Articles

Selenium-Catalyzed Conversion of Methyl Ketones into α-Keto Acetals

M. Tiecco,* L. Testaferri, M. Tingoli,* and D. Bartoli

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

Received December 20, 1989

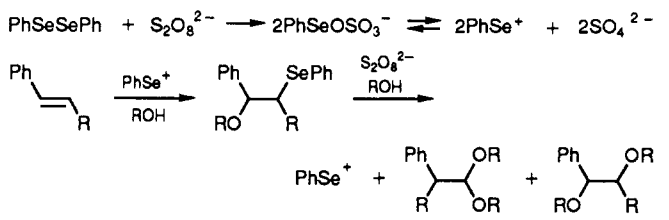
The reaction of methyl ketones with catalytic amounts of diphenyl diselenide and an excess of ammonium peroxydisulfate in methanol proceeds smoothly to afford α-keto acetals in good yield. In some cases reaction yields were increased by using stoichiometric amounts of PhSeSePh. It is suggested that the oxidation of PhSeSePh by $(NH_4)_2S_2O_8$ produces a very electrophilic phenylselenenylating agent that effects the methoxyselenenylation of the methyl ketones. The addition products so formed react with $(NH_4)_2S_2O_8$ to afford the methoxydeselenenylation products; the phenylselenenylating agent is thus regenerated. Thus, the entire process can be effected in one pot and with catalytic amounts of PhSeSePh. Some examples of the intramolecular version of this reaction are also reported.

Introduction

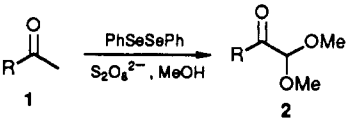
We have recently reported that the reaction of diphenyl diselenide with ammonium peroxydisulfate represents a simple and efficient method to produce an electrophilic phenylselenenylating agent in the absence of nucleophilic counterions.[1,2] This has considerable synthetic importance since it minimizes some undesirable side reactions usually encountered when benzeneselenenyl chloride is employed.[3] Our method has been successfully employed to effect the methoxy-,[1] hydroxy-,[1] and amidoselenenylation[2] of alkenes. Moreover, with use of alkenes containing internal nucleophiles, several selenium-induced ring-closure reactions have been carried out. Thus, unsaturated alcohols and amides, β-diketones, and β-keto esters, treated with PhSeSePh and $(NH_4)_2S_2O_8$ in nonnucleophilic solvents, gave cleanly the products of phenylselenoetherification in excellent yield.[4] The same process occurred with dienes and unsaturated ketones when the reactions were carried out in the presence of water or methanol, respectively.[4] Unsaturated acids, esters, and amides afforded the phenylselenolactonization products.[3] This process could be also effected starting from unsaturated nitriles when the reaction was carried out in dioxane in the presence of water and trifluoromethanesulfonic acid.[2]

A further interesting result was obtained in the course of our investigations on the alkoxyselenenylation of alkenes. Under the usual experimental conditions, the products of anti addition of the PhSe and OR groups to the double bond were cleanly obtained. However, in the presence of an excess of peroxydisulfate ion, the addition products were rapidly consumed to afford a mixture of 1,2- and 1,1-dialkoxyalkanes (Scheme I), regenerating the phenylselenium electrophilic species.[5] Thus, the entire process, consisting of the production of the cationic selenenylating reagent, alkoxyselenenylation of the alkenes, and alkoxydeselenenylation of the addition products, could be effected in one pot and with only catalytic amounts of diphenyl diselenide.[5] An excess of ammonium peroxydisulfate is obviously required. Under similar experimental conditions, vinyl halides were converted into α-alkoxy acetals.[6]

Scheme I



Scheme II



We now report that a similar process also occurs with methyl ketones 1. The reaction of aryl, vinyl, or alkyl methyl ketones with catalytic amounts of diphenyl diselenide and an excess of ammonium peroxydisulfate in methanol proceeds smoothly to afford the α-keto acetals 2 in good yield (Scheme II).

These monoprotected α-dicarbonyl compounds are important synthetic intermediates, and the reaction now described can therefore have some synthetic importance; moreover, this selenium-catalyzed transformation is interesting from a mechanistic point of view also.

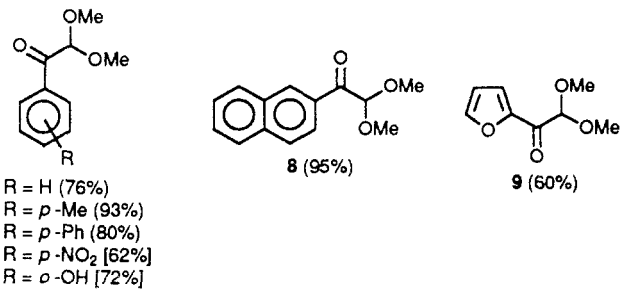
Results and Discussion

The experimental procedure to effect the conversion of methyl ketones into α-keto acetals is extremely simple and consists of refluxing the mixture of the ketone (2 mmol), the diphenyl diselenide (0.2 mmol), and ammonium peroxydisulfate (6 mmol) in methanol (15 mL) for a few hours. After the usual workup, PhSeSePh and compounds 2 can be obtained in pure form by column chromatography.

(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.
(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.; Chianelli, D.; Bartoli, D. *Tetrahedron* **1988**, *44*, 2273.

0022-3263/90/1955-4523$02.50/0

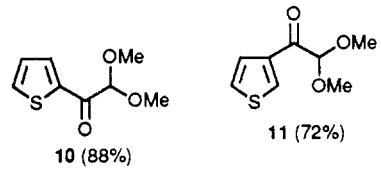
Chart I



3, R = H (76%)
4, R = *p*-Me (93%)
5, R = *p*-Ph (80%)
6, R = *p*-NO_2 [62%]
7, R = *o*-OH [72%]

8 (95%)

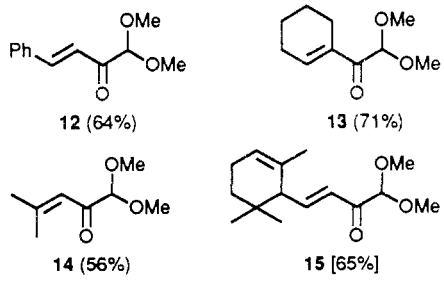
9 (60%)



10 (88%)

11 (72%)

Chart II



12 (64%)

13 (71%)

14 (56%)

15 [65%]

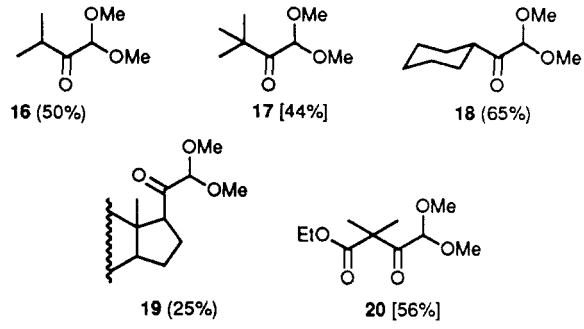
The products obtained from aryl methyl ketones are collected in Chart I. In this and in the following schemes and charts reaction yields are reported in parentheses; square brackets are employed to indicate that the reactions were effected with a stoichiometric amount of PhSeSePh. From these results it can be seen that the reaction can be applied to several types of aryl methyl ketones. Good results were obtained starting from the acetyl derivatives of benzene, naphthalene, furan, and thiophene; the reaction however does not proceed when acetylpyridines are used. Alkyl and aryl substituents are obviously fully compatible with the reagents employed. In the cases of the nitro- and the hydroxyacetophenones reaction yields were poor under the usual conditions. However, compounds **6** and **7** could be obtained in much better yield with a stoichiometric amount of PhSeSePh; this was almost quantitatively recovered at the end of the reaction. In these cases, as in some of those described below, more PhSeSePh is very likely necessary because some of the starting materials are consumed in reactions with the peroxydisulfate, when PhSeSePh is used in catalytic quantities.

The results obtained with some vinyl methyl ketones are indicated in Chart II. With these unsaturated substrates the reaction occurs selectively at the methyl group without touching the carbon–carbon double bond. From the reaction of α-ionone, compound **15** could be obtained in good yield only by using PhSeSePh in stoichiometric amounts.

A more complex picture emerged from the reactions of alkyl methyl ketones. Whenever the carbon atom in the 3-position was substituted, the reaction took place easily and the only products observed were those deriving from the conversion of the methyl group into the $CH(OMe)_2$ group. In the case of the pregnenolone acetate, a complex mixture was obtained and compound **19** (Chart III) could be isolated in 25% yield only.

When the reaction was applied to 2-hexanone, the expected product **21** (Chart IV) was obtained but a further

Chart III



16 (50%)

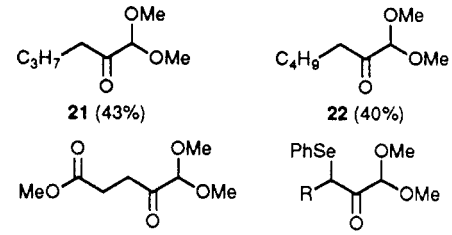
17 [44%]

18 (65%)

19 (25%)

20 [56%]

Chart IV



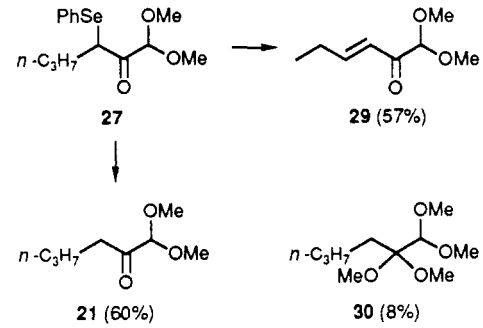
21 (43%)

22 (40%)

23 [50%]

24, R = Me [52%]
25, R = Et [59%]
26, R = *i*-Pr [77%]
27, R = *n*-Pr [62%]
28, R = *n*-Bu [62%]

Scheme III



27

29 (57%)

21 (60%)

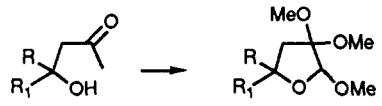
30 (8%)

product was isolated in 8% yield; this was identified as the β-phenylseleno-α-keto acetal **27**. Moreover, some starting ketone was also present. Similarly, starting from 2-heptanone, a mixture of **22**, **28** (7%), and unreacted ketone was obtained. The formation of these β-phenylseleno-α-keto acetals could not be avoided, and in some cases they were the main reaction products. For this reason, reactions with these types of substrates were carried out with a stoichiometric amount of PhSeSePh and the products **24**–**28**, indicated in Chart IV, were thus obtained. Under these conditions methyl levulinate afforded only compound **23**.

The β-phenylseleno-α-keto acetals **24**–**28** can be deselenenylated in several ways. Some examples are reported in Scheme III. Treatment of **26** or **27** with hydrogen peroxide in methanol afforded the vinyl α-keto acetals **14** and **29**, respectively. Very likely α-keto acetals can be obtained from these compounds by reductive deselenenylation with tin hydrides[7] or nickel boride.[8] We

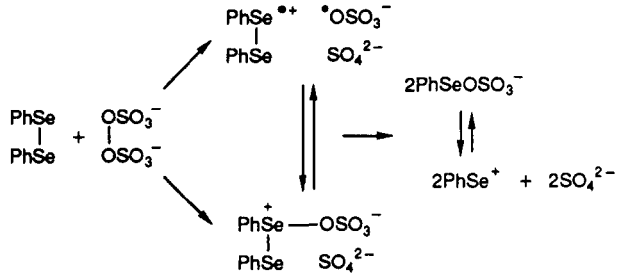
(7) (a) Clive, D. L. J.; Chittattu, G.; Wong, C. K. *J. Chem. Soc., Chem. Commun.* **1978**, 41. (b) Clive, D. L. J.; Chittattu, G. J.; Farina, V.; Kiel, W. A.; Menchen, S. M.; Russell, C. G.; Singh, A.; Wong, C. K.; Curtis, N. J. *J. Am. Chem. Soc.* **1980**, *102*, 4438. (c) Corey, E. J.; Pearce, H. L.; Szekely, I.; Ishiguro, M. *Tetrahedron Lett.* **1978**, 1023. (d) Nicolaou, K. C.; Barnette, W. E.; Magolda, R. L. *J. Am. Chem. Soc.* **1981**, *103*, 3480.

Scheme IV



31, R = R_1 = H [46%]
32, R = R_1 = Me [60%]
33, R = H, R_1 = Ph [57%]

Scheme V

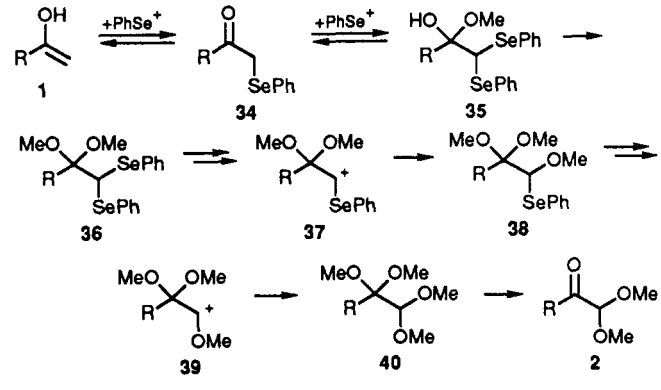


have found that the same process can be realized also by treating the β-phenylseleno-α-keto acetals in methanol with gaseous hydrogen chloride in the presence of a compound that can easily trap the phenylselenium cations, as also reported in a somewhat related procedure.[9] Thus, from the reaction of **27**, in the presence of styrene, compound **21** was obtained in good yield together with small amounts of the tetramethoxy derivative **30**. The benzeneselenenyl cation was trapped by the styrene to afford the methoxyphenylselenenylation product PhCH(OMe)-CH_2SePh. Other chemical transformations can be envisaged for compounds **24–28**; thus, these β-phenylseleno-α-keto acetals can be useful synthetic intermediates.

Finally, some experiments were carried out from β-hydroxy methyl ketones from which it was expected to obtain cyclic compounds. From the three examples reported in Scheme IV, it can be seen that the β-hydroxy groups indeed take part in the reaction and the cyclic acetals **31–33** are thus formed. It is interesting to note that in these cases the ketonic carbonyl group also is present as an acetal.

In order to explain the formation of α-keto acetals starting from the various types of methyl ketones, one has to assume that several reaction steps are involved. First of all the reaction of PhSeSePh with the peroxydisulfate anions generates the electrophilic phenylselenenylating reagent. As indicated in Scheme V, the first interaction of the two species can be seen as either an electron transfer or an S_N2 reaction. Fragmentation of the reactive intermediate so formed should afford the benzeneselenenyl cations and sulfate anions or the benzeneselenenyl sulfate or both. In any case, a strongly electrophilic phenylselenenylating species is produced in this way and this can easily add to several types of unsaturated compounds.[1-6,10] In the present case, as indicated in a simplified way in Scheme VI, we suggest that the addition takes place on the enolic form of the ketones **1** to afford the phenylseleno ketones **34**. It could now be suggested that these compounds react with the peroxydisulfate to afford the corresponding selenoxides from which the observed α-keto acetals are formed through a Pummerer reaction. Although this possibility cannot be ruled out, an alternative mechanism, similar to that proposed for the reactions of

Scheme VI



alkenes[5] and alkynes[10] with PhSeSePh and peroxydisulfate anions, can be suggested to operate in the present case. Thus, it can be expected that compounds **34** further react to give the methoxyselenenylation products **35** and eventually the diphenylselenodimethoxy derivatives **36**. It can also be suggested that **34** is first converted into the $PhCOCH(SePh)_2$ and that this compound then gives rise to **35** and **36**. In the presence of the peroxydisulfate anions compounds **36** can suffer deselenenylation to afford the selenium-stabilized carbocations **37**, which react with the solvent to give compounds **38**. Further deselenenylation should give the methoxy-stabilized carbocations **39** and hence the tetramethoxy derivatives **40**. Owing to their crowded structures these compounds are deprotected to afford the observed α-keto acetals **2**. This process can occur during the aqueous workup also. In the case of the intramolecular reactions this latter process probably does not occur because the deprotection of the carbonyl group would give rise to compounds in which steric restrictions are more severe than those experienced by compounds **31–33**.

This series of reactions would explain why PhSeSePh is only needed in catalytic amounts. From a stoichiometric point of view conversion of methyl ketones into α-keto acetals requires only methanol and peroxydisulfate anions as indicated in the equation reported in Scheme VI. In order to find some evidence to support the proposed reaction sequence, some parallel experiments were carried out. The reaction of acetophenone with stoichiometric amounts of PhSeSePh and $(NH_4)_2S_2O_8$ was investigated in some detail by analyzing the reaction mixture at various stages. The only reaction intermediate that could be identified from these experiments was the 1-phenyl-2-(phenylseleno)ethanone (**34**, R = Ph), which was present at the early stages of the reaction together with the unreacted acetophenone and the final product, 1-phenyl-2,2-dimethoxyethanone (**2**, R = Ph). When the 1-phenyl-2-(phenylseleno)ethanone was treated with ammonium peroxydisulfate in methanol, it was rapidly and quantitatively converted into the 1-phenyl-2,2-dimethoxyethanone. The 1-phenyl-1,1-dimethoxy-2,2-bis(phenylseleno)ethane (**36**, R = Ph), which could not be detected in these experiments, could instead be obtained independently from the reaction of phenylacetylene with PhSeCl in methanol.[10] This compound was stable in refluxing methanol, but as soon as some $(NH_4)_2S_2O_8$ was added, it was immediately and quantitatively converted into 1-phenyl-2,2-dimethoxyethanone (**2**, R = Ph). The observed behavior of 1-phenyl-2-(phenylseleno)ethanone and of 1-phenyl-1,1-dimethoxy-2,2-bis(phenylseleno)ethane suggests that compounds **34** and **36** can be reasonably

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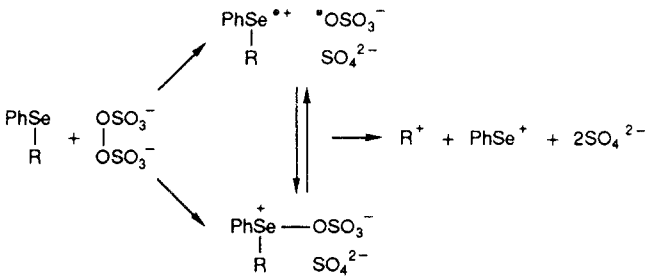
(9) Back, T. G.; Kerr, R. G. *Tetrahedron* **1985**, *41*, 4759.
(10) Unpublished results from this laboratory.

Scheme VII



considered as intermediate products in the conversion of methyl ketones **1** into α-keto acetals **2**. Finally, the structure of the cyclic acetals obtained from the reaction of the β-hydroxy methyl ketones suggests that the tetramethoxy derivatives **40** can be plausible intermediates in the reactions of the other methyl ketones also.

The methoxydeselenenylation process proposed to occur in compounds **36** to give **38** and in **38** to give **40** can be suggested to proceed either by attack of benzeneselenenyl cations on the selenium atom to give selenonium ion intermediates, which easily lose PhSeSePh, or in a way similar to that proposed in Scheme V for the reaction of diphenyl diselenide with peroxydisulfate anions. As indicated in Scheme VII, the interaction of these alkyl phenyl selenides with $S_2O_8^{2-}$ can be seen either as an electron transfer or as an S_N2 reaction from which selenium radical cation or selenonium ion intermediates are formed. Both these reactive species can suffer fragmentation at the alkylselenium bond to afford the carbocations **37** or **39**, the sulfate anions, and the benzeneselenenyl cations. The driving force for the fragmentation process is very likely the formation of stabilized carbocations. Indeed, also in the case of the reactions of the alkyl phenyl selenides deriving from the alkenes, indicated in Scheme I, it was observed that fragmentation occurred only in those cases in which stabilized carbocations could be formed.[5]

This type of deselenenylation of alkyl phenyl selenides is an interesting process that, to our knowledge, was never observed before and can be used to develop new organoselenium-based synthetic methods.

In conclusion, the results described in this paper indicate that α-keto acetals can be easily obtained from methyl ketones by taking advantage of the peculiar chemical behavior of organoselenium compounds. The simple procedure described here can have considerable synthetic importance since α-keto acetals and α-keto aldehydes have interesting properties that find several practical applications.[11-13] Moreover, α-keto acetals are stable synthetic equivalents of the very reactive α-keto aldehydes in which the most reactive carbonyl is protected; for this reason, these compounds are useful and versatile intermediates in organic synthesis.[14-25] Several procedures have been reported in the literature for the regioselective synthesis of α-keto acetals. However, in most cases these syntheses cannot find general application and often require several steps.[11,12,25-34] Among the various methods the one employing α,α-dichloro aldehydes as the starting materials seems to be very versatile.[35] Although other examples of conversion of methyl ketones into α-keto acetals can be found in the literature, the one-pot procedure described in this paper represents a substantial improvement with considerable advantages over the other previously described methods. Finally, from the mechanistic point of view this phenylselenium-catalyzed conversion of the COMe group into the $COCH(OR)_2$ group represents an interesting new process. The only other example in some way related to the now presented procedure seems to be the reaction of ArCOMe with SeO_2 affording the aromatic α-keto aldehydes.[36]

Other conversions have been realized in our laboratory that considerably extend the scope of the reaction of PhSeSePh with ammonium peroxydisulfate. Thus, for instance, both terminal and internal alkynes can be converted into the corresponding unprotected, monoprotected, or diprotected α-dicarbonyl compounds with water, alcohols, or glycols as solvents, respectively.[10] Moreover, from the reactions of β-diketones and β-keto esters in alcohols, monoprotected vicinal tricarbonyl compounds are obtained. These results will be described in forthcoming papers.

Experimental Section

Most of starting methyl ketones were commercial products that were used without further purification. Ethyl 2,2-dimethyl-3-oxobutanoate,[37] 4-hydroxy-2-butanone,[38] 4-hydroxy-4-methyl-2-pentanone,[39] and 4-hydroxy-4-phenyl-2-butanone[40] were prepared as described in the literature. Reaction products were identified by proton and carbon-13 NMR spectroscopy, mass spectrometry, and elemental analyses. Proton NMR spectra were recorded on 90-MHz Varian EM 390 and 200-MHz Bruker AC 200 instruments; carbon-13 NMR spectra were recorded at 50.32 MHz on a Bruker AC 200 instrument operating in the Fourier transform mode with proton decoupling throughout. $CDCl_3$ was used as the solvent and TMS as the reference. GLC analyses and MS spectra were carried out with a HP 5890 gaschromatograph (dimethyl silicone capillary column, 15.5 m) equipped with a HP 5971 mass-selective detector. Elemental analyses were carried out on a Carlo Erba 1106 elemental analyzer. Silica gel 60 (70–230 mesh) was used for column chromatography. Thin-layer chromatography

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(TLC) was performed on Merck silica gel 60 F-254.

Conversion of Methyl Ketones into α-Keto Acetals. General Procedure. A mixture of the methyl ketone (2 mmol), diphenyl diselenide (0.2 mmol), and ammonium peroxydisulfate (6 mmol) in methanol (15 mL) was stirred and refluxed for few hours. The progress of the reaction was monitored by TLC, GLC, and NMR. The reaction mixture was poured on water and extracted with chloroform. The organic layer was washed with water, dried, and evaporated. The reaction 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.

Reaction yields are indicated in Charts I–IV and Schemes III and IV. Reaction times are given in parentheses together with the physical, spectral, and analytical data of all the reaction products.

In some cases reactions were carried out on a large scale (20 mmol of ketones) with no substantial variations on reaction yields.

1-Phenyl-2,2-dimethoxyethanone (3): oil;[30,35] 2 h; ^{1}H NMR δ 8.15–8.00 (m, 2 H), 7.6–7.25 (m, 3 H), 5.2 (s, 1 H), 3.5 (s, 6 H); ^{13}C NMR δ 193.3, 133.5, 129.6, 128.4, 103.8, 54.6.

1-(4-Methylphenyl)-2,2-dimethoxyethanone (4): oil;[30] 2 h; ^{1}H NMR δ 8.0 (d, 2 H, J = 8.0 Hz), 7.25 (d, 2 H, J = 8.0 Hz), 5.2 (s, 1 H), 3.5 (s, 6 H), 2.4 (s, 3 H); ^{13}C NMR δ 192.7, 144.1, 131.3, 129.4, 128.9, 103.4, 54.2, 21.4.

1-[(1,1'-Biphenyl)-4-yl]-2,2-dimethoxyethanone (5): oil; 4 h; ^{1}H NMR δ 8.2–8.1 (m, 2 H), 7.75–7.35 (m, 7 H), 5.2 (s, 1 H), 3.55 (s, 6 H); ^{13}C NMR δ 192.4, 145.6, 139.2, 132.1, 129.6, 128.5, 127.8, 126.7, 126.5, 103.1, 54.1; MS, m/e (rel intens) 256 (1), 181 (4), 153 (3), 75 (100), 47 (7). Anal. Calcd for $C_{16}H_{16}O_3$: C, 74.99; H, 6.29. Found: C, 75.08; H, 6.37.

1-(4-Nitrophenyl)-2,2-dimethoxyethanone (6): mp 48–50 °C (lit.[41] mp 51–52 °C); 3 h; ^{1}H NMR δ 8.3 (s, 4 H), 5.05 (s, 1 H), 3.55 (s, 6 H); ^{13}C NMR δ 192.1, 138.1, 130.7, 123.3, 104.9, 55.3.

1-(2-Hydroxyphenyl)-2,2-dimethoxyethanone (7): oil; 1.5 h; ^{1}H NMR δ 11.8 (s, 1 H), 8.1 (dd, 1 H, J = 1.5 and 8.1 Hz), 7.8–6.8 (m, 3 H), 5.2 (s, 1 H), 3.5 (s, 6 H); ^{13}C NMR δ 198.8, 163.6, 136.9, 131.4, 118.9, 118.3, 103.7, 54.8; MS, m/e (rel intens) 196 (1), 165 (1), 121 (7), 93 (3), 76 (5), 75 (100), 65 (6), 47 (11). Anal. Calcd for $C_{10}H_{12}O_4$: C, 61.22; H, 6.17. Found: C, 61.31; H, 6.26.

1-(2-Naphthyl)-2,2-dimethoxyethanone (8): oil; 1 h; ^{1}H NMR δ 8.8–8.6 (m, 1 H), 8.15–7.8 (m, 4 H), 7.65–7.45 (m, 2 H), 5.35 (s, 1 H), 3.5 (s, 6 H); ^{13}C NMR δ 193.4, 135.9, 132.4, 131.8, 131.2, 129.8, 128.7, 128.2, 127.7, 126.6, 124.7, 103.8, 54.6; MS, m/e (rel intens) 230 (2), 155 (6), 127 (16), 75 (100), 47 (12). Anal. Calcd for $C_{14}H_{14}O_3$: C, 73.03; H, 6.13. Found: C, 73.14; H, 6.20.

1-(2-Furyl)-2,2-dimethoxyethanone (9): oil; 1.5 h; ^{1}H NMR δ 7.6 (dd, 1 H, J = 0.7 and 1.6 Hz), 7.35 (dd, 1 H, J = 0.7 and 3.6 Hz), 6.5 (dd, 1 H, J = 1.6 and 3.6 Hz), 5.1 (s, 1 H), 3.4 (s, 6 H); ^{13}C NMR δ 182.1, 150.0, 147.3, 120.8, 112.1, 102.3, 54.3; MS, m/e (rel intens) 139 (2), 95 (12), 75 (100), 67 (1), 47 (16). Anal. Calcd for $C_8H_{10}O_4$: C, 56.47; H, 5.92. Found: C, 56.38; H, 5.84.

1-(2-Thienyl)-2,2-dimethoxyethanone (10): oil; 4 h; ^{1}H NMR δ 8.0 (dd, 1 H, J = 1.2 and 3.9 Hz), 7.65 (dd, 1 H, J = 1.2 and 4.8 Hz), 7.1 (dd, 1 H, J = 3.9 and 4.8 Hz), 5.05 (s, 1 H), 3.55 (s, 6 H); ^{13}C NMR δ 186.9, 139.9, 134.8, 134.7, 128.2, 103.6, 54.5; MS, m/e (rel intens) 155 (1), 111 (11), 83 (3), 75 (100), 47 (15). Anal. Calcd for $C_8H_{10}O_3S$: C, 51.60; H, 5.41. Found: C, 51.67; H, 5.49.

1-(3-Thienyl)-2,2-dimethoxyethanone (11): oil; 2.5 h; ^{1}H NMR δ 8.4 (dd, 1 H, J = 1.2 and 3.0 Hz), 7.65 (dd, 1 H, J = 1.2 and 5.1 Hz), 7.3 (dd, 1 H, J = 3.0 and 5.1 Hz), 5.05 (s, 1 H), 3.5 (s, 6 H); ^{13}C NMR δ 188.25, 138.2, 134.95, 127.9, 125.7, 104.3, 54.7; MS, m/e (rel intens) 155 (1), 127 (5), 111 (12), 75 (100), 47 (19). Anal. Calcd for $C_8H_{10}O_3S$: C, 51.60; H, 5.41. Found: C, 51.52; H, 5.35.

1,1-Dimethoxy-4-phenyl-3-buten-2-one (12): oil;[42] 3 h; ^{1}H NMR δ 7.8 (d, 1 H, J = 16.5 Hz), 7.7–7.5 (m, 2 H), 7.5–7.2 (m, 3 H), 7.05 (d, 1 H, J = 16.5 Hz), 4.75 (s, 1 H), 3.5 (s, 6 H); ^{13}C NMR δ 193.7, 145.0, 134.7, 130.8, 128.9, 128.65, 120.95, 104.1, 54.5.

1-(1-Cyclohexenyl)-2,2-dimethoxyethanone (13): oil; 3 h; ^{1}H NMR δ 7.3–7.1 (m, 1 H), 5.0 (s, 1 H), 3.45 (s, 6 H), 2.4–2.15 (m, 4 H), 1.75–1.55 (m, 4 H); ^{13}C NMR δ 193.7, 143.6, 135.9, 102.2, 54.1, 26.0, 22.7, 21.6, 21.3; MS, m/e (rel intens) 184 (1), 153 (1), 109 (2), 93 (2), 75 (100), 47 (17). Anal. Calcd for $C_{10}H_{16}O_3$: C, 65.20; H, 8.75. Found: C, 65.29; H, 8.89.

1,1-Dimethoxy-4-methyl-3-penten-2-one (14): oil; 3 h; ^{1}H NMR δ 6.4–6.3 (m, 1 H), 4.5 (s, 1 H), 3.45 (s, 6 H), 2.2 (d, 3 H, J = 1.2 Hz), 1.95 (d, 3 H, J = 1.2 Hz); ^{13}C NMR δ 193.8, 128.8, 119.0, 104.4, 54.2, 27.8, 20.9; MS, m/e (rel intens) 118 (4), 117 (69), 75 (100), 55 (4), 47 (7), 43 (10). Anal. Calcd for $C_8H_{14}O_3$: C, 60.75; H, 8.92. Found: C, 60.90; H, 8.87. This compound was also obtained from **26** according to the following procedure. A mixture of **26** (1 mmol) and hydrogen peroxide (1.2 mmol) in methanol (10 mL) was stirred for 1 h at 0 °C. The solvent was evaporated, and the residue was chromatographed on silica gel with petroleum ether and ether (90:10) as eluant.

1,1-Dimethoxy-4-(2,6,6-trimethyl-2-cyclohexen-1-yl)-3-buten-2-one (15): oil; 3 h; ^{1}H NMR δ 6.9 (dd, 1 H, J = 10.2 and 16.0 Hz), 6.35 (d, 1 H, J = 16.0 Hz), 5.45 (br s, 1 H), 4.7 (s, 1 H), 3.44 (s, 6 H), 2.3 (d, 1 H, J = 10.2 Hz), 2.15–2.0 (m, 2 H), 1.65–1.4 (m, 4 H), 1.3–1.15 (m, 1 H), 0.95 (s, 3 H), 0.85 (s, 3 H); ^{13}C NMR δ 193.2, 150.8, 131.6, 126.1, 122.6, 102.8, 54.6, 54.1, 32.5, 31.3, 27.5, 26.8, 22.9, 22.7; MS, m/e (rel intens) 221 (1), 177 (1), 149 (1), 123 (1), 75 (100), 47 (6). Anal. Calcd for $C_{15}H_{24}O_3$: C, 71.40; H, 9.59. Found: C, 71.29; H, 9.47.

1,1-Dimethoxy-3-methyl-2-butanone (16): oil;[35] 3 h; ^{1}H NMR δ 4.6 (s, 1 H), 3.4 (s, 6 H), 3.0 (spt, 1 H, J = 7.0 Hz), 1.1 (d, 6 H, J = 7.0 Hz); ^{13}C NMR δ 208.7, 103.4, 54.4, 35.7, 18.1.

1,1-Dimethoxy-3,3-dimethyl-2-butanone (17): oil;[27,35] 3 h; ^{1}H NMR δ 4.85 (s, 1 H), 3.35 (s, 6 H), 1.2 (s, 9 H); ^{13}C NMR δ 207.7, 100.0, 53.8, 42.8, 26.1.

1-(1-Cyclohexyl)-2,2-dimethoxyethanone (18): oil;[27] 3 h; ^{1}H NMR δ 4.6 (s, 1 H), 3.45 (s, 6 H), 3.0–2.65 (m, 1 H), 2.0–1.2 (m, 10 H); ^{13}C NMR δ 207.9, 103.6, 54.6, 45.7, 28.45, 25.9, 25.7.

3-Hydroxy-21,21-dimethoxypregn-5-en-20-one (19): oil;[12] 3 h; ^{1}H NMR δ 5.35 (m, 1 H), 4.55 (s, 1 H), 3.9–2.7 (m, 6 H), 3.4 (s, 6 H), 2.7–0.7 (m, 16 H), 1.0 (s, 3 H), 0.65 (s, 3 H); ^{13}C NMR δ 206.1, 141.0, 121.3, 103.7, 71.6, 57.7, 57.2, 54.3, 50.1, 45.3, 42.3, 38.6, 37.4, 36.6, 32.0, 31.9, 31.7, 24.7, 23.8, 21.2, 19.4, 13.6.

Ethyl 4,4-dimethoxy-2,2-dimethyl-3-oxobutanoate (20): oil; 3 h; ^{1}H NMR δ 4.8 (s, 1 H), 4.15 (q, 2 H, J = 7.0 Hz), 3.35 (s, 6 H), 1.38 (s, 6 H), 1.2 (t, 3 H, J = 7.0 Hz); ^{13}C NMR δ 202.5, 173.0, 102.5, 60.9, 54.3, 54.2, 53.0, 21.8, 14.0. Anal. Calcd for $C_{10}H_{18}O_5$: C, 55.04; H, 8.31. Found: C, 55.13; H, 8.38.

1,1-Dimethoxy-2-hexanone (21): oil;[35] 2 h; ^{1}H NMR δ 4.45 (s, 1 H), 3.45 (s, 6 H), 2.55 (t, 2 H, J = 7.5 Hz), 1.85–1.1 (m, 4 H), 0.9 (t, 3 H, J = 7.5 Hz); ^{13}C NMR δ 205.7, 104.4, 54.7, 37.0, 25.1, 22.4, 13.8; MS, m/e (rel intens) 159 (1), 129 (10), 97 (4), 85 (10), 75 (100). This compound was also obtained from **27** according to the following procedure. A solution of **27** (1 mmol) and styrene (3 mmol) in methanol (10 mL), saturated with gaseous hydrochloric acid, was stirred, overnight, at room temperature. After the usual workup the reaction mixture was chromatographed on silica gel with petroleum ether and ether (90:10) as eluant. After $PhCH(OMe)CH_2SePh$[43] and compound **21**, a further product was isolated and was identified as **1,1,2,2-tetramethoxyhexane (30)**: oil; ^{1}H NMR δ 4.2 (s, 1 H), 3.5 (s, 6 H), 3.3 (s, 6 H), 1.85–1.15 (m, 6 H), 0.9 (t, 3 H, J = 7.0 Hz); ^{13}C NMR δ 106.7, 102.1, 56.9, 49.1, 32.2, 25.7, 23.4, 13.95; MS, m/e (rel intens) 175 (14), 131 (100), 101 (5), 75 (43), 57 (17), 47 (7). Anal. Calcd for $C_{10}H_{22}O_4$: C, 58.23; H, 10.75. Found: C, 58.31; H, 10.61.

1,1-Dimethoxy-2-heptanone (22): oil;[35] 2 h; ^{1}H NMR δ 4.45 (s, 1 H), 3.45 (s, 6 H), 2.55 (t, 2 H, J = 7.5 Hz), 1.85–1.1 (m, 6 H), 0.9 (t, 3 H, J = 7.5 Hz); ^{13}C NMR δ 205.5, 104.4, 54.7, 37.1, 31.4, 22.6, 22.4, 13.8; MS, m/e (rel intens) 143 (1), 99 (1), 75 (100), 55 (3), 47 (15).

Methyl 5,5-dimethoxy-4-oxopentanoate (23): oil;[44] 3 h; ^{1}H NMR δ 4.55 (s, 1 H), 3.65 (s, 3 H), 3.45 (s, 6 H), 2.9 (t, 2 H, J = 6.5 Hz), 2.6 (t, 2 H, J = 6.5 Hz); ^{13}C NMR δ 203.8, 172.8, 103.7, 54.6, 51.6, 32.2, 27.0; MS, m/e (rel intens) 173 (5), 159 (1), 75 (100), 47 (10).

1,1-Dimethoxy-3-(phenylseleno)-2-butanone (24): oil; 1 h; ^{1}H NMR δ 7.6–7.4 (m, 2 H), 7.4–7.2 (m, 3 H), 5.0 (s, 1 H), 4.2 (q, 1 H, J = 6.9 Hz), 3.4 (s, 3 H), 3.35 (s, 3 H), 1.45 (d, 3 H, J = 6.9 Hz); ^{13}C NMR δ 200.3, 136.1, 129.0, 128.8, 126.6, 101.2, 54.4, 53.9, 39.6, 15.8; MS, m/e (rel intens) 288 (1), 232 (1), 157 (3), 121 (5),

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105 (2), 75 (100), 47 (10). Anal. Calcd for $C_{12}H_{16}O_3Se$: C, 50.19; H, 5.62. Found: C, 50.26; H, 5.71.

1,1-Dimethoxy-3-(phenylseleno)-2-pentanone (25): oil; 5 h; ^1H NMR δ 7.55–7.4 (m, 2 H), 7.4–7.15 (m, 3 H), 5.0 (s, 1 H), 3.95 (t, 1 H, J = 7.3 Hz), 3.35 (s, 3 H), 3.3 (s, 3 H), 2.0–1.5 (m, 2 H), 0.95 (t, 3 H, J = 7.3 Hz); ^{13}C NMR δ 199.5, 135.9, 128.9, 128.7, 126.8, 101.3, 54.3, 53.9, 47.6, 23.1, 12.4; MS, m/e (rel intens) 302 (1), 232 (1), 157 (5), 121 (6), 75 (100), 47 (12). Anal. Calcd for $C_{13}H_{18}O_3Se$: C, 51.84; H, 6.02. Found: C, 51.78; H, 5.95.

1,1-Dimethoxy-4-methyl-3-(phenylseleno)-2-pentanone (26): oil; 6 h; ^1H NMR δ 7.55–7.35 (m, 2 H), 7.35–7.1 (m, 3 H), 4.9 (s, 1 H), 3.75 (d, 1 H, J = 10.1 Hz), 3.4 (s, 3 H), 3.35 (s, 3 H), 2.05 (dspt, 1 H, J = 6.6 and 10.1 Hz), 1.2 (d, 3 H, J = 6.6 Hz), 0.95 (d, 3 H, J = 6.6 Hz); ^{13}C NMR δ 198.9, 135.5, 129.1, 128.6, 127.8, 101.7, 55.3, 54.4, 54.1, 27.9, 21.3, 20.9; MS, m/e (rel intens) 316 (1), 232 (1), 159 (2), 157 (4), 121 (5), 75 (100), 55 (2), 47 (11). Anal. Calcd for $C_{14}H_{20}O_3Se$: C, 53.34; H, 6.39. Found: C, 53.40; H, 6.31.

1,1-Dimethoxy-3-(phenylseleno)-2-hexanone (27): oil; 6 h; ^1H NMR δ 7.55–7.35 (m, 2 H), 7.35–7.15 (m, 3 H), 5.0 (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 intens) 316 (1), 121 (6), 91 (2), 75 (100), 55 (5), 47 (12). Anal. Calcd for $C_{14}H_{20}O_3Se$: C, 53.34; H, 6.39. Found: C, 53.17; H, 6.47.

1,1-Dimethoxy-3-(phenylseleno)-2-heptanone (28): oil; 4 h; ^1H NMR δ 7.55–7.4 (m, 2 H), 7.4–7.2 (m, 3 H), 4.95 (s, 1 H), 4.05 (t, 1 H, J = 7.2 Hz), 3.4 (s, 3 H), 3.35 (s, 3 H), 1.9–1.1 (m, 6 H), 0.85 (t, 3 H, J = 7.2 Hz); ^{13}C NMR δ 199.7, 136.0, 129.0, 128.7, 126.8, 101.4, 54.3, 54.0, 45.8, 30.0, 29.4, 22.2, 13.8; MS, m/e (rel intens) 330 (1), 157 (3), 121 (4), 75 (100), 47 (6). Anal. Calcd for $C_{15}H_{22}O_3Se$: C, 54.71; H, 6.73. Found: C, 54.63; H, 6.64.

1,1-Dimethoxy-3-hexen-2-one (29). This compound was obtained from the reaction of **27** with hydrogen peroxide, according to the procedure described above for the reaction of **26**: oil; 1 h; ^1H NMR δ 7.15 (dt, 1 H, J = 6.7 and 16.6 Hz), 6.4 (d, 1 H, J = 16.6 Hz), 4.6 (s, 1 H), 3.4 (s, 6 H), 2.1 (quintet, 2 H, J = 6.7 Hz), 1.05 (t, 3 H, J = 6.7 Hz); ^{13}C NMR δ 193.6, 151.9, 124.1, 103.9, 54.5, 26.0, 12.1; MS, m/e (rel intens) 158 (1), 127 (2), 99 (2), 83 (4), 76 (5), 75 (100), 55 (7). Anal. Calcd for $C_8H_{14}O_3$: C, 60.75; H, 8.92. Found: C, 60.69; H, 9.05.

2,3,3-Trimethoxytetrahydrofuran (31): oil; 3 h; ^1H NMR δ 4.65 (s, 1 H), 4.15–3.85 (m, 2 H), 3.45 (s, 3 H), 3.35 (s, 3 H), 3.3 (s, 3 H). 2.3–1.9 (m, 2 H); ^{13}C NMR δ 108.9, 102.3, 64.9, 54.4, 51.05, 48.8, 30.3; MS, m/e (rel intens) 147 (1), 131 (20), 103 (44), 102 (100), 101 (24), 75 (32), 72 (24), 59 (47), 57 (77), 55 (22), 47 (10). Anal. Calcd for $C_7H_{14}O_4$: C, 51.85; H, 8.70. Found: C, 51.71; H, 8.82.

2,3,3-Trimethoxy-5,5-dimethyltetrahydrofuran (32): oil; 3 h; ^1H NMR δ 4.7 (s, 1 H), 3.45 (s, 3 H), 3.35 (s, 3 H), 3.3 (s, 3 H), 2.15 (d, 1 H, J = 12.0 Hz), 1.95 (d, 1 H, J = 12.0 Hz), 1.4 (s, 3 H), 1.35 (s, 3 H); ^{13}C NMR δ 109.2, 103.2, 80.3, 53.6, 50.3, 48.2, 41.8, 31.3, 28.9; MS, m/e (rel intens) 175 (2), 159 (1), 130 (12), 127 (12), 115 (100), 103 (23), 101 (21), 88 (13), 75 (12), 73 (23), 59 (22), 57 (4), 55 (9). Anal. Calcd for $C_9H_{18}O_4$: C, 56.83; H, 9.54. Found: C, 56.72; H, 9.41.

2,3,3-Trimethoxy-5-phenyltetrahydrofuran (33): oil; 2.5 h; ^1H NMR δ 7.3 (br s, 5 H), 5.15 (dd, 1 H, J = 6.0 and 10.8 Hz), 4.78 (s, 1 H), 3.5 (s, 3 H), 3.35 (s, 6 H), 2.5 (dd, 1 H, J = 6.0 and 12.6 Hz), 2.1 (dd, 1 H, J = 10.8 and 12.6 Hz); ^{13}C NMR δ 142.0, 128.4, 127.8, 126.6, 108.6, 102.9, 79.7, 55.0, 51.1, 49.1, 39.0; MS, m/e (rel intens) 178 (46), 147 (10), 121 (100), 105 (16), 104 (24), 103 (41), 91 (25), 77 (15), 75 (11), 59 (24). Anal. Calcd for $C_{13}H_{18}O_4$: C, 65.53; H, 7.61. Found: C, 65.61; H, 7.72.

1-Phenyl-2-(phenylseleno)ethanone (34). This product was isolated when the reaction was stopped after 0.5 h: oil;[45] ^1H NMR δ 7.95–7.75 (m, 2 H), 7.55–7.15 (m, 8 H), 4.15 (s, 2 H); ^{13}C NMR δ 196.0, 134.0, 133.1, 129.2, 128.7, 128.6, 128.0, 32.6; MS, m/e (rel intens) 276 (35), 157 (6), 105 (100), 91 (14), 77 (37).

Acknowledgment. Financial support from the CNR, Rome, Progetto Strategico "Processi di Trasferimento Monoelettronico", and Ministero della Pubblica Istruzione, Italy, is gratefully acknowledged.

Registry No. **3**, 6956-56-5; **4**, 54149-77-8; **5**, 127255-96-3; **6**, 21160-23-6; **7**, 127255-97-4; **8**, 127255-98-5; **9**, 127255-99-6; **10**, 127256-00-2; **11**, 127256-01-3; **12**, 55980-64-8; **13**, 127256-02-4; **14**, 127256-03-5; **15**, 127256-04-6; **16**, 56830-13-8; **17**, 38568-52-4; **18**, 55055-97-5; **19**, 127308-53-6; **20**, 127256-05-7; **21**, 6344-10-1; **22**, 6344-11-2; **23**, 66318-58-9; **24**, 127256-06-8; **25**, 127256-07-9; **26**, 127256-08-0; **27**, 127256-09-1; **28**, 127256-10-4; **29**, 127256-11-5; **30**, 127256-12-6; **31**, 127256-13-7; **32**, 127256-14-8; **33**, 127256-15-9; **34**, 35050-01-2; $PhCOCH_3$, 98-86-2; p-MeC_6H_4Ac, 122-00-9; p-PhC_6H_4Ac, 92-91-1; p-$O_2NC_6H_4Ac$, 100-19-6; o-HOC_6H_4Ac, 118-93-4; $PhCH{=}CHCOCH_3$, 122-57-6; $H_3CCOCH{=}C(CH_3)_2$, 141-79-7; $H_3CCOCH(CH_3)_2$, 563-80-4; $(CH_3)_3CCOCH_3$, 75-97-8; $EtOCOC(CH_3)_2COCH_3$, 597-04-6; $H_3C(CH_2)_3COCH_3$, 591-78-6; $H_3C(CH_2)_4COCH_3$, 110-43-0; $MeOCO(CH_2)_2COCH_3$, 6234-45-3; $H_3CCH_2COCH_3$, 78-93-3; $H_3C(CH_2)_2COCH_3$, 107-87-9; $HO(CH_2)_2COCH_3$, 590-90-9; $H_3CCOCH_2C(CH_3)_2OH$, 123-42-2; $HOCH(Ph)CH_2COCH_3$, 5381-93-1; $PhCH(OMe)CH_2SePh$, 63603-28-1; diphenyl diselenide, 1666-13-3; 2-acetylnaphthalene, 93-08-3; 2-furyl methyl ketone, 1192-62-7; 2-thienyl methyl ketone, 88-15-3; 3-thienyl methyl ketone, 1468-83-3; 1-(1-cyclohexenyl)ethanone, 932-66-1; 4-(2,6,6-trimethyl-2-cyclohexen-1-yl)-3-buten-2-one, 6901-97-9; 1-(1-cyclohexyl)ethanone, 823-76-7; 3-hydroxypregn-5-en-20-one, 38372-24-6.

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New Synthesis of the 6*H*-Pyrido[4,3-*b*]carbazoles Ellipticine and Olivacine via Cycloaddition of 2-Phenylsulfonyl 1,3-Dienes to Indoles

Jan-E. Bäckvall* and Niklas A. Plobeck

Department of Organic Chemistry, University of Uppsala, Box 531, S-751 21 Uppsala, Sweden

Received November 30, 1989

An efficient synthesis of the antitumor alkaloids ellipticine and olivacine, starting from indole, was developed. The cycloaddition of 3-(phenylsulfonyl)-2,4-hexadiene or 2-(phenylsulfonyl)-1,3-pentadiene to the magnesium salt of indole was followed by C–C–N chain addition via a Michael reaction. Subsequent Bischler–Napieralski cyclization and aromatization afforded ellipticine and olivacine, respectively.

Ellipticine, olivacine, and other 6*H*-pyrido[4,3-*b*]carbazoles have received much attention because of their antitumor activity.[1] As a consequence a great number of syntheses of ellipticine and related pyridocarbazole alka-

0022-3263/90/1955-4528$02.50/0