δ 4.25 (s, 1 H), 3.55 (s, 6 H), 3.3 (s, 6 H), 1.8–1.1 (m, 10 H), 0.9 (t, 3 H, *J* = 7.5 Hz); ^{13}C NMR δ 106.5, 102.0, 56.8, 49.0, 32.4, 31.7, 30.0, 23.4, 22.6, 13.9. MS *m/e* (rel intensity) 203 (12), 160 (12), 159 (100), 101 (8), 75 (61), 55 (11), 43 (26). Anal. Calcd for $C_{12}H_{26}O_4$: C, 61.51; H, 11.18. Found: C, 61.45; H, 11.10.

5,5-Dimethoxy-4-octanone (2f): oil; ^1H NMR δ 3.2 (s, 3 H), 2.55 (t, 1 H, *J* = 7.5 Hz), 1.9–1.1 (m, 3 H), 0.95 (t, 3 H, *J* = 7.5 Hz); ^{13}C NMR δ 209.2, 104.4, 49.3, 41.2, 35.3, 16.6, 14.2, 13.8; MS *m/e* (rel intensity) 157 (17), 117 (100), 71 (50). Anal. Calcd for $C_{10}H_{20}O_3$: C, 63.80; H, 10.71. Found: C, 63.65; H, 10.54.

2,2-Diethoxy-1,2-diphenylethanone (8g): oil;[40] ^1H NMR δ 8.15–7.95 (m, 1 H), 7.7–7.55 (m, 1 H), 7.4–7.2 (m, 3 H), 3.45 (q, 2 H, *J* = 7.5 Hz), 1.2 (t, 3 H, *J* = 7.5 Hz); ^{13}C NMR δ 195.3, 137.8, 134.6, 132.4, 129.9, 129.7, 128.8, 128.5, 128.2, 127.8, 126.8, 103.1, 58.0, 14.9; MS *m/e* (rel intensity) 239 (8), 179 (100), 151 (43), 123 (99), 105 (78), 79 (60), 77 (92).

2,2-Dimethoxy-2-(3-*tert*-butylphenyl)-1-phenylethanone and 2,2-Dimethoxy-2-phenyl-1-(3-*tert*-butylphenyl)ethanone (2h): ^1H NMR δ 8.2–7.8 (m, 2 H), 7.65–7.4 (m, 6 H), 7.4–7.1 (m, 10 H), 3.25 (s, 12 H), 1.3 (s, 9 H), 1.25 (s, 9 H).

(3-*tert*-Butylphenyl)phenylethanedione (3h): mp 53–55 °C; ^1H NMR δ 8.15–7.85 (m, 1 H), 7.85–7.15 (m, 2 H), 1.35 (s, 3 H); ^{13}C NMR δ 195.0, 194.8, 152.6, 134.9, 133.5, 133.2, 132.3, 130.1, 129.1, 128.9, 128.0, 126.3, 35.1, 31.3; MS *m/e* (rel intensity) 266 (1), 161 (100), 105 (19). Anal. Calcd for $C_{18}H_{18}O_2$: C, 81.18; H, 6.81. Found: C, 80.98; H, 6.68.

2,2-Dimethoxy-2-(2-bromophenyl)-1-phenylethanone (2i): mp 95–98 °C; ^1H NMR δ 8.3–8.05 (m, 1 H), 8.0–7.75 (m, 2 H), 7.5–7.0 (m, 6 H), 3.25 (s, 6 H); ^{13}C NMR δ 193.1, 137.1, 135.5, 134.4, 132.4, 130.4, 130.2, 129.6, 127.9, 127.1, 121.5, 101.1, 49.9; MS *m/e* (rel intensity) 303 (1), 231 (100), 229 (92), 185 (27), 183 (29), 157 (15), 155 (17), 135 (17), 105 (46). Anal. Calcd for $C_{16}H_{15}BrO_3$: C, 57.34; H, 4.51. Found: C, 57.43; H, 4.47.

(2-Bromophenyl)phenylethanedione (3i): mp 45–46 °C (lit.[41] mp 47–48 °C); ^1H NMR δ 8.2–7.9 (m, 2 H), 7.9–7.65 (m, 1 H), 7.65–7.3 (m, 6 H); ^{13}C NMR δ 194.1, 191.4, 136.1, 134.4, 134.2, 133.7, 132.8, 132.5, 130.3, 128.8, 127.8, 121.8; MS *m/e* (rel intensity) 288 (1), 185 (52), 183 (52), 157 (17), 155 (17), 105 (24), 77 (54).

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2,2-Dimethoxy-2-(4-fluorophenyl)-1-phenylethanone and 2,2-Dimethoxy-2-phenyl-1-(4-fluorophenyl)ethanone (2j): ^{1}H NMR δ 8.25–7.95 (m, 2 H), 7.7–6.95 (m, 7 H), 3.25 (s, 6 H); ^{13}C NMR δ 194.7, 193.3, 165.35 (d, $^1J_{CF}$ = 256 Hz), 162.9 (d, $^1J_{CF}$ = 249 Hz), 136.7, 134.2, 133.0, 132.65 (d, $^3J_{CCCF}$ = 9 Hz), 129.8, 128.9, 128.9 (d, $^3J_{CCCF}$ = 9 Hz), 128.5, 128.1, 126.8, 115.45 (d, $^2J_{CCF}$ = 21 Hz), 115.15 (d, $^2J_{CCF}$ = 21 Hz), 103.5, 103.3, 49.9.

(4-Fluorophenyl)phenylethanedione (3j): mp 64–65 °C (lit.[42] mp 64–65 °C); ^{1}H NMR δ 8.15–7.85 (m, 4 H), 7.7–7.35 (m, 3 H), 7.35–7.0 (m, 2 H); ^{13}C NMR δ 193.9, 192.6, 166.8 (d, $^1J_{CF}$ = 258 Hz), 134.9, 132.7 (d, $^3J_{CCCF}$ = 10 Hz), 129.9, 129.0, 116.35 (d, $^2J_{CCF}$ = 22 Hz); MS *m/e* (rel intensity) 228 (6), 123 (65), 105 (100), 95 (40), 77 (51).

From the reactions carried out in acetonitrile/ethylene glycol (5:1) the following products were obtained.

2-Phenyl-2,2′-bi-1,3-dioxolane (9a): mp 77–79 °C; ^{1}H NMR δ 7.6–7.4 (m, 2 H), 7.4–7.2 (m, 3 H), 5.15 (s, 1 H), 4.2–3.7 (m, 4 H), 3.75 (br s, 4 H); ^{13}C NMR δ 138.4, 128.3, 127.7, 126.9, 108.2, 105.1, 65.7, 65.6; MS *m/e* (rel intensity) 162 (1), 149 (100), 105 (70), 91 (4), 77 (37), 73 (18). Anal. Calcd for $C_{12}H_{14}O_4$: C, 64.86; H, 6.35. Found: C, 65.00; H, 6.48.

2-Phenylhexahydro-1,4-dioxino[2,3-*b*]-1,4-dioxin (10a): mp 114–116 °C; ^{1}H NMR δ 7.75–7.55 (m, 2 H), 7.45–7.2 (m, 3 H), 5.3 (s, 1 H), 4.25–3.9 (m, 4 H), 3.75–3.45 (m, 4 H); ^{13}C NMR δ 138.6, 128.9, 128.3, 126.8, 92.8, 62.3, 61.7; MS *m/e* (rel intensity) 222 (2), 149 (11), 123 (44), 105 (100), 77 (54), 73 (12). Anal. Calcd for $C_{12}H_{14}O_4$: C, 64.86; H, 6.35. Found: C, 64.71; H, 6.24.

2-*n*-Hexyl-2,2′-bi-1,3-dioxolane (9d): oil; ^{1}H NMR δ 4.8 (s, 1 H), 4.2–3.75 (m, 8 H), 1.8–1.5 (m, 2 H), 1.5–1.1 (m, 8 H), 0.9 (t, 3 H, *J* = 7.5 Hz); ^{13}C NMR δ 109.7, 104.8, 66.1, 65.2, 33.5, 31.6, 29.4, 22.3, 22.0, 13.8; MS *m/e* (rel intensity) 229 (1), 187 (1), 157 (100), 99 (17), 73 (29), 45 (17), 43 (30). Anal. Calcd for $C_{12}H_{22}O_4$: C, 62.59; H, 9.63. Found: C, 62.28; H, 9.50.

2-*n*-Hexylhexahydro-1,4-dioxino[2,3-*b*]-1,4-dioxin (10d): mp 40–42 °C; ^{1}H NMR δ 4.4 (s, 1 H), 4.2–3.8 (m, 4 H), 3.8–3.4 (m, 4 H), 1.9–1.5 (m, 2 H), 1.5–1.1 (m, 8 H), 0.9 (t, 3 H, *J* = 7.5 Hz); ^{13}C NMR δ 94.0, 93.5, 61.8, 61.0, 32.1, 31.7, 29.4, 22.5, 21.1, 13.9; MS *m/e* (rel intensity) 230 (2), 157 (27), 131 (6), 113 (18), 99 (10), 86 (16), 73 (100). Anal. Calcd for $C_{12}H_{22}O_4$: C, 62.59; H, 9.63. Found: C, 62.70, H, 9.74.

2,2′-Diphenyl-2,2′-bi-1,3-dioxolane (12f): oil;[7] ^{1}H NMR δ 7.5–7.3 (m, 2 H), 7.3–7.15 (m, 3 H), 3.8 (s, 4 H); ^{13}C NMR δ 139.2, 128.0, 127.9, 127.0, 110.3, 65.8; MS *m/e* (rel intensity) 149 (100), 105 (39), 77 (21).

5-(1,3-Dioxolan-2-yl)-4-octanone (11g): oil; ^{1}H NMR δ 4.2–3.85 (m, 2 H), 2.55 (t, 1 H, *J* = 7.5 Hz), 1.9–1.2 (m, 3 H), 0.95 (t, 3 H, *J* = 7.5 Hz); ^{13}C NMR δ 207.8, 109.6, 63.4, 38.8, 36.3, 16.6, 16.0, 14.0, 13.6; MS *m/e* (rel intensity) 127 (3), 115 (100), 71 (33). Anal. Calcd for $C_{10}H_{18}O_3$: C, 64.49; H, 9.74. Found: C, 64.61; H, 9.89.

2,2′-Di-*n*-propyl-2,2′-bi-1,3-dioxolane (12g): oil; ^{1}H NMR δ 4.2–3.8 (m, 4 H), 1.9–1.55 (m, 2 H), 1.55–1.15 (m, 2 H), 0.95 (t, 3 H, *J* = 7.5 Hz); ^{13}C NMR δ 113.3, 66.5, 36.4, 15.7, 14.3; MS *m/e* (rel intensity) 170 (1), 115 (100), 99 (3), 71 (19). Anal. Calcd for $C_{12}H_{22}O_4$: C, 62.59; H, 9.63. Found: C, 62.48; H, 9.54.

Reactions of Phenylacetylene 1a with PhSeCl. A mixture of **1a** (2 mmol), phenylselenenyl chloride (2 mmol), and $AgNO_3$ (2 mmol) in MeOH (15 mL) was stirred at rt for 1 h. The reaction mixture was poured into a NH_4OH solution and extracted with CH_2Cl_2. Pure **7a** and **20** were obtained after column chromatography on alumina with mixtures of petroleum ether and ether (from 97:3 to 90:10) as eluants.

In a second reaction phenylselenenyl chloride (2 mmol) and $AgNO_3$ (2.4 mmol) in MeOH (10 mL) were stirred for 1 h at rt. The resulting mixture was added to a solution of **1a** (4.4 mmol) in MeOH (5 mL), cooled with an ice bath, and stirred for 7 h. After the usual workup and column chromatography pure **7a** and **16a** were obtained.

Physical and spectral data of **16a** and **20** are given below.

1,1-Dimethoxy-1-phenyl-2,2-bis(phenylseleno)ethane (16a): oil; ^{1}H NMR δ 7.75–7.65 (m, 2 H), 7.45–7.00 (m, 13 H), 4.85 (s, 1 H), 3.28 (s, 6 H); ^{13}C NMR δ 138.7, 134.8, 131.4, 128.7, 128.6, 128.4, 128.2, 128.0, 127.6, 103.5, 55.4, 50.1; MS *m/e* (rel intensity) 478 (1), 444 (1), 321 (1), 290 (2), 167 (7), 164 (31), 151 (100), 121 (12), 105 (18), 77 (17). Anal. Calcd for $C_{22}H_{22}O_2Se_2$: C, 55.48; H, 4.66. Found: C, 55.57; H, 4.58.

2-Chloro-1,1-dimethoxy-1-phenyl-2-(phenylseleno)ethane (20): oil; ^{1}H NMR δ 7.85–7.6 (m, 4 H), 7.6–7.25 (m, 6 H), 5.55 (s, 1 H), 3.45 (s, 3 H), 3.35 (s, 3 H); ^{13}C NMR δ 135.1, 129.2, 128.9, 128.5, 128.4, 127.8, 102.9, 66.4, 50.3, 49.9; MS *m/e* (rel intensity) 356 (1), 325 (2), 289 (1), 234 (1), 210 (1), 151 (100), 105 (24), 77 (30). Anal. Calcd for $C_{16}H_{17}ClO_2Se$: C, 54.03; H, 4.82. Found: C, 54.12; H, 4.90.

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Stereospecific Palladium(II)-Catalyzed Cyclocarbonylation of 3-Aryl-1-propynes and Iodoarenes or Acid Chlorides To Form (*E*)-3-Arylidenebutenolides

Yujin Huang and Howard Alper*

Ottawa-Carleton Chemistry Institute, Department of Chemistry, University of Ottawa, Ottawa, Ontario, Canada K1N 6N5

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Iodoarenes react with 3-aryl-1-propynes and carbon monoxide, in the presence of palladium acetate and triphenylphosphine, to form (*E*)-arylidenebutenolides in 33–88% isolated yields. The same product is formed by substitution of acid chloride for a iodoarene.

Cyclocarbonylation reactions catalyzed by transition-metal complexes are useful for the synthesis of lactones and lactams, amongst other heterocyclic compounds. Recent examples include the cobalt carbonyl catalyzed conversion of β-epoxy alcohols to 2-*C*-(2,5-dihydro-2-oxo-3-phenylfur-5-yl)lactic acids,[1] the formation of 3(2*H*)-

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