extracted with EtOAc (3 × 100 mL) and with ether (3 × 100 mL). The organic extracts were combined, washed with saturated NaCl and with water, dried over $MgSO_4$, and concentrated. The dark residue (1.3 g) was chromatographed over silica gel. The fractions eluted with CCl_4–CH_2Cl_2 (1:1) gave 500 mg of syrup (12.4%) which showed a strong band at 1715 cm^{-1} in the IR. The ^1H NMR ($CDCl_3$) displayed signals at 8.05–7.3 (m, 4 H), 3.85 (s, 2 H), and 2.21 ppm (s, 3 H). Crystallization from $CHCl_3$–hexanes yielded 70 mg of **14**: mp 77–78 °C; mass spectrum, *m/e* 216 (M^+), 173, 154, 133; ^1H NMR ($CDCl_3$) 8.0 (d, J = 8 Hz, 2 H), 7.5 (d, J = 8 Hz, 2 H), 3.85 (s, 2 H), 2.21 (s, 3 H). The mother liquor after filtration of these crystals showed ^1H NMR and mass spectra very similar to those of the original syrup, indicating a mixture of **12** and **13**. In another experiment 2.5 g of phenylacetone in 5 mL of FSO_3H was stirred at room temperature for 1.75 h and added dropwise to a mixture of 75 mL of $CHCl_3$ and ice. The aqueous phase was extracted again with 75 mL of $CHCl_3$, and the combined organic extracts were washed with saturated NaCl solution (3 × 150 mL), dried over $MgSO_4$, filtered, and concentrated to yield 1.75 g of a light brown oil. The ^1H NMR disclosed that 50% of the starting material remained. The mixture was treated again with 5 mL of FSO_3H at room temperature for 20 h, yielding 1.70 g of crude product in which the starting material was absent (by NMR). After two recrystallizations from CCl_4–$CHCl_3$ and three from EtOH, 60 mg of **13** was obtained; mp 75.5–76 °C. Anal. Calcd for $C_9H_9SO_3F$: C, 49.99; H, 4.20. Found: C, 49.83; H, 4.29.

Reaction of Styrene Oxide with FSO_3H. Cold FSO_3H (8 mL) was added over 30 min to 2.2 g of styrene oxide in 30 mL of CCl_4 stirred in an ice–salt bath. The solution was stirred for 1 h, poured over ice, and extracted with CCl_4 (3 × 100 mL). The organic phase was washed with saturated $NaHCO_3$ and with water, dried over $MgSO_4$, filtered, and concentrated. The residue (500 mg) was purified by chromatography and recrystallized, yielding 120 mg (5.4%) of **5**.

Reaction of 2,4,6-Tribenzyl-*s*-trioxane with FSO_3H. Cold acid (2 mL) was added to 500 mg of the trioxane[24] in 5 mL of $CHCl_3$, which was kept at 0 °C. The mixture was stirred for 15 min, poured over ice, and extracted with $CHCl_3$ (2 × 100 mL). The extract was washed with $NaHCO_3$ and with water, dried over $MgSO_4$, and concentrated to give 100 mg of residue. Crystallization from isopropyl ether yielded 65 mg (14%) of **5**.

Reaction of 2-Methyl-3-phenyloxirane with FSO_3H. The starting material was obtained by epoxidation of β-methylstyrene (Aldrich), which contained 95% of the *E* isomer, with *m*-chloroperbenzoic acid. To 6 mL of FSO_3H cooled in an ice-bath was added 2.5 g of the epoxide dropwise in 50 min. The black reaction mixture was carefully added to ice in the presence of 200 mL of $CHCl_3$. After extraction of the aqueous phase, it was saturated with NaCl and extracted with 200 mL of $CHCl_3$. The combined organic extracts were washed with saturated NaCl solution (3 × 200 mL), dried over $MgSO_4$, filtered, and concentrated under vacuum to yield 2.2 g (88%) of an oil which had IR and ^1H NMR spectra superimposable with those of phenylacetone.

Acknowledgment. We are grateful to the National Institutes of Health (Grant No. GM 24144), the Robert A. Welch Foundation (Grant P-074), the TCU Research Foundation, the UICC Research Board, and the TCU Computer Center for partial support of this research.

Registry No. 1, 60727-92-6; 2, 77550-92-6; 3, 77550-05-1; 5, 66365-45-5; 6, 77550-06-2; 7, 77507-96-1; 8, 77550-07-3; 9, 77550-08-4; 10, 77550-09-5; 11, 77507-97-2; 12, 77507-98-3; 13, 77507-99-4; 14, 77508-00-0; fluorosulfuric acid, 15181-47-2; phenylacetaldehyde, 122-78-1; 2-phenylnaphthalene, 612-94-2; 2,4,6-tribenzyl-*s*-trioxane, 77550-10-8; diphenylacetaldehyde, 947-91-1; deoxybenzoin, 451-40-1; 2-phenylpropionaldehyde, 93-53-8; *p*-methylphenylacetaldehyde, 104-09-6; α-bromophenylacetaldehyde, 16927-13-2; 9-anthranaldehyde, 642-31-9; phenylacetone, 103-79-7; styrene oxide, 96-09-3; 2-methyl-3-phenyloxirane, 4436-22-0.

(24) Wittekind, R. R.; Lazarus, S. *J. Heterocycl. Chem.* **1971**, *8*, 495.

A Simple Method for the Efficient Synthesis of Unsaturated β-Dicarbonyl Compounds

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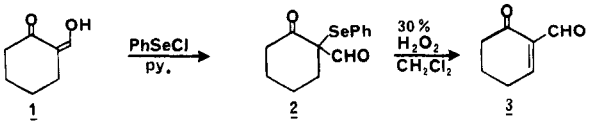
β-Dicarbonyl compounds which are substantially enolized can be readily converted to their corresponding unsaturated derivative by (a) selenation using a 1:1 complex of phenylselenenyl chloride/pyridine and (b) in situ oxidation with 30% H_2O_2 (after removal of the pyridine). The isolated yields of unsaturated β-dicarbonyl compounds obtained in this way are typically between 80% and 100%. If the selenation step (step a) is carried out in the presence of excess reagent, a slow "nonoxidative" elimination occurs. Synthetic and mechanistic details of this "nonoxidative" process are discussed.

Unsaturated β-dicarbonyl compounds are useful substrates for a number of important chemical reactions, including inter alia the Michael reaction and the Diels–Alder reaction. In principle, these materials can be prepared by DDQ oxidation of the corresponding saturated β-dicarbonyl compounds. In practice, the yields obtained from this procedure are usually only modest, presumably because of competitive over-oxidation.[2] In this article we report the results of a study involving reactions of a phenylselenenyl chloride/pyridine complex[3] with a variety of β-dicarbonyl compounds, which, when taken in the context of previous findings,[4] represents the simplest and most efficient method yet reported for the synthesis of unsaturated β-dicarbonyl compounds. The method is illustrated in Scheme I, using α-formylcyclohexanone. The results

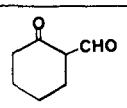
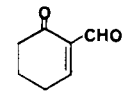
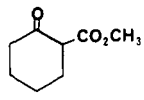
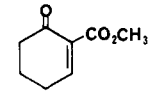
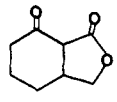
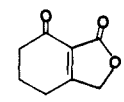
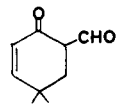
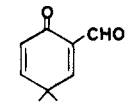
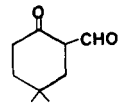
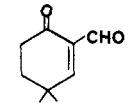
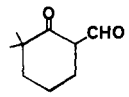
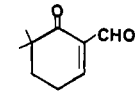
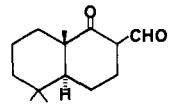
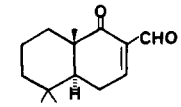
Scheme I



(1) Fellow of the Alfred P. Sloan Foundation, 1980–84.
(2) Walker, D.; Hebert, J. D. *Chem. Rev.* **1967**, *67*, 153.
(3) Zima, G.; Liotta, D. *Synth. Commun.* **1979**, *9*, 697.
(4) Reich et al. have previously selenated β-dicarbonyl compounds by first reacting these compounds with sodium hydride in anhydrous THF, followed by reaction of the resulting anion with phenylselenenyl chloride. See: Reich, H. J.; Renga, J. M.; Reich, I. L. *J. Am. Chem. Soc.* **1975**, *97*, 5434.

0022-3263/81/1946-2920$01.25/0

Table I

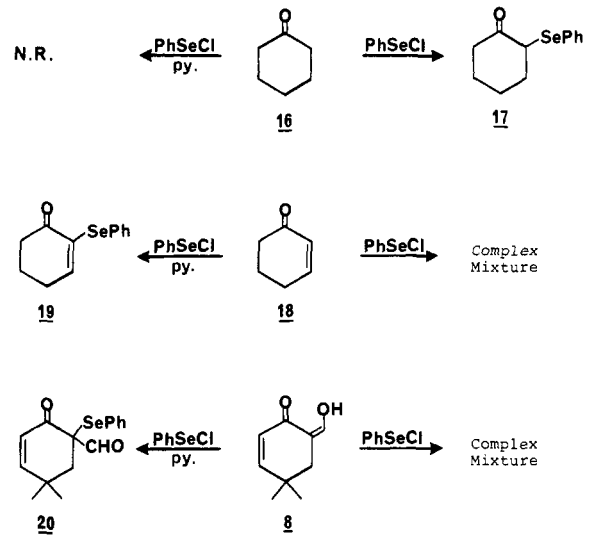
substrate	substrate no.	product	product no.	% yield
	1		3	85
	4		5	98
	6		7	85
	8		9	95
	10		11	85
	12		13	84
	14		15	100

of reaction of the complex with a number of structurally diverse β-dicarbonyl compounds and subsequent oxidation/elimination of the selenated intermediates are given in Table I.

In general, the reactions of carbonyl compounds with PhSeCl/pyridine (1:1) contrast markedly with those which are carried out in the absence of pyridine. For example, when PhSeCl is allowed to react with a saturated ketone, such as **16**, in ethyl acetate solution, the corresponding α-phenylselenenyl derivative is produced presumably via the enol form of the ketone.[5] If the reaction is carried out in the presence of 1 equiv of pyridine, no reaction occurs. Moreover, we have previously shown that unsaturated ketones, such as **18**, react with phenylselenenyl chloride/pyridine to give their corresponding 2-phenylselenenyl enones (e.g., **18** → **19**);[3] in the absence of pyridine only trace amounts of **19** are produced.

In the reactions of β-dicarbonyl compounds with PhSeCl, the pyridine dichotomy holds true. For example, addition of **8** to a chloroform or methylene chloride solution of PhSeCl yields a complex mixture of products.[6] However, if **8** is added to a chloroform solution of PhSeCl/pyridine (1:1), rapid and quantitative formation of **20** occurs.

We have found that the rate of selenation with PhSeCl/pyridine can be roughly correlated with the percent enol character of the starting β-dicarbonyl compounds. When the substrate in question exists to a substantial extent in its enol form, selenation is instantaneous at room temperature.[7] Substrates which are only slightly enolized



(e.g., diethyl ethylmalonate, **30**) react sluggishly with PhSeCl/pyridine (1 to 2 days) and often require the addition of excess reagent for complete selenation to occur.[8] Nonenolized substrates (e.g., most simple ketones and esters) completely fail to react with the complex.

Although the selenated intermediates can be isolated and purified by chromatography, we have found it most convenient to carry out the oxidation of these materials in situ. This is accomplished by removal of the pyridine with either dilute acid or water followed by the slow addition of 30% H_2O_2 to a stirred solution of the selenide at 0 °C. Failure to remove the pyridine causes a number of side reactions to occur and generally results in a substantial lowering of the overall yield of product. Unlike other selenide oxidative elimination processes, 30% H_2O_2 appears to be the reagent of choice for effecting these transformations. The use of other commonly employed oxidants (e.g., peracid or ozone)[3] results in poorer isolated yields.

The advantages of this approach over the existing methodology are obvious: (a) strong base (e.g., NaH) and anhydrous solvents are unnecessary; (b) reaction times are exceedingly short; (c) isolation of the intermediate selenides is unnecessary; (d) the reaction conditions are compatible with a variety of other functional groups (e.g., ketones, esters, alcohols, ethers, etc.); (e) the unsaturated products can usually be isolated in a high state of purity.

A curious feature of these selenation reactions is that in many cases the use of excess reagent results in the direct formation of the corresponding unsaturated β-dicarbonyl derivatives. For example, when 1 equiv of **8** is added to a $CDCl_3$ solution containing 2.1 equiv of PhSeCl/pyridine-d_5 in an NMR tube, one can initially record an NMR spectrum whose features are completely consistent with **20**. However, if the reaction is not quenched, signals attributable to **9** gradually "grow in" over a period of 24 h. After standard workup and purification, **9** is obtained in 77% yield. Similar "nonoxidative" eliminations have been observed in the reactions of PhSeCl/pyridine with most of the substrates listed in Table I. In all cases, the isolated yields of the products (50%–80%) were lower than those observed from the selenation–oxidation sequence shown in Scheme I.

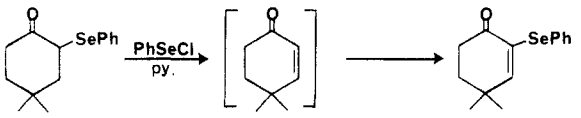
(5) Sharpless, K. B.; Lauer, R. F.; Teranishi, A. Y. *J. Am. Chem. Soc.* **1973**, *95*, 6137.

(6) The products obtained in this reaction have not been completely characterized.

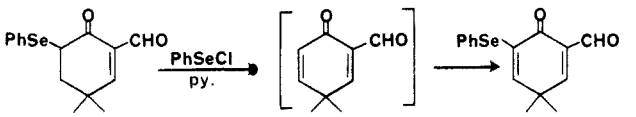
(7) All substrates listed in Table I react quite rapidly and often exothermically with PhSeCl/pyridine.

(8) The PhSeCl/pyridine complex decomposes slowly at room temperature. In slow reactions the decomposition of the complex competes with the selenation reaction and therefore necessitates the addition of excess reagent.

At present, our understanding of the mechanism of these "nonoxidative" elimination is incomplete. Nonetheless, we have identified several factors which appear to be important. First, those substrates which undergo this elimination process to a substantial extent (>10%) always possess an angular methyl group capable of a 1,3-diaxial interaction with the phenylseleno group. Thus, compounds **8**, **10**, **12**, and **14** all react with excess PhSeCl/pyridine to yield their corresponding unsaturated derivatives at a substantially faster rate than does **1**. Furthermore, both **21** and **24** undergo slow elimination with excess PhSeCl/pyridine to yield ultimately **23** and **25**, respectively.[9,10] Since in both of these compounds the phenylseleno groups are equatorial,[11] it is tempting to suggest that the elimination occurs in a conformation which places the phenylseleno group in an axial position.

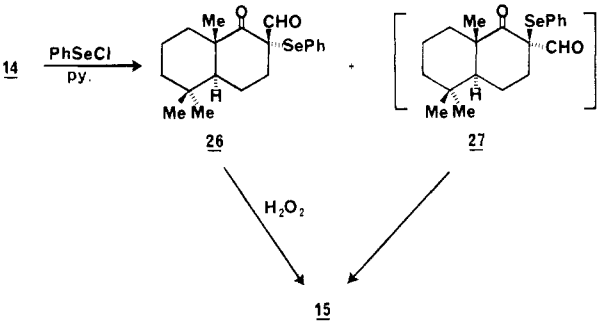


21 22 23



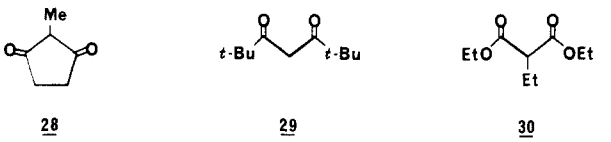
24 9 25

It is particularly noteworthy that when **14** is allowed to react with excess PhSeCl/pyridine at room temperature for 4 h, one observes by NMR a product mixture which consists of approximately 40% **15** and 60% of a material whose structure has been tentatively assigned as **26**. Upon exposure to 30% hydrogen peroxide solution, the mixture of **15** and **26** is quantitatively converted to **15**. The implication of these results is that unlike oxidative eliminations of selenides, "*nonoxidative*" *eliminations of α-phenylseleno ketones occur in a trans fashion.*[12,13]

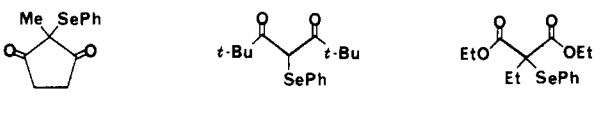


26 27 15

In principle, there are a number of possible explanations for the apparent rate accelerations observed in the reactions of β-dicarbonyl compounds possessing appropriately positioned angular substituents. One which we have considered is that these substrates for steric reasons preferentially undergo O-selenation, followed by a facile 1,4-elimination. In order to test this hypothesis, the selenation of three symmetrical substrates, **28–30**, was examined. For each case after selenation only symmetrical products **31–33** are formed, respectively, indicating that to the limits of our detection ability, only C-selenation is occurring.



28 29 30



31 32 33

In summary, in this paper we describe methodology which permits easy access to unsaturated β-dicarbonyl compounds as well as report synthetic and mechanistic details of the first observed "nonoxidative" elimination of phenylseleno ketones.

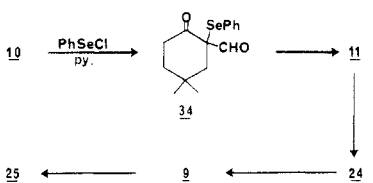
Experimental Section

General Methods. Melting points were determined with a capillary melting point apparatus. Infrared spectra were determined with Perkin-Elmer Model 257, 467, and 727 spectrophotometers. Nuclear magnetic resonance spectra were recorded with Varian Associates T-60, EM-360, and EM-390 spectrometers, and chemical shifts are reported in parts per million (δ) relative to an internal tetramethylsilane reference. Normal mass spectra were recorded with a Finnigan 4000 GC–MS system and a Varian Associates M-66 spectrometer. Precise mass measurements were carried out with the Varian Associates M-66 spectrometer. Reagents and solvents were purified by standard methods. Compounds **1** and **8** were prepared via a modification of the α-formylation procedure of Piers et al.[16] Compound **14** was prepared according to the method of Watt et al.[17] Compound **19** was prepared according to the method of Liotta and Zima.[3] Compounds **28–30** are commercially available. Compounds **21** and **24** were prepared according to the method of Sharpless.[5]

General Procedure for the Conversion of β-Dicarbonyl Compounds to Their Corresponding Unsaturated Derivatives via Scheme I. 4,4-Dimethyl-6-formylcyclohex-2-en-1-one, **8**, is used to illustrate a typical experimental procedure. PhSeCl (0.26 g, 1.05 equiv) is dissolved in 25 mL of CH_2Cl_2 and cooled to 0 °C, and 0.12 g (1.1 equiv) of pyridine is added. After 15 min,

(9) These reactions presumably occur through the intermediacy of **22** and **9**, respectively, which then react with an additional equivalent of PhSeCl/pyridine to yield the final products (see ref 3). The possibility that the final products are produced via the intermediacy of a bis(phenylseleno) ketone was considered and rejected on the basis that **17** reacts at an exceedingly slow trace of **19** was observed.

(10) Compound **24** is apparently also an intermediate in the one-flask oxidation sequence shown below. Curiously, by properly controlling the experimental conditions, either **11** or **25** can be obtained in good yield.



(11) In the NMR spectra of both **21** and **24**, the CHSePh of each compound appears as a clean doublet of doublets with coupling constants of approximately 10 and 4 Hz.

(12) Clearly, if these reactions were cis processes, both **26** and **27** would be capable of elimination.

(13) Professor R. H. Schlessinger (U. of Rochester) has independently reached the same conclusion with regard to a "nonoxidative" elimination which he and his co-workers observed in their synthesis of eriolanin. See: Roberts, M. R.; Schlessinger, R. H. *J. Am. Chem. Soc.* **1981**, *103*, 724. We thank Professor Schlessinger for informing us of his results prior to publication.

(14) Secor, H. V.; Bourlas, M.; DeBardeleben, J. F. *Experientia* **1971**, *28*, 18.

(15) Goldsmith, D. J.; Kezar, H. S. *Tetrahedron Lett.* **1980**, 3543.

(16) Piers, E.; Britton, R. W.; DeWall, W. *Can. J. Chem.* **1969**, *47*, 831.

(17) Snitman, D. L.; Tsai, M.-Y.; Watt, D. S.; Edwards, C. L.; Stotter, P. L. *J. Org. Chem.* **1979**, *44*, 2838.

0.20 g of **8** in 3 mL of CH_2Cl_2 is added and the mixture is stirred an additional 15 min.[7] The CH_2Cl_2 solution is extracted with two 5-mL portions of 10% HCl and cooled back to 0 °C, at which time 0.1 mL of 30% H_2O_2 is added. An additional 0.10 mL of 30% H_2O_2 is added after 10 min and again after 20 min. After an additional 10 min, 5 mL of H_2O is added and the CH_2Cl_2 layer is separated and washed with 5 mL of saturated $NaHCO_3$. After being dried over $MgSO_4$, the solution is filtered and the solvent evaporated in vacuo to yield 0.19 g of spectroscopically pure **9** (95% yield).

2-Formylcyclohex-2-en-1-one, 3. No additional purification is required (86% isolated yield). This material is somewhat unstable and should be used immediately after it is prepared: ^1H NMR (C_6D_6) 1.31–1.54 (m, 2), 1.65–1.89 (m, 2), 1.98 (t, J = 7 Hz, 2), 7.28 (t, J = 3 Hz, 1), 10.16 (s, 1); IR ($CHCl_3$) 1695, 1670, 1605 cm^{-1}; mass spectrum, m/e 124.

2-(Carbomethoxy)cyclohex-2-en-1-one, 5.[4] No additional purification is required (98% isolated yield): ^1H NMR ($CDCl_3$) 1.68–2.69 (m, 6), 3.86 (s, 3), 7.84 (t, J = 4 Hz, 1); IR ($CHCl_3$) 1750, 1715 cm^{-1}; mass spectrum, m/e 154.

8-Oxabicyclo[4.3.0]non-1-ene-3,9-dione, 7. No additional purification is required (85% isolated yield): mp 130–132 °C; ^1H NMR ($CDCl_3$) 2.10–2.95 (m, 6), 4.95 (s, 2); IR ($CHCl_3$) 1780, 1715 cm^{-1}; mass spectrum, m/e 152; precise mass calcd for $C_8H_6O_3$ m/e 150.031 68, found 150.031 12.

2-Formyl-4,4-dimethylcyclohexa-2,5-dien-1-one, 9.[14] No additional purification is required (95% isolated yield): mp 60–61 °C; ^1H NMR ($CDCl_3$) 1.40 (s, 6), 6.27 (d, J = 10 Hz, 1), 6.92 (dd, J = 20 Hz, J = 3 Hz, 1), 7.61 (d, J = 3 Hz, 1), 10.28 (s, 1); IR ($CHCl_3$) 1705, 1668 cm^{-1}; mass spectrum, m/e 150.

2-Formyl-4,4-dimethylcyclohex-2-en-1-one, 11. No additional purification is required (85% isolated yield): ^1H NMR ($CDCl_3$) 1.25 (s, 6), 1.88 (t, J = 8 Hz, 2), 2.58 (t, J = 8 Hz, 2), 7.47 (s, 1), 10.07 (s, 1); IR ($CHCl_3$) 1675, 1610 cm^{-1}; mass spectrum, m/e 152; precise mass calcd for $C_9H_{12}O_2$ m/e 152.083 72, found 152.082 87.

2-Formyl-6,6-dimethylcyclohex-2-en-1-one, 13. Further purification is accomplished by column chromatography on silica gel (84% isolated yield): ^1H NMR ($CDCl_3$) 1.14 (s, 6), 1.80 (t, J = 7 Hz, 2), 2.58 (dt, J = 7 Hz, 2), 7.70 (t, J = 4 Hz, 1), 10.08 (s, 1); IR ($CHCl_3$) 1680, 1609 cm^{-1}; mass spectrum, m/e 152; precise mass calcd for $C_9H_{12}O_2$ m/e 152.083 72, found 152.082 87.

5,5,9-Trimethyl-2-formyl-Δ^2-*trans*-1-octalone, 15.[15] No additional purification is required (100% isolated yield): mp 74–76 °C; ^1H NMR ($CDCl_3$) 0.99 (s, 3), 1.06 (s, 3), 1.13 (s, 3), 2.42–2.63 (m, 2), 1.15–1.98 (m, 7), 7.77 ("t", J = 4 Hz, 1), 10.04 (s, 1); IR ($CHCl_3$) 1680, 1650 cm^{-1}; mass spectrum, m/e 220.

General Procedure for Conversion of β-Dicarbonyl Compounds to Their Corresponding Unsaturated Derivatives via the "Nonoxidative" Elimination Process. 2-Formyl-4,4-dimethylcyclohexanone, **10**, is used to illustrate a typical experimental procedure. To a chloroform solution containing 0.75 g (3.90 mmol) of phenylselenenyl chloride is added via syringe 0.34 g (4.3 mmol) of pyridine under a nitrogen atmosphere. After temporarily immersing the reaction vessel in a cooling bath containing dry ice/carbon tetrachloride, 0.29 g (1.9 mmol) of 2-formyl-4,4-dimethylcyclohexanone, **10**, is added dropwise via syringe. After a few minutes the cooling bath is removed and the reaction mixture is allowed to stir at room temperature. The progress of the reaction can be monitored by NMR ($CDCl_3$) or by removal of aliquots and subsequent workup. In this case the reaction is complete in 3 days. After being quenched with a few drops of 10% HCl solution, the reaction mixture is washed with 10% HCl solution (3 × 25 mL), dried with $MgSO_4$, and stripped of solvent in vacuo. The resulting residue is then purified by silica gel chromatography, eluting first with hexane to remove any diphenyl diselenide and then with ether, to obtain 0.235 g of 4,4-dimethyl-2-formylcyclohex-2-en-1-one, **11** (81% yield).[14]

2-Methyl-2-(phenylselenenyl)cyclopentane-1,3-diones, 31. PhSeCl (0.03 g, 0.155 mmol) is dissolved in a 2.5 mL of $CDCl_3$. After the solution is cooled to 0 °C, 0.015 g (0.190 mmol) of pyridine is added. After the mixture stands for 10 min, 0.015 g (0.155 mmol) of **28**, dissolved in 1 mL of $CDCl_3$, is added via syringe. An instantaneous reaction occurs. The product was not isolated but was instead characterized via NMR: ^1H NMR ($CDCl_3$) 7.65–7.16 (m, 5), 3.1–2.4 (m, 4), 1.49 (s, 3).

2,2,4,4-Tetramethyl-4-(phenylselenenyl)heptane-3,5-dione, 32. PhSeCl (0.030 g, 0.155 mmol) is dissolved in 2.5 mL of $CDCl_3$. After the solution is cooled to 0 °C, 0.015 g (0.190 mmol) of pyridine is added. After the mixture stands for 10 min, 0.028 g (0.150 mmol) of **29**, dissolved in 1 mL of $CDCl_3$, is added via syringe. An instantaneous reaction occurs. The product was not isolated but was instead characterized via NMR: ^1H NMR ($CDCl_3$) 7.55–7.01 (m, 5), 1.15 (s, 18).

Diethyl 2-Ethyl-2-(phenylselenenyl)malonate, 33. PhSeCl (0.030 g, 0.155 mmol) is dissolved in 2.5 mL of $CDCl_3$. After the solution is cooled to 0 °C, 0.015 g (0.190 mmol) of pyridine is added. After the mixture stands for 10 min, 0.029 g (0.154 mmol) of **30**, dissolved in 1 mL of $CDCl_3$, is added via syringe. In order to obtain complete reaction, additional equivalents of PhSeCl/pyridine are added after 24 h and again after 48 h. The product was not isolated but was instead characterized via NMR: ^1H NMR ($CDCl_3$) 7.80–7.21 (m, 5), 4.55–4.10 (q, J = 7 Hz, 4), 2.27–1.80 (q, J' = 7 Hz, 2), 1.61–0.99 (2 overlapping t, J = 7, J' = 7 Hz, 9).

4,4-Dimethyl-6-(phenylselenenyl)-6-formylcyclohexenone, 20. PhSeCl (0.26 g, 1.35 mmol) is dissolved in 25 mL of CH_2Cl_2 and cooled to 0 °C, and 0.12 g (1.50 mmol) of pyridine is added. After 15 min, 0.20 g (1.30 mmol) of **8** in 3 mL of CH_2Cl_2 is added and the mixture is stirred an additional 15 min. The CH_2Cl_2 solution is extracted with two 5-mL portions of 10% HCl solution, dried ($MgSO_4$), and stripped of solvent to yield **20**. Compound **20** was not subjected to further purification but was instead oxidized directly to **9** (see general procedure): ^1H NMR of **20** ($CDCl_3$) 10.18 (s, 1), 7.62–7.06 (m, 5), 6.76 (d, J = 12 Hz, 1), 5.94 (d, J = 12 Hz, 1), 1.22 (s, 3), 1.00 (s, 3).

2-Formyl-4,4-dimethyl-6-(phenylselenenyl)cyclohexa-2,5-dienone, 25. PhSeCl (0.78 g, 4.05 mmol) is dissolved in 40 mL of CH_2Cl_2 and cooled to 0 °C and 0.36 g (4.50 mmol) of pyridine is added. After 15 min, 0.15 g (0.98 mmol) of **8** in 3 mL of CH_2Cl_2 is added. After 15 min the ice bath is removed and the solution is allowed to stir for approximately 45 h at room temperature. After being quenched with 1 mL of 10% HCl solution, the reaction mixture is washed with 10% HCl solution (3 × 25 mL), dried with $MgSO_4$, and stripped of solvent. the resulting residue is then purified by silica gel chromatography, eluting first with hexane to remove any diphenyl diselenide and then with ether, to obtain 0.195 g of **25** (65% yield): ^1H NMR ($CDCl_3$) 10.34 (s, 1), 7.75–7.08 (m, 6), 6.54 (d, J = 3 Hz, 1), 1.29 (s, 6); IR ($CHCl_3$) 1703, 1660 cm^{-1}; mass spectrum, m/e 306; precise mass calcd for $C_{15}H_{14}O_2{}^{80}Se$ m/e 306.015 87, found 306.015 27.

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