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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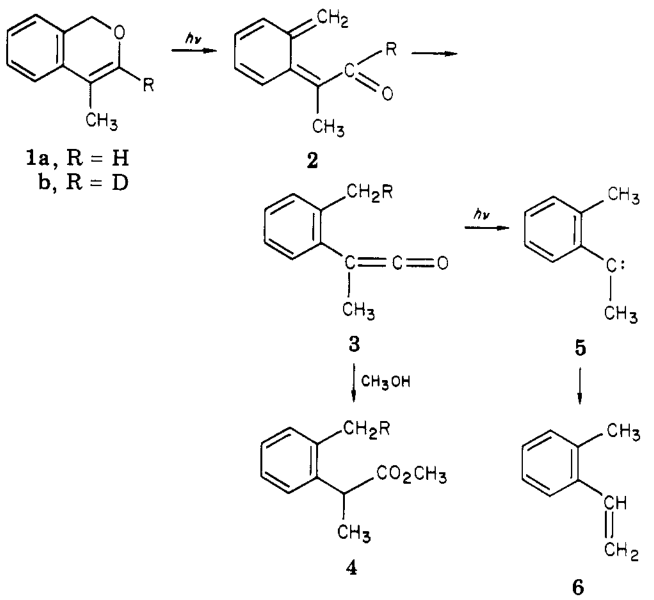
Diels–Alder reactions of *o*-quinodimethanes (*o*-xylylenes) with inter- and intramolecular dienophiles have been shown to have considerable utility for the synthesis of polycyclic ring systems.[1] Recently it has been reported[2] that various substituted isochromenes produce *o*-xylylene derivatives 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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(6) Although two stereoisomeric *o*-xylylenes could potentially be produced from 1, it is probable that only 2 is formed in this reaction.[2b]

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(9) The formation of carbenes upon irradiation of ketenes is a well-known photochemical reaction: W. Kirmse, "Carbene Chemistry", 2nd ed., Academic Press, New York, 1971, pp 9–16.

(10) Reference 9, pp 236–254.

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Photochemical Apparatus. Preparative irradiations employed a quartz immersion well and a Hanovia 450-W medium-pressure mercury-vapor lamp. Water jacketed vessels of 250 or 500 mL were used, and the solutions were purged continuously with a stream of oxygen-free nitrogen.[11] Analytical irradiations employed the same light source and immersion well, combined with a "merry-go-round" type apparatus with quartz photolysis tubes of ca. 15-mL capacity. Solutions (10 mL, 0.02 M in compound to be studied) were degassed with oxygen-free nitrogen[11] prior to irradiation.

3,3-Dideuterio-4-isochromanone. To a solution of 8.0 g (0.054 mol) of 4-isochromanone[12] in 40 mL of dry THF was added 40 mL of NaOD, prepared by reacting 0.4 g of sodium with 40 mL of D_2O. After the solution was stirred at room temperature for 20 min, the THF was removed in vacuo and the residue was extracted with dichloromethane. After the solution was dried over anhydrous Na_2SO_4, the solvent was removed in vacuo and the residue was treated as above a second time. Distillation gave 6.0 g (74%) of 3,3-dideuterio-4-isochromanone: NMR ($CDCl_3$) δ 4.87 (s, 2 H, benzylic H), 7.0–8.2 (m, 4 H, aromatic H). The singlet at δ 4.23 for the protons on C-3 of 4-isochromanone was entirely absent.

3-Deuterio-4-methylisochromene (1b). Compound **1b** was prepared from 3,3-dideuterio-4-isochromanone in the same manner[4] as the preparation of **1a** from 4-isochromanone: NMR ($CDCl_3$) δ 1.80 (s, 3 H, CH_3), 4.89 (s, 2 H, CH_2), 6.6–7.3 (m, 4 H, aromatics).

Methyl 2-(2-Methylphenyl)propanoate (4a). A solution of 0.15 g (0.91 mmol) of 2-(2-methylphenyl)propanoic acid[13] and 0.1 mL of H_2SO_4 in 5 mL of methanol was heated to reflux for 4 h. The reaction mixture was poured into water and extracted with ether, and the combined extracts were dried over anhydrous $MgSO_4$. Distillation gave 0.10 g (62%) of **4a**: bp 70–71 °C (0.5 mm); NMR ($CDCl_3$) δ 1.46 (d, J = 7 Hz, 3 H, $CHCH_3$), 2.35 (s, 3 H, o-CH_3), 3.62 (s, 3 H, OCH_3), 3.93 (q, J = 7 Hz, 1 H, $CHCH_3$), 7.0–7.4 (m, 4 H, aromatic H).

Anal. Calcd for $C_{11}H_{14}O_2$: C, 74.13; H, 7.91. Found: C, 74.02; H, 7.97.

Irradiation of 4-Methylisochromene (1a) in Benzene. A solution of 1.0 g of **1a** in 500 mL of benzene was irradiated for 30 min. After the solvent had been removed at 0 °C (0.25 mm), the crude residue showed a band at 2125 cm^{-1} in the IR spectrum. Distillation of the crude reaction mixture gave 0.10 g of **6**, bp 40 °C (10 mm). The IR and NMR spectra of this material were identical with those of an authentic sample. An analytical-scale photolysis of **1a** in benzene, followed by addition of methanol to convert **3a** to **4a**, showed, by GC analysis using biphenyl as an internal standard, that 60% of **1a** had reacted to produce 22% of **6** and 22% of **4**.

Irradiation of 4-Methylisochromene (1a) in Methanol. A solution of 1.0 g (6.1 mmol) of **1a** in 250 mL of methanol was irradiated for 30 min. Distillation gave 0.30 g (28%) of **4a**, bp 72–73 °C (1.0 mm). The IR and NMR spectra of this material were identical with those of an authentic sample.

Irradiation of 3-Deuterio-4-methylisochromene (1b) in Methanol. A solution of 1.0 g of **1b** in 250 mL of methanol was irradiated for 1 h. The solvent was removed in vacuo and the residue was chromatographed on silica gel, using 5% ether in hexane as eluant, to give 0.2 g of **4b**. The NMR spectrum of **4b** was identical with that of **4a** with the exception that the signal for the o-methyl group at δ 2.35 appeared as a triplet of lines of equal intensity (J_{H-D} = 2 Hz) that integrated for two protons.

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Registry No. **1a**, 32727-59-6; **1b**, 74082-01-2; **4a**, 74082-02-3; **4b**, 74082-03-4; **6**, 611-15-4; 3,3-dideuterio-4-isochromanone, 74096-70-1; 4-isochromanone, 20924-56-5; 2-(2-methylphenyl)propanoic acid, 62835-95-4.

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Halogenated Ketenes. 35. Cycloadditions of Halogenated Ketenes and Tetramethoxyethylene. Semisquaric Acid Derivatives

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The (2 + 2) cycloaddition of the electron-rich tetraalkoxyethylenes with some aldoketenes has been described by Bellus[1,2] as an intermediate step in the synthesis of squaric acid and 2-substituted semisquaric acid derivatives. We have recently reported on the cycloaddition of some tetraalkoxyethylenes with trimethylsilylketene to yield the tetraalkoxy-2-(trimethylsilyl)cyclobutanones which undergo acid-catalyzed hydrolysis to give semisquaric acid.[3] We now wish to report the cycloaddition of methylchloro-, dichloro-, and phenylchloroketenes with tetramethoxyethylene to yield the 2-chlorotetramethoxycyclobutanones. Hydrolysis of these cycloadducts results in ring cleavage to yield acyclic products. However, reduction of the 2-chlorotetramethoxycyclobutanones to the cyclobutanols and hydrolysis yield 2-substituted semisquaric acid derivatives.

This procedure involves the in situ generation of the ketene by the triethylamine dehydrohalogenation of α-chloropropionyl chloride, dichloroacetyl chloride or α-chlorophenylacetyl chloride in the presence of tetramethoxyethylene to produce the cyclobutanone in high yields (Scheme I).

The cycloaddition produces 2-substituted 2-chloro-3,3,4,4-tetramethoxycyclobutanones (**1a–c**) in high yields, which is consistent with yields (>80%) reported for the cycloaddition of tetraalkoxyethylene with aldoketenes.[1,2]

The adducts **1a** and **1b** are liquids which could be vacuum distilled whereas **1c** is a solid and was purified by sublimation. The infrared absorption spectra for the 2-halocyclobutanones revealed the carbonyl bands at 1800–1815 cm^{-1}.

The NMR spectrum of 2-methyl-2-chloro-3,3,4,4-tetramethoxycyclobutanone (**1a**) revealed a multiplet, δ 3.45–3.60, representing the 12 protons (4-OCH_3). This multiplet is expected since each set of protons on the four methoxy groups are nonequivalent. The NMR spectrum of 2,2-dichloro-3,3,4,4-tetramethoxycyclobutanone (**1b**) revealed two peaks, δ 3.45 (2-OCH_3) and 3.55 (2-OCH_3). In the case of **1c**, 2-chloro-2-phenyl-3,3,4,4-tetramethoxycyclobutanone, the NMR spectrum had a multiplet, δ 3.35 (3-OCH_3), and a singlet at δ 2.98 (1-OCH_3). The chemical shift of the C(3)-methoxy protons cis to the phenyl is shifted upfield due to the shielding effect of the benzene ring.

It was reported that the cycloadducts of tetraalkoxyethylene and aldoketenes could be hydrolyzed to squaric acid or semisquaric acid by 18% HCl. It is apparent that the cycloadducts of tetramethoxyethylene and disubstituted ketenes reported in this paper cannot be hydrolyzed to semisquaric acid derivatives because of the lack of an enolizable hydrogen. However, hydrolysis of these cycloaddition products could lead to cyclobutanediones or ring-opened acyclic products. Hydrolysis of the dichloro

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