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A Two-Step Conversion of α,β-Unsaturated Ketones to Their α-Carbalkoxy or α-Carbamoyl Derivatives

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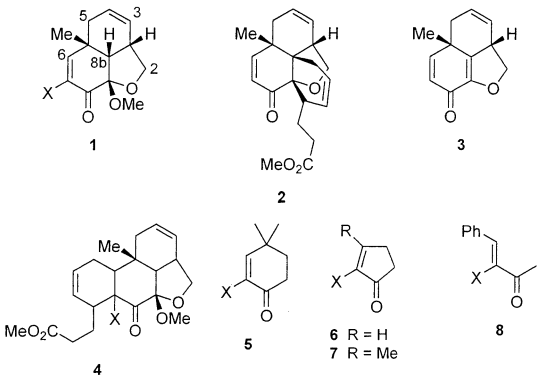
Abstract: Several enones are converted into their α-iodo derivatives in excellent yields and carbonylated with palladium catalysis in the presence of alcohol or amines to the α-carbonyl enones in satisfactory yields.

The notoriously poor dienophilic character of cyclohexenones has curtailed their use in natural products synthesis. This deficiency has been addressed, by Liu and co-workers in particular, by the placement of an electron-withdrawing group (EWG) at C-2 of the cycloalkenone. They have prepared 2-carbalkoxy- and 2-cyanocycloalkenones from the corresponding cycloalkanones via enolate quenching and selenoxide elimination and convincingly demonstrated their value as dienophiles for the construction of many terpenoid ring systems.[1,2]

In the course of synthetic studies related to the pentacyclic fungal metabolites of the viridin group,[3] we were able to develop a two-step synthesis of the tricycle **1a** that represents rings A, B, and E of these compounds. Although the cyclohexenone moiety of **1a** added readily to reactive isobenzofuranoid dienes and was a valuable dienophile for the synthesis of pentacyclic marine quinones,[4] it was of little use in reactions with simple dienes with or without Lewis acid catalysis. For example, the reaction of **1a** with methyl (*E*)-4,6-heptadienoate catalyzed by 10 mol % of aluminum chloride at room temperature for 4 days led to a 7% yield of an adduct whose structure **2** was confirmed by X-ray crystallography. Under other conditions with various Lewis acids, solvents and temperatures the only identifiable product obtained was dienone **3** (the putative precursor of **2**) and its 2,2a dehydro derivative, with none of the desired adduct **4a** at all (Chart 1).

Since we were unable to adapt the method[5] used for preparing **1a** to the synthesis of an α-EWG substituted

CHART 1



a: X =H; **b:** X = I; **c:** X = Br; **d:** X = CO_2Me; **e:** X = CO_2Et; **f:** X = CO_2Bu; **g:** X = $CONEt_2$; **h:** X = CONHBu; **i:** X = $CON(CH_2CH_2)_2O$

enone in good yield, we set out to devise a synthetically useful conversion of **1a** to **1d** in order to improve the electrophilicity of the enone double bond. Treatment of **1a** with iodine and pyridine in dichloromethane[6,7] produced the α-iodoenone **1b** in excellent yield (99%). Lithium−iodine exchange could not be successfully accomplished with *n*-butyl or *tert*-butyllithium at temperatures between −95 and −78 °C, but the Heck carbalkoxylation applied previously to vinyl iodides[8] and 5-iodo-2,3-dihydropyridones[9] was an effective alternative. Treatment of **1b** with methanol, 2,6-lutidine, palladium acetate and 1,3-bis(diphenylphosphino)propane (5 mol % each) in THF under carbon monoxide (750 psi) at 60 °C for 48 h produced a 62% yield of the derived α-carbomethoxyenone **1d**.[10] The reaction was plagued by irreproducible yields however, and this was eventually traced to the sodium thiosulfate that was used in the previous step for destroying excess iodine. Evidently, very small residues of sulfur compounds, contaminating the iodoenone, poison the palladium catalyst and reduce its efficacy. Using ascorbic acid[11] in place of the thiosulfate solved this problem and **1a** could be converted to **1d** in two steps in reproducibly good yields (>60%). The Lewis acid catalyzed cycloaddition of **1d** with methyl (*E*)-4,6-heptadienoate did proceed with the desired regioselectivity to produce **4d**, but in an unacceptably low yield (12−15%)

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TABLE 1. Carbonylation of α-Haloenones in the Presence of Alcohol and Amine Nucleophiles

entry	substrate	nucleophile	product	isolated yield (%)
1	**1b**	MeOH	**1d**	62
2	**1b**	$HNEt_2$	**1g**	62
3	**1b**	*n*-$BuNH_2$	**1h**	33
4	**1b**	morpholine	**1i**	55
5	**5b**	MeOH	**5d**	68
6	**5b**	*n*-BuOH	**5f**	62
7	**5b**	$HNEt_2$	**5g**	64
8	**5b**	morpholine	**5i**	77
9	**6b**	MeOH	**6d**	55
10	**6b**	EtOH	**6e**	58
11	**6c**	MeOH	**6d**	29
12	**6c**	EtOH	**6e**	28
13	**7b**	MeOH	**7d**	42
14	**7c**	MeOH	**7d**	13
15	**8b**	MeOH	**8d**	51

and accompanied by much decomposition. This reaction could not be used in a viable synthetic route to viridin, but in view of the amply demonstrated value[1,13] of α-carbalkoxyenones in synthesis we set out to evaluate the scope of the two step α-carbalkoxylation with several enone bromides and iodides. The outcome of these investigations is discussed below and summarized in Table 1.

Yields of α-haloenones were excellent in the cyclic examples (**5**−**7**) but much less satisfactory with the acyclic enones.[7] Iodides gave better results in the carbonylation than bromides (entries 11, 12, and 14) and primary amines (entry 3) were inferior to secondary amines in the reaction (entries 3, 4, 7, and 8). Thiols could not be used in the reaction; the starting iodoenones were recovered probably due to poisoning of the palladium catalyst. The reaction failed with both 2-iodo and 2-iodo-3-methyl cyclohexenones. Aromatization to phenolic products took place together with deiodination. This seems to be the usual outcome[12] with iodocyclohexenones that do not contain a quaternary carbon atom in the ring. Within these limitations our two-step α-carbalkoxylation appears to be a convenient method that could be used for improving the reactivity of enones in both cycloaddition and conjugate addition[1a,13] processes. A particularly good illustration of its value is found in a comparison of it with the existing five-step method[13,14] for converting cyclopentenones **6a** and **7a** to their α-esters **6e** and **7e**, respectively.

Experimental Section[15]

7-Iodo-8a-methoxy-5a-methyl-2a,5,5a,8,8a,8b-hexahydro-2*H*-naphtho[1,8-*bc*]furan-8-one (1b). A solution of naphthofuran **1a** (0.094 g, 0.42 mmol) in 10 mL of 1:1 pyridine and CCl_4 was cooled to 0 °C. A solution of iodine (0.453 g, 1.79 mmol) in 5 mL 1:1 pyridine−CCl_4 was slowly added dropwise. The dark mixture was stirred for 3 h at 0 °C, and then diluted with ether. The ether extract was washed sequentially with cold HCl (1 M), saturated ascorbic acid solution, and water and then dried ($MgSO_4$), filtered, and concentrated under reduced pressure. Flash chromatography (1:1 ether−hexane) afforded iodide **1b** as a yellow solid (0.148 g, quantitative). Mp: 81−82 °C. IR: 2930, 1700, 1454, 1053 cm^{-1}. ^1H NMR: 1.25 (s, 3H, R-CH_3), 1.89−2.08 (m, 2H, H-5), 2.64 (dd, J = 0.9, 9.2 Hz, 1H, H-8b), 3.02 (m, 1H, H-2a), 3.26 (s, 3H, R-OCH_3), 3.78 (dd, J = 3.1, 8.6 Hz, 1H, H-2), 4.15 (dd, J = 7.3, 8.6 Hz, 1H, H-2), 5.77 (br s, 2H, H-3 and H-4), 7.35 (s, 1H, H-6). ^{13}C NMR: 28.1, 37.3, 37.6, 39.5, 51.1, 53.8, 73.0, 98.1, 102.7, 125.6, 129.4, 166.5, 186.3. Anal. Calcd for $C_{13}H_{15}O_3I$: C, 45.11; H, 4.37. Found: C, 45.23; H, 4.47.

Typical Procedure for the Amino- and Alkoxycarbonylation of α-Haloenones: Synthesis of 7-Carbomethoxy-8a-methoxy-5a-methyl-2a,5,5a,8,8a,8b-hexahydro-2*H*-naphtho-[1,8-*bc*]furan-8-one (1d). To a solution of iodide **1b** (401 mg, 1.16 mmol) in THF (30 mL) were added MeOH (250 μL), 2,6-lutidine (300 μL), $Pd(OAc)_2$ (14 mg, 0.06 mmol), and dppp (25 mg, 0.06 mmol), and the reaction mixture was placed under a CO atmosphere (750 psi) in a pressure reactor, which was then heated at 60 °C for 48 h. The resulting solution was diluted with Et_2O and washed with water. The aqueous layer was extracted with Et_2O, the combined organic phases were dried (Na_2SO_4), and the solvent was removed under reduced pressure. Flash chromatography (50% Et_2O in hexane) gave **1d** as a light yellow solid (203 mg, 0.73 mmol, 63% yield). Mp: 80−82 °C. IR: 2952, 1744, 1722, 1436, 1275, 1131 cm^{-1}. ^1H NMR: 1.25 (s, 3H, R-CH_3), 1.80 (br d, J = 16.7 Hz, 1H, H-5), 2.02 (dd, J = 4.4, 16.7 Hz, 1H, H-5), 2.57 (dd, J = 1.3, 9.0 Hz, 1H, H-8b), 2.98 (m, 1H, H-2a), 3.25 (s, 3H, R-OCH_3), 3.79 (s, 3H, R-CO_2CH_3), 3.86 (dd, J = 1.8, 8.6 Hz, 1H, H-2), 4.13 (dd, J = 6.6, 8.6 Hz, 1H, H-2), 5.72 (br s, 2H, H-3 and H-4), 7.60 (s, 1H, H-6). ^{13}C NMR: 27.3, 34.2, 36.4, 36.8, 50.4, 52.3, 53.9, 72.9, 105.2, 124.8, 128.4, 131.3, 163.6, 164.4, 188.3. HRMS (EI) *m*/*z*: required for $C_{15}H_{18}O_5$ 278.1154, found 278.1150. Anal. Calcd for $C_{15}H_{18}O_5$: C, 64.74; H, 6.52. Found: C, 64.60; H, 6.39.

7-Diethylaminocarbonyl-8a-methoxy-5a-methyl-2a,5,-5a,8,8a,8b-hexahydro-2*H*-naphtho[1,8-*bc*]furan-8-one (1g) was prepared from iodide **1b** as a light brown solid. Mp: 55−58 °C. IR: 2972, 1692, 1635, 1458, 1433, 1049 cm^{-1}. ^1H NMR: 1.11 (t, J = 7.1 Hz, 3H, $R_2NCH_2CH_3$), 1.18 (t, J = 7.1 Hz, 3H, R_2-NCH_2CH_3), 1.27 (s, 3H, R-CH_3), 1.96 (br d, J = 16.5 Hz, 1H, H-5), 2.04 (br d, J = 16.5 Hz, 1H, H-5), 2.65 (dd, J = 0.9, 9.3 Hz, 1H, H-8b), 3.04 (m, 1H, H-2a), 3.20 (q, J = 7.1 Hz, 2H, R_2-NCH_2CH_3), 3.32 (s, 3H, R-OCH_3), 3.45 (m, 2H, $R_2NCH_2CH_3$), 3.81 (dd, J = 3.0, 8.6 Hz, 1H, H-2), 4.15 (dd, J = 7.2, 8.6 Hz, 1H, H-2), 5.79 (m, 2H, H-3 and H-4), 6.75 (s, 1H, H-6). ^{13}C NMR: 12.8, 14.2, 28.1, 34.9, 37.2, 37.4, 39.2, 42.7, 50.6, 53.5, 72.9, 103.2, 125.6, 129.7, 136.6, 156.0, 165.4, 188.2. HRMS (EI) *m*/*z*: required for $C_{18}H_{25}NO_4$ 319.1784, found 319.1799.

7-Butylaminocarbonyl-8a-methoxy-5a-methyl-2a,5,5a,8,-8a,8b-hexahydro-2*H*-naphtho[1,8-*bc*]furan-8-one (1h) was prepared from iodide **1b** as a light yellow solid. Mp: 61−62 °C. IR: 3359, 2959, 1694, 1661, 1532, 1458, 1048 cm^{-1}. ^1H NMR: 0.90 (t, J = 7.3 Hz, 3H, RNH$(CH_2)_3CH_3$), 1.26 (s, 3H, R−CH_3), 1.34 (m, 2H, RNH$(CH_2)_2CH_2$Me), 1.52 (m, 2H, RNHCH_2CH_2Et), 1.87 (br d, J = 16.4 Hz, 1H, H-5), 2.03 (br d, J = 16.4 Hz, 1H, H-5), 2.58 (d, J = 8.9 Hz, 1H, H-8b), 2.98 (m, 1H, H-2a), 3.25 (s, 3H, R−OCH_3), 3.31 (m, 2H, RNHCH_2Pr), 3.76 (dd, J = 3.1, 8.5 Hz, 1H, H-2), 4.12 (dd, J = 7.2, 8.5 Hz, 1H, H-2), 5.74 (m, 2H, H-3 and H-4), 7.85 (s, 1H, H-6), 8.09 (br s, 1H, RN*H*Bu). ^{13}C NMR: 13.8, 20.2, 28.1, 31.4, 34.8, 37.2, 37.5, 39.3, 50.5, 52.9, 73.2, 104.4, 125.7, 129.2, 130.0, 162.0, 166.9, 192.2. HRMS (EI) *m*/*z*: required for $C_{18}H_{25}NO_4$ 319.1784, found 319.1770.

8a-Methoxy-5a-methyl-7-morpholinocarbonyl-2a,5,5a,8,-8a,8b-hexahydro-2*H*-naphtho[1,8-*bc*]furan-8-one (1i) was prepared from iodide **1b** as a light brown oil. IR: 2963, 1692, 1639, 1435, 1275, 1114 cm^{-1}. ^1H NMR: 1.20 (s, 3H, R-CH_3), 1.85 (br d, J = 16.5 Hz, 1H, H-5), 2.01 (br d, J = 16.5 Hz, 1H, H-5), 2.58 (d, J = 9.0 Hz, 1H, H-8b), 2.99 (m, 1H, H-2a), 3.21 (s, 5H, R-OCH_3, overlapping RN$(CH_2CH_2)_2$O), 3.49−3.70 (m, 6H, RCON-$(CH_2CH_2)_2$O), 3.75 (dd, J = 2.8, 8.5 Hz, 1H, H-2), 4.05 (dd, J = 7.2, 8.5 Hz, 1H, H-2), 5.72 (m, 2H, H-3 and H-4), 6.86 (s, 1H,

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(15) For general experimental details see ref 4. Assignments of ^1H NMR signals were made with the aid of 2D and decoupling methods and by comparisons with spectra of similar compounds prepared in our laboratory.

H-6). ^{13}C NMR: 27.8, 35.0, 37.1, 37.3, 42.2, 47.0, 50.2, 53.2, 66.5, 66.7, 73.0, 103.3, 125.4, 129.4, 135.4, 158.7, 164.3, 187.6. HRMS (EI) *m/z*: required for $C_{18}H_{23}NO_5$ 333.1576, found 333.1564.

Reaction of 1a with Methyl (*E*)-4,6-Heptadienoate. Naphthofuranone **1a** (0.21 g, 0.93 mmol) was mixed with freshly distilled methyl (*E*)-4,6-heptadienoate (1.3 g, 9.3 mmol) in dry CH_2Cl_2 (5 mL), and to the resulting solution was added $AlCl_3$ (14 mg, 0.1 mmol). After being stirred at room temperature for 4 days, the reaction was quenched with water, and the products were extracted into CH_2Cl_2. The organic extract was washed with brine, dried (Na_2SO_4), and concentrated under reduced pressure. Flash chromatography (20% EtOAc in hexane) led to the isolation of **3** (51 mg, 29% yield), its 2,2a-dehydro derivative (15 mg, 8% yield), and adduct **2** (22 mg, 7% yield), all of which crystallized from ether to give colorless needles, colorless plates, and shiny plates, respectively. Analytical data for **2**: ^{1}H NMR: 1.18 (s, 3H, R-CH_3), 1.61 (m, 1H, R−CH_2CH$_2$CO$_2$Me), 1.89), 1.61 (m, 1H, R-CH_2CH$_2$CO$_2$Me), 1.95 (dd, J = 6.35, 17.3 Hz, 1H, H-8), 2.01 (dd, J = 7.0, 15.4 Hz, 1H, H-1), 2.19 (ddd, J = 2.9, 5.3, 17.3 Hz, 1H, H-8), 2.41 (t, J = 8.0 Hz, 2H, R-CH$_2$CH_2CO$_2$Me), 2.45 (dt, J = 2.7, 15.4 Hz, 1H, H-1), 2.67 (m, 1H, H-11), 2.88 (ddd, J = 3.0, 6.5, 9.6 Hz, 1H, H-4), 3.28 (dd, J = 8.7, 11.4 Hz, 1H, R-CH_2O-R′), 3.65 (s, 3H, R-CO$_2$CH_3), 3.91 (t, J = 8.7 Hz, 1H, R-CH_2O-R′), 5.61 (dt, J = 3.0, 10.0 Hz, 1H, H-10), 5.81 (m, 1H, H-9), 5.96 (ddd, J = 2.8, 6.9, 9.6 Hz, 1H, H-2), 6.16 (ddd, J = 2.9, 6.6, 9.6 Hz, 1H, H-3), 6.20 (d, J = 10 Hz, 1H, H-6), 6.68 (d, J = 10 Hz, 1H, H-7). ^{13}C NMR: 25.1, 29.9, 30.3, 33.4, 36.5, 36.7, 39.6, 51.4, 51.5, 52.1, 70.4, 90.6, 125.6, 126.3, 126.8, 131.1, 132.1, 160.3, 173.9, 193.1. HRMS (EI) *m/z*: required for $C_{20}H_{24}O_4$ 329.1753, found 329.1735. Anal. Calcd for $C_{20}H_{24}O_4$: C, 73.15; H, 7.37. Found: C, 72.90; H, 7.28. Analytical data for **3**. Mp: 86−88 °C. IR: 2878, 1680, 1646, 1130 cm^{-1}. ^{1}H NMR: 1.28 (s, 3H, R-CH_3), 2.09 (dm, J = 17.9 Hz, 1H, H-5), 2.32 (dm, J = 17.9 Hz, 1H, H-5), 3.91 (m, 1H, H-2a), 4.03 (dd, J = 8.3, 10.3 Hz, 1H, H-2), 4.84 (dd, J = 8.3, 9.9 Hz, 1H, H-2), 5.75 (br s, 2H, H-3 and H-4), 6.20 (d, J = 9.8 Hz, 1H, H-7), 6.90 (d, J = 9.8 Hz, 1H, H-6). ^{13}C NMR: 21.6, 37.8, 39.6, 40.6, 76.2, 125.5, 126.4, 128.5, 139.7, 147.4, 154.9, 177.7. HRMS (EI) *m/z*: required for $C_{12}H_{12}O_2$ 188.0837, found 188.0848. Anal. Calcd for $C_{12}H_{12}O_2$: C, 76.57; H, 6.43. Found: C, 76.36; H, 6.23. Analytical data for **5a-methyl-5a,8-dihydro-5*H*-naphtho[1,8-*bc*]furan-8-one** (2,2a-dehydro derivative of **3**). IR: 1656, 1446, 1066, 826, 668 cm^{-1}. ^{1}H NMR: 1.36 (s, 3H, R-CH_3), 2.30 (dm, J = 17.3 Hz, 1H, H-5), 2.46 (ddd, J = 0.9, 5.8, 17.3 Hz, 1H, H-5), 5.94 (ddd, J = 2.6, 5.8, 9.7 Hz, 1H, H-4), 6.24 (d, J = 9.7 Hz, 1H, H-7), 6.54 (ddd, J = 0.9, 3.0, 9.7 Hz, 1H, H-4), 6.96 (d, J = 9.7 Hz, 1H, H-6), 7.49 (s, 1H, H-2). ^{13}C NMR: 25.8, 33.4, 36.3, 118.1, 120.8, 127.9, 130.1, 140.7, 144.2, 144.8, 152.7, 174.3. HRMS (EI) *m/z*: required for $C_{12}H_{10}O_2$ 186.0681, found 186.0686.

2-Carbomethoxy-4,4-dimethyl-2-cyclohexen-1-one (5d) was prepared from iodide **5b**[7] as a colorless oil, and the ^{1}H NMR spectrum recorded was in complete agreement with the data reported in the literature.[1d] ^{1}H NMR: 1.24 (s, 6H, R-CH_3), 1.90 (m, 2H, H-5), 2.54 (m, 2H, H-6), 3.80 (s, 3H, R-CO$_2$CH_3), 7.36 (t, J = 1.0 Hz, 1H, H-3).

2-Carbobutoxy-4,4-dimethyl-2-cyclohexen-1-one (5f) was prepared from iodide **5b**[7] as a yellow oil. IR: 2961, 1741, 1713, 1690, 1467, 1272 cm^{-1}. ^{1}H NMR: 0.93 (t, J = 7.2 Hz, 3H, R-CO$_2$-(CH$_2$)$_3$CH_3), 1.22 (s, 6H, R-CH_3), 1.42 (m, 2H, R-CO$_2$(CH$_2$)$_2$CH_2-Me), 1.63 (m, 2H, R-CO$_2$CH$_2$CH_2Et), 1.88 (m, 2H, H-5), 2.52 (m, 2H, H-6), 4.18 (t, J = 6.7 Hz, 2H, R-CO$_2$CH_2Pr), 7.27 (t, J = 0.9 Hz, 1H, H-3). ^{13}C NMR: 13.6, 19.0, 27.3, 30.5, 33.3, 35.1, 35.3, 65.0, 130.3, 163.6, 164.9, 194.4. HRMS (EI) *m/z*: required for $C_{13}H_{20}O_3$ 224.1412, found 224.1409.

2-Diethylaminocarbonyl-4,4-dimethyl-2-cyclohexen-1-one (5g) was prepared from iodide **5b**[7] as a light brown oil. IR: 2964, 1683, 1636, 1430, 1362, 1284 cm^{-1}. ^{1}H NMR: 1.05 (t, J = 7.1 Hz, 3H, R-CON(CH$_2$CH_3)$_2$), 1.14 (t, J = 7.1 Hz, 3H, R-CON-(CH$_2$CH_3)$_2$), 1.18 (s, 6H, R-CH_3), 1.88 (m, 2H, H-5), 2.49 (m, 2H, H-6), 3.09 (q, J = 7.1 Hz, 2H, R-CON(CH_2CH$_3$)$_2$), 3.40 (q, J = 7.1 Hz, 2H, R-CON(CH_2CH$_3$)$_2$), 6.63 (s, 1H, H-3). ^{13}C NMR: 12.9, 14.1, 27.6, 32.9, 34.4, 35.7, 39.2, 43.1, 135.9, 156.4, 166.9, 195.7. HRMS (EI) *m/z*: required for $C_{13}H_{21}NO_2$ 223.1572, found 223.1557.

4,4-Dimethyl-2-morpholinocarbonyl-2-cyclohexen-1-one (5i) was prepared from iodide **5b**[7] as a yellow oil. IR: 2960, 1682, 1634, 1434, 1360, 1114 cm^{-1}. ^{1}H NMR: 1.20 (s, 6H, R-CH_3), 1.90 (t, J = 6.8 Hz, 2H, H-5), 2.51 (t, J = 6.8 Hz, 2H, H-6), 3.20 (t, J = 4.8 Hz, 2H, RN(CH_2CH$_2$)$_2$O), 3.62 (t, J = 4.8 Hz, 2H, RN(CH$_2$CH_2)$_2$O), 3.68 (br s, 4H, RN(CH_2CH_2)$_2$O), 6.76 (s, 1H, H-3). ^{13}C NMR: 27.4, 33.0, 34.3, 35.5, 42.0, 47.4, 66.6, 66.7, 134.9, 158.4, 165.7, 195.3. HRMS (EI) *m/z*: required for $C_{13}H_{19}NO_3$ 237.1365, found 237.1364.

2-Carbomethoxy-2-cyclopenten-1-one (6d) was prepared from either iodide **6b**[6] or bromide **6c**[14] as a light yellow oil, and the ^{1}H NMR spectrum recorded was in complete agreement with the data reported in the literature.[16] ^{1}H NMR: 2.50 (m, 2H, H-4), 2.71 (m, 2H, H-5), 3.79 (s, 3H, R-CO$_2$CH_3), 8.41 (t, J = 3.2 Hz, 1H, H-3).

2-Carbethoxy-2-cyclopenten-1-one (6e) was prepared from either iodide **6b**[6] or bromide **6c**[14] as a yellow oil, and the ^{1}H NMR spectrum recorded was in complete agreement with the data reported in the literature.[16] ^{1}H NMR: 1.35 (t, J = 6.9 Hz, 3H, R-CH_3), 2.56 (m, 2H, H-4), 2.75 (m, 2H, H-5), 4.30 (q, J = 6.9 Hz, 2H, R-CO$_2$CH_2Me), 8.40 (t, J = 3.3 Hz, 1H, H-3).

2-Carbomethoxy-3-methyl-2-cyclopenten-1-one (7d) was prepared either from iodide **7b**[6] or bromide **7c**[14] as a yellow oil, and the ^{1}H NMR spectrum recorded was in complete agreement with the data reported in the literature.[17] ^{1}H NMR: 2.39 (s, 3H, R-CH_3), 2.52 (m, 2H, H-4), 2.70 (m, 2H, H-5), 3.85 (s, 3H, R-CO$_2$CH_3).

(*Z*)-3-Carbomethoxy-4-phenyl-3-buten-2-one (8d) was prepared from iodide **8b**[6] as a light orange oil, and the ^{1}H NMR spectrum recorded was in complete agreement with the data reported in the literature.[18] ^{1}H NMR (200 MHz, CDCl$_3$) δ: 2.42 (s, 3H, R-COCH_3), 3.84 (s, 3H, R-CO$_2$CH_3), 7.42 (m, 5H, R-C$_6H_5$), 7.58 (s, 1H, H-3).

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Supporting Information Available: X-ray crystallographic data for adduct **2** and copies of ^{1}H NMR spectra of **1g**−**i**, **5f**,**g**,**i**, and the 2,2a-dehydro derivative of **3**. This material is available free of charge via the Internet at http://pubs.acs.org.

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