O-*p*-bromobenzenesulfonylhomolupinine ester was not purified but converted by heating to 90° in a rotatory evaporator for 2 hr into 250 mg of the internal quaternary salt, mp 138°.

Anal. Calcd for $C_{17}H_{24}O_3NSBr$: C, 50.7; H, 5.97; N, 3.48; Br, 19.80. Found: C, 50.56; H, 5.83; N, 3.39; Br, 19.79.

Iodide (Vd). The brosylate (44.5 mg) was dissolved in 5 ml of methylene chloride; then sodium iodide (20 mg) in 2 ml of acetone was added and the sodium brosylate filtered. The residue after evaporation, 30 mg, was crystalline. Recrystallization from ethanol–ether gave leaflets, mp 332–333° dec.

Anal. Calcd for $C_{11}H_{20}NI$: C, 45.02; H, 6.82. Found: C, 44.91; H, 6.90.

Nmr spectra were recorded on a Varian A-60 spectrometer using chloroform-*d*.

The **infrared data** were obtained on a Perkin-Elmer grating spectrophotometer.

Acknowledgment. This research was carried out during the tenure of the author's stay as a visiting scientist with the Pure Chemistry Division of the National Research Council in Ottawa, Canada. Grateful acknowledgment is hereby made to the Council, in particular to Dr. Léo Marion, former Vice-President, to Dr. W. G. Schneider, Vice-President, and to Dr. O. E. Edwards, Organic Chemistry Section. Thanks are due to Mr. H. Seguin for the microanalyses.

Photochemical Synthesis. XI. On the Mechanism of the Maleate–Cyclohexene Cycloaddition

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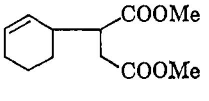
Contribution from the Department of Chemistry, University of Western Ontario, London, Canada.

Received October 1, 1965

Abstract: The composition of the bicyclo[4.2.0]octane dicarboxylic ester mixture produced by the irradiation of dimethyl maleate in cyclohexene varies with the temperature of irradiation. Since the intervention of excited cyclohexene molecules is improbable, this and the formation of *trans*-fused products requires that part of the product, at least, be formed through a discrete diradical intermediate. The sensitized reaction, using sensitizers of E_{T} from 40 to 84 kcal/mole, shows a similar, but different, temperature dependence and the product analysis is independent of the E_{T}. A triplet–triplet energy transfer mechanism is indicated for this process, and at least part of the directly formed product appears to be formed through the singlet.

In a previous paper in this series[1] the products obtained in the photochemical addition of dimethyl maleate to cyclohexene and to cyclopentene were described.[3] It was found that, in addition to the allylic addition products, such as cyclohex-2-enyl succcinic ester (**1**) and bicyclohexenyl (**2**), a number of saturated dicarboxylic esters, formed by cycloaddition, were obtained. Those isolated in the cyclohexene series were bicyclo[4.2.0]octane derivatives and included members of both the *cis*- and *trans*-fused systems, specifically esters **3**–**6**.

The *cis,cis,endo* isomer, isolated in a small amount by Barltrop,[4] was present in our system in too small quantities for investigation: its exiguousness is probably to be attributed to the steric compression in this molecule. No obvious explanation for the absence of the *trans,cis* isomer is available unless it be present as an unseparated very minor component of the peak containing **3**.



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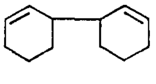

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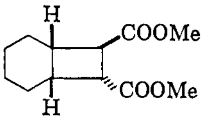

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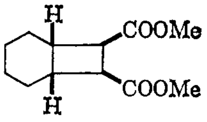

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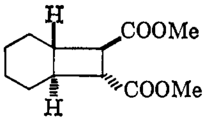

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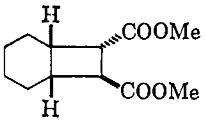

6

Present detailed knowledge concerning the photochemical cycloaddition process is comparatively sparse, though presently attracting attention,[4,5] and the present instance appeared suitable for further study as regards the nature of the species involved.

Results

A. Ground-State Charge-Transfer Complexes. No indication of additional or modified absorption was found with dimethyl maleate in cyclohexene (as distinct from that of the components) although complex

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[1] P. de Mayo, S. T. Reid, and R. W. Yip, *Can. J. Chem.*, **42**, 2828 (1964); see also ref 2.

[2] P. de Mayo, R. W. Yip, and S. T. Reid, *Proc. Chem. Soc.*, **54** (1963).

[3] The addition of maleic anhydride to cyclohexene has also been reported recently.[4]

[4] R. Robson, P. W. Grubb, and J. A. Barltrop, *J. Chem. Soc.*, 2153 (1964); see also J. A. Barltrop and R. Robson, *Tetrahedron Letters*, 597 (1963).

[5] (a) S. J. Cristol and R. L. Snell, *J. Am. Chem. Soc.*, **76**, 5000 (1954); (b) P. E. Eaton, *ibid.*, **84**, 2454 (1962); (c) P. de Mayo and H. Takeshita, *Can. J. Chem.*, **41**, 440 (1963); (d) H. J. F. Angus and D. Bryce-Smith, *J. Chem. Soc.*, 4791 (1960); (e) E. Grovenstein, Jr., and D. V. Rao, *Tetrahedron Letters*, No. 4, 148 (1961); (f) E. J. Corey, J. D. Bass, R. Le Mahieu, and R. B. Mitra, *J. Am. Chem. Soc.*, **86**, 5570 (1964); (g) G. O. Schenck and R. Steinmetz, *Tetrahedron Letters*, No. 21, 1 (1960); (h) G. O. Schenck, W. Hartmann, and R. Steinmetz, *Chem. Ber.*, **96**, 498 (1963).

Table I. Solvent Dependence of the Intensity of Absorption at 250 mμ of Dimethyl Fumarate

Solvent	ϵ	$\epsilon_s - \epsilon_c$
Cyclohexane	360[a] ($=\epsilon_c$)	
Cyclohexane + 4% cyclohexene	400	40
Oct-1-ene	530	170
cis-Dichloroethylene	740	380
2,5,5-Trimethylhex-2-ene	750	390
Cyclohexene	1080	720

[a] Kosower[6] records ϵ_{260} mμ = 250 in isooctane for diethyl fumarate. [b] Concentration 0.01 *M*.

Table II. Composition of Saturated Ester Mixture Obtained under Various Conditions from Dimethyl Maleate and Dimethyl Fumarate[a]

Conditions	Ester,[b] %			
	3	**4**	**5**	**6**
2537 A (M)	68.1 ± 0.3	14.6 ± 0.2	116 ± 0.3	5.7 ± 0.2
2537 A (F)	75.8 ± 0.3	7.8 ± 0.2	10.6 ± 0.3	5.8 ± 0.2
~2900 A (M)	69.7 ± 1.0	14.2 ± 0.6	10.4 ± 0.3	5.6 ± 0.6
4-Methylacetophenone (SM)	62.7 ± 0.3	11.0 ± 0.2	17.7 ± 0.3	8.6 ± 0.2
4-Methylacetophenone (SF)	63.9 ± 0.3	10.9 ± 0.2	17.1 ± 0.3	8.2 ± 0.2
Benzene (SM)	61.9 ± 0.3	118. ± 0.2	17.3 ± 0.3	9.0 ± 0.2
Phenanthrene (SM)	62.5 ± 0.2	11.3 ± 0.1	17.7 ± 0.2	8.5 ± 0.1
Pyrene (SM)	64.4 ± 0.3	10.5 ± 0.2	17.3 ± 0.2	7.8 ± 0.2
9,10-Dibromoanthracene (SM)[c]	(64.7)	(10.0)	(17.2)	(8.1)

[a] M = dimethyl maleate, F = dimethyl fumarate, S = sensitized experiment. [b] Average of at least four determinations except under *c*. [c] Single determination because of corrosion of detector by decomposition products.

formation has been reported[4] between maleic anhydride and cyclohexene. Dimethyl fumarate, on the other hand, shows a distinct enhancement of the intensity of absorption of the already reported[6] n → π* transition. This enhancement (Table I) is concentration and solvent dependent, and appears to be due to the superimposition of a charge-transfer band on the n → π* absorption.

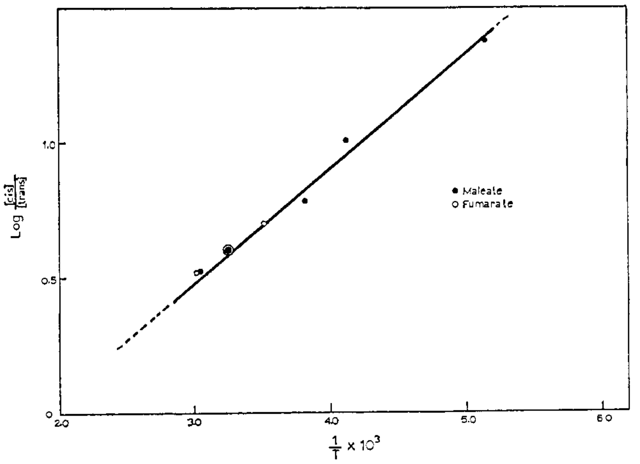

Figure 1. Relationship of *cis–trans* fusion proportions to temperature in the direct irradiation.

B. Direct Irradiations. The quantum yields for total saturated ester product at 2537 A and near 2900 A were found to be close ϕ = 0.011 ± 0.0015 and 0.0105 ± 0.0015, respectively) as was the composition[7] of the saturated ester mixture (**3–6**) (Table II). The composition of the mixture obtained by the irradiation of dimethyl fumarate differed in the proportions of the *cis*-fused esters, but little in that of the *trans*-fused esters. These formed about 17% of the total ester product and consisted of **5** and **6**[8] in the ratio of nearly 2:1.

The variation in ratio of the *cis*- to *trans*-fused products obtained with unfiltered light (Vycor) was determined over the range −76 to +56° for dimethyl maleate (Table III). Over this limited range log [*cis*]/[*trans*] *vs.* 1/*T* gave an apparently linear plot (Figure 1). Determination of the *cis–trans* fusion ratio for dimethyl fumarate over the range 11 to 58° (limited by the lesser solubility of dimethyl fumarate) gave points falling on the same line obtained by the usual least-squares method.

Table III. *cis-trans* Fusion Ratio Variation with Temperature of Esters from Dimethyl Maleate and Dimethyl Fumarates[a]

T, °C	*cis*, %	*trans*, %
	Maleate	
54	77.0 ± 0.2	23.0 ± 0.2
34	80.0 ± 0.2	20.0 ± 0.2
−11	86.0 ± 0.2	14.0 ± 0.2
−40	91 ± 0.3	9 ± 0.3
−76	96 ± 0.5	4 ± 0.5
	Fumarate	
58	77.6 ± 0.2	22.4 ± 0.2
34	80.0 ± 0.3	20.0 ± 0.3
11	83.4 ± 0.3	16.6 ± 0.3

[a] Average of four runs.

C. Sensitized Irradiations. The photochemical cycloaddition of both dimethyl maleate and dimethyl fumarate could be induced by sensitizers absorbing all the incident light. The composition of the saturated ester mixture (Table II) appeared similar from both esters and with all sensitizers. The sensitizers varied in transition energy (E_T) over a range of 40 kcal/mole from 9,10-dibromoanthracene (E_T = 40[9]) through pyrene (E_T = 48.7[10]), phenanthrene (E_T = 62.2[10]), 4-

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[6] W. D. Closson, S. F. Brady, E. M. Kosower, and P. K. C. Huang, *J. Org. Chem.*, **28**, 1161 (1963).

[7] As indicated in the tables the analytical method gave mean deviations that were higher than were desired, but it is believed nevertheless that the conclusions drawn are within the defined limits.

[8] In our first communication[2] the remaining stereochemistry of the *trans,trans* isomers was not assigned. Our diacid of mp 182° appears to be that assigned the stereochemistry of **6** by Barltrop.[4] The acid, mp 202°, must then be the alternative *trans,syn,trans* isomer **5**.

[9] G. S. Hammond and J. Saltiel, *J. Am. Chem. Soc.*, **85**, 2515 (1963).

[10] W. G. Herkstroeter, A. A. Lamola, and G. S. Hammond, *ibid.*, **86**, 4537 (1964).

methylacetophenone (E_T = 73.6[11]), and benzene (E_T = 84.06[12]).

The sensitized cycloaddition was also temperature dependent and was studied over a very limited range (−22 to +46°) using 4-methylacetophenone as the sensitizer (Table IV). The values obtained do not fall on the plot (Figure 1) obtained for the direct irradiation.

Table IV. *cis–trans* Fusion Ratio Variation with Temperature of Esters Obtained by the Sensitized[a] Addition of Dimethyl Maleate to Cyclohexene

T, °C	*cis*, ±0.5 %	*trans*, ±0.5 %
46	69.9	30.1
26	74.0	26.0
5	75.6	24.4
−22	76.1	23.9

[a] Sensitized with approximately 0.05 *M* 4-methylacetophenone. Averages of four runs.

D. Attempted Quenching Experiments. The possibility that triplets could be involved in the direct irradiation pathway suggested the use of low-energy acceptors to quench these triplets: the effect of the quenching should be reflected both in a lowered quantum yield for total saturated ester products. In the case of addition proceeding by parallel singlet and triplet pathways, a change in the composition of the product would also be expected. The concentration of the quencher first used, naphthalene,[13] was limited by its absorption at 2537 A, but up to 3.12 × 10^{-3} *M* (Table V) the quantum yield appeared unaffected. Calculation of the diffusion constant[14] and thence the rate constant[15] for triplet maleate–naphthalene collisions in cyclohexene gives a figure of near 1.5 × 10^{10} l. mole^{-1} sec^{-1}. At the concentration used this implies an interval of the order of 2.5 × 10^{-8} sec. If quenching is diffusion controlled the mean lifetime of any quenchable excited species should be less than this.

Table V. The Attempted Quenching of Naphthalene in the Addition of Dimethyl Maleate to Cyclohexene

Run	[Maleate] × 10^2	[Nap] × 10^3	Φ at 2537 A × 10^2
1	4.98	1.48	1.00
2	5.10	2.27	1.08
3	5.09	2.81	1.08
4	5.04	3.12	1.08

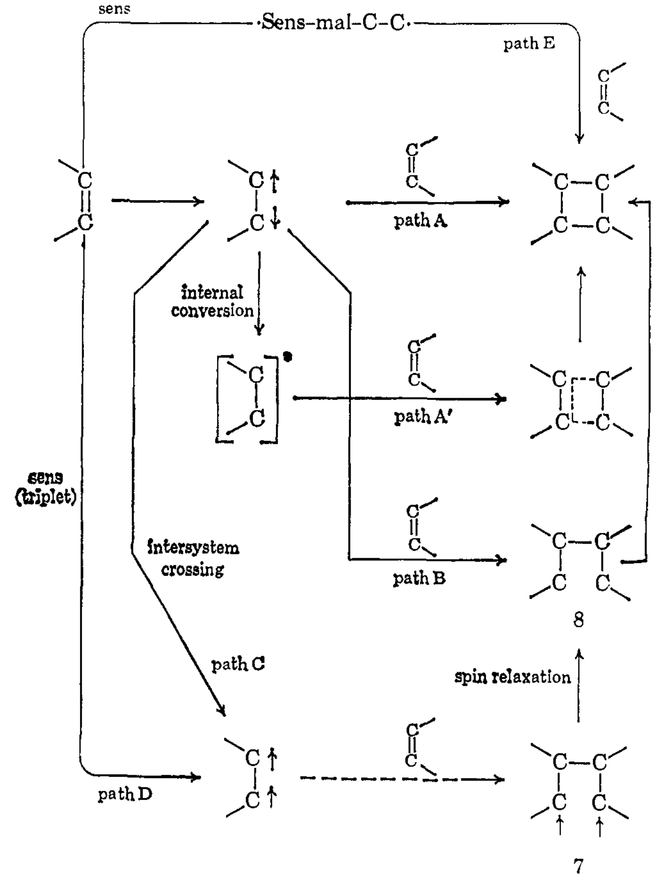
The use of azoethane as a quencher[16] permitted the use of higher concentrations (0.017 and 0.107 *M*), but no change in *cis–trans* fusion rates was observed in irradiation near 2900 A. Oxygen could conceivably have been active as a quencher, and an attempt was made to use it, but without success: analysis was impracticable because of the profusion of irrelevant products.

An attempt was made to provide opportunity for preferential singlet decay by dilution of the medium with cyclopentane. If the singlet and triplet lifetimes were appreciably different, a change in ester composition might be observed in a reaction occurring through parallel pathways. No significant change in the *cis–trans* fusion ratio was observed even when 95% of the cyclohexene was replaced with cyclopentane. The [*cis*]/[*trans*] ratio obtained at 28.5 ± 0.05° was 4.03 ± 0.08°. The estimated value at this temperature is 4.07. With 80% of the cyclohexene replaced by cyclopentane the ratio obtained at 31 ± 0.05° was 3.98 ± 0.06. The estimated value is 4.03.

Discussion

The cycloaddition of a molecule energized by the absorption of radiation to a double bond may be envisaged as proceeding by one of three main pathways: through the excited singlet or lowest triplet, or through the vibrationally excited ground state. The place of the present four-center addition, as regards orbital symmetry, in the general scheme of cycloaddition reactions has been discussed very recently by Hoffmann and Woodward.[17] These authors conclude that continuous formation of both bonds (Scheme I, path A) is permitted for the excited singlet, but is disfavored for the ground state (path A′).[18] Excited singlet addition

Scheme I



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(11) D. R. Arnold, private communication.

(12) D. S. McClure, *J. Chem. Phys.*, **19**, 670 (1951).

(13) A. Beckett and G. Porter, *Trans. Faraday Soc.*, **59**, 2038 (1963); W. M. Moore and M. Ketchum, *J. Am. Chem. Soc.*, **84**, 1368 (1962).

(14) P. Chang and C. R. Wilke, *J. Phys. Chem.*, **59**, 592 (1955).

(15) G. V. Schulz, *Z. Physik. Chem.*, **8**, 284 (1956).

(16) R. E. Rebbert and P. Ausloos, *J. Am. Chem. Soc.*, **87**, 1847 (1965).

(17) R. Hoffmann and R. B. Woodward, *ibid.*, **87**, 2046 (1965).

(18) For a review of ground-state reactions see J. D. Roberts and C. M. Sharts, *Org. Reactions*, **12**, 1 (1962).

may thus be stereospecific. It should be noted that at some point electron demotion is required, and that this point (unless there be a third singlet different from S_0 and S_1) occurs after the process of bond formation has begun. If demotion does not occur then the formation of the cyclobutane in the excited state may be energetically impossible. Photochemically induced triplet addition (path C) might not be expected to be stereospecific since bond rotation in an intermediate biradical (7) could compete with ring closure. Such is the case in the addition of triplet methylene to simple olefins.[19] Before cyclization, and assuming there is no alternative mode of cyclization permitting spin conservations (see below), spin inversion to **8** is required. Should spin inversion be both necessary and slow, competitive polymerization may intervene. It seems probable that such spin inversion is not slow[20] since the addition of triplet methylene to double bonds leads to cyclization.[21]

The assumption that no alternative mode of cyclization from the triplet (7) other than that proceeding with prior spin relaxation may require modification, particularly if the excited molecule has at its disposal a means of transference of spin. Thus, in the present instance, the addition of maleate to cyclohexene, the electron is adjacent to one of the ester carbonyl groups. Direct cyclization might, in principle, then lead to cyclobutane formation with concomitant generation of the carbonyl triplet. However, the energetics of the system, bearing in mind the high energy expected of the resultant saturated carbonyl triplet, render this process improbable. Thus at the outset it could be expected that stereospecific addition probably involved the excited singlet, and that the triplet addition would not be stereospecific. It could not be concluded that the converse, that a nonstereospecific addition implied participation of a triplet, would hold.

As a preliminary step a search for the possible existence of ground-state charge transfer complexes was made. If one such existed in the case of one isomer, and if it had strong absorption, then predominant energy absorption would be by that isomer even if it were present in very minor amount.

No complex formation of cyclohexene was observed with dimethyl maleate,[22] but enhanced though weak absorption near 2500 A was indeed observed with dimethyl fumarate. That this was charge-transfer complex absorption was indicated by its dependence on concentration and on the nature of the olefin (Table I) when this was varied. But since in the maleate direct irradiations epimerization was not carried further than about 2%, the amount of light absorbed by any such complex formed would be, at the concentration used, very small. As far as the present evidence allows conclusions to be drawn, the existence of the complex is, as far as the cycloaddition of dimethyl maleate is concerned and probably over-all, without mechanistic importance. This is borne out by the identity of the quantum yield and product analysis at 2537 and near 2900 A.

The possibility was considered that cycloaddition might proceed through the intermediacy of excited cyclohexene. The absorbance of the hydrocarbon is low at 2537 A compared with the esters, and reaction in this manner would indicate a quantum yield near unity, a possibility contraindicated by the large amount of polymer produced. Near 2900 A, where the absorbance of the maleate and cyclohexene are comparable, a change in quantum yield of well over an order of magnitude would be indicated. Addition of directly excited cyclohexene to ground-state maleic ester is not therefore a plausible hypothesis. Energy transfer from excited maleic ester to cyclohexene would be expected to be inefficient[23] and, as with the direct cyclohexene excitation, would not be expected to lead to the observed products.[24]

The cycloaddition products are thus most probably formed by the addition of excited maleate to cyclohexene. It then can be concluded that the formation of the *trans*-fused adducts, because of the spatial requirements for effective overlap, excludes processes A (and A′) for at least that portion of the saturated ester products.

Given a difference in the activation energy of *cis* and *trans* cyclization in this two-step process the composition of the mixture of cyclobutane esters formed through 7 should be temperature dependent, and this was found to be the case, both for maleate and for fumarate.[27] The two-step addition thus demonstrated suggested, but did not require, triplet intermediates.

Recently it has been established that a number of cycloadditions may be induced through the agency of sensitizers.[5h,29–32] In addition, evidence has been presented to indicate that at least some of these reactions are initiated by triplet–triplet energy transfer (path D).[30,31,33] According to a different concept[34] the specific formation of sensitizer–adduct biradicals (path E) has been proposed. These are then suggested to collapse directly to ground-state sensitizer and adduct.

The cycloaddition of dimethyl maleate could be induced with benzophenone and with acetophenone under

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[19] *Cf. inter alia*, F. A. L. Anet, R. F. W. Bader, and A. M. van der Auwers, *J. Am. Chem. Soc.*, **82**, 3217 (1960).

[20] L. K. Montgomery, K. Schueller, and P. D. Bartlett, *ibid.*, **86**, 622 (1964).

[21] K. R. Kopecky, G. S. Hammond, and P. Leermakers, *ibid.*, **83**, 2397 (1961).

[22] A complex has been reported between maleic anhydride and cyclohexene.[4]

[23] The energy of the triplet state of cyclohexene is not known; ethylene (D. F. Evans, *J. Chem. Soc.*, 1735 (1960)) is 83 kcal. Dimethyl maleate (see later) appears to be in the region of 70 kcal, and it seems improbable that the substitution and incorporation of ethylene into a ring could lower the triplet state sufficiently such that efficient transfer from the planar maleate molecule to the cyclohexene could occur.

[24] High-energy carbonyl sensitizers do not add to alkenes, for instance, and form oxetanes, but effect energy transfer.[25] The excited alkenes may then dimerize.[26]

[25] D. R. Arnold, R. L. Hinman, and A. H. Glick, *Tetrahedron Letters*, **No. 22**, 1425 (1964).

[26] D. R. Arnold, D. J. Trecker, and E. B. Whipple, *J. Am. Chem. Soc.*, **87**, 2596 (1965); D. Scharf and F. Korte, *Tetrahedron Letters*, **No. 13**, 821 (1963).

[27] *trans*-Fused cycloaddition products recently have been obtained Barltrop[4] and by Corey.[5f,28]

[28] E. J. Corey, R. B. Mitra, and H. Uda, *J. Am. Chem. Soc.*, **86**, 485 (1964).

[29] G. O. Schenck, I. von Wilucki, and C. H. Krauch, *Chem. Ber.*, **95**, 1409 (1963).

[30] N. J. Turro and G. S. Hammond, *J. Am. Chem. Soc.*, **84**, 2841 (1962).

[31] G. S. Hammond and R. S. H. Liu, *ibid.*, **85**, 477 (1963).

[32] G. O. Schenck and R. Steinmetz, *Tetrahedron Letters*, **No.** 21, 1 (1960).

[33] R. S. H. Liu, N. J. Turro, and G. S. Hammond, *J. Am. Chem. Soc.*, **87**, 3406 (1965).

[34] G. O. Schenck and R. Wolgast, *Naturwiss.*, **48**, 737 (1961); **49**, 36 (1962); G. O. Schenck and R. Steinmetz, *Bull. Soc. Chim. Belges*, **71**, 781 (1962).

conditions in which the ketone absorbed all the light, but by-products made analysis unsatisfactory. Sensitizers which were more satisfactory included 4-methylacetophenone, pyrene, phenanthrene, benzene, and, in part, 9,10-dibromoanthracene. The product analysis obtained for the saturated esters apparently was independent of the sensitizer.

The mechanism involving actual addition of the sensitizer to the addend molecule may be represented in the present specific case of maleate (or fumarate) cycloaddition as follows.

$$\text{sens} \xrightarrow{h\nu} \text{sens}^{*} \xrightarrow{\text{maleate}} \cdot\text{sens–mal}\cdot \xrightarrow{\text{cyclohexene}}$$

$$\cdot\text{sens–mal–cyclohexene}\cdot \longrightarrow \text{sens} + \text{adduct}$$

It seems improbable that sensitizers of such different types could, when incorporated into a trimolecular biradical, lead to its collapse in an identical manner. Aside from the question of the geometry of the sensitizer moiety adopted in the trimolecular complex for stabilization of the radical, it is surely to be expected that the steric requirements of the sensitizer would affect the orientation of the "maleate" and cyclohexene moieties in the transition state for collapse, and hence the composition of the ester mixture. We are therefore led to conclude that here also triplet–triplet transfer is implicated.

After this section of our work was completed, Hammond reported a detailed study of the maleic–fumaric ester geometrical isomerism.[35] This was not found to be induced at appreciable rates by sensitizers having excitation energies below 59 kcal/mole. Although figures for quantum yields are not available the cycloaddition process appears to proceed approximately at rates of the same order of magnitude with the different sensitizers, as judged by the amounts of product obtained. By whatever means the same diradical (**7**) must be formed, but whether by nonvertical excitation of methyl maleate to a skew triplet of much lower energy than had been expected followed by addition, or by some other route, is presently unclear. Certainly, although the estimation of the singlet–triplet excitation energy, as indicated by ethyl iodide solution spectra, of methyl maleate and fumarate was exceedingly tentative, the results we had obtained were in agreement with Hammond's[35] in that they appeared to be in the region of 70 and 60 kcal/mole, respectively. Under these circumstances all the sensitizers used with the exception of benzene and 4-methylacetophenones should be incapable of efficient excitation transfer to the planar triplets.

One possibility is that energy transfer from the sensitizer takes place by a nonspectroscopic transition to a skew cyclohexene triplet. This could be expected to be even less efficient than transfer to a skew maleate, though the inefficiency may be partly compensated by the high concentration of cyclohexene. It is also required, however, that the cyclohexene triplet react exceedingly rapidly with ground-state maleate relative to cyclohexene to overcome the now adverse concentration effect. It is known, though, that excited cycloalkenes such as norbornene dimerize readily on activation,[26] and although quantitative data are not available, it seems improbable that this should be an important contributing process.

The fact that in the sensitized reaction the product analysis, whether the starting material was maleate or fumarate, appeared the same clearly indicated that the stereochemical identity of the starting ester is lost, as is not the case with the direct irradiation at 2537 A. This is in agreement with the suggested path D for this process. Also in agreement is the fact that the sensitized reaction showed some temperature dependence.

For the direct irradiation two possibilities must be considered. Either the direct reaction goes entirely by a single pathway or by two (or more) concurrent processes. If the first case is correct, A (and A′) must be excluded for this because the products contain more *trans*-carboxyl esters than could be formed by direct addition of fumarate at the extent of conversion. In addition, the presence of *trans*-fused products has already rendered these routes suspect. Path C has already been bespoken and cannot represent the sole route. Direct evidence to support or exclude path B is not available. This pathway may be such that electron demotion occurs after formation of the first bond, but the degree of stereospecificity to be expected of such a process is unknown.

If the second case is correct, then one of the two pathways should be C, that of the triplet, and it may be noted that the ratio of the two *trans*-fused products (**5** and **6**) is 2:1 both in the direct and sensitized reactions. If it be assumed that all the *trans*-fused material in the direct irradiation is formed through the triplet pathway with accompanying *cis*-fused products in the proportions indicated in the sensitized reactions, then about two-thirds of the total direct ester products is accounted for. The remainder consists of *cis*-fused products in the ratio of roughly 3.5:1 *trans–cis* carboxyl. The same computation applied to the fumarate irradiation again leaves about one-third of the total product to be formed by other than the triplet pathway. In this case the material is, within the experimental error, entirely *cis*-fused, *trans* carboxyl (**3**).

It would seem that in this postulated second route some mechanism for carboxyl inversion must be provided (other than through the triplet) which does not apparently reach completion, and which is proceeding at a rate comparable with ring closure. Again, path B could be relevant, as could conceivably charge-transfer complexes of the excited ester with ground-state cyclohexene. *In any event, it would appear very probable that at least part of the directly formed material is generated through a singlet pathway*, a process for which there is at present little analogy.[36]

Attempted modifications of the relative importance of the singlet and triplet components of the direct addition by quenching with naphthalene were ineffective (Table V). This was attempted before it was appreciated that sensitizers of very low E_{T} could be used for the addition. However, the high-energy *planar* triplets would be expected to be quenched at a rate which was diffusion controlled. Under the present conditions, therefore, if these triplets are generated then they must have a lifetime of less than 2.5×10^{-8} sec. If the decay is to a

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

(36) For a discussion of the singlet dimerization of anthracene see E. J. Bowen, *Advan. Photochem.*, 1, 23 (1963); see also, D. Bryce-Smith and A. Gilbert, *J. Chem. Soc.*, 918 (1965), with regards to the cycloaddition of maleic anhydride to benzene.

low-energy species, as indicated by the energy-transfer experiments, which then adds to the cyclohexene, then the lifetime of this species remains indeterminate.

Attempted quenching with azoethane was ineffective even at high concentration and the use of oxygen led to a proliferation of products. Dilution of the medium with cyclopentane, thus prolonging the time between effective collisions, did not change the *cis,trans* fusion ratio. If more singlets were able to cross over to the triplet manifold before addition, a change could have been manifest in this ratio. That it did not change may merely mean that the triplets also have increased modes of decay available to them with longer lifetime.

No comment has yet been made as to the excited state involved in this reaction. No specific evidence is available, but the following observations are pertinent. The $n \rightarrow \pi^*$ singlet transition of fumaric ester occurs near 2500 A (~112 kcal) and the π,π^* near 2120 A (~138 kcal). The (n,π^*) singlet–triplet splitting, because of orthogonality, would be expected to be small, and the question is whether the π,π^* splitting is sufficiently large to render the π,π^* triplet of lower energy then the n,π^*. The relevant triplet transition has, as has been mentioned, an energy of 70 and 60 kcal for maleate and fumarate. Even allowing for some uncertainty in the energies of the transition it seems very improbable that the n,π^* splitting could be as large as 40 kcal. Most splittings recorded involving carbonyl groups appear to be of the order of about one-quarter of this value. The π,π^* splitting should be larger because of the greater overlap and might attain the ~70 kcal indicated: this is of the order of that found for alkenes. For these reasons the excited state in the presently reported reactions is considered to be more probably π,π^*.

Experimental Section

Materials. Acetophenone and 4-methylacetophenone were reagent grade further fractionated and had n^{13}D 1.5349 and n^{20}D 1.5338, respectively. Azoethane was prepared according to the method of Renaud and Leitch.[37] Cyclohexene was prepared by the dehydration of cyclohexanol, and was stored over zinc dust. Prior to use it was filtered through alumina under nitrogen. Phenanthrene (BDH) was freed from anthracene by the method of Backmann and Kloetzel.[38] Pyrene (Aldrich) was crystallized from carbon tetrachloride and converted to the picrate which was crystallized from ethanol and from benzene. Decomposition of the picrate on alumina gave the hydrocarbon, recovered recrystallized from carbon tetrachloride. 9,10-Dibromoanthracene was prepared according to the method of Heilbron and Heaton[39] and dimethyl maleate according to Clemo and Graham.[40] Dimethyl fumarate (K and K Laboratories) was used without further purification.

Charge-Transfer Spectra. Solutions of 0.1, 0.01, and 0.001 *M* maleate in cyclohexene were prepared and the absorption spectra were compared with a cyclohexene reference. Solutions of dimethyl maleate in cyclohexane (0.125, 0.0104, and 0.000228 *M*) also were compared with a cyclohexane reference. Comparison of the absorption curves with appropriate correction did not show the presence of new or increased absorption.

Similar plots for dimethyl fumarate (which showed the shoulder near 250 mμ reported by Kosower[6]) showed a distinct enhancement in this region.

Temperature Studies. A quartz unsilvered dewar was fitted with 1.1-cm diameter windows as described by Hirshberg and Fischer[41] the temperature being recorded continuously with an iron–constantan thermocouple inserted between the dewar walls and the cell. The reaction vessel was a 1-cm path rectangular quartz cell (5 ml) equipped at the joint with a grease trap. It could be connected to a vacuum source for degassing.

Temperatures were maintained by the following means: −76°, methanol–carbon dioxide; −40 to −10°, boiling liquid nitrogen; +56°, filtered air heated in a copper spiral.

Dry cyclohexene was introduced into the cell which contained from 10 to 23 mg of dimethyl maleate or dimethyl fumarate (degassed to remove moisture) and previously dried under high vacuum. The solution itself was then degassed at −76° to 0.1 mm. No change in product analysis was observed with no degassing and degassing to 0.035 mm.

The light source for these experiments was a collimated beam from an Osram HB$_0$ 200 W mercury arc. In sensitized experiments Corning CS 0-52 and 7069 filters were interposed.

Product Analysis. The product of irradiations after evaporation of the solvent was ozonized in CH_2Cl_2 (25 ml) at −76° for approximately 20 min. After evaporation of solvent *in vacuo*, 6 ml of 5% aqueous H_2O_2 was added and the mixture was warmed at 80–90° for 5 min. Solid $NaHCO_3$ was added to the cooled mixture until it was basic. The saturated ester was extracted with $CHCl_3$. The amount of maleate consumed was between 3 and 7% in all cases, and in this region the product analysis appeared independent of the time of irradiation. The saturated products were analyzed on a 20 ft × 18 in. 2.5% Carbowax 20M on Chromosorb P column at 210°.

Quantum Yields at 2537 and near 2900 A. The source for the 2537-A light was a 100-w U medium-pressure mercury arc, the collimated beam being passed through Bausch and Lomb monochromator. Because of the low intensity a half-band width of 25 mμ was employed. The incident light on the cell was approximately 5×10^{14} quanta/sec. For the 290-mμ region an Osram HBO 200-w high-pressure arc was used (half-band width 12 mμ). A significant proportion of light from the 2968-A line was thus transmitted. The total incident light on the cell was approximately 3×10^{15} quanta/sec. In this case the relative effective absorbancies of the cyclohexene and dimethyl maleate under these exact conditions were measured actinometrically. It was found that 83% of the light was absorbed by the maleate. Very high purity in cyclohexene was essential.

A beam splitter of the type described by Porter[42] was used, calibration giving ^TR as 10.0 at 2890 A and 9.1 at 2537 A. With the 254-mμ light, absorption of radiation was over 99.99%. With the longer wavelength a second actionometer cell was placed behind the sample cell. No correction was made for reflection. Actinometry was by the ferrioxalate method of Hatchard and Parker,[43] the solutions being stirred by bubbling nitrogen.

To reduce errors due to sampling and injection (glpc) the quantity of adducts formed was measured relative to a known amount of benzophenone. This was added to the irradiated solution (approximately 5×10^{-2} *M* in dimethyl maleate) in the amount of 1 ml of solution containing 2.7 mg/25 ml to 2 ml of irradiated solution. The benzophenone ester relative response (in CS_2) was determined separately.

Sensitized Cycloadditions. The light source for all except the benzene experiments was the Osram HBO 200-w arc. A 6.5-cm cylindrical cell of 2-cm path length was used. For 4-methylacetophenone the Corning filters CS 0-52 and 7-60 were used. For phenanthrene, pyrene, and 9,10-dibromoanthracene a solution of naphthalene (12.8 g/l.) in cyclohexane was used (path length 1 cm). The concentrations of dimethyl maleate varied from 0.045 to 0.12 *M*; those of the sensitizers were 0.13, 0.04, 0.023, and 0.16 *M*, respectively. The benzene irradiation was performed at 2537 A using a Srinivasan–Griffin reactor (S.N.E. Ultraviolet Co.) with a tubular cell. This was immersed in a bath with a cooling coil. Over 98.4% of the light was absorbed by the benzene.

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