at 1 atm was 137–139° (lit.[14] bp 137–138°), and its reaction with KO-*t*-Bu–DMSO gave **2**.

If the addition of bromine was carried out at −78° over 3 hr (with 2 hr additional stirring) using chloroform as solvent, glc showed less than 2% of product other than **3**, which could be isolated as above in 90% yield.

Isolation of 4.—If the undistilled product mixture from the room-temperature bromination of **2** was allowed to sit at −20° for 4 days, 4.1 g of straw-colored crystals could be isolated by filtration. The melting point was found to be 159–161° after recrystallization (chloroform) and sublimation (80–100°, 1 mm). The partial mass spectrum (70 eV) was as follows: *m/e* 404, 402, 400, 398, 396 (1:4:6:4:1), 323, 321, 319, 317 (1:3:3:1, M − Br), 242, 240, 238 (1:2:1, M − 2Br), 161, 159 (1:1, M − 3Br). Additional spectral data follow: ir (KBr) 3045 (w), 2993 (w), 1465 (s), 1441 (s), 1237 (s), 1205 (s), 1121 (w), 1098 (m), 877 (s), 866 (s), 740 (s), 665 (vs), 568 (m), and 499 cm^{-1} (m); pmr[15] δ 4.19 (s); uv (pentane) λ_{max} 218 nm (log ϵ 4.09) and 251 (4.03).

Anal. Calcd for $C_6H_8Br_4$: C, 18.03; H, 2.02; Br, 79.96. Found: C, 18.12; H, 1.93; Br, 80.14.

***tert*-Butylacetylene (1).**—To 115 g (0.710 mol) of KO-*t*-Bu[16] was added 150 ml of fresh (dry) DMSO, and the suspension was stirred for 30 min. Dibromide **3** (87.2 g, 0.357 mol) was added dropwise over 1 hr, and then the mixture was warmed slowly and distilled through a 9-in. Vigreux column to give 26.7 g (0.326 mol, 91.3%) of the acetylene, bp 36–38° (lit.[1] bp 36.4–37.8°). The product was >99% pure by glc. Spectral data for **1** follow: ir 3310 (vs), 2985 (vs), 2145 (m), 1480 (s), 1460 (s), 1370 (s), 1260 (vs), 1215 cm^{-1} (s); pmr[12] δ 1.21 (s, 9 H), 1.91 (s, 1 H).

Bromination of 5.—Reaction of **5** with 1 equiv of bromine at −10° as previously described[8] led to a mixture of two products as described in the text. Dibromide **7** could be isolated therefrom, showing (after recrystallization from chloroform) mp 43–44° (lit.[8] mp 47°); ir (chloroform) 3000 (m), 2940 (m), 1450 (m), 1385 (m), 1200 (s), 1070 (m), 930 (m), 870 cm^{-1} (m); pmr[15] δ 1.88 (s, 6 H), 4.00 (s, 4 H).

Bromination of 5 with Excess Bromine.—To 1.82 g (22.2 mmol) of the diene in a flask fitted with a reflux condenser atop an addition funnel was added 7.10 g (44.4 mmol) of bromine over 30 min. The addition is highly exothermic, with the reaction mixture staying at 60°. During the last half of the addition HBr was liberated copiously, and crystalline material began to form. Chloroform (5 ml) was added, and the solution was filtered to give 550 mg of **8**: mp (after recrystallization from chloroform) 138–140°; pmr[15] δ 2.12 (s, 6 H), 4.09 (d, J = 11.5 Hz, 2 H), 4.36 (d, J = 11.5 Hz, 2 H);[17] ir (chloroform) 2850 (m), 1440 (w), 1380, (w), 1257 (w), 1010 (w), 855 cm^{-1} (w); mass spectrum, no parent ion from 20 to 70 eV, very intense isotope clusters in the region *m/e* 322 (q, M − Br) and 242 (t, M − 2Br).

Anal. Calcd for $C_6H_{10}Br_4$: C, 17.94; H, 2.51; Br, 79.56. Found: C, 17.74; H, 2,06; Br, 79.56.

The filtrate from above was further diluted with 40 ml of chloroform, washed with dilute sodium thiosulfate, and dried over magnesium sulfate. Removal of solvent and two short-path distillations afforded **9**, bp 76–78° (0.15 mm). The yield of **9** was 1–2 g, depending on the pot temperature, as decomposition took place. Spectral data follow: pmr[15] δ 1.97 (s, 3 H), 4.05 (s, 2 H), 4.15 (s, 2 H), 4.20 (s, 2 H); ir (neat) 2960 (m), 1640 (m), 1450 (s), 1380 (s), 1300 (m), 1200 (vs), 948 (m), 880 (s), 860 (s), 700 cm^{-1} (s); mass spectrum (45 eV) *m/e* 318, 320, 322, 324 (1:3:3:1).

Anal. Calcd for $C_6H_9Br_3$: C, 22.46; H, 2.83; Br, 74.71. Found: C, 22.57; H, 2.28; Br, 75.14.

Registry No.—**1**, 917-92-0; **2**, 558-37-2; **3**, 640-21-1; **4**, 30432-16-7; **5**, 513-81-5; **7**, 34619-20-0; **8**, 24173-07-7; **9**, 38400-50-9; 1-bromo-3,3-dimethylbutane, 1647-23-0.

Acknowledgment.—The authors gratefully acknowledge the financial assistance provided by Research Corporation in the form of a Frederick Gardner Cottrell Grant.

---

[14] L. Schmerling and J. P. West, *J. Amer. Chem. Soc.*, **74**, 3592 (1952).

[15] Deuteriochloroform solution.

[16] This was prepared in the conventional way (L. F. Fieser and M. Fieser, "Reagents for Organic Synthesis," Wiley, New York, N. Y., 1967) from metallic potassium and *tert*-butyl alcohol. After evacuation for 2 hr at 145° (1 mm), the product was 73% (w/w) butoxide and 27% alcohol.

[17] The absorptions at δ 4.09 and 4.36 actually constitute an (AB) pattern, the nonequivalence caused by the neighboring asymmetric center

---

Reactions of Lone Pair Electron Donors with Unsaturated Electrophiles. I. The Addition of Tetrahydrofuran and Oxetane to Dimethyl Acetylenedicarboxylate[1]

GORAN AHLGREN[2]

Department of Organic Chemistry, Royal Institute of Technology, S-10044 Stockholm 70, Sweden

Received October 10, 1972

Tetrahydrofuran and oxetane give cis-trans isomeric 1:1 adducts with dimethyl acetylenedicarboxylate. The reaction can be initiated thermally, photochemically, or by free-radical sources. All three processes are shown to be free-radical chain reactions, presumably involving a vinyl radical intermediate, formed by addition of an ether radical to the dimethyl acetylenedicarboxylate. Possible mechanisms for the chain initiations in the thermal and photochemical reactions are discussed. Secondary isomerizations take place in the photochemical reactions, yielding vinyl ethers through a shift of the double bond.

The addition of cyclic ethers to unsaturated substrates has attracted some attention in recent years. Tetrahydrofuran (THF) adds to maleic anhydride,[3] diethyl maleate,[3] and azodicarboxylate[4] to give α-substituted tetrahydrofuranes by formal addition of the α-C–H ether bond across the unsaturated linkage. These reactions take place by initiation with dibenzoyl peroxide or azoisobutyronitrile and by direct irradiation; they are believed to be radical chain reactions involving THF radicals. Similarly, THF has been added to 7,7,8,8-tetracyanoquinodimethane and tetracyanoethylene by direct irradiation.[5] Tetrahydropyran and *p*-dioxane will not produce 1:1 adducts with unsaturates under these conditions.[3] They can, however, be added to diethyl maleate and various simple olefins under ketone-sensitized uv irradiation[6]; in this case, a radical chain reaction was believed to be initiated by hydrogen abstraction by the excited ketone.[6]

Recently, Singh reported on the photochemical addition of THF, tetrahydropyran, and *p*-dioxane to dimethyl acetylenedicarboxylate (DMAD).[7] He found that THF adds to DMAD by direct irradiation to give

---

[1] Presented in part at the XXIII International Congress of Pure and Applied Chemistry, Boston, Mass., 1971.

[2] Department of Chemistry, University of California, Berkeley, Calif. 94720, where this work was completed.

[3] R. L. Jacobs and G. C. Ecke, *J. Org. Chem.*, **28**, 3036 (1963).

[4] R. Askani, *Chem. Ber.*, **98**, 2551 (1965).

[5] J. Diekmann and C. J. Pedersen, *J. Org. Chem.*, **28**, 2879 (1963).

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

[7] P. Singh, *J. Org. Chem.*, **37**, 836 (1972).

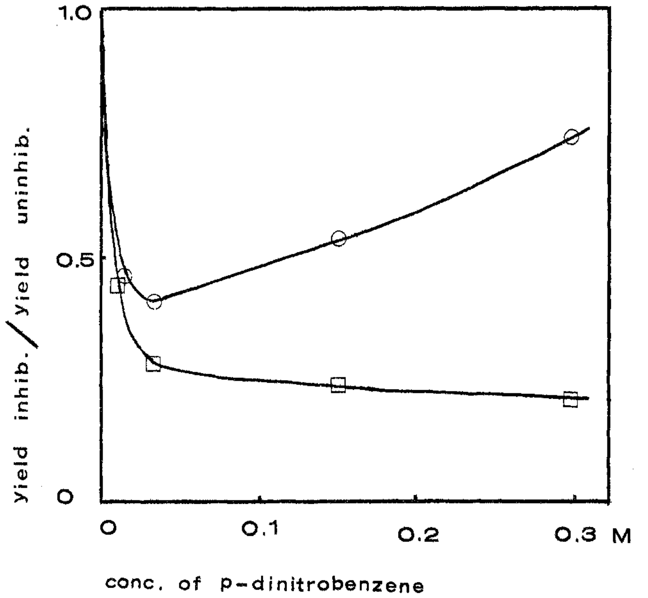
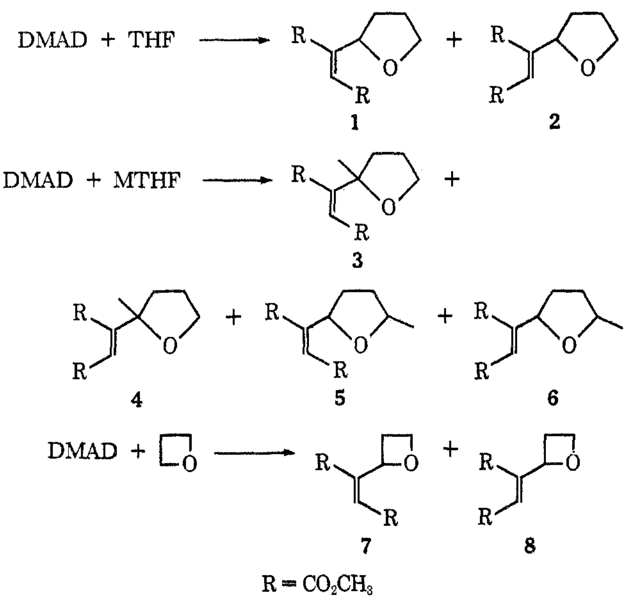


Figure 1.—Yields of trans product (1) (□) and cis product (2) (○) in the presence of scavenger relative to the yields in the unscavenged reaction *vs.* scavenger concentration.

a mixture of dimethyl tetrahydro-2-furylfumarate (**1**) and dimethyl tetrahydro-2-furylmaleate (**2**) (Scheme I); tetrahydropyran and *p*-dioxane give the corresponding products by sensitization with acetone. A free-radical chain mechanism was proposed; in the unsensitized THF addition, the radical chain was postulated to be initiated by unidentified and undetected impurities. In our study of the free radical, thermally, and photochemically initiated additions of cyclic ethers to DMAD, we have reached a different conclusion regarding the mechanism of radical formation in these systems. Furthermore, our primary results from the photochemical addition of THF to DMAD differ somewhat from those reported by Singh.

SCHEME I



Results

Free Radical Initiated Additions.—A solution of DMAD and a small amount of dibenzoyl peroxide in excess THF give the adducts **1** and **2** in a ratio of *ca.* 70:30[8] at 65°. The total yield is 62%. Similarly, 2-methyltetrahydrofuran (MTHF) gives a mixture of products **3–6** in a total yield of *ca.* 90% with relative ratios of *ca.* 6:2:1:1.[8] Dibenzoyl peroxide will also initiate addition of oxetane to DMAD, resulting in a mixture of the products **7** and **8** in a ratio of *ca.* 2:1. Tetrahydropyran and oxepane do not add to DMAD under these conditions.

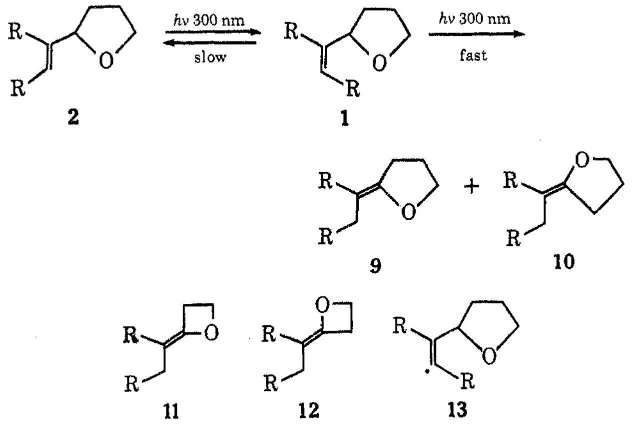
Thermal Additions.—In the absence of radical initiators, the addition of THF to DMAD still takes place, but at a much slower rate. The ratio of the adducts **1** and **2** is similar to that obtained in the free-radical initiated addition. A slight variation in the ratio with respect to change in temperature was observed, ranging from 76:24 at 5° to 70:30 at 135.° The yield at 135° is 20% based on the total amount of DMAD used; this cannot be increased further by prolonged reaction time and/or higher temperatures (150°). Most of the remaining DMAD is left unreacted.

The reaction is partially quenched when *p*-dinitrobenzene is present in the reaction mixture. At high concentrations of *p*-dinitrobenzene, the formation of the cis isomer **2** is promoted while the amount of trans isomer **1** formed remains approximately at the same residual level (Figure 1). The adducts **1** and **2** do not undergo cis–trans isomerization when heated in THF in the presence of *p*-dinitrobenzene.

With MTHF, a mixture of products **3–6** is formed in the same relative ratios as in the radical addition. The total yield is *ca.* 30%. Similarly, oxetane adds to DMAD, giving the adducts **7** and **8** in a ratio of *ca.* 2:1. Tetrahydropyran and oxepane do not give any adducts with DMAD under these conditions.

Photochemical Additions.—Irradiation of a THF solution of DMAD at 3000 Å initially gives the adducts **1** and **2** in a ratio similar to that obtained in the free-radical initiated and thermal additions (*ca.* 70:30). With continued irradiation, however, the ratio of **1** to **2** decreases while the build-up of two new products, vinyl ethers **9** and **10** (Scheme II), is observed. After

SCHEME II



---

[8] Initial ratios; the product mixture isomerized slightly under the experimental conditions. (See Experimental Section.)

48 hr of irradiation the total yield of 1:1 adducts is 80%, with a product ratio of *ca.* 1:5:2:2 (**1**:**2**:**9**:**10**). Separate irradiation of the primary trans adduct **1** in a methanol solution results in rapid and virtually quantitative formation of a 3:2 mixture of the vinyl ethers **9** and **10**. Similar treatment of the cis isomer **2** also yields a 3:2 mixture of **9** and **10** but at a considerably slower rate.

Furthermore, the photochemical addition of MTHF to DMAD will also initially give the products **3**–**6** in ratios similar to those obtained in the free-radical initiated and thermal additions.

In agreement with the report by Singh,[7] we found that tetrahydropyran does not add photochemically to DMAD by direct irradiation. This is also the case with oxepane. Oxetane, however, adds smoothly to DMAD, giving products analogous to those obtained with THF. The final products are a mixture of the isomers **11** and **12**.

Product Isomerization.—In order to determine the thermodynamic ratio of the cis–trans isomers **1** and **2**, each of these was treated with a small amount of thiophenol in benzene solution.[9] After exposure to sunlight for 1 week, both samples showed a 50:50 composition of **1** and **2**. When **1** and **2** were heated separately to 150° in THF solution for 24 hr no isomerization occurred.

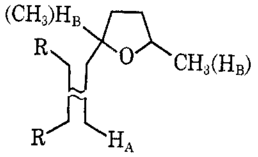
Characterization of Products and Analysis of Product Mixtures.—The composition of the product mixtures was determined by vpc and the different isomers were separated by preparative vpc and characterized by their spectral properties (*i.e.*, ir, mass spectra, and nmr).

The products **1**–**4** as characterized by Singh[7] are in perfect agreement with our structural assignments to these adducts based on spectral and chemical behavior. Nmr data which are crucial for the structure determination of compounds **5**–**8** and **9**–**12** are given in Tables I and II, respectively. For comparison the previously characterized products **1**–**4** are also described (Table I). The cis isomers **2**, **4**, and **6** were separated from their trans counterparts by hydrolysis of the product mixtures with subsequent distillation; this produced the cyclic anhydrides, which were then reesterified. In the product mixture from the addition of MTHF, the isomers **4** and **5** could not be separated by vpc. The cis isomer **4** was separated by preparative vpc from the mixture of cis isomers **4** and **6** obtained from the hydrolysis–distillation–reesterification sequence. Thus, the only isomer which could not be isolated was **5**. The ratio of the isomers **4** and **5** in the product mixtures was obtained by integration of the vinylic region in the nmr spectra of the crude product mixtures; the absolute yields were obtained from the vpc peak corresponding to the sum of **4** and **5**.

The products from the addition to the 2 and 5 position of MTHF were identified by inspection of their nmr spectra. The olefinic protons and the 2-methyl group of the isomers **3** and **4** appear as singlets, in contrast to the isomers **5** and **6**, in which the corresponding absorptions appear as doublets owing to allylic coupling of the vinyl protons and vicinal coupling of the methyl groups.

The secondary photoproducts **9** and **10** show the strong -C=C- ir absorbtions characteristic of vinyl ethers. However, the stereochemical assignment of the individual cis and trans isomers is only tentative and is based on the difference in shielding in the nmr spectra of the isomeric pairs, as inferred from inspection of molecular models.

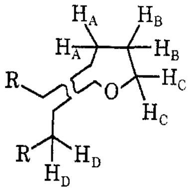
TABLE I[a]



Compd	H_A	H_B	CH_3
1	6.55 d J = 1.0 Hz	5.2 t b J = 7 Hz	
2	6.15 d J = 1.3 Hz	4.7 t b J = 6 Hz	
3	6.70 s		1.5 s
4	6.10 s		1.5 s
5	6.55 d J = 1.0 Hz	5.2 t b J = 7 Hz	Two doublets centered at 1.2[b]
6	6.20 d J = 1.5 Hz	4.7 t b J = 7 Hz	1.30 d J = 5 Hz[b] 1.35 d J = 6 Hz
7	6.7 d J = 0.5 Hz	6.0 t b J = 8 Hz	
8	6.4 d J = 1.0 Hz	5.5 t b J = 8 Hz	

[a] Nmr data for the products from the addition of THF, MTHF, and oxetane to DMAD. Chemical shifts are given in δ units in $CDCl_3$ solution relative to TMS as internal standard. [b] Two absorptions due to syn and anti isomerism. Abbreviations: s, singlet; d, doublet; t, triplet; b, broadened.

TABLE II[a]



Compd	H_A	H_B	H_C	H_D
9	3.2 t J = 8 Hz	2.2 m	4.2 t J = 7 Hz	3.4 s
10	2.8 t J = 7 Hz	2.2 m	4.4 t J = 7 Hz	3.2 s
11	3.5 t J = 6 Hz		4.9 t J = 6 Hz	3.1 s
12	3.4 t J = 6 Hz		4.9 t J = 6 Hz	3.0 s

[a] Nmr data for the secondary products in the photoaddition of THF and oxetane to DMAD. Chemical shift values are given in δ units in $CDCl_3$ solution relative to TMS as internal standard. Abbreviations: s, singlet; t, triplet; m, multiplet. In addition, these compounds all show an absorption at 3.7, two partially overlapping singlets (CH_3O–).

Discussion

The rather effective and clean free-radical initiated additions of THF, MTHF, and oxetane to DMAD should be of some preparative value. As has been pointed out by others in regard to analogous reactions,[3] the reaction is apparently a radical chain reaction involving ether radicals formed by hydrogen abstraction

---

(9) C. Walling and W. Helmreich, *J. Amer. Chem. Soc.*, **81**, 1144 (1959); J. C. Kampmeier and G. Chen, *ibid.*, **87**, 2608 (1965).

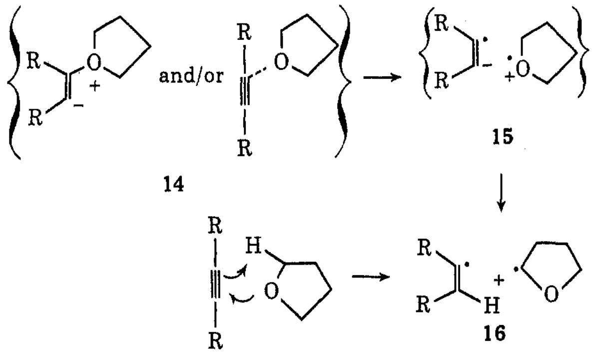
of the radicals from the decomposing initiator. In our case, the vinyl radical **13**, formed by addition of a THF radical to DMAD, is likely to be the chain-carrying species, as proposed by Singh for the photochemical addition.[7]

As we have shown, the product ratio is not the thermodynamic ratio. The stereochemical features of vinyl radicals have recently been reviewed by Singer.[10] Vinyl radicals can assume either linear (sp-hybridized) or bent (sp^2-hybridized) configurations. In the latter case, inversion can be either fast or slow in relation to hydrogen abstraction from a solvent molecule. In the case of a linear or bent and rapidly inverting vinyl radical, the product ratio depends only on the difference in the free energy levels of the two transition states leading to cis and trans product, respectively, and is in no way related to the free energy levels of the products, or to the populations of the two bent forms (Curtin–Hammet principle).[11] When the rate of inversion of a bent radical decreases in relation to the rate of scavenging (product formation), the relative populations of the two bent forms become important. In the limiting case, the product ratio reflects the stereochemistry of the initial addition step. This does not seem to be a likely alternative in our case, since radicals are generally considered to add stereospecifically trans to acetylenes.[10] Assuming a linear or bent and rapidly inverting radical, the product ratio 70:30 corresponds to a *ca.* 0.6 kcal/mol difference in free energy between the transition states giving **1** and **2** from the vinyl radical **13**.

The thermal and primary photochemical additions of THF, MTHF, and oxetane to DMAD are, in our opinion, of considerable mechanistic interest. These additions give product ratios similar to those obtained in the free-radical initiated additions (Scheme I). This shows that vinyl radicals are intermediates also in the former cases. Thus, the photochemical and thermal additions are also radical chain reactions, involving ether radicals. This is further supported by the fact that the thermal addition is partially quenched by a radical scavenger such as *p*-dinitrobenzene.[12] The thermal addition seems to be self-inhibiting, since complete conversion of DMAD cannot be achieved.

THF is known to be extremely prone to peroxide formation in the presence of oxygen. To avoid the possibility of a free-radical reaction initiated by the decomposition of peroxides and other impurities, great care was taken to purify the reactants. Excluding the possibility of initiation by peroxide impurities, we will discuss some reasonable mechanisms for the thermal and photochemical formation of THF radicals i in these systems. Even though no evidence for a charge-transfer complex (**14**) could be found by inspection of the uv spectrum of DMAD in THF,[13] the photochemical addition may proceed *via* an anion–cation radical pair **15** formed by the excitation of such a complex (**14**), since this seems to be a frequent process in related systems. A related mechanism is believed to operate in the photochemical oxidation of THF, where a charge-transfer complex between THF and oxygen has been shown to be an intermediate.[14] Photoaddition of THF to quaternary salts of pyridylethylenes is also believed to proceed *via* electron transfer–proton transfer–radical coupling.[15] Tetracyanoethylene has been shown to form a charge-transfer complex with THF, which on irradiation gives the tetracyanoethylene anion radical.[16] In addition, THF adds photochemically to tetracyanoethylene (see above). In our case, proton transfer within the anion–cation radical pair **15** should give the radical pair **16**, which by diffusion gives free radicals to start a radical chain reaction. A similar mechanism may also be important in the thermal reaction. Alternatively, the electron transfer–proton transfer process may be concerted, giving the radical pair **16** directly (Scheme III). This should be an attractive alternative, particularly for the thermal addition, since formation of high-energy intermediates would be avoided.

SCHEME III



The behavior of the thermal reaction in the presence of high scavenger concentrations deserves attention (Figure 1). The yield of the trans product **1** decreases sharply to a constant value on increasing concentrations of scavenger, while the yield of the cis isomer **2**, after an initial sharp decrease, shows a steady increase. This indicates that an alternative mechanism for the formation of the cis isomer **2** becomes important. *p*-Dinitrobenzene is an acceptor and may catalyze a polar addition when present in high concentrations.[17] Furthermore, the residual formation of the trans isomer **2** at a constant level at high concentrations of scavenger indicates that the reaction has partial cage character, with a cage factor of 0.2.

Only the four- and five-membered cyclic ethers add to DMAD in the free-radical initiated, thermally, and direct photochemically initiated reactions, while the six- and seven-membered cyclic ethers are unreactive under these conditions. This behavior parallels the reports of the free-radical and photochemical additions of cyclic ethers to substrates such as diethyl maleate

---

(10) L. A. Singer, "Selective Organic Transformations," Vol. II, B. S. Thyagarajan, Ed., Wiley-Interscience, New York, N. Y., 1972.

(11) E. L. Eliel, "Stereochemistry of Carbon Compounds," McGraw-Hill, New York, N. Y., 1962, pp 237–239.

(12) E. G. Janzen and B. L. Blackburn, *J. Amer. Chem. Soc.*, **91**, 4481 (1969); E. G. Janzen and J. L. Gerlock, *ibid.*, **91**, 3108 (1969).

(13) When DMAD was added to carefully purified MTHF at room temperature a faint but distinct pink color developed in the solution, which remained for several days. Product formation occurred simultaneously.

(14) V. I. Stenberg, C. T. Wang, and N. Kulevsky, *J. Org. Chem.*, **35**, 1774 (1970); V. I. Stenberg, R. D. Olson, C. T. Wang, and N. Kulevsky, *ibid.*, **32**, 3227 (1967).

(15) J. W. Happ, M. T. McCall, and D. G. Whitten, *J. Amer. Chem. Soc.*, **93**, 5496 (1971).

(16) D. F. Ilten and M. Calvin, *J. Chem. Phys.*, **42**, 3760 (1965).

(17) Reflux of a THF solution of DMAD in the presence of boron trifluoride etherate gave pure cis adduct **2**. However, this result has been shown not to be readily reproducible, the reason for which is under investigation.

and simple olefins and has been mentioned above. Generally, six-membered cyclic ethers add to unsaturates only by ketone-sensitized irradiation.[6] This divergent behavior in the series of cyclic ethers may be related to the stereochemical features of their α hydrogens. In the relatively planar four- and five-membered cyclic ethers, the α hydrogens are eclipsed with the oxygen lone pairs, while the α hydrogens of the less rigid six- and seven-membered cyclic ethers are less sterically restricted.[18] This special feature of the former ethers might render their α hydrogens more susceptible to both hydrogen abstraction by a chain-transfer agent and to radical initiation *via* a mechanism as outlined above. In our opinion, this stereochemical feature of the cyclic ethers should be more important than the effect of decreasing donor strength with increasing ring size,[19,20] which might be associated with their interaction with electrophiles. The differences in donor strength in the series of cyclic ethers are not great enough to account for the striking change in behavior within the series.

From this discussion it can be concluded that the ketone-sensitized photochemical additions of cyclic ethers to unsaturates are different in nature from the corresponding reaction in the presence of free radical initiators and by direct irradiation. Ketone–ether exciplexes may be intermediates in the sensitized photochemical abstractions.

The secondary photochemical isomerizations of **1** and **2** and **7** and **8** to vinyl ethers **9–12** should be of some preparative interest. Our results indicate that **9** and **10** are formed solely from the trans isomer **1** (Scheme II). The cis isomer **2** probably gives **9** and **10** *via* slow cis–trans isomerization. As soon as it is formed, the trans isomer undergoes isomerization to **9** and **10**. This process is another example of photodeconjugation of acyclic α,β-unsaturated esters. Our results are in complete agreement with what has been found to be general behavior in similar systems.[21,22] These reactions have been shown to proceed from an excited singlet state *via* a cyclic transition state to give an enol, which is subsequently ketonized. The hydrogen transfer step has been looked upon as a sigmatropic 1,5 shift or an intramolecular hydrogen abstraction.[22]

Experimental Section

Spectra.—Ir data are given in reciprocal centimeters. The nmr spectra were run on a Varian T-60 spectrometer in $CDCl_3$ solution. Chemical shifts are given in δ units relative to TMS as internal standard. The mass spectra were run on a LKB 9000 gas chromatograph–mass spectrometer at an electron potential of 70 eV. (For vpc columns, see below.)

Gas Chromatography.—In the analytical work, products **1–6** were separated on a 6 ft × 0.125 in., 5% PDEAS (phenyldiethanolamine succinate), Chromosorb W column at 180–200°. Products **9–12** were separated on a UC-298 (silicone rubber) Hewlett-Packard column at 160–200°. The chromatograms were integrated with a Varian 480 electronic digital integrator and/or by the cutting and weighing technique. For the preparative work, a 12 ft × 0.25 in., 30% PDEAS, Chromosorb W column and a 6 ft × 0.25 in., 10% SE-30 Chromosorb W column were used.

Materials.—THF (Mallinckrodt analytical grade) and MTHF (Fluka) were purified by refluxing over potassium benzophenone ketyl in an atmosphere of purified nitrogen followed by distillation. Oxetane (Aldrich) was refluxed over $LiAlH_4$. Tetrahydropyran (Merck) and oxepane (Aldrich) were used as received. DMAD (Aldrich) was vacuum distilled and stored at 5° before use. Before use, THF, MTHF, and oxetane were subjected to the ferric thiocyanate peroxide test.[23] No peroxides could be detected. By applying this test to ethyl ether solutions of dibenzoyl peroxide, it was found that peroxide was easily detected down to concentrations of 1×10^{-5} *M*.

Dibenzoyl Peroxide Initiated Additions. A. Addition of THF to DMAD.—Three 200-mg (0.83 mmol) portions of Bz_2O_2 were added to a refluxing solution of 5.0 g (35.2 mmol), in 25 ml (0.3 mol) of THF, with 12-hr intervals. After 36 hr, excess THF was evaporated and the residue was taken up in ether and washed with saturated aqueous $NaHCO_3$ solution and water. After drying and evaporation, 7.2 g of a crude material was isolated. For further purification, the material was distilled to give 4.7 g of a 64:36 mixture of **1** and **2** at 90–100° (0.1 mm), yield 62.5%. The isomers were isolated by preparative vpc. Spectral data of **1** and **2** were in general accord with those given by Singh.[7] Before the second addition of Bz_2O_2 the ratio of **1** and **2** was 70:30. When more Bz_2O_2 was added in order to complete the reaction, partial isomerization of the initial product mixture took place to a mixture that was enriched in the cis isomer **2**. This was due to secondary isomerization, as shown by treating a refluxing THF solution of a 70:30 mixture of **1** and **2** with Bz_2O_2. This resulted in isomerization of the 70:30 mixture to the thermodynamic 50:50 mixture.

B. Addition of MTHF to DMAD.—A 50-mg (0.2 mmol) portion of dibenzoyl peroxide was added to a refluxing solution of 0.84 g (5.9 mmol) of DMAD in 5 ml (50 mmol) of MTHF. After 12 hr all the DMAD had reacted (vpc) and the total yield of 1:1 adducts was estimated to be 90% (vpc, naphthalene as internal standard). Excess MTHF was evaporated and the isomers **3** and **6** were isolated by preparative vpc. On all columns tried the isomers **4** and **5** did not separate but eluted as a mixture. However, the isomer **4** could be isolated by preparative vpc of the mixture of cis isomers **4** and **6** (see below). Having isolated **4**, the nmr spectrum of **5** was obtained by subtracting the spectrum of **4** from that of the mixture of **4** and **5**. Our spectral data for **3** and **4** are in general agreement with what has been reported by Singh.[7] Nmr data for **5** and **6** are given in Table I and, for comparison, nmr data for **3** and **4**. By the method mentioned previously, the relative ratios of the products **3**, **4**, **5**, and **6** were found to be 6:2:1:1.

C. Addition of Oxetane to DMAD.—A 50-mg (0.2 mmol) portion of Bz_2O_2 was added to a refluxing solution of 0.2 g (1.4 mmol) of DMAD in 2 ml (30 mmol) of oxetane. After refluxing for 8 hr, two partially resolved peaks in the vpc showed the formation of two 1:1 adducts in a ratio of *ca.* 2:1. The yield was estimated to be 50%. After evaporation of excess oxetane, nmr of the crude mixture showed the major adduct to be **7** and the minor **8** by comparison with the nmr spectra of the corresponding THF adducts. For nmr see Table I.

Solutions of DMAD in tetrahydropyran and oxepane were subjected to the same treatment. No 1:1 adducts or other products could be detected or isolated.

Thermal Additions.—For analytical work, a stock solution of 5.0 g (35.2 mmol) of DMAD, 0.1 g (0.78 mmol) of naphthalene (internal vpc standard), and 25 ml (0.31 mol) of THF (MTHF respectively) was prepared and kept under nitrogen before immediate use.

A. Addition of THF to DMAD.—Samples (1 ml) were syringed from the stock solution and placed in glass ampoules which were sealed after purging with nitrogen. Samples were kept at 5°, room temperature, and 135°. In each case, **1** and **2** were formed in ratios ranging from 76:24 at 5° to 70:30 at 135° (vpc). A maximum yield of 20% was achieved after 24 hr at 135° (based on the total amount of DMAD and measured by vpc in comparison with standard solutions of **1** and **2**). No other products could be detected by vpc, and the remaining 80% DMAD seemed to be left largely unreacted.

To a series of samples, 2 mg (0.012 mmol), 5 mg (0.030 mmol), 25 mg (0.149 mmol), and 50 mg (0.298 mmol) of *p*-dinitrobenzene were added, respectively. These were kept at 135° for 4

---

[18] E. M. Arnett and C. Y. Wu, *J. Amer. Chem. Soc.*, **84**, 1684 (1962).

[19] M. Brandon, M. Tamres and S. Searles, Jr., *ibid.*, **82**, 2129 (1960); M. Tamres and M. Brandon, *ibid.*, **82**, 2134 (1960).

[20] S. Searles, Jr., and M. Tamres, "The Chemistry of the Ether Linkage," S. Patai, Ed., Wiley, New York, N. Y., 1967, p 243.

[21] M. J. Jorgensen and S. Patumvapibal, *Tetrahedron Lett.*, 489 (1970).

[22] J. A. Barltrop and J. Wills, *ibid.*, 4987 (1968).

[23] F. T. Weiss, "Chemical Analysis," Vol. 32, Wiley-Interscience, New York, N. Y., 1970, p 224.

hr, and subsequently analyzed by vpc. Yields of **1** and **2** relative to an untreated sample heated similarly are given in Figure 1.

B. Addition of MTHF to DMAD.—A 1-ml sample from the stock solution was kept at 135° for 24 hr in a sealed tube, and subsequently analyzed by vpc. The yield of 1:1 adducts was 30% based on the total amount of DMAD (vpc). The main part of the DMAD was left unreacted and the ratio of the isomers **3**, **4**, **5**, and **6** was 6:2:1:1. After 0.2 hr at room temperature, a faint pink color developed in the stock solution. Vpc showed simultaneously an initially fast product formation; after 4 days at room temperature, the pink tinge faded away. A substantial amount of products **3–6** had formed at that time.

C. Addition of Oxetane to DMAD.—A 0.1-g (0.7 mmol) portion of DMAD in 1 ml (15 mmol) of oxetane was kept at 135° in a sealed tube for 4 hr. Vpc showed the formation of **7** and **8** in a ratio of *ca.* 2:1. The yield was estimated to be 30%.

Solutions of DMAD in tetrahydropyran and oxepane were subjected to similar treatment. No 1:1 adducts or other products could be detected or isolated.

Photochemical Additions. A. Photoaddition of THF to DMAD.—A solution of 3.0 g (21.1 mmol) of DMAD in 50 ml (0.62 mol) of THF was degassed by purging with nitrogen and then irradiated in a Pyrex vessel in a Rayonet photoreactor equipped with 3000-Å lamps. After very low conversion (*ca.* 5 min), the ratio of the products **1** and **2** formed was 70:30 (vpc). After 48 hr of irradiation, excess THF was evaporated. Vpc analysis showed the presence of four products. By distillation of the crude mixture (4.3 g), 2.2 g of a 1:5 mixture of **1** and **2** was collected at 90–100° (0.1 mm). In addition, at 130–140° (0.1 mm), 1.4 g of a 1:1 mixture of **9** and **10** was collected. The total yield of 1:1 adducts was 80%. The mixture of **9** and **10** was separated by preparative vpc (SE-30). Elementary analyses follow. *Anal.* Calcd for **9**: C, 56.07; H, 6.59. Found: C, 55.85; H, 6.45. For **10**: Found: C, 55.78; H, 6.47. **9** and **10** showed the following spectral characteristics. **9**: nmr, see Table II; ir C═O 1740, 1710, -C═C- 1640 (strong); mass spectrum parent ion m/e 214, base peak m/e 123. **10**: nmr, see Table II; ir C═O 1735, 1680, -C═C- 1640 cm^{-1} (strong); mass spectrum parent ion m/e 214, base peak m/e 155. The photoproducts **9** and **10** were also obtained by irradiation (3000 Å) of **1** and **2** in a methanol solution. After 12 hr irradiation of **1**, the conversion to 3:2 mixture of **9** and **10** was virtually quantitative (vpc). Irradiation of **2** under similar conditions also gave a 3:2 mixture of **9** and **10** but at a much slower rate. After 96 hr irradiation *ca.* 90% of **2** had reacted. In addition some polymer was formed.

B. Photoaddition of MTHF to DMAD.—Irradiation of a solution of 0.1 g (0.7 mmol) of DMAD in 2 ml of MTHF under the conditions described previously gave initially a 6:2:1:1 mixture of the products **3**, **4**, **5**, and **6** (vpc).

C. Photoaddition of Oxetane to DMAD.—A solution of 0.5 g (3.5 mmol) of DMAD in 10 ml (0.15 mol) of oxetane was irradiated in a Pyrex vessel in a Rayonet photoreactor equipped with 3000-Å lamps. The reaction was followed by vpc, which showed initial formation of the two primary products **7** and **8** in a ratio of *ca.* 2:1. These were subsequently transformed into two new products, **11** and **12** (ratio 6:2, 46 hr irradiation). After evaporation of excess oxetane, the mixture of **11** and **12** was separated from the product mixture by preparative vpc. **11** and **12** were not easily separated by preparative vpc, but samples which were enriched in both isomers could be obtained. The structural assignments of **11** and **12** are based on comparison of the nmr spectra of these enriched mixtures with the nmr spectra of **9** and **10**. Total yield was *ca.* 80%.

Similar irradiations of tetrahydropyran and oxepane solutions of DMAD gave no adduct formation.

Isomerization of the Adducts 1 and 2.—A 50-mg (0.235 mmol) portion of **1** in 1 ml of benzene was treated with 10 mg (0.09 mmol) of thiophenol and exposed to sunlight. Vpc analysis at different intervals showed slow isomerization of **1** to a mixture of **1** and **2**. After 1 week, the ratio of **1** and **2** was 50:50 and did not change further. The same result was obtained when **2** was treated similarly.

Isolation of the Cis Isomers 2, 4, and 6.—The product mixtures from the additions of DMAD to THF and MTHF, respectively, were hydrolyzed by refluxing in NaOH–methanol solution overnight. After acidification and extraction with ether and water, the ether layer was evaporated and the residue was distilled. At 80–90° (0.1 mm), tetrahydro-2-furylmaleic anhydride was collected: ir C═O 1840, 1770, -C═C- 1650 cm^{-1}; nmr δ 2.0 (m, 4 H), 4.0 (m, 3 H), 4.8 (t, J = 6 Hz, 1 H), 6.8 (d, J = 1 Hz, 1 H). This material was refluxed overnight in methanol solution with a trace of sulfuric acid. Usual work-up gave pure **2**. In a similar way, a mixture of **4** and **6** was isolated from the mixture of **3**, **4**, **5**, and **6**. The ratio of **4** and **6** was shown to be 8:2 in the mixture obtained from the thermal addition.

Registry No.—**1**, 33536-59-3; **2**, 28864-83-7; **3**, 33536-63-9; **4**, 33536-64-0; **5**, 33522-13-3; **7**, 38229-58-2; **8**, 38229-59-3; **9**, 38229-60-6; **10**, 38229-61-7; **11**, 38229-62-8; **12**, 38229-63-9; THF, 109-99-9; MTHF, 96-47-9; DMAD, 762-42-5; oxetone, 503-30-0.

Acknowledgment.—I would like to thank Professors J. A. Kampmeier, B. Akermark, and W. G. Dauben for fruitful discussions, their interest and support of this work, which was made possible in part by a grant from the Swedish Board of Technical Development (STU). Furthermore, I am greatly indebted to Miss Marta Kilgour for editorial assistance.