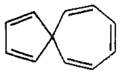
Synthesis of Spiro[4.6]undecane-1,6-dione

Thomas N. Wheeler,* Clifford A. Jackson,[1] and Kirk H. Young[1]

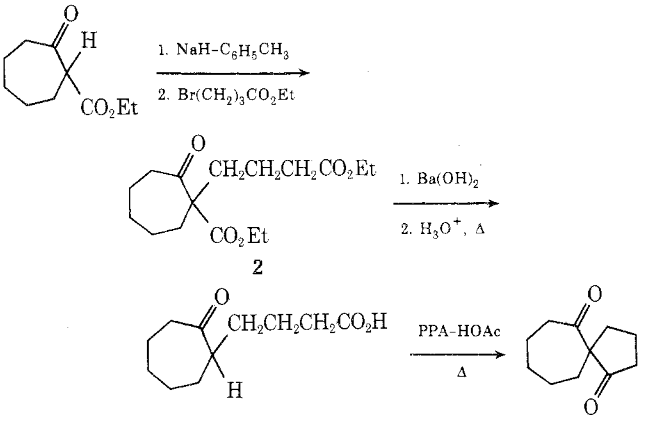
Department of Chemistry, Florida Technological University, Orlando, Florida 32816

Received October 2, 1973

As a part of our long-range objective of exploring the chemistry of spirarenes,[2,3] we have undertaken the synthesis of spiro[4.6]undeca-1,3,6,8,10-pentaene (**1**). An attractive precursor in the synthesis of **1** is the previously unknown spiro[4.6]undecane-1,6-dione (**4**). We now wish to report the synthesis of **4**, prepared as shown, *via* an acid-catalyzed intramolecular Claisen condensation of 4-(2′-oxocycloheptyl)butyric acid (**3**).



1



The acid-catalyzed intramolecular Claisen condensation represents a reaction type which only recently has been exploited as a means of synthesizing in moderate to high yields nonenolizable β-diketones.[4] Our procedure is an extension of the work of Gerlach and Müller, who have reported[5,6] that 4-(2′-oxocyclopentyl)butyric acid undergoes cyclization with polyphosphoric acid–acetic acid solution to give an 85% yield of spiro[4.4]nonane-1,6-dione. The lower yield in the synthesis of **4** (52%) as compared to that of spiro[4.4]nonane-1,6-dione is presumably due to the higher strain energy of the former.

The structure of the spiro ketone **4** was confirmed by physical methods. The infrared spectrum of **4** showed $\bar{\nu}_{max}$ at 1735 and 1695 cm^{-1} due to the carbonyl stretching frequency of cyclopentanone and cycloheptanone rings, respectively. The nmr, uv, mass spectrum, and composition analysis are all consistent with the structure proposed for **4**.

The acid-catalyzed intramolecular Claisen condensation described here offers a facile method for the synthesis of spirocyclic 1,3-diketones. Furthermore, this method should be general and provide an alternate synthetic route to spiro molecules in which at least one of the rings is a five- or six-membered ring.

Experimental Section[7]

Preparation of Diethyl 4-(1′-Carbethoxy-2′-oxocycloheptyl)-butyrate (2).[8] The keto diester **2** was prepared by the general procedure of Huisgen and Pawallek.[8] A 56% yield of **2** was obtained as a clear oil: bp 133–137° (0.10 mm) [lit.[8] bp 110–115° (0.01 mm)]; ir (CCl_4) 1730 (ester C=O), 1700 (cycloheptanone C=O), 1175 cm^{-1}; nmr (CCl_4) δ 1.40 (6 H, six lines), 1.40–2.20 (m, 12 H), 2.20–2.90 (m, 4 H), 4.30 (m, 4 H).

Preparation of 4-(2′-Oxocycloheptyl)butyric Acid (3).[9] The keto acid **3** was obtained by the procedure of Kimeki and Bien.[9] An 84% yield of **3** was obtained as a clear oil: bp 142–145° (0.15 mm) [lit.[9] bp 138–140° (0.01 mm)]; ir (CCl_4) 3400–3000 and 2700–2400 (OH), 1700 (C=O), 935 cm^{-1}; nmr ($CDCL_3$) δ 2.1–1.0 (m, 12 H), 2.9–2.1 (m, 3 H), 11.26 (s, 1 H).

Preparation of Spiro[4.6]undecane-1,6-dione (4). To a stirred solution of 34.1 g (0.10 mol) of polyphosphoric acid[10] and 65.0 g (1.08 mol) of purified glacial acetic acid[11] under N_2 was added (dropwise) 10.0 g (0.051 mol) of **3**. The reaction mixture was heated for 6 hr at 100° in an oil bath, cooled, poured onto ice, and extracted with benzene (3 × 100 ml). The combined benzene extracts were washed with saturated $NaHCO_3$ (3 × 100 ml) and dried ($MgSO_4$), and the benzene was removed. Vacuum distillation of the residue gave 4.75 g (52%) of **4** as a clear, colorless oil: bp 101–103° (1.25 mm); ir (CCl_4) 1735 (cyclopentanone C=O), 1695 (cycloheptanone C=O), 1145 cm^{-1}; uv (95% ethanol) λ_{max} 303 nm (ϵ 127); nmr (CCl_4) δ 2.90–1.0 (m); mass spectrum (70 eV) *m/e* (rel intensity) 180 (23, M$^+$), 152 (16), 135 (16), 125 (25), 124 (17), 123 (25), 110 (17), 97 (24), 96 (31), 95 (22), 81 (38), 79 (18), 69 (15), 68 (15), 67 (37), 57 (28), 55 (88), 54 (17), 53 (17), 43 (100), 39 (39).

Anal. Calcd for $C_{11}H_{16}O_2$: C, 73.30; H, 8.95. Found: C, 73.45; H, 8.75.

Acknowledgment. We gratefully acknowledge the support of this work by the donors of the Petroleum Research Fund, administered by the American Chemical Society, and thank Dr. George Hertel of Florida Technological University for providing the mass spectra.

Registry No.—**2**, 50987-56-9; **3**, 33366-38-0; **4**, 50987-57-0.

References and Notes

(1) Petroleum Research Fund Undergraduate Research Participants, summer 1973.
(2) H. E. Simmons and T. Fukunaga, *J. Amer. Chem. Soc.*, **89**, 5208 (1967).
(3) R. Hoffmann, A. Imamura, and G. D. Zeiss, *J. Amer. Chem. Soc.*, **89**, 5215 (1967).
(4) Y. Kos and H. J. E. Lowenthal, *J. Chem. Soc.*, 605 (1963).
(5) H. Gerlach and W. Müller, *Helv. Chim. Acta*, **55**, 2277 (1972).
(6) H. Gerlach and W. Müller, *Angew. Chem., Int. Ed. Engl.*, **11**, 1030 (1972).
(7) Ir spectra were recorded with a Perkin-Elmer Model 457 spectrometer. Ultraviolet spectra were determined in 95% ethanol with a Beckman DK-2A spectrometer. Nmr spectra were obtained with a Varian T-60 spectrometer using TMS as an internal standard. The mass spectra were obtained at an ionizing energy of 70 eV on a magnetic sector mass spectrometer with a modified Nier-type source. This mass spectrometer was constructed by Dr. George Hertel of Florida Technological University. Microanalyses were performed by Robertson Laboratory, Florham Park, N. J.
(8) R. Huisgen and D. Pawallek, *Justus Liebigs Ann. Chem.*, **641**, 71 (1961).
(9) D. Kimeki and S. Bien, *J. Chem. Soc.*, 5345 (1961).
(10) Matheson Coleman and Bell polyphosphoric acid, practical, was used without further purification.
(11) Commercial glacial acetic acid was treated with 5% (by weight) $KMnO_4$ and distilled. This material was redistilled from P_2O_5.

Utilization of the 1,4-Conjugated Wittig Reaction for the Synthesis of Substituted 1,3-Cyclohexadienes

Albert Padwa* and Lee Brodsky

Department of Chemistry, State University of New York at Buffalo, Buffalo, New York 14214

Received November 7, 1973

Despite the enormous success of the Wittig reaction for the preparation of olefins,[1-4] this method does have certain limitations. One complication is that the alkylidenephosphorane can function as a proton acceptor and promote enolate condensation reactions.[1] Another side reaction that occasionally occurs in the 1,4 addition of the alkylidenephosphorane to the β-carbon atom of a conjugate ketone.[5] We now report a study which shows that the Michael addition of certain alkylidenephosphoranes with α,β-unsaturated ketones can be advantageously utilized for the synthesis of substituted 1,3-cyclohexadienes.