$1]^+$ ion. By contrast the methane chemical ionization mass spectra of both isomers are very similar, with the base peak occurring at $[M + 1 - 90]^+$. On the other hand the isobutane chemical ionization spectra of **2** and **4** were not informative because of the poor reactivity of the reagent.

Conclusions

The examples presented above provide new evidence about functional group interactions during ionic vapor-phase reactions of alkyl siliconium ions. The vapor-phase reaction of these ions with sample molecules containing a trimethylsilyl function results in exchange of methyl groups as well as the entire trimethylsilyl group. The extent of intermolecular exchange of either the methyl groups or the entire trimethylsilyl function is in part determined by the acidity of the trimethylsilyl derivative. This indicates that a finite lifetime is probably required for the postulated intermediates to effect methyl group scramble. Recognition of ionically induced trimethylsilyl group exchanges such as the ones reported here is important in analytical studies of trimethylsilyl derivatives, since in the spectra of the latter compounds much of the structural information is carried by ions containing the silyl function. The data presented also point out that stereochemical factors play a significant role in vapor-phase reactions. Unlike proton transfer reactions from NH_4^+ or CH_5^+, which are generally not sterically "sensitive", chemical ionization studies with alkyl siliconium ions may provide important information about stereochemical requirements in vapor-phase ionic reactions.

Experimental Section

Chemical ionization mass spectra were obtained with a modified CEC 21-110B mass spectrometer.[11] All spectra were recorded at ion source pressures of 0.2 Torr, temperatures of 100–135°, a repeller field of 10 V/cm, and ion-accelerating voltage of 8 kV. The total filament emission current was 100 μA and the electron energy was 400 V. The ion beam was focussed for maximum secondary ion intensity at *m/e* 161. The principal ions in the spectrum of tetramethylsilane at ion source pressure of 0.2 Torr and temperature of 125° occurred at *m/e* 73 (75% Σ_{40}), 131 (2.5% Σ_{40}), 145 (<1% Σ_{40}), and 161 (18% Σ_{40}). Trimethylsilyl derivatives of the compounds investigated were prepared according to established procedures.[12] The samples were introduced into the ion source *via* the standard solid probe inlet of the mass spectrometer.

Acknowledgment.—Financial support by the National Institutes of Health (GM-13901, GM-16216, and GM-02055) is gratefully acknowledged.

Registry No.—**1**, 6221-89-2; **2**, 6221-90-5; **3**, 42449-18-3; **4**, 42449-19-4; **5**, 42449-20-7; **6**, 7604-82-2; **7**, 18603-17-3; **8**, 29881-28-5; **9**, 42449-24-1; **10**, 18406-56-9.

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(11) (a) J. H. Futrell and L. H. Wojcik, *Rev. Sci. Instrum.*, **42**, 244 (1971); (b) I. Dijidic, D. M. Desiderio, M. S. Wilson, P. F. Crain, and J. A. McCloskey, *Anal. Chem.*, **43**, 1877 (1971).

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Synthesis, Structure, and Conformation of 10,15-Dihydro-1,6,11-trihydroxy-2,7,12-trimethoxy-4,9,14-trimethyl-5*H*-tribenzo[*a*,*d*,*g*]cyclononene and Its Tripropyl Analog

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Acid-catalyzed condensation of 6-hydroxymethyl-4-methylguaiacol produced a new cyclic trimer similar to cyclotriveratrylene (CTV). Its structure was determined by proton magnetic resonance spectroscopy and mass spectrometry to be 10,15-dihydro-1,6,11-trihydroxy-2,7,12-trimethoxy-4,9,14-trimethyl-5*H*-tribenzo[*a*,*d*,*g*]-cyclononene (**3**). In contrast to CTV, neither **3** nor its triacetate **3a** adopt rigid "crown" conformations normal for compounds of this type; nor do they form inclusion complexes. Similar properties were exhibited by the tripropyl analog, 10,15-dihydro-1,6,11-trihydroxy-2,7,12-trimethoxy-4,9,14-tripropyl-5*H*-tribenzo[*a*,*d*,*g*]cyclononene (**4**) and its triacetate **4a**.

Although originally described as a dimer[1] and subsequently as a hexamer,[2] the condensation product of veratrole with formaldehyde under acid conditions, with the general formula $(C_9H_{10}O_2)_n$, has been shown by Lindsey,[3] Erdtman, *et al.*,[4] and others[5-8] to be in fact a trimer ($n = 3$). The trivial name for this trimer, cyclotriveratrylene (CTV), was coined by Lindsey.[3]

The stereochemistry of this tribenzocyclononene system has been investigated by several groups.[3-8] On the basis of pmr spectra, CTV adopts a rigid "crown" conformation. This is also the most stable conformation for cyclononatriene,[9] although here interconversion between two equivalent "crown" conformations occurs at room temperature. However, unlike cyclononatriene, CTV does not show any tendency to invert its conformation, even at 200°.[5,6] CTV forms clathrate complexes with a large number of organic compounds[10] suggesting that this molecule must adopt a rigid nonplanar conformation.

An alternative conformation proposed in the literature is a flexible "saddle" form, which would be ex-

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(1) G. M. Robinson, *J. Chem. Soc.*, **107**, 267 (1915).

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(6) B. Miller and B. D. Gesner, *Tetrahedron Lett.*, **No. 38**, 3351 (1965).

(7) T. Sato and K. Uno, *J. Chem. Soc., Chem. Commun.*, 579 (1972); *J. Chem. Soc., Perkin Trans. 1*, 895 (1973).

(8) A. Goldup, A. B. Morrison, and W. G. Smith, *J. Chem. Soc.*, 3864 (1965).

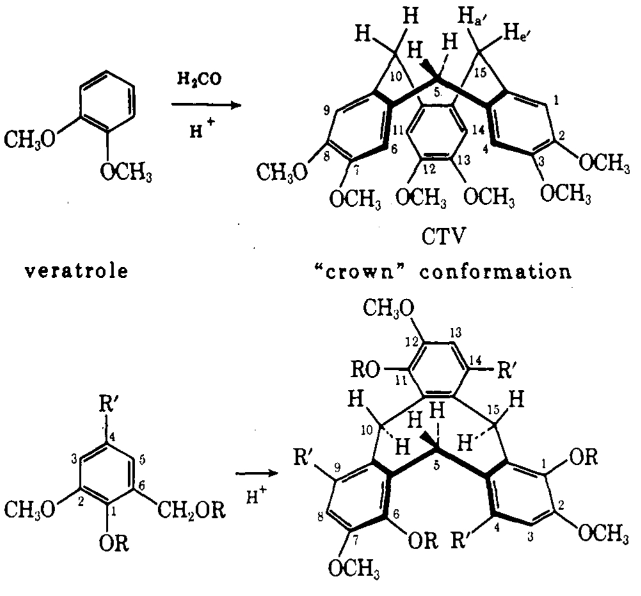
(9) P. Radlick and S. Winstein, *J. Amer. Chem. Soc.*, **85**, 344 (1963); K. G. Untch and R. J. Kurland, *ibid.*, **85**, 346 (1963).

(10) V. Gaglioti, A. M. Liquori, N. Galo, E. Giglio, and M. Scrocco, *J. Inorg. Nucl. Chem.*, **8**, 572 (1958).

TABLE I

PMR SPECTRAL DATA. FIRST-ORDER CHEMICAL SHIFTS (δ VALUES, $CDCl_3$ SOLUTIONS)

	Aromatic(s)	Methylene	Methoxyl	Methyl	Propyl α	Propyl β	Propyl γ	OH(s)	Acetate(s)
1	6.55 (2)	4.58	3.70	2.20				6.05, 2.2	
1a	6.70 (2)	4.95	3.69	2.16					2.12, 1.98
2	6.56 (2)	4.64	3.78		2.46	1.58	0.82	6.25, 2.9	
2a	6.74, 6.69	4.96	3.72		2.48	1.58	0.92		2.23, 1.98
3	6.50	4.02	3.76	2.22				5.5	
3a	6.58	3.86	3.73	2.25					2.08
4	6.47	4.07	3.72		2.63	1.28	0.83	5.6	
4a	6.57	3.90	3.72		2.56	1.28	0.86		2.06



1, 1a, 2, 2a

3, 3a, 4, 4a

"saddle" conformation

1,3, R = H, R′ = CH_3

1a, 3a, R = $COCH_3$; R′ = CH_3

2,4, R = H; R′ = C_3H_7

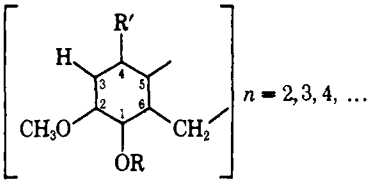
2a, 4a, R = $COCH_3$; R′ = C_3H_7

pected to interconvert readily among three equivalent structures. Cookson, *et al.*,[5] found evidence for such a form for cyclotriveratrylen-5-one and the derived methylcarbinol; unlike the 5-methylene analog these showed no tendency to revert to "crown" conformations. They also observed that cyclotriveratrylen-5-ol preferentially adopts the rigid "crown" conformation (β alcohol). Although they were able, by carefully controlling the reaction conditions, to synthesize this secondary alcohol in the flexible "saddle" conformation (α alcohol), it readily and quantitatively converted into the rigid "crown" form. They did not observe any conversion of the β alcohol into the α alcohol.

During studies on resin formation from lignin hydrogenolysis products, the acid-catalyzed condensation of 6-hydroxymethyl-4-methylguaiacol (**1**) was examined. The resulting syrup was acetylated prior to gas-liquid chromatographic (glc) analysis. It was found to contain relatively low-molecular-weight products. This acetylated syrup, on standing in aqueous ethanol overnight, deposited crystals whose retention time of 51 min, although considerably longer than those of the acetylated dimeric products previously obtained[11] from **1** and alkali, was indicative of a relatively low degree of polymerization.

The structures of this crystalline product and of that produced from 6-hydroxymethyl-4-propylguaiacol (**2**) were established by pmr and mass spectrometry.

The pmr spectrum of **3a** (see Table I) is very simple: all five resonances are sharp singlets with an integrated ratio of 1:2:3:3:3. The signal at δ 6.58 corresponds to the aromatic protons while the signal for the methylene groups appears at δ 3.86. The remaining signals at δ 3.73, 2.25, and 2.08 are due to the methoxyl, methyl, and acetate groups, respectively. This is in full accordance with a flexible structure interconverting rapidly at room temperature with two other equivalent conformations (see above) making similar protons groupwise equivalent. Also, it indicates a 1,2,4-substitution pattern on each aromatic ring as in **3a**. However, these data do not specify the degree of polymerization, since any molecule in this series where $n = 2, 3, 4\ldots$ undergoing rapid conformational interconversions would exhibit these pmr parameters. However, the method of synthesis, similarities with CTV, and the retention time for **3a** (51 *vs.* 71 min for CTV) suggest that $n = 3$; this was confirmed by mass spectrometry.



CTV shows the two methylene protons as an AB quartet, with $J = 14$ Hz, at δ 4.70 and 3.45.[3-7] In **3**, **3a**, **4**, and **4a** the methylene protons are equivalent and appear close to the average of the shifts observed for CTV. Further, it has been shown[4-7] that CTV does not undergo conformational interconversions at temperatures up to 200°. CTV is locked in a "crown" conformation. In contrast, several conformations of compounds **3**, **3a**, **4**, and **4a** appear to be rapidly interconverting at room temperature, since all resonances [in $CDCl_3$, $(CD_3)_2CO$, C_6D_6, CS_2, and CD_2Cl_2] are groupwise equivalent.

Further evidence of this flexibility was obtained by observing the pmr spectra at low temperatures in CD_2Cl_2. The chemical shift(s) of the aromatic protons for **3a** and **4a** are temperature dependent and become separated into two discrete resonances. Table II lists these chemical shifts for **3a** and **4a** at the various temperatures studied. Compounds **3** and **4** were not at the slow exchange limit at −108.5°, broad singlets being observed at δ 6.50.

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[11] G. E. Troughton and J. F. Manville, *Can. J. Forest Res.*, **2**, 271 (1972).

TABLE II

VARIABLE TEMPERATURE PMR DATA OF **3a** AND **4a**

Temp, °C	Aromatic proton chemical shifts(s)[a] **3a**	**4a**
+35	6.63 (3)	6.60 (3)
−58.5	6.64 (3)	6.63 (3)
−68.5		6.64 (3)
−78.5	~6.67 (3)	~6.65 (3)
−88.5[b]	6.73 (1), 6.66 (2)	6.78 (1), 6.58 (2)
−98.5	6.75 (1), 6.66 (2)	6.80 (1), 6.58 (2)
−108.5[c]	6.87 (1), 6.66 (2)	6.82 (1), 6.58 (2)[d]

[a] Shifts in CD_2Cl_2–10% TMS. [b] At the slow exchange limit, two separate resonances for the aromatic protons might be expected. Examination of the Dreiding molecular models for these compounds shows that two of the aromatic rings are below the plane of the methylene groups, the third is above this plane. Thus it is reasonable to find two aromatic protons resonating together even though they are diastereotopic groups. [c] Compounds **3** and **4** were not at the slow exchange limit at this temperature and were observed as broad singlets at δ 6.50. [d] In CS_2 the chemical shifts (δ) are 6.62 (1) and 6.42 (2).

The cyclotribenzylene ring system can exist in five distinct conformational modes, two of which are rigid; the remaining three are conformationally mobile. These are given in Chart I together with the expected pmr observation for the aromatic proton resonance(s) at the exchange limits (intensity ratios in parentheses).

CHART I

	No. of aromatic proton resonances Fast	Slow
1. Rigid "saddle" (C_1 symmetry)	n.a.	2 (2:1) or 3 (1:1:1)
2. Rigid "crown" (C_3 symmetry)	n.a.	1
3. Interconverting "crown" ⇄ "crown"	1	No change
4. Interconverting "crown" ⇄ "saddle"	1	3; possibly 2 or 4
5. Interconverting "saddle" ⇄ "saddle"	1	2 (2:1) or 3 (1:1:1)

Scrutiny of Table II indicates that the first possibility is excluded by the room temperature pmr data. Conformations 2 and 3 are excluded by the two distinct resonances in a ratio of 2:1 obtained below −60°. Two possibilities remain, that of an interconverting "crown" ⇄ "saddle" conformational mode or a conformationally mobile "saddle" form.

Even though the pmr data do not exclude the interconverting "crown" ⇄ "saddle" conformation, literature data on this cyclotribenzylene ring system make this possibility unlikely. Thus, for molecules in this ring system to undergo "crown" ⇄ "saddle" conformational interconversions, a *necessary condition* is that at least one of the ring carbons C-5, C-10, or C-15 be an sp^2 carbon.[12] All other molecules studied, in this ring system, are either locked in the "crown" conformation[4-7] or exist solely in the flexible "saddle" conformation,[5-8] with no "crown" form observable. Examples are CTV and its methylcarbinol which are reported to be exclusively in the rigid "crown" and flexible "saddle" conformations, respecitvely.

Since compounds **3**, **3a**, **4**, and **4a** do not satisfy the necessary sp^2 condition for the interconverting "crown" ⇄ "saddle" conformational mode, and yet they are conformationally mobile, they must be interconverting between "saddle" conformations.

This result was not expected in view of the stability exhibited[4-7] by CTV in the "crown" conformation. Exclusive adoption of a flexible "saddle" conformation must reflect strong nonbonded interactions between the 4 and 6, 9 and 11, and 14 and 1 substituents on adjacent aromatic rings which would result if these molecules were to exist in the "crown" conformation. CPK Precision [Corey–Pauling atomic models with Kolton connectors (CPK)] and Dreiding molecular models of these compounds reveal that these nonbonded interactions are minimized in the "saddle" form.[13] Also it would be most difficult for these molecules to interconvert with the "crown" form due to the excessive bond/angle strain necessary to force these models to adopt this alternative conformation. In fact, it is not possible to construct a CPK molecular model of **3**, **3a**, **4**, and **4a** in the "crown" form due to the bulkiness of the substituents. Thus it is most likely that these molecules formed by acid-catalyzed ring closure of their respective benzyl alcohols exist exclusively in flexible "saddle" conformations.

Further evidence for the adoption of "saddle" conformations was obtained by attempts to determine clathrate formation for these compounds (**3a** and **4a**). Pmr spectroscopy was used to examine crystals obtained from several of the solvents listed by Gaglioti, *et al.*,[10] which are known to form inclusion complexes with CTV. Complete absence in the pmr spectra of signals due to the crystallizing solvent indicated that clathrate formation had not occurred for **3a** and **4a**. These results strongly suggest that their inability to form clathrate complexes is directly related to the fact that they do not adopt the "crown" conformation of CTV. Compounds **3** and **4** both exhibited pmr parameters consistent with a flexible conformation.

The mass spectrum of **3a** exhibited a molecular ion peak (M) at *m/e* 576, confirming that it is indeed a cyclic trimer. In contrast to the spectrum of CTV,[2] there is no M − 2 peak. The first major fragment occurs at *m/e* 534 which corresponcs to loss of ketene from one of the acetates. Peaks at *m/e* 193 and 383 (sum 576) arise from the fission of the molecule with formation of the ions $^{1}/_{3}$ M + 1 and $^{2}/_{3}$ M − 1, respectively. Similarly, for the decomposition of M − 42 ion, *m/e* 534, peaks arise at 151 and 383 or 193 and 341. The base peak at *m/e* 341 corresponds to $^{2}/_{3}$ M − 1 − ketene. The next abundant ion fragment *m/e* 299 (92%) corresponds to the further loss of ketene from the *m/e* 341 ion. A larger peak corresponding to loss of 32 mass units from the above (*m/e* 299) fragmention is observed at *m/e* 267. No metastable transitions were observed in the mass spectrum so that the origin of some peaks remains a matter of conjecture.

The mass spectrum obtained for **4a** exhibited major ion fragments analogous to those observed for **3a**, but at higher *m/e* values (multiples of 28 mass units) corresponding to the replacement of methyl with propyl groups.

We feel that the above data are consistent with the proposed structures and conformations for the crystal-

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(12) Since the β alcohol does not convert into the "saddle" conformation,[5] cyclotriveratrylen-5-ol does not undergo "crown" ⇄ "saddle" conformational interconversions.

(13) A similar conclusion was formulated by Meth-Cohn[14] following recent studies on the cyclic trimer produced from 2,5-dimethylthiophene and formaldehyde.

(14) O. Meth-Cohn, *Tetrahedron Lett.*, **No. 2**, 91 (1973).

line products obtained from acid-catalyzed condensations of 4-alkyl-6-hydroxymethylguaiacols. This class of 1,2,4-trisubstituted cyclotribenzylenes appears to adopt only the flexible "saddle" conformation in contrast to CTV (2,3 disubstituted) which is locked in the "crown" conformation. This represents the first example of conformational control by aryl substitution pattern in the cyclotribenzylene system.

Experimental Section

The reaction mixtures were fully acetylated (pyridine–acetic anhydride 1:1 v/v) prior to pmr or glc analyses. Pmr spectra were normally recorded on a Varian HA-100 spectrometer using $CDCl_3$ as solvent and TMS as internal reference. The low-temperature experiments were recorded on a Varian XL-100 instrument in CD_2Cl_2 with 10% TMS. Glc analyses were obtained from a Varian Model 1520 gas chromatograph using a 6 ft × $^1/_8$ in. stainless steel column packed with 5% SE-30 coated on Chromosorb W (60–80 mesh). The column was temperature programmed from 90 to 250° at 6°/min and then held isothermally. The nitrogen carrier-gas flow rate was 20 ml/min. The injector port was maintained at 230° and flame-ionization detection was used. Ir spectra (KBr pellet) were recorded on a Perkin-Elmer 521 spectrophotometer. Low-resolution mass spectra were run on a MS-12 spectrometer. Melting points were determined on a Fisher-Johns melting point apparatus and are uncorrected.

Cyclization.—6-Hydroxymethyl-4-methylguaiacol (1) and 6-hydroxymethyl-4-propylguaiacol (2) were prepared by the procedure of Marton, *et al.*,[15] and their purity checked by pmr spectroscopy. Cyclization was effected by heating 2 g of 1 or 2, 20 ml of water, and 7.5 ml of concentrated HCl under reflux for 2 hr. The reaction mixture was neutralized, extracted with ether, dried (Na_2SO_4), and evaporated (reduced pressure) to a syrup. After acetylation the reaction product was crystallized from ethanol. 10,15-Dihydro-1,6,11-triacetoxy-2,7,12-trimethoxy-4,9,14-trimethyl-5*H*-tribenzo[*a,d,g*]cyclononene (**3a**) (0.61 g, 27%) had mp 280–282°; ν_{max} 1745, 1585, 1445, 1352, 1300, 1120, 1090, 1000, 915, 870, and 820 cm^{-1}; M^+ 576; retention time 51 min.

10,15-Dihydro-1,6,11-triacetoxy-2,7,12-trimethoxy-4,9,14-tripropyl-5*H*-tribenzo[*a,d,g*]cyclononene (**4a**) (0.57 g, 25%) had mp 207–209°; ν_{max} 1745, 1585, 1440, 1352, 1295, 1165, 1090, 1010, 870, and 820 cm^{-1}; M^+ 660; retention time 91 min.

De-O-acetylation.—Compounds **3a** and **4a** were de-O-acetylated by treating them with excess $LiAlH_4$ in THF. After recrystallization from aqueous ethanol, **3** was obtained as white crystals, mp *ca.* 135° dec. Somewhat impure (rust color) **4** was obtained from **4a** and had a melting point range of >10° at *ca.* 190° dec. Pmr indicated only traces <5% of impurities.

10,15-Dihydro-1,6,11-trihydroxy-2,7,12-trimethoxy-4,9,14-trimethyl-5*H*-tribenzo[*a,d,g*]cyclononene (**3**) had ν_{max} 3430, 1585, 1440, 1280, 1230, 1200, 1175, 1090, 1025, 905, and 820 cm^{-1}; M^+ 450.

10,15-Dihydro-1,6,11-trihydroxy-2,7,12-trimethoxy-4,9,14-tripropyl-5*H*-tribenzo[*a,d,g*]cyclononene (**4**) had ν_{max} 3530, 3495, 1585, 1450, 1270, 1230, 1180, 1090, 1005, 900, and 820 cm^{-1}; M^+ 534.

Acknowledgments.—We thank L. Rozon and D. Watson for technical assistance in the preparation of these compounds, and Dr. Ian Armitage for helping to obtain the low-temperature pmr spectra at the University of British Columbia.

Registry No.—**1**, 7452-08-6; **1a**, 42214-44-8; **2**, 32359-71-0; **2a**, 42214-46-0; **3**, 42214-47-1; **3a**, 42214-48-2; **4**, 42214-49-3; **4a**, 42319-50-6.

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[15] J. Marton, T. Marton, S. K. Falkenhag, and E. Adler, *Advan. Chem. Ser.*, **No. 59**, 125 (1966).

Photochemical and Acid-Catalyzed Rearrangements of Tricyclo[4.4.2.0]dodecanones[1,2]

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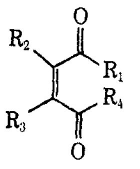
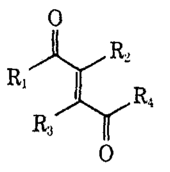
Photoannulations of transoid 2-ene-1,4-diones with ethylene and 2-butyne are described. An efficient synthesis of bicyclo[4.4.0]dec-1(6)-ene-2,7-dione (7) in two steps from 1,5-decalindiol has been accomplished. Acid-catalyzed and photochemical isomerizations of 11,12-dimethyltricyclo[4.4.2.0]dodec-11-ene-2,7-dione (10), the adduct of 7 and 2-butyne, are presented.

Although cycloaddition reactions of cisoid 2-ene-1,4-dione systems with acetylenes, olefins, and other enes are well documented,[3] the involvement of molecules containing transoid 2-ene-1,4-dione moieties in such reactions is not. In this paper we report that the latter enediones are effective partners in photocycloadditions with olefins and acetylenes.



cisoid 2-ene-1,4-dione



transoid 2-ene-1,4-dione

Irradiation of 1[4] in hexane through uranium glass[5] at room temperature with 2-butyne very quickly and cleanly produced the β,γ-unsaturated dione **3**. Irradiation (Pyrex) of **1** at low temperature[6] in methylene chloride saturated with ethylene likewise gave a single adduct, **4** (Scheme I).

Since rearrangement studies with **3** and **4** would certainly be complicated by the presence of the angular methyl group, we required the parent enedione **7**. The electronic effect of the methyl group in methylfuran is apparently essential for conjugate addition to cyclohexenone to occur; thus furan could not be added to cyclohexenone under the same reaction conditions.

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[1] Presented in part by N. P. Peet at the 164th National Meeting of the American Chemical Society, New York, N. Y., Aug 30, 1972, Abstract ORGN 86.

[2] Grateful acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for their generous support of this research.

[3] Consider the number of examples in which quinones, benzoquinones, and maleic anhydrides have been used in photocycloaddition reactions: M. E. Kuehne and H. Linde, *J. Org. Chem.*, **37**, 4031 (1972); S. P. Pappas, B. C. Pappas, and N. A. Portnoy, *ibid.*, **34**, 520 (1969); I. W. J. Still, M. W. Kwan, and G. E. Palmer, *Can. J. Chem.*, **46**, 3731 (1968); W. L. Dilling, *Chem. Rev.*, **66**, 373 (1966).

[4] M. A. Tobias, *J. Org. Chem.*, **35**, 267 (1970).

[5] When a Pyrex glass filter was employed in the preparation of **3**, two additional products were observed in the irradiation solution by glpc.

[6] The apparatus used for low-temperature irradiation was similar to that described by D. C. Owsley and J. J. Bloomfield, *J. Chem. Soc. C*, 3445 (1971).