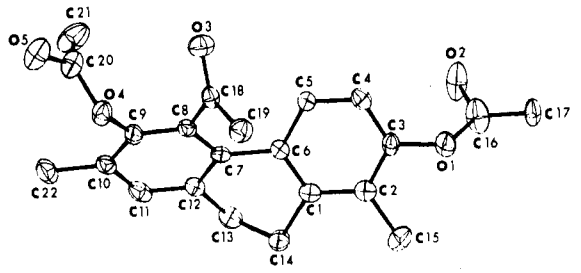

Figure 1. Molecular structure of juncunone diacetate with atoms displayed as 30% probability ellipsoids for thermal motion. Hydrogen atoms are not shown.

As a check on the stability of the instrument and the crystal, two reflections were measured after every 50 reflections; the standards fluctuated within a range of ±2%.

One independent quadrant of data was measured out to $2\theta = 50°$; a slow scan was performed on a total of 1808 reflections. Since these data were scanned at a speed which would yield a net count of 4000, the calculated standard deviations were all very nearly equal. No reflection was subjected to a slow scan unless a net count of 20 was obtained in the prescan. On the basis of these considerations, the data set of 1808 reflections (used in the subsequent structure determination and refinement) was considered observed and consisted mainly of those for which $I > 3\sigma(I)$. The intensities were corrected for Lorentz and polarization effects but not for absorption ($\mu = 0.93$ cm^{-1}).

The structure was solved by direct methods using the program MULTAN[6] and refined by full-matrix least-squares techniques[7] to give discrepancy indexes of $R = 0.088$ and $R_w = 0.096$ which are calculated as in eq 1 and 2. Carbon and oxygen atoms were

$$R = \sum||F_o| - |F_c||/\sum|F_o| \quad (1)$$

$$R_w = [\sum w(|F_o| - |F_c|)^2/\sum w(F_o)^2]^{1/2} \quad (2)$$

refined with anisotropic thermal parameters. All hydrogen atoms were located on a difference Fourier map. Those of the methyl substituents were refined as rigid groups. One of the acetate groups was disordered about the C–O bond; the occupancy factors converged at 0.60 and 0.40. The bond lengths and angles agree well (esd's of 0.008 Å and 0.6°, respectively) with generally accepted values.[8]

Acknowledgment. This work was supported by a grant from the National Cancer Institute (2-ROI-CA13268), National Institutes of Health, Bethesda, MD. We thank Dr. Sidney McDaniel for collection of plant material.

Registry No. 1, 62023-90-9; 3, 77305-81-8; 4, 77305-82-9.

Supplementary Material Available: The fractional coordinates (Table I), important bond distances and angles (Table II), and a complete listing of structure factor amplitudes (13 pages). Ordering information is given on any current masthead page.

(5) J. Holton, M. F. Lappert, D. G. H. Ballard, R. Pearce, J. L. Atwood, and W. E. Hunter, *J. Chem. Soc., Dalton Trans.*, 45 (1979).
(6) G. Germain, P. Main, and M. M. Woolfson, *Acta Crystallogr., Sect. A*, **27**, 368 (1971).
(7) The following crystallographic programs were used: D. J. Hodgson's version of Dellaca and Robinson's Fourier program as locally implemented for the UNIVAC 1110, University of Alabama; W. R. Busing, K. O. Martin, and H. A. Levy, "A Fortran Crystallographic Least-Squares Program", Report ORNL-TM 305, Oak Ridge National Laboratory, Oak Ridge, TN, 1965; C. Johnson, "ORTEP, A Fortran Thermal-Ellipsoid Plot Program", Report ORNL-3794, Oak Ridge National Laboratory, Oak Ridge, TN, 1965; W. R. Busing, K. O. Martin, and H. A. Levy, "ORFFE, A Fortran Crystallographic Function and Error Program", Report ORNL-TM 306, Oak Ridge National Laboratory, Oak Ridge, TN, 1964.
(8) O. Kennard, D. G. Watson, F. H. Allen, N. W. Issacs, W. D. S. Motherwell, R. C. Pettersen, and W. G. Town, Eds., "Molecular Structures and Dimensions", Vol. A1, N. V. A. Oosthoek, Utrecht, The Netherlands, 1972.

Synthesis of Bicyclo[3.3.0]oct-1(2)-en-3-one

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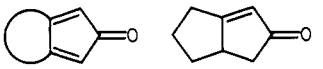
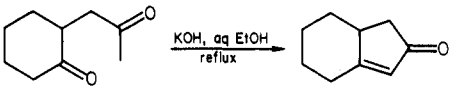
In connection with a project on the synthesis of cyclopentadienones containing a ring fused to the C3–C4 bond, as in **1**, we required the title compound **2**. Surprisingly this relatively simple enone, which is of current interest because the ring system is present in many biologically active natural products, has eluded synthesis.



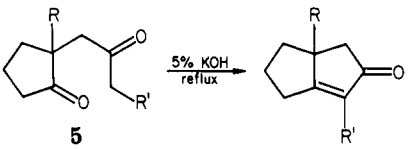
1 **2**

A variety of condensations which might reasonably be expected to give **2** have failed. For example, although base-catalyzed intramolecular aldol condensation of **3**[1]



3 **4** (83%)

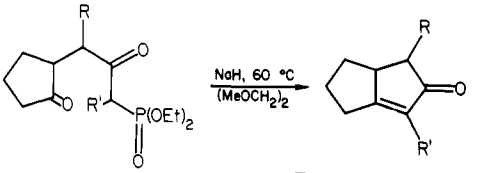
gives a good yield of the next higher homologue **4** and similar conditions give simple methyl derivatives of **2** (i.e., **6**–**8**), these methods failed to give **2** from **5** (R = R′ = H). Only complex intractable mixtures were obtained.[2]



5

6,[1] R = CH_3; R′ = H (79%)
7,[2] R = H; R′ = CH_3 (83%)
8,[1] R = R′ = CH_3 (88%)

In a very recent paper[3] the Wadsworth–Emmons modification of the Wittig reaction also failed when applied to **2**. Thus whereas **7** and **10** could be obtained in good yield, only a "tarry mass" was obtained when the same procedure was applied to **9** (R = R′ = H).[4]



9

7, R = H; R′ = CH_3 (80%)
10, R = CH_3; R′ = H (70%)

We have been able to prepare the long-sought **2** in 38% overall yield from the known precursors **11**[5] and **12**.[6] Carefully controlled conditions are required for the hydrolysis and decarboxylation of **12**. An improved procedure for the synthesis of **11** is given in the Experimental Section. By Becker's procedure,[6] cyclization of **11** with

(1) Miyashita, M.; Yanami, T.; Yoshikoshi, A. *J. Am. Chem. Soc.* **1976**, *98*, 4679 and earlier references cited therein.
(2) Paul, H.; Wendel, I. *Chem. Ber.* **1957**, *90*, 1342.
(3) Bailey, M. J.; Cooper, K.; Pattenden, G. *Tetrahedron Lett.* **1981**, 257. Since it may lead to some confusion, we call attention to the fact that the title and text of this paper give an incorrect (indeed, impossible) name to these compounds.
(4) At 25 °C with 2 equiv of NaH the authors isolated a novel dimer of **2** and "in only one experiment" were they able to isolate a "small amount" of **2**.
(5) Herz, W. *J. Am. Chem. Soc.* **1956**, *78*, 1485.
(6) Becker, D.; Brodsky, N. C.; Kalo, J. *J. Org. Chem.* **1978**, *43*, 2557.

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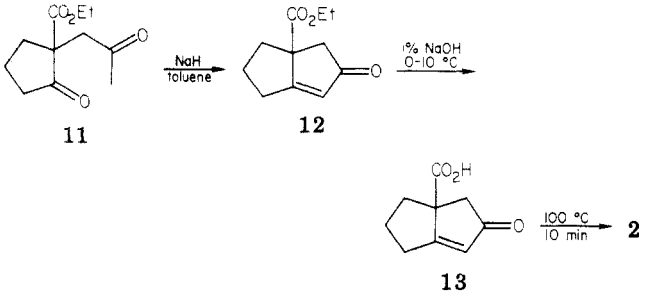
sodium hydride in toluene gave keto ester **12**.[7] After



bulb-to-bulb distillation, crude **12** was hydrolyzed under exceptionally mild conditions, 1% aqueous NaOH at 0–10 °C for 1.5 h. Extraction of the nonhydrolyzable impurities with chloroform and acidification gave the crude keto acid **13**, which was readily decarboxylated in a few minutes on a steam bath. The product **2** was >95% pure by NMR and GC but could be further purified if necessary by preparative GC.

Enone **2** is a mobile liquid with an exceptionally sweet aroma. Its structure was clear from its spectral properties. In particular the IR and UV spectra showed a conjugated cyclopentenone, the proton NMR spectrum showed one vinyl proton (δ 5.86), and the ^{13}C NMR spectrum and mass spectra were also consistent with the structure. In particular the IR and UV spectra showed a conjugated cyclopentenone, the proton NMR spectrum showed one vinyl proton (δ 5.86), and the ^{13}C NMR spectrum and mass spectra were also consistent with the structure. Finally chemical transformations of **2**, to be described in conjunction with the synthesis of **1**, confirm the structure.

The synthesis of **2** described here makes the substance available in amounts sufficient for further chemical manipulation.

Experimental Section

2-Acetonyl-2-(ethoxycarbonyl)cyclopentanone (11). (a) 2-(Ethoxycarbonyl)-2-propargylcyclopentanone (14). To a refluxing solution of potassium (26.2 g, 0.67 mol) in *tert*-butyl alcohol (850 mL) was added, under nitrogen and over 15 min, neat 2-(ethoxycarbonyl)cyclopentanone (95 g, 0.61 mol). After 15 min of further reflux, propargyl bromide (90.6 g, 0.61 mol) was added over 45 min (exothermic reaction). The *tert*-butyl alcohol (~600 mL) was removed by distillation and the cooled remaining mixture was poured onto ice (500 g). The organic layer was washed with water (3 × 200 mL), concentrated under reduced pressure, taken up in chloroform (750 mL), dried ($MgSO_4$), and distilled to give 95.6 g (81%) of pure **14**, bp 107 °C (4 torr), as a colorless liquid: IR (neat) 3280 (m), 2980 (m), 1750 (vs), 1725 (vs), 1470 (w), 1450 (w), 1425 (w), 1405 (w), 1330 (m), 1015 (m), 930 (w), 860 (w), 810 (w) cm^{-1}; ^1H NMR (250 MHz, $CDCl_3$) δ 1.247 (t, 3 H, J = 7.3 Hz), 2.046 (t, 1 H, J = 2.7 Hz), 2.06–2.60 (m, 6 H), 2.680 and 2.687 (dd, 2 H, J = 2.7 and 17 Hz), 4.158 (q, 2 H, J = 7.3 Hz); ^{13}C NMR ($CDCl_3$) δ 14.04, 19.79, 23.13, 32.57, 38.20, 58.75, 61.64, 70.99, 79.97, 170.23, 213.11; mass spetrum, m/e (relative intensity) 194 (5), 166 (38), 149 (26), 138 (53), 121 (79), 120 (28), 111 (54), 110 (31), 109 (37), 93 (92), 92 (44), 91 (96), 79 (74), 78 (30), 77 (95), 67 (40), 65 (84), 64 (23), 53 (32), 51 (22), 43 (27), 41 (37), 39 (100). Anal. Calcd for $C_{11}H_{14}O_3$: C, 68.02; h, 7.27. Found: C, 68.09; H, 7.34.

(b) Hydration of 14. A mixture of **14** (86 g, 0.44 mol), methanol (600 mL), water (150 mL), mercuric oxide impregnated Dowex 50 H^+ resin[8] (2.0 g, 200–400 mesh), and concentrated sulfuric acid (4 drops) was stirred at room temperature for 60 h, then filtered, and concentrated under vacuum. The residue was taken up in chloroform (400 mL) and the aqueous layer was extracted with chloroform (100 mL). The combined organic layers were dried ($MgSO_4$) and distilled to give 93.0 g (99%) of **11** as a colorless liquid: IR (neat) 2945 (m), 2910 (m), 1750 (vs), 1720 (vs), 1450 (m), 1420 (m), 1405 (s), 1368 (s), 1325 (m), 1282 (m), 1255 (m), 1230 (s), 1168 (s), 1148 (s), 1110 (m), 1050 (w), 1030 (m), 970 (w), 940 (w), 920 (w), 858 (w) cm^{-1}; ^1H NMR (250 MHz, $CDCl_3$) δ 1.237 (t, 3 H, J = 7.3 Hz), 2.099 (d, 1 H, J = 18.3 Hz), 2.147 (s, 3 H), 1.95–2.65 (m, 6 H), 3.184 (d, 1 H, J = 18.3 Hz), 4.141 (q, 2 H, J = 7.3 Hz); ^{13}C NMR ($CDCl_3$) δ 13.97, 19.79, 29.86, 33.24, 37.55, 47.42, 57.44, 61.44, 170.45, 205.14, 214.26; mass spectrum, m/e (relative intensity) 212 (0.4), 167 (12), 166 (34), 141 (7), 139 (15), 138 (7), 124 (21), 123 (26), 113 (13), 111 (32), 110 (8), 97 (17), 95 (28), 71 (8), 68 (8), 67 (20), 55 (13), 43 (100). Anal. Calcd for $C_{11}H_{16}O_4$: C, 62.25; H, 7.60. Found: C, 62.14; H, 7.70.

Bicyclo[3.3.0]oct-1(2)-en-3-one (2). To a refluxing mixture of sodium hydride (4.0 g, 0.167 mol) in anhydrous toluene (300 mL) was added under nitrogen over 2 h a solution of **11** (8.0 g, 0.039 mol) in toluene (200 mL), and the resulting mixture was refluxed for 18 h. The mixture was cooled to 10 °C and carefully acidified with 10% hydrochloric acid (90 mL). The aqueous layer was separated and washed with ether (3 × 50 mL), and the combined organic layers were washed with saturated brine (50 mL) and dried ($MgSO_4$). After the solvent was removed under reduced pressure, the residue was distilled bulb-to-bulb at 100 °C (0.1 torr) to give 4.44 g of crude keto ester **12**. This product was treated with 1% aqueous sodium hydroxide (100 mL) for 1.5 h at 0–10 °C. The resulting mixture was washed with chloroform (50 mL), acidified with 10% hydrochloric acid, and extracted with chloroform (3 × 50 mL). The extract was dried ($MgSO_4$) and the solvent was removed under reduced pressure to give a clear oil. This oil (impure **13**) was heated on a steam bath for 10 min (gas evolution), diluted with chloroform, washed with 5% aqueous sodium hydroxide (25 mL), and dried ($MgSO_4$) and the solvent evaporated to give 1.75 g (38% from **11**) of a mobile, sweet-smelling liquid which by NMR and GC was >95% pure **2**. Further purification was possible by preparative GC (5% FFAP on Chromosorb W-AWDMCS, 0.25 in. × 6 ft column, 160 °C): IR (neat) 2968 (s), 2875 (m), 1705 (vs), 1625 (s), 1452 (m), 1375 (w), 1315 (m), 1258 (w), 1176 (m), 1158 (m), 1108 (w), 1082 (w), 1028 (w), 932 (w), 872 (m), 835 (w), 819 (w) cm^{-1}; UV (MeOH) λ_{max} 228 nm (ϵ 12 200), 293 (62); ^1H NMR ($CDCl_3$) δ 1.7–3.0 (m, 9 H), 5.86 (br s, 1 H); ^{13}C NMR ($CDCl_3$) δ 25.55, 26.30, 31.16, 42.36, 46.74, 124.79, 191.41, 210.93; mass spectrum, m/e (relative intensity) 122 (100), 121 (31), 107 (22), 95 (5), 94 (72), 79 (52); high-resolution mass spectrum, calcd for $C_8H_{10}O$ 122.07260, found 122.07317.

Acknowledgment. We are indebted to the National Institutes of Health (GM 15997) and the National Science Foundation (CHE 80-17746) for financial support of this research.

Registry No. **2**, 72200-41-0; **11**, 61771-77-5; **12**, 65898-66-0; **13**, 77320-45-7; **14**, 77320-46-8; 2-(ethoxycarbonyl)cyclopentanone, 611-10-9; propargyl bromide, 106-96-7.

(7) Use of other bases in this cyclization, such as potassium hydride or potassium *tert*-butoxide in refluxing toluene or THF, gave no yield improvement.

(8) Newman, M. S. *J. Am. Chem. Soc.* **1953**, *75*, 4740.

Anodic Fluorination of Benz[*a*]anthracene

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Whereas benz[*a*]anthracene (**1**) is a weak carcinogen, its 12-methyl (**2a**), 7-methyl (**3a**), and 7,12-dimethyl (**4a**) analogues become increasingly more carcinogenic.[1] All

