(0.01 *M*) in acetonitrile–water (95:5) was irradiated in a Pyrex vessel with a General Electric 1000-W photochemical lamp for 425 sec. The solution was then shaken with a mixture of 150 ml of dichloromethane and 100 ml of aqueous 2 *M* sodium chloride solution. The organic layer was separated, washed with additional salt solution, dried, concentrated, and subjected to gas chromatography on a Hewlett-Packard Model 720 gas chromatograph equipped with dual 10 ft × 0.25 in. columns of 4.5% silicone gum rubber (GE-SE-52) on Chromosorb G. Only two substances were obtained from the reaction mixture: 1-cyanonaphthalene (51%) and unreacted 1-nitronaphthalene (31%). These compounds were characterized by their retention times, by infrared spectra, and by mixture melting point with authentic samples.

Registry No.—I, 31657-32-6; II, 31657-33-7; III, 31657-34-8; IV, 31657-35-9; 1-nitronaphthalene, 86-57-7; cyanide, 57-12-5; 4-methoxy-1-nitronaphthalene, 4900-63-4; decyl 4-nitrophenyl ether, 31657-37-1; 4-nitroanisole, 100-17-4; pyridine, 110-86-1; *N*-(1-naphthyl)pyridinium picrate, 31657-38-2; 1-bromo-4-(4′-decyloxyphenoxy)butane, 31657-39-3.

Photochemical [2 + 2] Cycloaddition Reactions at Low Temperatures. Synthesis of Bridgehead Substituted Bicyclo[*n*.2.0]dicarboxylates from Maleic Acid Derivatives and Ethylene

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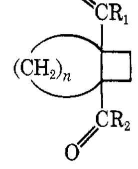
Received July 1, 1971

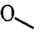
Irradiation through quartz at −65° or lower of ethylene saturated dichloromethane solutions of dimethyl cyclobutene-1,2-dicarboxylate, dimethyl cyclopentene-1,2-dicarboxylate, and cyclohexene-1,2-dicarboxylic anhydride produces the corresponding bicyclo [2.2.0], [3.2.0], and [4.2.0] derivatives in nearly quantitative yield in preparatively useful amounts with high quantum efficiency. Dimethyl cyclohexene-1,2-dicarboxylate does not add ethylene under a wide variety of experimental conditions. Maleic anhydride readily adds ethylene at low temperature in acetone to give a mixture of the maleic anhydride–acetone oxetane (21%) and cyclobutane-1,2-dicarboxylic anhydride (57%), while in an unreactive solvent the cyclobutane is the sole product (70%). Dimethyl acetylenedicarboxylate also reacts readily at low temperatures to add two molecules of ethylene to produce a 9:1 mixture (60–66% yield) of dimethyl bicyclo[2.2.0]hexane-1,4-dicarboxylate and dimethyl bicyclopropyl-1,1′-dicarboxylate. Dimethyl bicyclo[2.2.0]hexane-1,4-dicarboxylate is thermally converted to dimethyl α,α′-dimethyleneadipate with a half-life at 75° of about 53 min.

Photochemical [2 + 2] cycloaddition of olefins and/or acetylenes has provided an excellent route to a number of substituted cyclobutane and cyclobutene derivatives.[1–3] In most of the prior work, however, substituted olefins or acetylenes were the ground-state partners in the cycloadditions, giving substituted cyclobutanes or cyclobutenes. The use of ethylene[3] as the ground-state partner in [2 + 2] cycloadditions to give 1,2-disubstituted cyclobutanes has received much less attention. Furthermore, ethylene addition to a cyclic maleic acid derivative to give bridgehead dicarboxylate derivatives of bicyclo[*n*.2.0]alkanes has only recently been described.[4]

The use of low temperatures to carry out a variety of photochemical transformations can offer a number of distinct advantages. Among these are fewer undesirable side products which result from thermal reactions of the photoproduct, higher quantum yields, and greater solubility of gaseous reactants. We wish to report the results of some of our studies on the preparation of some 1,(*n* + 2)-bicyclo[*n*.2.0]alkanedicarboxylate derivatives **1**, where *n* = 2, 3, 4, by the photochemical cycloaddition of ethylene to the appropriate cyclic maleic acid derivatives, which show the advantages of low temperature preparative photochemistry.



1

where $R_1 = R_2 = OR', OH; R_1 =$ 

Results and Discussion

The additions of ethylene to dimethyl cyclobutene-1,2-dicarboxylate (**2**), dimethyl cyclopentene-1,2-dicarboxylate (**3**), and cyclohexene-1,2-dicarboxylic anhydride (**4**) were carried out by irradiation of solutions of each substrate at −70° in dichloromethane through quartz using a variable-temperature preparative photochemical reactor of our own design.[4a] Excellent yields of the bicyclo[*n*.2.0]alkane derivatives **5**–**7** were obtained in each case (eq 1–3). The use of low temperature and dichloromethane solvent to carry out these transformations is critical. For example, **2** gives a vari-

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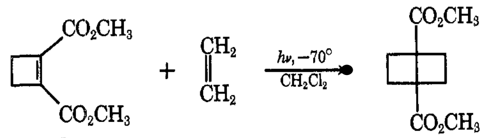
(1) Several reviews on these syntheses have appeared: (a) P. E. Eaton, *Accounts Chem. Res.*, **1**, 50 (1968); (b) W. L. Dilling, *Chem. Rev.*, **69**, 845 (1969); (c) P. G. Bauslaugh, *Syn.*, 287 (1970); (d) G. O. Schenck and R. Steinmetz, *Bull. Soc. Chim. Belg.*, **71**, 781 (1962).

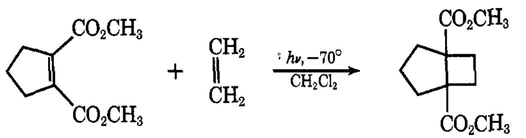
(2) For syntheses of cyclobutanes and cyclobutenes from substituted olefins and acetylenes, *cf.* (a) E. J. Corey, J. D. Bass, R. Lemathieu, and R. B. Mitra, *J. Amer. Chem. Soc.*, **86**, 5570 (1964); (b) R. L. Cargill, J. R. Damewood, and M. M. Cooper, *ibid.*, **88**, 1330 (1966); (c) G. O. Schenck, W. Hartmann, and R. Steinmetz, *Chem. Ber.*, **96**, 498 (1963); (d) R. Steinmetz, W. Hartmann, and G. O. Schenck, *ibid.*, **98**, 3854 (1965); (e) G. R. Evanega and D. L. Fabiny, *Tetrahedron Lett.*, 2241 (1968); (f) H. Yamazaki and R. J. Cretanovi, *J. Amer. Chem. Soc.*, **91**, 521 (1969); (g) W. L. Dilling, T. E. Tabor, F. P. Boer, and P. P. North, *ibid.*, **92**, 1399 (1970).

(3) For cyclobutane synthesis with ethylene, *cf.* (a) H.-D. Scharf and F. Korte, *Chem. Ber.*, **98**, 764 (1965); (b) *Angew. Chem., Int. Ed. Engl.*, **4**, 429 (1965); (c) Y. Yamada, H. Uda, and K. Nakanishi, *Chem. Commun.*, 423 (1966); (d) P. H. Nelson, J. W. Murphy, J. A. Edwards, and J. H. Fried, *J. Amer. Chem. Soc.*, **90**, 1307 (1968); (e) P. E. Eaton, Abstracts of Papers, 156th National Meeting of the American Chemical Society, San Francisco, Calif., April 1968; (f) P. E. Eaton and K. Nyi, *J. Amer. Chem. Soc.*, **93**, 2786 (1971); (g) W. C. Agosta and W. W. Lowrance, *Tetrahedron Lett.*, 3053 (1969).

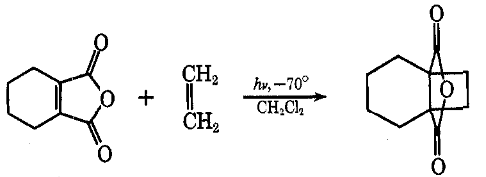
(4) (a) D. C. Owsley and J. J. Bloomfield, *Org. Prep. Proced., Int.*, **3**, 61 (1971); (b) *J. Amer. Chem. Soc.*, **93**, 782 (1971).



2 **5** (100%) (1)



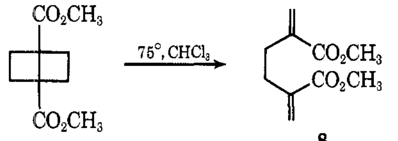
3 **6** (89%) (2)



4 **7** (99%) (3)

ety of products upon irradiation in ether at 0° in the presence of ethylene. The quantum efficiency of the photoreaction of **3** with ethylene drops off dramatically in dichloromethane at 10° (*vide infra*).

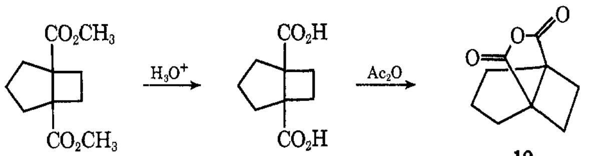
A structure proof of **5** is afforded by its facile rearrangement to the known dimethyl α,α'-dimethyleneadipate[5] (**8**) in quantitative yield (eq 4). Measurements of the isomerization rate at 75° gave a first-order rate constant of $2.2 \pm 0.4 \times 10^{-4}$ sec^{-1}.[4b,6] The rate of isomerization of **5** is approximately 10^8 times faster than that calculated for the rate of isomerization of unsubstituted bicyclo[2.2.0]hexane to 1,5-hexadiene ($k_{75°} = 4 \times 10^{-12}$ sec^{-1}).[7]



5 **8** (4)

$k = 2.2 + 0.4 \times 10^{-4}$ sec^{-1}

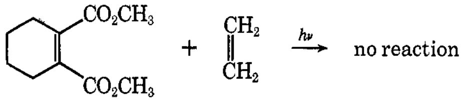
The structure and stereochemistry of the bicyclo[3.2.0]heptane derivative **6** was proved by hydrolysis to the diacid **9** and its subsequent conversion to the cyclic anhydride **10** (eq 5).



6 **9** **10** (5)

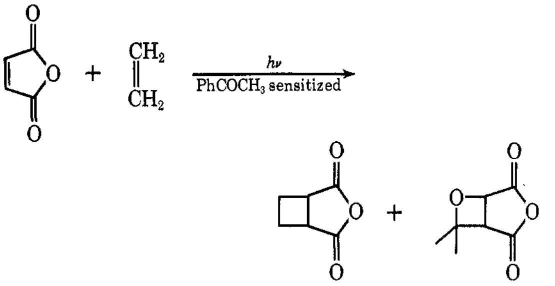
The structure of the bicyclo[4.2.0]octane derivative **7** was proved by comparison with an authentic sample.[8]

Strongly contrasting with the high reactivities of the cyclic maleic anhydride derivatives **2**, **3**, and **4** toward ethylene is dimethylcyclohexene-1,2-dicarboxylate (**11**) which could not be induced to react with ethylene under a variety of conditions (*vide infra*, eq 6).



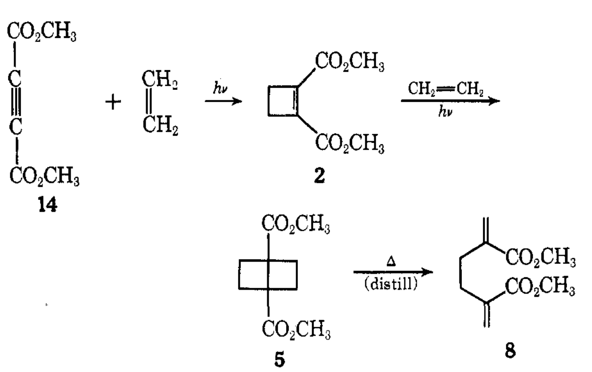
11 (6)

The direct synthesis of cyclobutane-1,2-dicarboxylic anhydride **12** from ethylene and maleic anhydride has not previously been reported (eq 7), even though there are numerous examples of either the reaction of substituted maleic anhydrides with ethylene or of substituted olefins with maleic anhydride.[1-3] For this reaction both the solvent and the reaction temperature are critical. At 5–10° reaction times are of the order of 1 week and the reactions are accompanied by polymer formation on the lamp housing. In acetone solvent, the formation of the oxetane[9] **13** represents an important side reaction. At or below −65°, the photolysis mixtures are quite clean and reaction times are on the order of 1–2 days. However, in acetone oxetane formation is still important, while in ethyl acetate **12** is produced in 71% yield as the sole product. None of the desired cycloaddition was observed in ether at 5–10°, but a white polymer was rapidly produced.



12, 50–71% **13** (in acetone solvent) (7)

The cycloaddition of two molecules of ethylene to dimethyl acetylenedicarboxylate (**14**) offers an attractive, one-step synthesis of dimethyl α,α'-dimethyleneadipate (**8**) *via* a thermal rearrangement of the bicyclo[2.2.0]hexane derivative **5** (eq 8). Thus, irradiation of a solution of **14** through quartz in dichloromethane at −80° and subsequent distillation afforded a 63% yield of a 9:1 mixture of **8** and an isomer **15** (eq 9). Monitoring



14 **2** **5** **8** (8)

$$14 + 2CH_2{=}CH_2 \xrightarrow[CH_2Cl_2]{h\nu,\ -80°} 8 + 15\ (63\%) \qquad (9)$$

$$9{:}1$$

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[5] C. S. Marvel and S. D. Vest, *J. Amer. Chem. Soc.*, **81**, 984 (1959).

[6] The isomerization rate constant for **5** → **8** was incorrectly reported in our preliminary communication of this work (ref 4b). A complete study of the kinetics of this isomerization is now in progress in collaboration with J. Chickos of the University of Missouri, St. Louis.

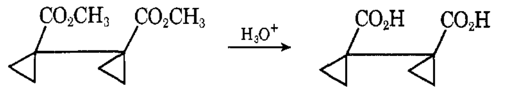
[7] (a) For a review of bicyclo[2.2.0]hexane chemistry, *cf.* K. B. Wiberg, *Advan. Alicycl. Chem.*, **2**, 230 (1968); (b) C. Steel, R. Zand, P. Hurwitz, and S. G. Cohen, *J. Amer. Chem. Soc.*, **86**, 679 (1964).

[8] (a) E. Vogel, D. Roos, and K. H. Disch, *Justus Liebigs Ann. Chem.*, **653**, 55 (1962); (b) R. A. Martin, Dissertation, University of Oklahoma, 1969.

[9] N. J. Turro and P. A. Wriede, *J. Org. Chem.*, **34**, 3562 (1969).

the reaction by glc showed that **2** was reacting very rapidly since it could not be detected.

That the minor product of the photolysis, **15**, was isomeric with both **5** and **8** was shown by its mass spectrum (see Experimental Section). The nmr and ir spectra of **15** are compatible with its formulation as dimethyl bicyclopropyl-1,1′-dicarboxylate.[10a] Final structure proof was afforded by its hydrolysis to the known bicyclopropyl-1,1′-dicarboxylic acid (**16**, eq 10).[10] The formation of **15** is not surprising in that similar structures have been found in the photosensitized additions of maleic anhydride to acetylene and propyne,[11,12] of 3,6-dihydrophthalic anhydride to 2-butyne,[13] and of acetylenedicarboxylic acid to 1,4-cyclohexadiene.[14]



(10)

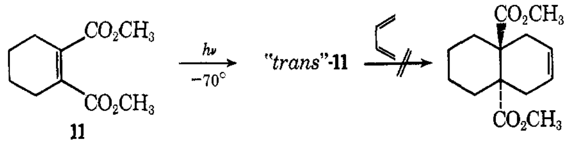
15 **16**

The solvent and temperature are again very important in the reaction of dimethyl acetylenedicarboxylate (**14**) with ethylene. Our experiments show that in ether solvent the primary reaction of **14** occurs with solvent rather than with ethylene. This type of behavior has previously been observed in cyclic ether solvents with both **14** and with diethyl fumarate,[15,16] in which the triplet states of these molecules are certainly involved.

The concerted cycloaddition of ground-state ethylene to an electronically excited π system to form a cyclobutane is a symmetry-allowed process.[17] However, it has been shown that the addition of substituted ethylenes to cyclic α,β-unsaturated ketones occurs through the triplet state of the ketones and that the products are derived from ring closures and intramolecular disproportionations of diradical intermediates.[1,2a] These data rule out a concerted reaction in these systems.

The nature of the excited state which is involved in the addition of ethylene to the cyclic maleic acid derivatives **2**–**4** cannot be ascertained on the basis of our data. The fact that one and only one product is formed in each case does not rule out the triplet states of **2**–**4** in the cycloadditions. This is supported by the fact that the same product is obtained in both the photosensitized[8] and unsensitized reaction of cyclohexene-1,2-dicarboxylic anhydride (**4**) with ethylene. Furthermore, no data have been obtained on the quantum yields of intersystem crossing from an excited singlet state to a triplet state of any cyclic or noncyclic maleic or fumaric acid derivative.[18]

The nonreactivity of dimethyl cyclohexene-1,2-dicarboxylate (**11**) toward ethylene was initially quite surprising. However, dimethyl cyclobutene-1,2-dicarboxylate (**2**), dimethyl cyclopentene-1,2-dicarboxylate (**3**), cyclohexene-1,2-dicarboxylic anhydride (**4**), and maleic anhydride all react with ethylene and make up a series of conformationally rigid molecules, while **11** may have some rotational freedom about the carbon–carbon double bond in the excited state. Therefore, it appears that the excited state of **11** may be conformationally different from those of **2**–**4** and maleic anhydride and may even be a "*trans*"-cyclohexene. 1-Acetylcyclohexene has been shown to undergo isomerization to a trans form.[1a] In an attempt to try to trap a hypothetical "*trans*"-**11**, a photolysis was performed in the presence of a large excess of butadiene at −70° (eq 11). No Diels–Alder product was formed (eq 11).



(11)

11

Baird[19] has noted that the equilibrium conformation of the lowest $^3\pi,\pi^*$ in a vibrationally relaxed, conjugated polyene has one of the double bonds twisted at an angle of 90°. Moreover, Lim, Li, and Li[20] have described the importance of out-of-plane vibrations in the vibronic coupling of n,π^* and π,π^* states of heteroaromatic and aromatic carbonyl compounds. Thus, the excited states of **11** may not only differ conformationally from those of **2**–**4** and maleic anhydride but also may differ electronically. Studies are presently under way to clarify this point.[18]

The formation of dimethyl bicyclopropyl-1,1′-dicarboxylate (**15**) in the photoaddition of ethylene to dimethyl acetylenedicarboxylate (**14**) needs to be discussed in some detail. Because similar products have been found in photoadditions which involve acetylenes as the ground-state partners,[11–14] the production of a product containing cyclopropane rings from an electronically excited acetylene must involve intermediates common to both types of reactions.

Hartmann[11] has proposed two types of intermediates to account for the formation of cyclopropyl compounds from triplet maleic anhydride and acetylene (eq 12, 13). Diradical intermediate **17** could give cyclobutene by spin relaxation and ring closure, while the carbene intermediate **18** could rearrange to cyclobutene.[21]

In Hartmann's case,[11] either intermediate can explain the results. However, the finding of bicyclopropyl compound **15** in the present case poses problems for an intermediate analogous to **17** and its reaction with ethylene (eq 14).

The site at which ethylene is required to attack **20** in order to ultimately give **15** is the site that is most sterically hindered and is the site at which the radical center is most highly stabilized. No products which would result from ethylene attack at the alternate site on **20** [*e.g.*, dimethyl cyclohexene-1,2-dicarboxylate (**11**)] have been found. Thus, because **11** is stable under these conditions (*vide supra*) an attack of ethylene on

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[10] (a) J. M. Conia and J. M. Denis, *Tetrahedron Lett.*, 3445 (1969) (ir and nmr spectra of the diethyl ester); (b) L. Eberson, *Acta Chem. Scand.*, **13**, 46 (1959).

[11] W. Hartmann, *Chem. Ber.*, **102**, 3974 (1969).

[12] G. Klotzenberg, P. G. Fuss, and J. Leitch, *Tetrahedron Lett.*, 3409 (1966).

[13] R. Askani, *Chem. Ber.*, **98**, 3618 (1965).

[14] M. Takahashi, Y. Kitahara, I. Murata, T. Nitta, and M. C. Woods, *Tetrahedron Lett.*, 3409 (1966).

[15] P. Singh, *ibid.*, 2155 (1970).

[16] I. Rosenthal and D. Elad, *Tetrahedron*, **23**, 3193 (1967).

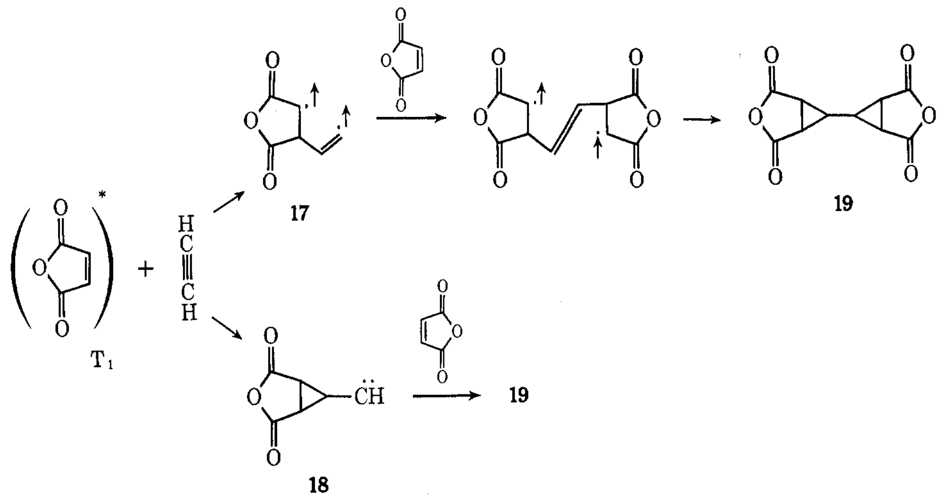
[17] *Cf.* R. B. Woodward and and R. Hoffmann, *Angew. Chem., Int. Ed. Engl.*, **8**, 781 (1969), and references cited therein.

[18] We have obtained emission spectra of **2–4**, **14**, maleic anhydride, and maleic and fumaric esters. Quantum yields and lifetimes of fluorescence and phosphorescence are presently being studied in collaboration with D. R. Kearns of the University of California, Riverside.

[19] N. C. Baird, *Mol. Photochem.*, **2**, 153 (1970).

[20] E. C. Lim, Y. H. Li, and R. Li, *J. Chem. Phys.*, **53**, 2443 (1970).

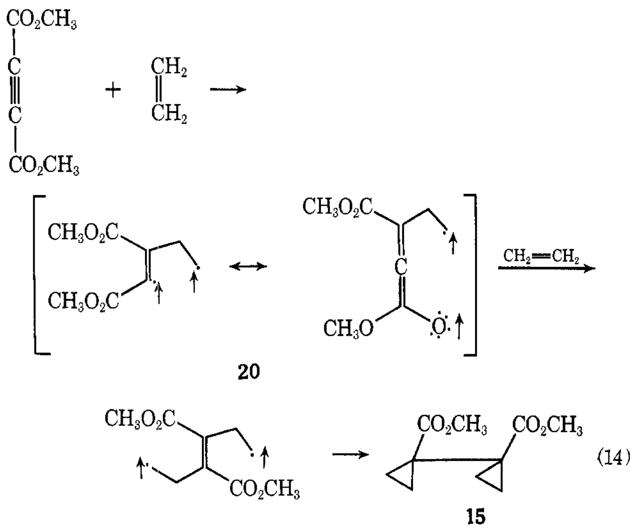
[21] L. Friedman and H. Schechter, *J. Amer. Chem. Soc.*, **82**, 1002 (1960).



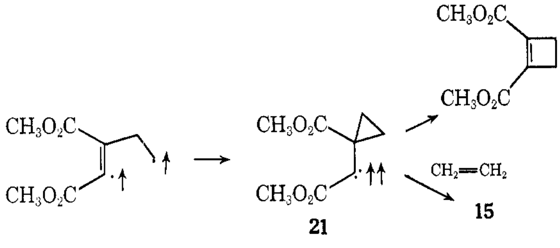
(12)

(13)

20 is not very likely. An alternative pathway for decomposition of 20 is rearrangement to a triplet carbene 21 which is stabilized by an adjacent carbomethoxyl group (eq 15).[22] Askani's work[13] has a great deal of bearing on this point. The photosensitized addition of 2-butyne to 3,6-dihydrophthalic anhydride was found to give the products shown in eq 16, but **24a–c** were not reported.

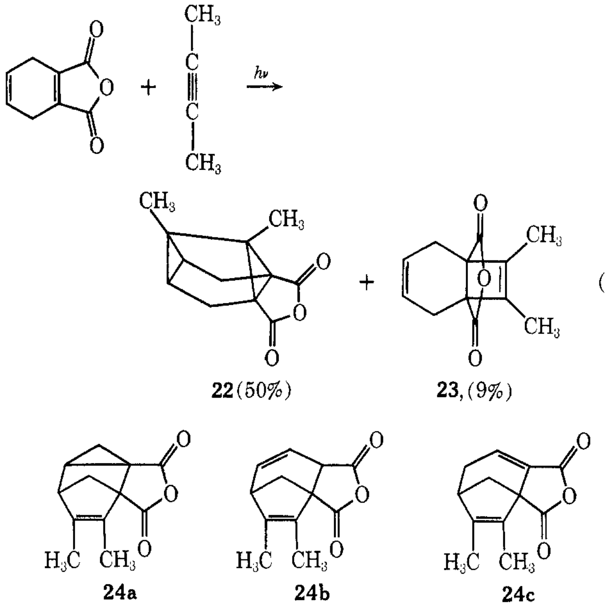


(14)

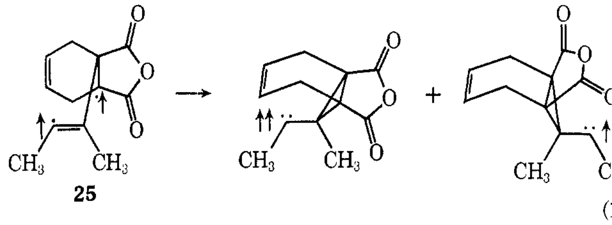


(15)

The formation of **22** and **23** in 50 and 9% yields, respectively, and the absence of products such as **24a–c** strongly implies (1) formation of carbenes as intermediates and (2) their formation either directly or before spin–spin relaxation can occur in an intermediate such as **25** (eq 17).

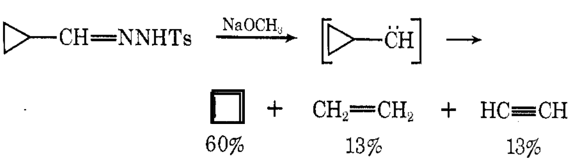


(16)



(17)

The work of Friedman[21] and others[23,24] shows that cyclopropyl conjugated carbenes either rearrange to cyclobutenes or decompose to olefins and acetylenes (eq 18).



(18)

Application of the principle of microscopic reversibility to the previous results on cyclopropyl conjugated carbenes[21,23,24] implies that these species could be formed from acetylenes and olefins under photochemical conditions. The production of the cyclobutene (**2**) and bicyclo[2.2.0]hexane (**5**) derivatives from excited singlet dimethyl acetylenedicarboxylate and ethylene *via* a concerted process has not been discussed. Indeed, it may be the major pathway which produces **5**.

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[22] W. Kirmse, "Carbene Chemistry," Academic Press, New York, N. Y., 1964, Chapter 6, p 95.

[23] W. Kirmse and K. H. Pook, *Chem. Ber.*, **98**, 4022 (1965).

[24] S. J. Cristol and J. K. Harrington, *J. Org. Chem.*, **28**, 1413 (1963).

However, this pathway does not explain the formation of the bicyclopropyl derivative **15**. Therefore, it may be likely that a multiplicity of pathways is necessary to account for the formation of both **5** and **15**.

Experimental Section

Microanalyses were carried out by Alfred Bernhardt Mikroanalytisches Laboratorium. Nmr spectra were recorded on either a Varian Associates T-60 or A-56/60 nmr spectrometer. Mass spectra were obtained on a Varian MAT CH-7 instrument.

Materials.—Dichloromethane (Mallinckrodt), tetrahydrofuran (THF) (Fisher), methanol (Mallinckrodt, anhydrous), and ethylene (Matheson, C. P. grade) were used without further purification. Pimelic acid (Eastman) was recrystallized from water. Thionyl chloride (Fisher reagent) and phosphorus pentachloride (J. T. Baker) were used directly from the bottle. Dimethyl acetylenedicarboxylate (Eastman White Label) was distilled before use. Dimethyl cyclobutene-1,2-dicarboxylate was prepared from 1,2-dicyanocyclobutane.[8,25] Cyclohexene-1,2-dicarboxylic anhydride was prepared by the phosphorus pentoxide catalyzed isomerization of 4-cyclohexene-1,2-dicarboxylic anhydride.[26] Dimethyl cyclopentene-1,2-dicarboxylate was prepared as previously described.[4a]

Reaction Kinetics.—The rate of the transformation **5** → **8** was followed at 75° in a Varian Associates A-56/60 nmr spectrometer with variable temperature probe. The probe temperature was calibrated by following the chemical shift of the hydroxyl protons of ethylene glycol as they varied with temperature. A solution of 50 μl of **5** in 0.5 ml of $CDCl_3$ with TMS and 20 μl of $CHCl_3$ as internal standards was prepared in an nmr tube. The reaction was followed by integrating the rise of the vinyl (at δ 6.06 and 5.47 ppm) and methoxy resonances (at δ 3.70 ppm) of **8** and the fall of the methoxy resonance of **5** (at δ 3.53 ppm). First-order plots were obtained which were linear to 3 half-lives. A first-order rate constant of 1.85×10^{-4} sec^{-1} was obtained for the rise of the vinyl protons of **8**, while a rate constant of 2.53×10^{-4} sec^{-1} was obtained for either the fall of the methoxy resonance of **5** or the rise of the methoxy resonance of **8**. We have no adequate explanation at present for these differences.[6]

Dimethyl Cyclohexene-1,2-dicarboxylate (11).—A solution of 100.0 g (0.66 mol) of cyclohexene-1,2-dicarboxylic anhydride[26] and 0.1 g of *p*-toluenesulfonic acid hydrate was prepared and stirred in 700 ml of methanol for 36 hr at room temperature. After the methanol had been stripped from the reaction mixture, the resulting clear oil was added to 156.8 g (0.75 mol) of phosphorus pentachloride in 500 ml of benzene. The mixture was stirred for 4 hr and was added to 1500 ml of absolute methanol. The methanol was chilled in a −8° cold bath and the rate of addition of the benzene solution was kept such that the temperature of the methanol never rose above −2°. The methanolic solution was concentrated *in vacuo* to yield an oil which was taken up in water (500 ml) and extracted four times with 400-ml portions of ether. The ether was washed four times with 200-ml portions of a 10% sodium bicarbonate solution and twice with 200-ml portions of water. It was then dried over magnesium sulfate and concentrated *in vacuo* to yield 86.1 g of a clear oil. The oil was fractionated through a 6-in. Vigreux column to yield 68.9 g (0.35 mol, 53%) of dimethyl cyclohexene-1,2-dicarboxylate, bp 84–85° (0.3 mm) [lit.[27] 75° (0.2 mm)].

Photochemical Cycloadditions. General Procedure.—All photochemical cycloadditions of ethylene were carried out using the variable temperature preparative reactor[4a] except where noted. Unless stated otherwise, the general procedure was as follows. The compound to be photolyzed was dissolved in 2800 ml of solvent in the reactor. Nitrogen was bubbled through the solution during cool down to −70 to −80°. Ethylene was then bubbled into the solution for 15–20 min at a flow rate of 6 l./min. Once the lamp was turned on, a flow rate of ethylene of 50–100 ml/min was maintained throughout the photolysis. All photolyses except for maleic anhydride reactions were carried out using unfiltered light from an Hanovia 450-W medium-pressure mercury arc.

Dimethyl Bicyclo[2.2.0]hexane-1,4-dicarboxylate (5).—Dimethyl cyclobutene-1,2-dicarboxylate[25] (**2**) (10 g, 0.058 mol) was irradiated in 2800 ml of dichloromethane for 2 hr at −70°. Then the −70° solution was sucked directly into a rotary film evaporator, the evaporation flask of which was held at −15° with an ice–acetone bath as the dichloromethane was stripped at 10-mm pressure. The flask was allowed to warm to 0° in order to remove the last traces of solvent. Dimethyl bicyclo[2.2.0]-hexane-1,4-dicarboxylate (**5**) was obtained in this manner in 100% yield (10.65 g, 0.0588 mol) as a low melting solid, liquid at room temperature. This material showed a single, sharp peak on glc (10 ft × $^1/_{16}$ in. with 3% SE-30 on Aeropak 30, 125°) which had a retention time of 7.2 min, identical with its rearrangement product, dimethyl α,α'-dimethyleneadipate (**11**): nmr δ 3.53 (singlet, 6 H), 3.0–2.0 ppm (multiplet, 8 H); mass spectrum *m/e* (rel intensity) 198 (0.12), 107 (48), 79 (100), 77 (48), 59 (71), 39 (90).

Anal. Calcd for $C_{10}H_{14}O_4$: C, 60.59; H, 7.12. Found: C, 60.66; H, 7.22.

Attempted Photoaddition of Ethylene to 2 at 0°.—A mixture of 4.0 g (0.023 mol) of **2** in 800 ml of ether was prepared in a small reactor fitted with a quartz immersion well and gas dispersion tube. The ether solution was saturated with ethylene by bubbling the gas through it for 1 hr. The solution was then irradiated with an Hanovia 450-W medium-pressure mercury arc for 30 min at 0°. Glc examinations of the reaction mixture (SE-30, 125°) at the end of this time indicated that all of the starting diester had reacted. A complex mixture of products was produced which was shown to be the result of ether incorporation by nmr analysis.

Dimethyl Bicyclo[3.2.0]heptane-1,5-dicarboxylate (6).—Dimethyl cyclopentene-1,2-dicarboxylate (**3**) (27.6 g, 0.15 mol) was irradiated for 3 hr in 2800 ml of dichloromethane at −70°. After the reaction mixture had been concentrated *in vacuo*, the 30.6 g (96%) of crude product which remained was distilled through a short Vigreux column to yield 28.2 g (0.138 mol, 89%) of analytically pure dimethyl bicyclo[3.2.0]heptane-1,5-dicarboxylate (**6**): bp 75.5–76° (0.2 mm); nmr (CCl_4 solvent, TMS reference) δ 3.58 (singlet, 6 H), 2.57 (complex multiplet, 6 H), 1.6 ppm (complex multiplet, 4 H); n^{25}_{D} 1.4691.

Anal. Calcd for $C_{11}H_{16}O_4$: C, 62.25; H, 7.60. Found: C, 62.04; H, 7.75.

Addition of Ethylene to Dimethyl Cyclopentene-1,2-dicarboxylate (3) at 10°.—In another experiment, 92.0 g (0.5 mol) of **3** was irradiated for 6 days at 10° in 4500 ml of methylene chloride saturated with ethylene. Glc (SE-30, 125°) showed that only approximately 40% of **3** had been consumed. The solution was concentrated to a volume of 2800 ml and irradiated in the variable temperature reactor at −70° in the presence of ethylene for 18 hr to complete the photolysis. A yield of 80.4 g (0.38 mol, 76%) of **6** was obtained.

Bicyclo[3.2.0]heptane-1,5-dicarboxylic Acid (9).—Dimethylbicyclo[3.2.0]heptane-1,5-dicarboxylate (**6**) (80.4 g, 0.38 mol) was refluxed for 24 hr in 400 ml of 6 *N* HCl. The product which crystallized from the solution was recrystallized from water to yield 43.0 g (0.24 mol, 63%) of **9**, mp 214–214.8°.

Anal. Calcd for $C_9H_{12}O_4$: C, 58.69; H, 6.57. Found: C, 58.73; H, 6.42.

Bicyclo[3.2.0]heptane-1,5-dicarboxylic Anhydride (10).—A solution of 43.0 g (0.24 mol) of bicyclo[3.2.0]heptane-1,5-dicarboxylic acid (**9**) and 0.1 g of *p*-toluenesulfonic acid hydrate was prepared in 250 ml of acetic anhydride in a 500-ml round-bottomed flask equipped with reflux condenser and drying tube. The solution was heated on the steam bath for 24 hr. White crystals were deposited upon cooling of the solution. The product was isolated by suction filtration and was recrystallized from hot carbon tetrachloride to yield 31.4 g (0.195 mol, 81%) of **10**: mp 133–133.4°; ir 1865, 1935, 1780 cm^{-1} (cyclic anhydride).

Anal. Calcd for $C_9H_{10}O_3$: C, 65.05; H, 6.07. Found: C, 64.89; H, 6.03.

Bicyclo[4.2.0]octane-1,6-dicarboxylic Anhydride (7).—A solution of 10.0 g (0.066 mol) of cyclohexene-1,2-dicarboxylic anhydride (**4**) in 2800 ml of methylene chloride was irradiated for 2 hr at −70°. When the reaction mixture was concentrated *in vacuo*, 11.80 g (0.066 mol, 99%) of **7** was obtained. It had melting point, mixture melting point (108–110°), and glc retention time identical with an authentic sample;[8] ir 1850 and 1790 cm^{-1} (cyclic anhydride); nmr (CCl_4 solvent, TMS reference)

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(25) (a) W. H. Perkin, Jr., *J. Chem. Soc.*, **65**, 950 (1894); (b) D. Seebach, *Chem. Ber.*, **97**, 2953 (1964); (c) F. B. Kipping and J. J. Wren, *J. Chem. Soc.*, 1773 (1967).

(26) M. E. Bailey and E. D. Amstutz, *J. Amer. Chem. Soc.*, **78**, 3828 (1956).

(27) A. L. Barney and H. B. Stevenson, U.S. Patent 2,870,196 (Jan 20, 1959); *Chem. Abstr.*, **53**, 11237*g* (1959).

δ 2.34 (singlet, 4 H), 1.88 (multiplet, 4 H), and 1.5 ppm (multiplet, 4 H).

Attempted Photoaddition of Ethylene to Dimethyl Cyclohexene-1,2-dicarboxylate (**11**).—The photoaddition of ethylene to dimethyl cyclohexene-1,2-dicarboxylate (**11**) was attempted under a variety of conditions in the variable temperature apparatus. The procedures followed for the mechanical handling of the apparatus were as previously described. Table I gives the conditions used in these experiments. No cycloaddition product could be observed by glc.

TABLE I

ATTEMPTED PHOTOADDITION OF ETHYLENE TO **11**

Solvent[a]	Temp, °C	Filter	Sensitizer
Ether	−80	None	None
Dichloromethane	−73	None	None
Dichloromethane	−73	Pyrex	Acetophenone
Dichloromethane	27	Pyrex	Acetophenone
Acetone	−78	None	Acetone
Dichloromethane[b]	−70	None	None (400 g of butadiene added)

[a] All reactions were run with 29.7 g (0.15 mol) of **11** in 2800 ml of solvent. [b] 2400 ml of solvent.

Cyclobutane-1,2-dicarboxylic Anhydride (**12**).—The addition of ethylene to maleic anhydride in acetone, acetonitrile, ethyl acetate, and ether at 10 and −65° is summarized in Table II. The reactions carried out at 10° were conducted under nitrogen in a flask of appropriate volume with Pyrex-filtered light from a 450-W Hanovia medium-pressure mercury arc. Photolyses at low temperature were carried out in the low temperature reactor[4a] as described above except that a Pyrex filter was used. All reactions were photosensitized by addition of 5 g of acetophenone per mole of anhydride.

TABLE II

ADDITION OF ETHYLENE TO MALEIC ANHYDRIDE

Solvent	Temp, °C	Time	Yield,[a] %
Acetone (5 l.)	10	7 days	50[b]
Acetone (2800 ml)	−65	29 hr	57[c]
Acetonitrile (1300 ml)	10	7 days	68[d]
Ethyl acetate (2800 ml)	−65	44 hr	71[e]
Ether (5 l.)	10	7 days	0[f]

[a] Based on unrecovered maleic anhydride. [b] 196 g (2.0 mol) of maleic anhydride gave 72 g of product and 85 g of starting material. The crude reaction mixture showed oxetane by glc and nmr, but the distilled product contained only cyclobutanedicarboxylic anhydride. [c] 98 g (1.0 mol) of maleic anhydride gave 31.2 g of oxetane and after crystallization and distillation 72.2 g of cyclobutanedicarboxylic anhydride. [d] 98 g (1.0 mol) of maleic anhydride gave 65 g of the desired product and 23 g of starting material. [e] 98 g (1.0 mol) of maleic anhydride gave 71.6 g of desired product, 19.0 g of starting material, and 3.5 g of cyclobutane-1,2,3,4-tetracarboxylic dianhydride, mp 299–300° [G. W. Griffin, J. E. Basinski, and A. F. Vellturo, *Tetrahedron Lett.*, 13 (1960)]. [f] 98 g (1.0 mol) of maleic anhydride gave only a white polymer and none of the desired product.

The reactions were worked up by concentrating the reaction mixture *in vacuo* and fractionally distilling the product. The structure of **12** was proved by comparison with an authentic sample prepared from 1,2-dicyanocyclobutane.[25a] The presence of the maleic anhydride–acetone oxetane **13** was inferred by its characteristic nmr frequencies at δ 5.25 (doublet), 1.67 (singlet), and 1.42 ppm (singlet).[9] Oxetane **13** tended to polymerize on attempted distillation or crystallization and was not isolated. Distillation of the reaction mixtures which contained oxetane **13** gave no oxetane in the distillate. Glc analyses were carried out on a 10 ft × $^{1}/_{8}$ in. 1% OV-17 on Chromosorb G column programmed at 10°/min from 70 to 180°.

Dimethyl α,α′-Dimethyleneadipate (**8**) **from Dimethyl Acetylenedicarboxylate** (**14**).—Dimethyl acetylenedicarboxylate (**14**) (14.2 g, 0.1 mol) was irradiated for 18 hr at −80° in 2800 ml of dichloromethane. After the solvent had been distilled from the reaction mixture *in vacuo*, the resulting yellow oil was distilled at 71–74° (0.2 mm) through a short Vigreux column to yield 12.5 g (0.063 mol, 63%) of a 9:1 mixture of **8** and **15**. The analysis was carried out at 125° on the 10 ft × $^{1}/_{16}$ in. SE-30 column previously described. Retention times follow: **15**, 6.2 min, and **8**, 7.2 min. Dimethyl α,α′-dimethyleneadipate was crystallized from low boiling petroleum ether: mp 25–26° (lit.[5] 25–26°); nmr δ 6.18 (doublet, 2 H), 5.55 (broad singlet, 2 H), 3.70 (singlet, 6 H), 2.55 ppm (broad singlet, 4 H); mass spectrum *m/e* (relative intensity) 198 (0.4), 166 (32), 107 (100), 79 (58), 59 (35).

A sample of **15** was collected by preparative glc (10 ft × 0.25 in. 15% Apiezon L on Chromosorb W, 140°): ir 3090, 1725 cm^{-1}; nmr δ 3.5 (singlet, 6 H), 1.4–1.1 (complex multiplet, 4 H), 0.8–0.5 ppm (complex multiplet, 4 H); mass spectrum *m/e* (relative intensity) 198 (11), 183 (21), 167 (32), 166 (49), 151 (23), 139 (42), 107 (28), 106 (25), 79 (100), 77 (39), 59 (59), 28 (48).

The photoaddition may also be run on a larger scale. Thus, 50.0 g (0.325 mol) of **14** in 125 ml of dichloromethane was dripped from a Hershberg addition funnel into a photolyzing solution of ethylene in 2600 ml of dichloromethane in the variable temperature reactor at −80° over an 8-hr period. The solution was irradiated through quartz for a total of 52 hr with a 450-W medium-pressure mercury arc. The photolysis mixture was concentrated *in vacuo* and the residue was passed down a falling film molecular still at 110° (0.5 mm). A total of 49.1 g of a clear oil was collected. The oil was fractionated through a short Vigreux column. The first fraction, bp 28–30° (0.2 mm), contained 6.4 g (0.045 mol) of **14**. The product mixture which weighed 36.9 g (0.186 mol, 66%) had bp 45–50° (0.05 mm).

Bicyclopropyl-1,1′-dicarboxylic Acid (**16**).—Dimethyl bicyclopropyl-1,1′-dicarboxylate (**15**) (100 mg, 0.5 mmol) was refluxed for 12 hr in 5 ml of 10% ethanolic KOH solution. The solution then was acidified with HCl and extracted three times with 15 ml of ether. The ether extracts were dried over magnesium sulfate and concentrated *in vacuo* to yield a tan solid. The tan solid was recrystallized from aqueous acetic acid to yield 52 mg (0.31 mmol, 63%) of bicyclopropyl-1,1′-dicarboxylic acid, mp 268–275° (sealed tube) (lit.[10b] 256–275°).

Attempted Photoaddition of Ethylene to Dimethyl Acetylenedicarboxylate (**14**) **in Ether.**—Using the dropping funnel technique discussed above, 50.0 g of **14** in 125 ml of ether was added over 6 hr to 2600 ml of ether saturated with ethylene at −80° in the variable temperature reactor. The solution was irradiated through quartz with the 450-W medium-pressure mercury arc for 18 hr. Work-up of the photolysis mixture yielded 71 g of an oil which showed at least seven components on glc (SE-30 column, 125°). The nmr spectrum of the oil showed that ether had participated in the reaction.

Registry No.—**3**, 13368-79-1; **5**, 31947-22-5; **6**, 31947-23-6; **7**, 6537-91-3; **8**, 31952-35-9; **9**, 31952-36-0; **10**, 31952-37-1; **12**, 4462-96-8; **15**, 29547-69-1; ethylene, 74-85-1; maleic anhydride, 108-31-6.