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}; ^1H 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}; ^1H 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}; ^1H 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}; ^1H 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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[1] This work was supported by Grant CA-07394 of the National Cancer Institute, DHEW.

[2] Postdoctoral Research Associate.

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which was dissolved in 50 mL of chloroform and diluted with petroleum ether to yield 6.8 g (87% based on recovery of 1.6 g of ester of 1), mp 158 °C, from the mother liquor by chromatography over basic alumina.

When the above reaction was tried in *o*-dichlorobenzene at reflux for 10 h (occasional addition of BF_3 etherate) a 90% yield of 1, based on recovery of 20% diethyl 3-methoxyphthalate, was obtained.

Registry No. 1, 14963-96-3; diethyl acetylenedicarboxylate, 762-21-0; potassium acid acetylenedicarboxylate, 928-04-1; 1-methoxy-1,4-cyclohexadiene, 2886-59-1; diethyl 3-methoxyphthalate, 38157-42-5.

Photochemistry of 4-Methylisochromene and 1,5-Hydrogen Migration in the Resulting *o*-Xylylene

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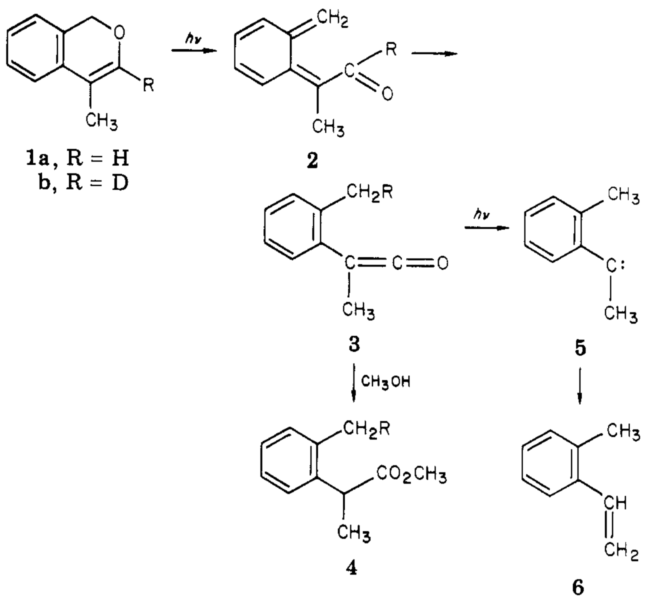
Diels–Alder reactions of *o*-quinodimethanes (*o*-xylylenes) with inter- and intramolecular dienophiles have been shown to have considerable utility for the synthesis of polycyclic ring systems.[1] Recently it has been reported[2] that various substituted isochromenes produce *o*-xylylene derivatives upon UV irradiation. Our interest[3] in the synthetic use of photochemically generated *o*-xylylenes lead us to investigate the potential of this reaction as a source of *o*-xylylenes for synthesis. We report here our studies of the photochemical behavior of 4-methylisochromene (1), which show that the Diels–Alder reaction of the initially produced *o*-xylylene cannot compete with a rapid 1,5-hydrogen migration.

Irradiation of **1a**[4] in benzene produced two products whose relative yields depended on the duration of the irradiation. One of these was identified as *o*-methylstyrene (**6**) by isolation and comparison with an authentic sample. The other product was unstable and could not be isolated in pure form. However, after the solvent was removed at low temperature, the crude photolysis products showed a band in the IR spectrum at 2125 cm^{-1}, suggesting that this product was a ketene.[5] Irradiation of **1a** in methanol gave ester **4a** in 28% yield. The ester was identified by isolation and comparison with an independently synthesized sample. Irradiation of **1a** in benzene, followed by addition of methanol, gave **4a** and **6** in 22% yield each. Upon irradiation of **1a** in purified acetonitrile the same photoproducts as those produced in benzene were observed.

In order to help establish the mechanism for this reaction, the behavior of **1b** was investigated. Irradiation of **1b** in methanol gave ester **4b**. In the NMR spectrum of **4b**, the signal for the *o*-methyl group appeared as a triplet ($J_{\text{D-H}}$ = 2 Hz) integrating for two protons, thus establishing the position of the deuterium.

Scheme I



Although these experiments support the formation of *o*-xylylene **2** as a primary photoproduct of **1**, we were unable to trap **2** with dienophiles. No evidence for the formation of cycloadducts was found when **1a** was irradiated in a mixture of benzene and cyclohexene or in acetonitrile with maleic anhydride as the dienophile.

A mechanism which accounts for these observations is outlined in Scheme I. Irradiation of **1** produces *o*-xylylene **2**,[6] similar to the behavior proposed for other isochromenes[2] and 1,2-dihydronaphthalenes.[7,8a] This intermediate either returns to **1** or undergoes a 1,5-hydrogen (or deuterium) migration to give ketene **3**. Similar 1,5-hydrogen migrations have been observed for other *o*-xylylenes,[8] including one, very similar to **2**, that is produced upon irradiation of 4-phenylisothiochromene.[2a] In the presence of methanol, ketene **3** is trapped as methyl ester **4**. In the absence of methanol, **3** undergoes a secondary photoreaction to give carbene **5**,[9] which rearranges to **6**.[10] The observation that we were unable to trap **2** with dienophiles indicates that the 1,5-hydrogen migration is much faster than the Diels–Alder reaction in this system. The 1,5-hydrogen migration must also be fast enough to preclude the photochemical (4 + 2) cycloaddition that has been observed with the *o*-xylylenes produced from 3-substituted isochromenes.[2]

Experimental Section

NMR spectra were obtained on a Varian EM-360 spectrometer, using tetramethylsilane as internal standard. IR spectra were obtained with a Perkin-Elmer 337 spectrometer. GC analyses employed a Hewlett-Packard 5750 chromatograph coupled to a Columbia Scientific Industries CSI 38 digital integrator. Unless otherwise specified a 1.8 m × 3.2 mm column with 10% Silicone Gum Rubber UCW-982 on 60/80 Chromosorb W was used. Elemental analyses were obtained from Atlantic Microlab, Inc., Atlanta, GA.

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