methylene)camphor, Dr. C. S. Pak for early determinations of CD spectra of 1 and 5–7, and Dr. F. S. Steinberg for establishing a modified synthesis of 1.

Registry No. 1, 74033-52-6; 2, 74033-53-7; 3, 16161-84-5; 5, 29583-35-5; 6, 40550-41-2; 7, 464-49-3; 8, 10292-98-5; 9, 25861-51-2; 2-methylenebornane, 5655-58-3.

A New Synthesis of Cyclic Allenic Esters[1]

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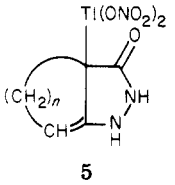
Previous studies[2,3] have demonstrated the generality of the conversion of 3,4-polymethylene-2-pyrazolin-5-ones to cycloalkene-1-carboxylic acids in two steps: first by conversion to the 4-halo-3,4-polymethylene-2-pyrazolin-5-one and then by a ring-opening reaction with aqueous sodium hydroxide. In related work, Taylor's group[4] has converted 3,4-dialkyl-2-pyrazolin-5-ones directly to acyclic allenic esters using thallium(III) nitrate and methanol, a reaction which simultaneously involved putting on the leaving groups in the 4-position of the pyrazolin-5-one and ring opening. There has been much interest in the synthesis[5] and reactions[6] of allenic acids and esters, and in this paper, we describe an extension of this reaction to the synthesis of the difficult-to-obtain 1-carbomethoxy cyclic allenic esters from the readily available cycloalkanones.

For purposes of clarity, the overall synthetic route is shown in Scheme I.

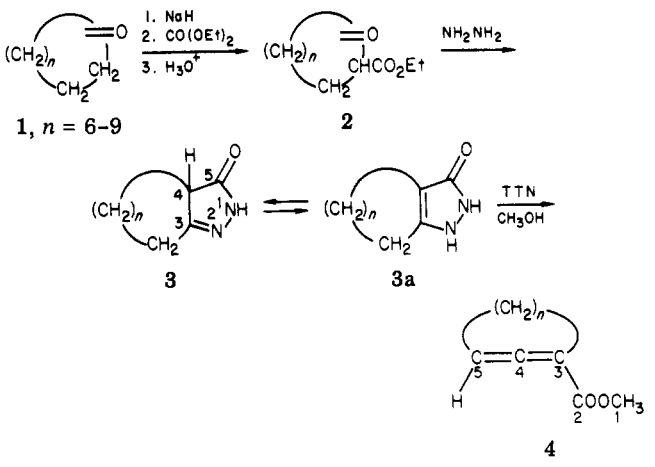
The first step in the synthesis invovled the conversion of the cycloalkanone 1 to the respective β-keto ester 2, which was readily accomplished by reaction of 1 with sodium hydride and diethyl carbonate. The second step involved reaction of 2 with hydrazine hydrate to form the corresponding 3,4-polymethylene-2-pyrazolin-5-one, 3. Compound 3 was converted to the cyclic allenic ester 4 by reaction with thallium(III) nitrate (TTN) and methanol.

The conversion of 3 to allenic esters[4] can be explained by electrophillic thallation of the enamine (3-pyrazolin-5-one) tautomer[7] 3a followed by loss of proton at the 3-substituted methylene position to give the cyclic alkylidene pyrazolidone 5. Subsequent oxidation of the hydrazo bond



5

Scheme I



of 5 by TTN and ring opening with methanol would give the cyclic allenic ester 4. Previous evidence that 5-pyrazolones undergo oxidation to oxopyrazoles[8] supports this explanation.

The structures of 4 (n = 6–9) were supported by spectral and analytical data. In general, the infrared spectra of the cyclic allenes showed a sharp absorption near 1960 cm^{-1}, corresponding to the allene linkage, and one around 1720 cm^{-1}, indicative of the carbonyl stretching frequency of the allenic ester. The proton magnetic resonance spectra of 4 showed a complex multiplet ranging from 0.90–2.50 ppm downfield from Me_4Si, assigned to the methylene hydrogens, a singlet of area 3 hydrogens near 3.70 ppm, and a multiplet or broad triplet of area 1 near 5.60 ppm, attributed to the methyl ester and vinyl hydrogens, respectively. ^{13}C nuclear magnetic resonance spectra of 4 exhibited an extreme downfield shift and weak absorption (small NOE) of the central allenic (C_4) carbon (208.5 to 211.1 ppm) which is consistent with data reported by Friedel and Retcofsky[9] and Stens and co-workers[10] for acylic allenes. The very low position of the central allenic carbon makes ^{13}C NMR an important tool for investigating molecular structures of this type. The cumulative olefinic resonances of the C_3 and C_5 carbons range from 96.25 to 101.19 ppm and 91.62 to 96.14 ppm, respectively, giving a total spread of the allenic carbons of 120 ppm as compared to 140 ppm for the acyclic case.[9] The methylene bridge carbons, the methyl ester carbon (C_1), and carbonyl ester carbon (C_2) all exhibit chemical shift values in expected areas.[11]

The preparation of 1-substituted cyclic allenes through the cyclic 5-pyrazolone appears to be most promising in that the method could be used as a general synthesis of lower or higher cyclic allene systems and utilizes readily available cycloalkanones as starting materials.

Experimental Section

All melting and boiling points were uncorrected. IR spectra were determined with a Perkin-Elmer Model 621 double-beam spectrophotometer and were calibrated vs. polystyrene. ^1H NMR spectra were recorded on a Perkin-Elmer 60-MHz R20A spectrometer with tetramethylsilane as an internal standard. ^{13}C NMR

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spectra were taken on a Varian CFT-20 spectrometer with proton noise decoupling, operating in the pulse Fourier transform mode with deuterium lock. Analyses were done by Galbraith Laboratories, Inc., Knoxville, TN.

2-Carbethoxycycloalkanones, 2 (n = 6–9). The method of Rhoades[12] et al. involving carbethoxylation by diethyl carbonate and sodium hydride was used in the preparation of 2-carbethoxycyclononanone (76%), 2-carbethoxycyclodecanone (69%), 2-carbethoxycycloundecanone (71%), and 2-carbethoxycyclododecanone (73%). **2** (n = 9) was also prepared by the method of Shahak[13] involving carbethoxylation by triethyl phosphonoformate–sodium hydride in 68% average yield.

3,4-Polymethylene-2-pyrazolin-5-one, 3 (n = 6–9). The method of Silveira, Mehra, and Atwell[2] was used in the preparation of **3**. All yields of **3** (n = 6–9) were in excess of 95%.

Cyclic Allenic Methyl Esters, 4 (n = 6–9). To a 250-mL flask containing 4.5 mmol of **3** was added 30 mL of methanol. In another 250-mL flask, 3.5 g (9 mmol) of thallium(III) nitrate (TTN) was added to 40 mL of methanol. TTN was prepared as previously[14] except the acid wash with dilute HNO_3 was omitted for on washing all crystals dissolved. The solution of TTN was transferred to the flask containing the pyrazolone–methanol mixture and the resulting solution was stirred with a magnetic stirrer for 30 min. The precipitated thallium(I) nitrate was removed by vacuum filtration and the filtrate was extracted several times with 50-mL portions of chloroform. The combined extracts were dried with anhydrous Na_2SO_4 overnight, filtered, rinsed with an additional 20 mL of chloroform, and passed through a 60–100 mesh Florisil (10 g) column. After all the extracts had been eluted from the column, an additional 30 mL of chloroform was added and the chloroform was removed under reduced pressure at 40 °C to give the pure allenic esters **4**.

4 (n = 6): 49% average yields; n^{22}_D 1.5050; IR (CCl_4) 1709, 1960 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.90–2.50 (complex m, 12 H), 3.71 (s, 3 H), 5.70 (m, 1 H). Anal. Calcd for $C_{11}H_{16}O_2$: C, 73.33; H, 8.88. Found: C, 73.16; H, 8.87.

4 (n = 7): 57% average yields; n^{22}_D 1.5035; IR (CCl_4) 1721, 1961 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.90–2.50 (complex m, 14 H), 3.70 (s, 3 H), 5.50 (m, 1 H); ^{13}C NMR ($CDCl_3$) δ 21.16–26.68 ($(CH_2)_7$), 51.50 (C_1), 94.38 (C_5), 99.21 (C_3), 167.13 (C_2), 209.31 (C_4). Anal. Calcd for $C_{12}H_{18}O_2$: C, 74.23; H, 9.28. Found: 74.19, 9.36.

4 (n = 8): 57% average yields; n^{22}_D 1.5010; IR (CCl_4) 1721, 1961 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.90–2.50 (complex m, 16 H), 3.72 (s, 3 H), 5.66 (7, 1 H); ^{13}C NMR ($CDCl_3$) δ 22.82–28.03 ($(CH_2)_8$), 51.15 (C_1), 96.14 (C_5), 101.19 (C_3), 167.56 (C_2), 208.50 (C_4). Anal. Calcd for $C_{13}H_{20}O_2$: C, 75.00; H, 9.62. Found: C, 75.13; H, 9.68.

4 (n = 9): 54% average yields; n^{22}_D 1.5012; IR (CCl_4) 1721, 1960 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.90–2.50 (complex m, 18 H), 3.70 (s, 3 H), 5.33 (t, 1 H); ^{13}C NMR ($CDCl_3$) δ 20.61–26.26 ($(CH_2)_9$), 50.84 (C_1), 91.62 (C_5), 96.25 (C_3), 166.80 (C_2), 211.06 (C_4). Anal. Calcd for $C_{14}H_{22}O_2$: C, 75.68; H, 9.91. Found: C, 75.40; H, 9.91.

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Registry No. **1** (n = 6), 3350-30-9; **1** (n = 7), 1502-06-3; **1** (n = 8), 878-13-7; **1** (n = 9), 830-13-7; **2** (n = 6), 4017-57-6; **2** (n = 7), 4017-58-7; **2** (n = 8), 4017-59-8; **2** (n = 9), 4017-60-1; **3** (n = 6), 63657-98-7; **3** (n = 7), 63657-99-8; **3** (n = 8), 63658-00-4; **3** (n = 9), 63658-01-5; **4** (n = 6), 74143-60-5; **4** (n = 7), 74143-61-6; **4** (n = 8), 74143-62-7; **4** (n = 9), 74143-63-8.

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Synthesis of 3-Methoxyphthalic Anhydride[1]

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Because of the possible use of 3-methoxyphthalic anhydride, **1**, for the synthesis of 8-methoxy- and 11-methoxy-7,12-dimethylbenz[a]anthracenes we wished to prepare a quantity of this material. The best known route appeared to us to be the reaction of dihydroanisole with dimethyl acetylenedicarboxylate[3,4] in the presence of dichloromaleic anhydride (DCMA)[4] to prepare dimethyl 3-methoxyphthalate followed by conversion to **1**. We used diethyl acetylenedicarboxylate instead of dimethyl acetylenedicarboxylate because the diethyl ester was preparable in higher yield from the precursor, the potassium acid salt of acetylenedicarboxylic acid (Aldrich). We obtained diethyl 3-methoxyphthalate in 86% yield.

The conventional route to 3-methoxyphthalic anhydride from dialkyl 3-methoxyphthalates involves alkaline hydrolysis followed by anhydride formation.[3] However, because of the high water solubility of 3-methoxyphthalic acid this route was supplanted by a direct conversion of the diethyl ester to **1** by heating with a small amount of boron trifluoride etherate.

Experimental Section[5]

Diethyl Acetylenedicarboxylate. A stirred mixture of 304 g of potassium acid acetylenedicarboxylate, 600 mL of absolute ethanol, and 600 mL of benzene was slowly treated with 150 g of concentrated H_2SO_4. The mixture was held at reflux into a Dean–Stark trap for 24 h, during which the lower layer was occasionally removed.[6] After a conventional workup 325 g (95%) of diethyl ester was obtained, bp 78–83 °C (1–1.5 mm) [lit.[6] bp 60–62 °C (0.3 mm)], suitable for use in the next step.

1-Methoxy-1,4-cyclohexadiene. To a solution of 440 mL of ethanol and 163 g (1.5 mol) of anisole in 1–6 L of liquid ammonia in a three-necked flask fitted with a stirrer and dry ice–isopropyl alcohol cooled reflux condenser was slowly added during 1.5 h 88 g of clean cut sodium in small pieces. After 1 h more, about 2 g of solid sodium benzoate was added to destroy the blue color. After the ammonia evaporated, the product was extracted with three 500-mL portions of pentane. The combined extracts were passed through a funnel containing $MgSO_4$. The pentane was distilled and then 150 g (91%) of the product, bp 145–147 °C, was obtained.

Diethyl 3-Methoxyphthalate. To 350 mg of dichloromaleic anhydride[7] in a 1-L two-necked flask fitted with a reflux condenser, dropping funnel, and magnetic stirrer was added 50 mL of a mixture of 110 g of 1-methoxy-1,4-cyclohexadiene and 173 g of diethyl acetylenedicarboxylate. The flask was heated with an oil bath to 125 °C when the evolution of ethylene started. The remaining mixture was added during 30 min and the temperature was raised to 150 °C and slowly to 200 °C and kept here for 3 h. Vacuum distillation afforded 217 g (86%) of diethyl 3-methoxyphthalate, bp 168–172 °C (2–3 mm).

3-Methoxyphthalic Anhydride (1). A mixture of 12.6 g of diethyl 3-methoxyphthalate and 1.5 mL of boron fluoride etherate was heated under reflux at 160–165 °C for 1 h. The temperature was slowly raised (with darkening) to 180–185 °C for 3 h. Vacuum distillation afforded a solid distillate, bp 205–215 °C (0.2 mm),

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