1.5297, and shown by infrared to contain 35 ± 2% of 1,1-dimethyl-7-methoxytetralin and 65 ± 2% of the 6-methoxy isomer. Similarly, the alcohol fraction was shown by infrared to contain 2 ± 1% of 5-(*p*-anisyl)-2-methyl-2-pentanol in 4-*p*-anisyl-4-methyl-1-pentanol.

The Acidic Acetolysis of 4-(*p*-Anisyl)-4-methyl-1-pentyl *p*-Bromobenzenesulfonate.—To 1000 ml of dry acetic acid at 100.0° was added 10.0 g of the bromobenzenesulfonate. After 47 hr at 100.0° the solvolysis solution was poured into water and the products were extracted, reduced, and chromatographed as described above. The first fraction, eluted with pentane, 1.7 g, bp 105–107° (2.5 mm), $n^{25}\text{D}$ 1.5288, was pale yellow. The infrared analysis of the mixture indicated it to be 40 ± 5% 1,1-dimethyl-6-methoxytetralin and 60 ± 5% of the 7-methoxy isomer.

The second fraction was eluted with ether. This product, 2.75 g, bp 135–138° (1.5 mm), $n^{25}\text{D}$ 1.5227, had an infrared spectrum identical with that of the starting alcohol, 4-(*p*-anisyl)-4-methyl-1-pentanol.

The Acetolysis Products from 4-Methyl-4-phenyl-1-butyl *p*-Bromobenzenesulfonate.—A solution of 15 ml of 1.00 *M* lithium acetate in dry acetic acid and 1500 ml of dry acetic acid was heated to 100.0° and 12.0 g of the bromobenzenesulfonate was added. In 5 hr another 20 ml of 1 *M* lithium acetate in acetic acid was added and after 90 more hr at 100.0° the solvolysis solution was cooled and poured into water. The products were extracted with five portions of pentane and isolated as in the above examples. Pentane elution of the products from alumina gave 0.70 g of hydrocarbons, bp 60° (1.5 mm), $n^{25}\text{D}$ 1.5217, and elution with ether gave 4.40 g of alcohols, bp 112–115° (2 mm), $n^{25}\text{D}$ 1.5162.

The hydrocarbon fraction reacted slowly with potassium permanganate in acetone. Quantitative hydrogenation of a 0.3121-g sample at 27° and 750 mm in acetic acid with 10% Pd/C took up 4.7 ml of hydrogen. A second sample, 0.2350 g, at 30° and 747 mm, took up 3.2 ml of hydrogen (9.4% and 8.4% olefin, respectively).

The infrared spectrum of the hydrogenated hydrocarbons, $n^{25}\text{D}$ 1.5195, was generally very similar to that of 1,1-dimethyltetralin except for a band of medium intensity at 695 cm^{-1} and a small increase in intensity of absorption in the 1075–1300-cm^{-1} region. The 695-cm^{-1} band is present in both possible hydrogenated olefins, 2-methyl-2-phenylpentane and 4-methyl-1-phenylpentane. However, the absence of any appreciable absorption at 740 cm^{-1} indicates that there is less than *ca.* 2% of the second isomer present. A 20% solution of 2-methyl-2-phenylpentane in 1,1-dimethyltetralin will account for the 695-cm^{-1} band but not the 1075–1300 cm^{-1} discrepancy. Considering both the hydrogenation data and the infrared data, the mixture probably contains *ca.* 80% of 1,1-dimethyltetralin, *ca.* 10% of 2-methyl-2-phenylpentane, and *ca.* 10% of some other unknown product.

Registry No.—VI, 33214-69-6; VII, 33214-70-9; X, 33214-69-6; 3-(4-acetamidophenyl)-3-methylbutyric acid, 33214-72-1; 3-(4-acetamido-3-nitrophenyl)-3-methylbutyric acid, 33214-73-2; 3-methyl-3-(3-nitrophenyl)butyric acid, 33214-35-6; 3-(*m*-anisyl)-3-methylbutyric acid, 33214-36-7; 3-(*p*-anisyl)-3-methylbutyric acid, 1136-01-2; 3-(*o*-anisyl)-3-methylbutyric acid, 33214-38-9; 4-(*m*-anisyl)-4-methylpentanoic acid, 33214-39-0; 3-(*p*-anisyl)-1-bromo-3-methylbutane, 33214-40-3; 4-(*p*-anisyl)-4-methylpentanoic acid, 23203-48-7; 4-methyl-4-pentanolacetone, 3123-97-5; 1-bromo-3-methyl-3-phenylbutane, 1197-97-3; 4-methyl-4-phenylpentanoic acid, 4408-55-3; 3-(3,4-dimethoxyphenyl)-3-methylbutyric acid, 33214-44-7; 3-(3,4-dimethoxyphenyl)-3-methyl-1-butanol, 33214-45-8; 1-bromo-3-(3,4-dimethoxyphenyl)-3-methylbutane, 33214-46-9; 4-(3,4-dimethoxyphenyl)-4-methylpentanoic acid, 3754-68-5; 4-(*m*-anisyl)-3,3-dimethylbutanoic acid, 25380-95-4; 4-(*m*-anisyl)-3,3-dimethyl-1-butanol, 33214-48-1, 33214-49-2 (Br); 3,3-dimethyl-4-(*p*-nitrophenyl)butyric acid, 33209-64-2; 4-(*p*-aminophenyl)-3,3-dimethylbutyric acid, 33209-65-3; 4,3-dimethyl-4-(*p*-hydroxyphenyl)butyric acid, 33209-66-4; 4-(*p*-anisyl)-3,3-dimethylbutyric acid, 33209-67-5; 4,4-dimethyl-6-methoxy-1-tetralone, 23203-51-2; 1,2-dimethyl-7-methoxynaphthalene picrate, 33209-69-7; 4,4-dimethyl-1-tetralone, 2979-69-3; 4,4-dimethyl-7-nitro-1-tetralone, 33209-71-1; 4,4-dimethyl-7-hydroxy-1-tetralone, 33209-72-2; 4,4-dimethyl-7-methoxy-1-tetralone, 23203-49-8; 1,2-dimethyl-6-methoxynaphthalene picrate, 33209-74-4; 4-*o*-anisylbutyric acid, 33209-75-5, 33209-76-6 (Et ester); 5-(*o*-anisyl)-2-methyl-2-pentanol, 33209-77-7; 4,4-dimethyl-8-methoxynaphthalene, 33209-78-8; 4,4-dimethyl-8-hydroxy-1-tetralone, 33209-79-9; 1,2-dimethyl-5-methoxynaphthalene picrate, 33209-80-2; ethyl 4-*p*-anisylbuyrate, 4586-89-4; 5-(*p*-anisyl)-2-methyl-1-pentanol, 33209-82-4; 5-(*p*-anisyl)-2-methyl-2-pentanol, 4586-90-7.

Photoaddition Reactions. II.[1] Photoaddition of Dimethyl Acetylenedicarboxylate to Cyclic Ethers

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The photoinitiated free-radical addition of tetrahydrofuran, 2-methyltetrahydrofuran, 1,4-dioxane, and tetrahydropyran to dimethyl acetylenedicarboxylate is found to give cis and trans 1:1 adducts. The products were isolated and characterized. The reaction has been found to be specific in that the trans adducts predominate over the cis.

Dimethyl acetylenedicarboxylate (DMAD, **2**), one of the most versatile acetylenes, has played an important role in organic synthesis because it undergoes a wide variety of thermal cycloaddition and conjugate addition reactions.[4] Very little is, however, known about its photochemical reactions. Photoaddition of **2** to benzene has been reported to give dimethyl cyclooctatetraene-1,2-dicarboxylate,[5,6] and norbornene and pyrrole have been reported to give 1:1 photoadducts with DMAD.[7,8] Recently, the photoaddition of DMAD to two molecules of ethylene has also been re-

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[1] Paper I: P. Singh, *J. Org. Chem.*, **36**, 3334 (1971).

[2] Syva Research Institute, 3221 Porter Drive, Palo Alto, Calif. 94304.

[3] Part of this work was carried out at the Department of Chemistry, The University, Southampton, England.

[4] R. Fuks and H. G. Viehe in "Chemistry of Acetylenes," H. G. Viehe, Ed., Marcel Dekker, New York, N. Y., 1969, Chapter 8, pp 460–520, 550–567, and 574–575.

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[6] D. Bryce-Smith and J. E. Lodge, *J. Chem. Soc.*, 695 (1963).

[7] M. Hara, Y. Odaira, and S. Tsutsumi, *Tetrahedron*, **22**, 95 (1966).

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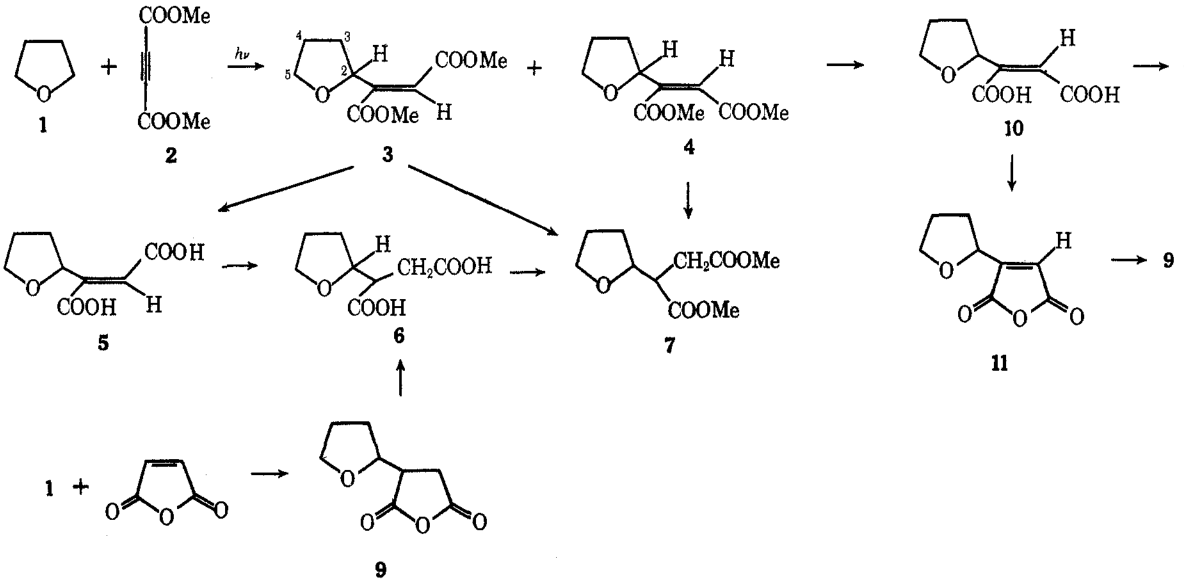
SCHEME I



ported.[9] Jacobs and Ecke reported free radical initiated addition of cyclic ethers to maleic anhydride but failed to get any adduct with DMAD.[10] Ether free radicals have been reported to be relatively unstable at elevated temperatures and tend to disproportionate, which in the case of cyclic ethers results in ring opening of the ether ring.[11] Ring opening of cyclic ethers seldom takes place at room temperature, thus giving an excellent chance of addition of 2 to cyclic ether free radicals generated by ultraviolet light at room temperature.[12,13] In fact, efficient addition of cyclic ether free radicals generated photochemically to both alkenes and alkynes have been reported.[14-16] We wish now to report that dimethyl acetylenedicarboxylate also undergoes efficient addition with cyclic ethers under the influence of ultraviolet light.[17]

Results

Reported below are the 1:1 addition reactions of DMAD (2) to tetrahydrofuran, 2-methyltetrahydrofuran, 1,4-dioxane, and tetrahydropyran. Unless stated otherwise, the reactions were carried out by ultraviolet irradiation, through a Pyrex filter, with a 450-W Hanovia lamp.

Irradiation of DMAD for 20 hr in tetrahydrofuran with a 250-W Hanovia lamp gave 1:1 adducts **3** and **4** in *ca.* 60% yield. The photoadducts were separated by preparative glpc, and their structures are based on analytical and spectral data. The nmr spectrum of **3** showed its vinylic proton as a doublet at δ 6.42 with a coupling constant of 0.5 Hz. The splitting of this proton is due to its long-range coupling with the tetrahydrofuryl methine proton, as was evident by its collapse to a sharp singlet when decoupled from the C-2 methine proton at δ 5.12. The vinylic proton of **4** appeared as a doublet at δ 6.07, showing its long-range coupling with the C-2 methine proton as 2.0 Hz. The large allylic coupling constant observed in **4** indicated a cisoid relationship of the C-2 methine protons as shown, while the small allylic coupling constant in **3** is in agreement with their transoid relationship.[18-20] The low-field chemical shift of the vinylic proton in **3** as compared to that of its isomer **4** is due to deshielding by methyl ester groups on the adjacent carbon atom.[21,22] The structures **3** and **4** were secured by hydrogenation of these photoadducts to dimethyl tetrahydro-2-furylsuccinate (**7**). Both the diesters **3** and **4** gave on saponification their corresponding diacids **5** and **10**, respectively. The diacid **10**, on being heated at 110° for 30 min, was quantitatively dehydrated to tetrahydro-2-furylsuccinic anhydride (**9**)[10] (Scheme I). The diacid **10**, therefore, is tetrahydro-2-furylmaleic acid, and the stereochemistry of the ester groups in **4** must be cis as shown. The diacid **5**, obtained by saponification of **3**, was recovered unchanged under similar conditions; the trans relationship of the acid groups in **5**, and hence the ester groups in **3**, is therefore assigned. It is interesting to point out that prolonged heating of the trans diacid **5** at 180° resulted in considerable charring and afforded the anhydride **11** in a poor yield (10%),[23] in agreement with the ob-

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[12] D. Elad in "Organic Photochemistry," Vol. 2, O. L. Chapman, Ed., Marcel Dekker, New York, N. Y., 1969, pp 202–208.

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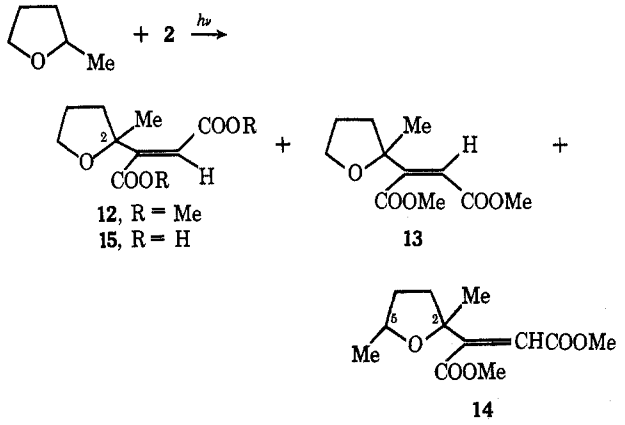
[21] L. M. Jackman and R. H. Wiley, *J. Chem. Soc.*, 2881, 2886 (1960).

[22] "Varian NMR Spectra Catalogue," Spectra No. 212 and 213.

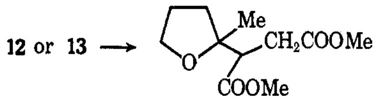
[23] Based on this evidence and the presence of a strong fragment at M − 18 in the mass spectrum of **5** the major adduct **3** was tentatively considered in our preliminary communication to be a derivative of maleic acid. However, comparative studies on both the isomers **5** and **10** have revealed that our earlier assignment of cis stereochemistry to the adduct **3** is in error and it should now be considered as trans.

servation that fumaric acid on being heated at elevated temperature gives maleic anhydride.[24]

To determine the effect of an alkyl-substituted ether ring on the mode of addition, a solution of 2 in tetrahydro-2-methylfuran was irradiated. After 6 hr 1:1 adducts **12**–**14**, in a relative ratio of 7:2:1, respectively, were obtained in *ca.* 40% yield. The photolysis mixture was resolved by preparative glpc. The minor adduct **13**, obtained in a relative yield of 10%, could also be obtained by further irradiation of the major adduct **12**. Both the adducts **12** and **13** consumed 1 mol of hydrogen to give the same saturated diester **16**, suggesting that these adducts are stereochemically related to each other. The nmr spectrum of **12** showed its vinylic proton as a singlet at δ 6.62 while the same proton in **13** appeared as a singlet at δ 5.98. A considerable downfield shift of the vinylic proton in **12** as compared to the same proton in its isomer **13** requires the cis relationship of the vinylic proton with the ester group (and hence, the trans relationship between the methyl ester groups).[21] The low-field chemical shift of the C-2 methyl group at δ 1.42 in **12** as compared to that of its isomer **13** at δ 1.39 is also in agreement with its cisoid relationship with the ester group.[25] The dicarboxylic acid **15**, obtained by saponification of the diester **12**, could not be dehydrated to its anhydride. Based on these arguments, and by analogy with the photoaddition of tetrahydrofuran to DMAD, the major and the minor isomers are assigned structures **12** and **13**, respectively.



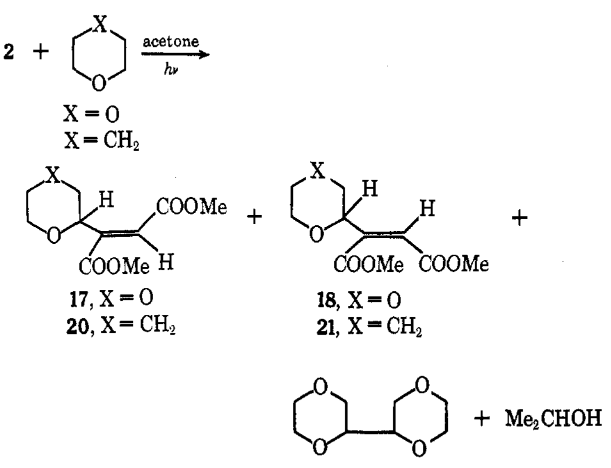
12, R = Me
15, R = H
13
14



16

The third compound, formed in a relative yield of 20% (nmr analysis), could not be obtained in pure form and is tentatively assigned structure **14** on the basis of its spectral data.

The photoaddition of DMAD (2) to six-membered cyclic ethers, 1,4-dioxane and tetrahydropyran, was also investigated. Ultraviolet irradiation of 1,4-dioxane in DMAD in the presence of acetone afforded the 1:1 photoadducts **17** and **18** (18% yield) in a relative ratio of 4:1, respectively, in addition to substantial amounts of 2-propanol and dehydro-1,4-dioxane dimer **19**.[26] Similarly, 1:1 adducts **20** and **21** were obtained (36% yield) in a relative ratio of 3.5:1 when a solution of 2 in tetrahydropyran was irradiated in the presence of acetone. A substantial amount of 2-propanol was also obtained as a by-product. The structures of the photoadducts **17**, **18**, **20**, and **21** are in excellent agreement with their spectral data (see Experimental Section).



17, X = O
20, X = CH₂
18, X = O
21, X = CH₂
19

Discussion

The photoaddition of cyclic ethers to DMAD, induced directly or initiated with acetone by ultraviolet light, to give 1:1 adducts has been found to be quite a general reaction. The possibility that the primary step involved excitation of DMAD, followed by addition of the excited diester molecule to cyclic ethers to give the products observed, though tempting, is ruled out on the basis of its nonreactivity with 1,4-dioxane and tetrahydropyran in the absence of acetone. The formation of dehydro-1,4-dioxane dimer **19** and 2-propanol during the photolysis of 1,4-dioxane in DMAD (2) in the presence of acetone strongly suggests that the reactions in this system (and probably in all the other systems studied here) are free-radical reactions. The possibility that ether free radicals are produced by hydrogen expulsion from excited ether molecules is highly improbable.[15,27] The formation of ether free radicals **22**, as a result of hydrogen atom abstraction from ethers by other radicals formed during irradiation, is considered to be the key step in the photoaddition reactions (Scheme II).

The addition of tetrahydrofuran as well as of 2-methyltetrahydrofuran to DMAD could be affected without a photoinitiator, using ultraviolet light filtered through Pyrex. This is attributed to impurities present in commercial ethers which could act as photoinitiator.[15] Indeed, photoaddition of purer tetrahydrofuran (refluxed over lithium aluminum hydride) to DMAD was slow and gave the 1:1 adducts **3** and **4** in a poor yield (10%).

The radical addition of ethers to DMAD could occur both cis and trans, giving the cis and trans products, respectively. The photoaddition of ethers to DMAD

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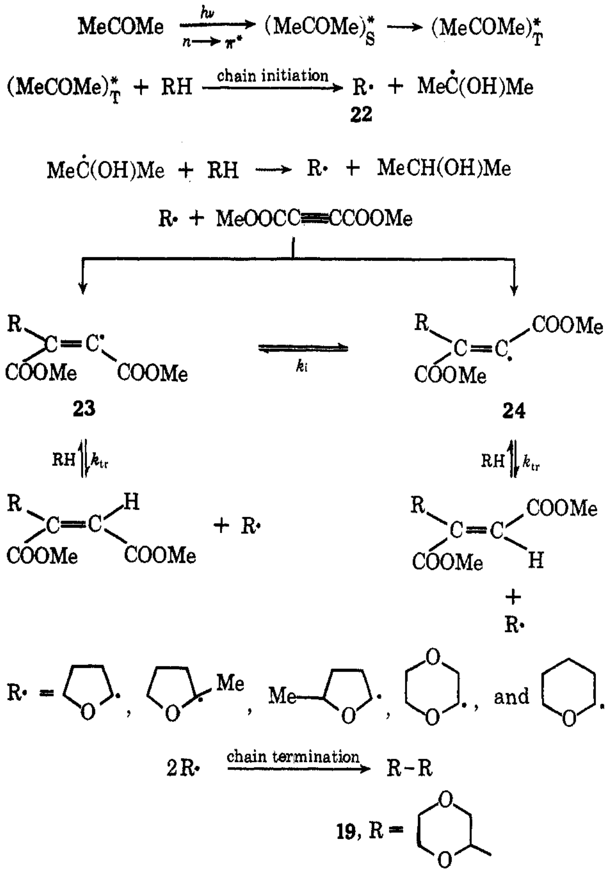
[24] "The Merck Index," P. G. Stecher, Ed., Merck and Co., Inc., N. J., 1968, pp 474 and 639.

[25] M. Cais in "The Chemistry of Alkenes," S. Patai, Ed., Interscience, London, 1964, pp 988–992.

[26] A white, fluffy solid, mp 103–110°, was also obtained which could not be identified. Based on spectral data the solid is tentatively considered to be a telomer of 1,4-dioxane and DMAD.

[27] G. Porter, "XIII-e Counseil de Chimie Solvay Report," Bruxelles, Oct 1965, p 29.

SCHEME II



has been found to be stereoselective in that the trans adducts predominate as a result of a preferential trans addition mechanism.[28-30] The preferential formation of the trans adducts does not necessarily mean that the stereochemistry of the intermediate radicals is trans, as the rate of invertion, K_i, of radicals **23** and **24** is much faster than their chain transfer, K_{tr}, steps.[31] The stereoselective trans addition of DMAD to cyclic ethers is probably due to a substantial difference in free energies of the transition states for the conversion of the intermediate radicals **23** and **24** to the products.[29] The formation of considerable amount of the cis adduct **13** after prolonged irradiation of DMAD in tetrahydrofuran is attributed to further isomerization of the trans adduct **12** under experimental conditions.[32,33] Indeed, the compound **13** could be obtained by ultraviolet irradiation of **12**.

Experimental Section

Melting points and boiling points are uncorrected. Ir spectra were recorded on a Unicam SP 200 spectrometer. Unless stated otherwise, nmr spectra were recorded on a Varian A-60 spectrometer; the values are given in δ units downfield from tetramethylsilane as internal standard. Mass spectra were recorded on an MS-12 instrument and tlc separations were accomplished on silica plates. Unless mentioned otherwise, gas chromatographic separations were achieved using a 6 ft × 0.25 in., 10% Carbowax on Chromosorb W column. For photochemical reactions, the reaction mixtures were thoroughly flushed with nitrogen before ultraviolet irradiations.

Solutions in organic solvents were dried over anhydrous magnesium sulfate.

Photolysis of Dimethyl Acetylenedicarboxylate (DMAD, 2) in Tetrahydrofuran. Formation of Dimethyl Tetrahydro-2-furylfumarate (3) and Dimethyl Tetrahydro-2-furylmaleate (4).—A solution of DMAD (**2**) (8.2 g, 0.058 mol) in tetrahydrofuran (200 ml) was irradiated with a 250-W Hanovia lamp contained in a water-cooled Pyrex well immersed in the solution. Glpc analysis (304 column[34] at 105°) of the reaction mixture after 1.5 hr irradiation showed the formation of adducts **3** and **4** in a relative ratio of 6:1, respectively. The relative ratio of **3** and **4** after 3-hr irradiation was 4:1 and their ratio changed to *ca.* 2:1 after further photolysis for 2 hr. The irradiation was stopped after 20 hr and removal of the excess of reactants under reduced pressure gave compounds **3** and **4** as a light yellow oil (7.5 g, 60%) in a relative ratio of 1:1. The mixture could not be distilled without extensive decomposition and was separated by preparative glpc.[35]

The diester **3**, a colorless, mobile liquid, showed the following spectral data: ir (CCl_4) 1730 (C=O), 1650 (C=C), 1065 (COC), and 1020 cm^{-1}; mass spectrum (70 eV) *m/e* (rel intensity) 214 (2, M^+), 183 (30), 182 (100, base peak), 155 (25), 154 (50), 124 (34), 113 (40), 71 (26), 59 (37), 53 (35), and 41 (40); nmr (CCl_4) δ 1.7–2.3 (m, 4 H, C-3 and C-4 ring methylenes), 3.68 (s, COOMe), 3.73 (s, COOMe), 3.6–4.0 (m, C-5 ring methylene) (total 8 H), 5.12 br (t, 1 H, J = 7 Hz, C-2 methine proton), and 6.42 (d, 1 H, J = 0.5 Hz, vinylic proton). The triplet at δ 5.12 was reduced to a broad singlet when decoupled from the protons at δ 3.6–4.0 and the doublet at δ 6.42 was a sharp singlet when irradiated at the C-2 methine proton (at δ 5.12).

Anal. Calcd for $C_{10}H_{14}O_5$: C, 56.07; H, 6.59. Found: C, 55.83; H, 6.85.

The diester **4**, with longer retention time, was a colorless oil: ir (CCl_4) 1735 (C=O), 1655 (C=C), and 1065 cm^{-1} (ether); nmr (CCl_4) δ 1.9–2.2 (m, 4 H, C-3 and C-4 ring methylenes), 3.73 (s, COOMe), 3.87 (s, COOMe), 3.6–4.0 (m, $-CH_2O-$) (total 8 H), 4.60 (triplet of doublets, 1 H, J_1 = 7.5, J_2 = 2.0 Hz, ring methine), and 6.07 (d, 1 H, J = 2.0 Hz, vinylic proton). The doublet at δ 6.07 was reduced to a sharp singlet when decoupled from the methine proton at δ 4.60.

The analytical sample was purified by preparative glpc.

Anal. Calcd for $C_{10}H_{14}O_5$: C, 56.07; H, 6.59; mol wt, 214. Found: C, 56.35; H, 6.47; mol wt, 214 (mass spectrum).

When pure tetrahydrofuran, refluxed over lithium aluminum hydride for 2 days, was used the reaction was very slow and afforded the adducts **3** and **4** in 10% yield after 30 hr irradiation.

Tetrahydro-2-furylfumaric Acid (5).—The dimethyl tetrahydro-2-furylfumarate (**3**) (450 mg) in methanol (20 ml) was refluxed with 5% aqueous sodium hydroxide (4 ml) on a steam bath. After 5 hr the reaction mixture was cooled and stripped of methanol under reduced pressure. The residue was diluted with water (35 ml) and extracted with chloroform. The aqueous layer was cooled in ice and acidified (pH 4) with 5% aqueous, cold hydrochloric acid. The solution was saturated with ammonium chloride and extracted with ethyl acetate. Removal of the solvent from the dried extract gave diacid **5** as a thick oil (380 mg) which solidified when set aside at 5°. The solid was crystallized twice from chloroform–petroleum ether (bp 30–60°) to give colorless crystals of **5**: mp 112–114°; ir ($CHCl_3$) 3600–2500 br (COOH), 1705 (C=O), 1645 (C=C), and 1050 cm^{-1} (ether); uv max (95% EtOH) 206 nm (log ϵ 3.96); nmr ($CDCl_3$) δ 1.9–2.3 (m, 4 H), 3.8–4.3 (m, 2 H), 5.3–5.7 (m, 1 H, C-2 ring methine), 7.08 br (s, 1 H, vinylic proton), and 9.6 br (s, 2 H, absent when washed with D_2O, acid protons); mass spectrum (70 eV) *m/e* (rel intensity) 168 (85, $M^+ - H_2O$), 140 (90), 128 (11), 122 (18), 112 (24), 99 (100, base peak), 95 (90), 71 (61), 55 (46), 43 (40), 42 (77), and 41 (90).

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(29) J. A. Kampmeier and G. Chen, *ibid.*, **87**, 2608 (1965).

(30) W. E. Truce and G. C. Wolf, *J. Org. Chem.*, **36**, 1727 (1971).

(31) L. A. Singer and J. Chen, *Tetrahedron Lett.*, 4849 (1969), and references cited therein; for a review on stereochemical features of vinyl free radicals see L. A. Singer, *Intra-Sci. Chem. Rep.*, **4**, 139 (1970).

(32) G. S. Hammond, J. Saltiel, A. A. Lamola, N. J. Turro, J. S. Bradshaw, D. O. Cowan, R. C. Counsell, V. Vogt, and C. Dalton, *J. Amer. Chem. Soc.*, **86**, 3197 (1964).

(33) C. S. Angadiyavar and M. V. George, *J. Org. Chem.*, **36**, 1589 (1971).

(34) Perkin-Elmer 5 ft × 0.125 in. silicon gum rubber SE-30 on Chromosorb W.

(35) A partial separation of the mixture could, however, be achieved by its quick distillation under reduced pressure. The earlier fractions were rich in the trans isomer **3** while the later fractions were mostly the cis isomer **4**. In addition, a considerable amount of a nondistillable polymer was left behind in the distillation pot.

Anal. Calcd for $C_8H_{10}O_5$: C, 51.61; H, 5.41. Found: C, 51.89; H, 5.49.

Tetrahydro-2-furylmaleic Acid (10).—The dimethyl tetrahydro-2-furylmaleate (4) was saponified as above and diacid **10** was obtained as colorless crystals (crystallized from chloroform–30–60° petroleum ether): mp 84–86°; ir ($CHCl_3$) 3600–2500 br, 1700, 1645, and 1065 cm^{-1}; nmr ($CDCl_3$) δ 1.8–2.2 (m, 4 H), 3.7–4.2 (m, 2 H), 5.4–5.8 (m, 1 H), 6.65 (d, 1 H, J = 1.5 Hz, vinylic proton), and 9.3 br (s, 2 H, absent when washed with D_2O). The 70-eV mass spectrum of **10** was very similar to that of its isomer **5** and demonstrated its base peak at m/e 168 ($M^+ - H_2O$).

Anal. Calcd for $C_8H_{10}O_5$: C, 51.61; H, 5.41. Found: C, 51.75; H, 5.68.

Hydrogenation of Diacid 5 (and Diacid 10). Formation of Tetrahydro-2-furylsuccinic Acid (6).—The unsaturated diacid **5** (60 mg, 0.3 mmol) in ethanol was hydrogenated over 5% Pd on charcoal. The uptake of hydrogen was complete in 45 min. The solution was filtered, and removal of ethanol gave **6** as a thick liquid (55 mg, 90%) which crystallized when set aside. Recrystallization from methanol–chloroform afforded white crystals of **6**, mp and mmp with authentic tetrahydro-2-furylsuccinic acid (see below) 142–144° (lit.[15] mp 142–144°).

Hydrogenation of the diacid **10** also afforded acid **6** in 80% yield.

Tetrahydro-2-furylsuccinic Anhydride (9).—The title compound **9** was obtained as a colorless, mobile liquid in 50% yield by peroxide-initiated free-radical addition of maleic anhydride to tetrahydrofuran according to the method of Jacobs and Ecke.[10] The adduct **9**, bp 107–111° (0.1 mm), had the following spectral data: ir (neat) 1865, 1792, 1225, 1070, and 925 cm^{-1}; nmr ($CDCl_3$) δ 1.8–2.4 (m, 4 H, methylenes of the furyl ring), 2.8–3.5 (m, 3 H, anhydride ring protons), 2.6–4.0 (m, 2 H, $-CH_2O-$), and 4.1–4.5 (m, 1 H, $-CH_2OCH-$).

Tetrahydro-2-furylsuccinic Acid (6).—Tetrahydro-2-furylsuccinic anhydride (**9**) (2.0 g) in methanol (10 ml) was stirred at room temperature with 5% aqueous sodium bicarbonate (50 ml). After 3 hr the unreacted anhydride was extracted with chloroform. The aqueous layer was cooled and acidified with 2% hydrochloric acid. The solution was saturated with ammonium chloride and extracted with ethyl acetate. Removal of the solvent from the dried extract gave a thick liquid (800 mg) which solidified when set aside. Recrystallization from methanol–chloroform gave microcrystals of tetrahydro-2-furylsuccinic acid (**6**), mp 142–144°.

Anal. Calcd for $C_8H_{12}O_5$: C, 51.06; H, 6.43. Found: C, 50.95; H, 6.68.

Dimethyl Tetrahydro-2-furylsuccinate (7).—The mixture of adducts **3** and **4** was hydrogenated over 5% Pd on charcoal. Usual work-up afforded **7** as a colorless liquid, which was identified as dimethyl tetrahydro-2-furylsuccinate by spectral, tlc, and glpc comparison with an authentic sample (obtained by esterification of authentic diacid **6**). The diester **7** showed the following spectral data: ir (neat) 1740 and 1070 cm^{-1}; nmr (CCl_4) δ 1.6–1.9 (m, 4 H), 2.4–3.0 (m, 3 H), 3.68 (s), 3.72 (s), 3.5–4.1 (m) (total 9 H).

The analytical sample was purified by preparative glpc.

Anal. Calcd for $C_{10}H_{16}O_5$: C, 55.54; H, 7.46. Found: C, 55.82; H, 7.71.

Tetrahydro-2-furylmaleic Anhydride (11).—The tetrahydro-2-furylmaleic acid (**10**) (40 mg) was heated at 110° in a drying pistol containing phosphorus pentoxide. After 30 min the reaction mixture was cooled and purification by tlc gave anhydride **11** as an oil (25 mg), ir (neat) 1815 and 1770 cm^{-1}.

The analytical sample was purified by preparative glpc.

Anal. Calcd for $C_8H_8O_4$: C, 57.14; H, 4.80. Found: C, 57.41; H, 5.07.

The anhydride **11** obtained above was hydrogenated over 5% Pd on charcoal and there was obtained tetrahydro-2-furylsuccinic anhydride (90%), identical in all respects to an authentic sample of **9** (spectral and glpc comparison).

Action of Heat on Tetrahydro-2-furylfumaric Acid (5).—The diacid **5** (50 mg) was heated for 4 hr at 180° under an atmosphere of nitrogen. There was considerable charring and the reaction mixture had turned dark brown. Analysis of the product by tlc (benzene–ether, 1:1) showed it to be a complex mixture. Preparative tlc of the mixture afforded tetrahydro-2-furylmaleic anhydride (**11**, 5 mg, *ca.* 10%) along with unreacted **5** (10 mg, 20%).

The diacid **5** was quantitatively recovered when heated for 30 min at 110° in the presence of phosphorus pentoxide.

Photolysis of DMAD in 2-Methyltetrahydrofuran. Formation of Dimethyl Tetrahydro-2-(2-methylfuryl)fumarate (12), Dimethyl Tetrahydro-2-(2-methylfuryl)maleate (13), and the Diester 14.—A solution of DMAD (1.5 g, 0.01 mol) in 2-methyltetrahydrofuran (10 ml) was irradiated in a Pyrex tube with a 450-W Hanovia lamp. Glpc analysis of the reaction mixture after 4-hr irradiation showed the formation of only one product, **12**. The contents were further irradiated for 18 hr, and analysis by glpc showed an additional broad peak with longer retention time. The relative area under these glpc peaks was 5:2. Removal of the reactants under reduced pressure afforded a pale yellow oil (1.5 g). The oil was chromatographed on a silica column, and elution with benzene–ether (9:1) afforded adducts **12–14** (950 mg, 39%) as a colorless liquid. The mixture of the adducts was further separated by preparative glpc (column temperature 190°).

The major fraction **12** (shorter glpc retention time) was obtained as a colorless, mobile liquid: ir ($CHCl_3$) 1720 (C=O), 1645 (C=C), 1055 (ether), and 1018 cm^{-1}; nmr (CCl_4) δ 1.47 (s, 3 H, C-2 Me), 1.7–2.1 (m, 4 H, C-3 and C-4 ring methylenes), 3.70 and 3.77 (singlets, ester groups), 3.5–3.9 (m, C-5 methylene) (total 8 H), and 6.62 (s, 1 H, vinylic proton); mass spectrum (70 eV) m/e (rel intensity) 228 (2.7, M^+), 213 (25, M^+ − Me), 196 (23), 181 (24), 137 (12), 113 (21), 109 (14), 85 (50), 59 (31), 53 (22), and 43 (100, base peak).

Further purification of **12** by preparative glpc furnished an analytical sample.

Anal. Calcd for $C_{11}H_{16}O_5$: C, 57.88; H, 7.07. Found: C, 58.13; H, 7.25.

The minor fraction (longer glpc retention time) was also a colorless liquid and was assigned structure **14**: ir ($CHCl_3$) 1725, 1645, 1435, 1065, and 1020 cm^{-1}; nmr (CCl_4) δ 1.20 (d, J = 6 Hz, C-5 Me), 1.7–2.3 (m, C-3 and C-4 methylenes), 3.72 (s, COOMe), 3.77 (s, COOMe), 3.5–4.0 (m, ring methine), and 6.35 br (s, vinylic proton).

The nmr spectrum of the minor adduct also showed singlets at δ 1.39 and 5.98 in a relative ratio of 3:1, assigned to the methyl and vinyl protons of **13** (see below), the cis stereoisomer of **12**.

Anal. (mixture of **13** and **14**). Calcd for $C_{11}H_{16}O_5$: C, 57.88; H, 7.07; mol wt, 228. Found: C, 57.75; H, 7.34; mol wt, 228 (mass spectrum).

The relative ratio of the photoadducts **12**, **13**, and **14**, determined by areas under their vinylic signals at δ 6.62, 5.98, and 6.35 in the nmr spectrum of the crude reaction mixture, was 15:4:2, respectively.

Photoisomerization of the Photoadduct 12 to the Diester 13.—A solution of adduct **12** (100 mg) and acetone (0.5 ml) was irradiated in a Pyrex tube. After 15 hr the ratio of **12**:**13** as found by glpc was 1:4. The solvent was evaporated and the mixture was resolved by preparative glpc. The compound **13**, a colorless liquid, showed the following spectral data: ir ($CHCl_3$) 1724, 1650, 1055, and 1020 cm^{-1}; nmr (CCl_4) δ 1.39 (s, 3 H), 1.7–2.2 (m, 4 H), 3.68 and 3.74 (s), 3.6–3.9 (m) (total 8 H), and 5.98 (s, 1 H, vinylic proton).

Anal. Calcd for $C_{11}H_{16}O_5$: C, 57.88; H, 7.07. Found: C, 58.14; H, 7.29.

Tetrahydro-2-(2-methylfuryl)fumaric Acid (15).—The diester **12** (114 mg) was hydrolyzed with 5% aqueous sodium hydroxide as outlined above and there was obtained diacid **15** (78 mg) as a thick liquid which solidified after prolonged standing. Two crystallizations from chloroform–30–60° petroleum ether afforded microcrystals of **15**: mp 105–107°; ir ($CHCl_3$) 3600–2400, 1703, 1650, 1400, 1260, and 1040 cm^{-1}; nmr ($CDCl_3$) δ 1.60 (s, 3 H), 1.8–2.4 (m, 4 H), 3.7–4.1 (m, 2 H), 6.97 (s, 1 H, vinylic proton), and 9.7 br (s, 2 H, absent when washed with D_2O).

Anal. Calcd for $C_9H_{12}O_5$: C, 54.00; H, 6.00. Found: C, 54.28; H, 5.95.

The diacid **15** was recovered unchanged when heated at 110° for 60 min in a drying pistol containing phosphorus pentoxide. No anhydride was formed when the diacid **15** was treated with trifluoroacectic anhydride in the presence of pyridine according to Duckworth's method.[36]

Photoaddition of DMAD to 1,4-Dioxane. Formation of 2-

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[36] A. C. Duckworth, *J. Org. Chem.*, **27**, 3146 (1962).

Propanol, Dehydro-1,4-dioxane Dimer 19, and the Diesters 17 and 18.—A solution of DMAD (2.0 g, 15.3 mmol) and 1,4-dioxane (10 ml) in acetone (10 ml) was irradiated in a Pyrex tube with a 450-W Hanovia lamp. After 6 hr the photolysis was stopped and the solution was distilled on a steam bath. Glpc analysis of the distillate on both polar and nonpolar columns showed, in addition to acetone and dioxane, the presence of 2-propanol. The residue was chromatographed on a silica column. Earlier eluents with benzene gave white crystals of meso and *dl* forms, mp 155–157° and 131–133°, of dioxane dimer **19**[37] (560 mg) followed by a colorless, fluffy solid, mp 103–110°. The solid could not be crystallized from a host of solvents and is tentatively considered to be a telomer of 1,4-dioxane and DMAD from its spectral data: ir (Nujol) 1725 cm^{-1}; the nmr spectrum in $CDCl_3$ showed a broad singlet at δ 3.7 superimposed on a multiplet at δ 3.6–4.1 and a multiplet at δ 4.6–5.4. Further elution with benzene–ether (4:1) gave a mixture of adducts **17** and **18** as a pale yellow, mobile liquid (550 mg, 18%). The mixture was resolved by preparative glpc.

The major glpc fraction was a colorless liquid and is assigned structure **17**: ir (neat) 1730 (C=O), 1658 (C=C), and 1060 cm^{-1} (ether); nmr (CCl_4, 100 MHz) δ 3.72 and 3.80 (singlets, methyl esters), 3.5–3.9 (m, ring methylenes) (total 12 H), 4.1–4.4 (m, 1 H, ring methine), and 6.20 (s, 1 H, vinylic proton).

Anal. Calcd for $C_{10}H_{14}O_6$: C, 52.17; H, 6.13; mol wt, 230. Found: C, 52.41, H, 5.97; mol wt, 230 (mass spectrum).

The minor product **18**, which had spectral data similar to those of its isomer **17**, showed in its nmr the vinylic proton as a doublet at δ 6.32 (J = 1.5 Hz). The relative ratio of **17** and **18** in the mixture as determined by areas under its nmr signals at δ 6.2 and 6.32 was 4:1, respectively.

The analytical sample of **18** was obtained by further purification by preparative glpc.

Anal. Calcd for $C_{10}H_{14}O_6$: C, 52.17; H, 6.13. Found: C, 51.98; H, 6.33.

When DMAD in 1,4-dioxane was irradiated in the absence of acetone for 20 hr only the starting material could be recovered quantitatively.

Photoaddition of DMAD to Tetrahydropyran. Formation of Dimethyl Tetrahydro-2-pyrylfumarate (20) and Dimethyl Tetrahydro-2-pyrylmaleate (21).—A solution of DMAD (2.0 g, 15.3 mmol) and tetrahydropyran (10 ml) in acetone (10 ml) was irradiated with a 450-W Hanovia lamp. Usual work-up after 15 hr gave, in addition to 2-propanol, a mixture of adducts **20** and **21** in a relative ratio of 3.5:1, respectively, as a colorless liquid (1.2 g, 36%). The mixture was separated by preparative glpc.

The major fraction **20** with shorter retention time showed the following spectral data: ir (neat) 1725, 1645, 1070, and 1015 cm^{-1}; nmr ($CDCl_3$) δ 1.3–2.1 (m, 6 H), 3.71 (s), 3.75 (s), and 3.6–4.1 (m) (total 8 H), 5.20 br (t, 1 H, J = 6.0 Hz, C-2 methine proton), and 6.41 br (s, 1 H, vinylic proton).

Anal. Calcd for $C_{11}H_{16}O_5$: C, 57.88; H, 7.07. Found: C, 58.11; H, 7.35.

The minor adduct **21** (longer retention time) had the following spectral data: ir (neat) 1730, 1658, 1040, and 1025 cm^{-1}; nmr ($CDCl_3$) δ 1.4–2.1 (m, 6 H), 3.68 (s), 3.72 (s), and 3.5–4.0 (m) (total 8 H), 5.1–5.3 (m, 1 H, C-2 methine proton), and 6.10 (d, 1 H, J = 1.5 Hz, vinyl proton).

Anal. Calcd for $C_{11}H_{16}O_5$: C, 57.88; H, 7.07. Found: C, 57.69; H, 7.40.

Registry No.—**2,** 762-42-5; **3,** 33536-59-3; **4,** 28864-83-7; **5,** 33536-61-7; **6,** 10486-63-2; **7,** 33522-10-0; **9,** 7370-72-1; **10,** 28864-84-8; **11,** 33522-12-2; **12,** 33536-63-9; **13,** 33536-64-0; **14,** 33522-13-3; **15,** 33536-65-1; **17,** 33536-66-2; **18,** 33536-67-3; *dl*-**19,** 3333-27-5; *meso*-**19,** 3443-36-5; **20,** 33531-70-3; **21,** 33531-71-4.

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[37] G. Sosnovsky, *J. Org. Chem.*, **28**, 2934 (1963).

The Influence of Structure on the Rate of Thermal Rearrangement of Aryl Propargyl Ethers to the Chromenes. The *gem*-Dimethyl Effect

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The rates of first-order thermal cyclizations of a group of para-substituted aryl propargyl ethers p-Z-C_6H_4-$OCRR'C{\equiv}CH$ with R, R′ = H or CH_3 were determined in *o*-dichlorobenzene as a function of Z (OCH_3, NHAc, H, Cl, CN, NO_2) and of the number of CH_3 groups. Where R and R′ are both H (*k* values extrapolated to 189.8°) or where R was CH_3 and R′ was H (*k* values extrapolated to 161.6°), the points followed an adequate Hammett relationship using σ^+ ($\rho = -0.43$) although the NO_2 and CN did not give a good fit for R = R′ = H, and *p*-Cl was faster than *p*-H for R = H, R′ = CH_3. The attempted Hammett plot for the *gem*-dimethyl analogs, R = R′ = CH_3, had a paraboloid shape, *e.g.*, X = NHAc and X = NO_2 had about the same rate, with X = H at a minimum (*k* values extrapolated to 161.6°). The $\Delta S^{\ddagger}$ and $\Delta H^{\ddagger}$ followed no obvious order. The results are best explained by assuming that the "*gem*-dimethyl effect" results from an increase in the proportion of the rotamer with the ethnyl group positioned near the benzene ring, *i.e.*, the rotamer best positioned for reaction, when no hydrogen is available to rotate to that position, and that activation of the position meta to the substituent Z, at least by the electron-withdrawing groups, exists. Preparative runs showed that an essentially quantitative yield of 2-methyl- or 2,2-dimethyl-3-chromenes could be obtained in *o*-dichlorobenzene, and this solvent is preferred to *N,N*-diethylaniline at least for cyclization of 4-nitrophenyl propargyl ether.

Initial reports[1] of desirable analgetic and related activities of *p*-acetamidophenyl *tert*-butyl ether led us to prepare 3-(4-acetamidophenoxy)-3-methylbutyne [**1c**, Z = $NHC(O)CH_3$]. The method used involved reduction of the corresponding 3-(4-nitrophenoxy) compound **1c**, Z = NO_2, to the amino compound (iron and a trace of acid, with initial purification by steam distillation) and acetylation of that under mild conditions. Although the nitro compound gave the theoretical titer for acetylenic hydrogen, the amino compound produced by this procedure gave a low and variable acetylenic hydrogen titer. Acetylation and purification of the resulting acetylamino compound gave us as a major product in several preparations one or the other of the two isomeric products, one giving the theoretical titer for acetylenic hydrogen, the other giving none. The

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[1] See M. Harfenist and E. Thom, *J. Org. Chem.*, **36**, 1171 (1971), for references.