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STEREOCHEMISTRY AND MECHANISM OF THE [2 + 2] AND [4 + 2] PHOTOCYCLOADDITION OF ALKENES AND DIENES TO PUMMERER'S KETONE

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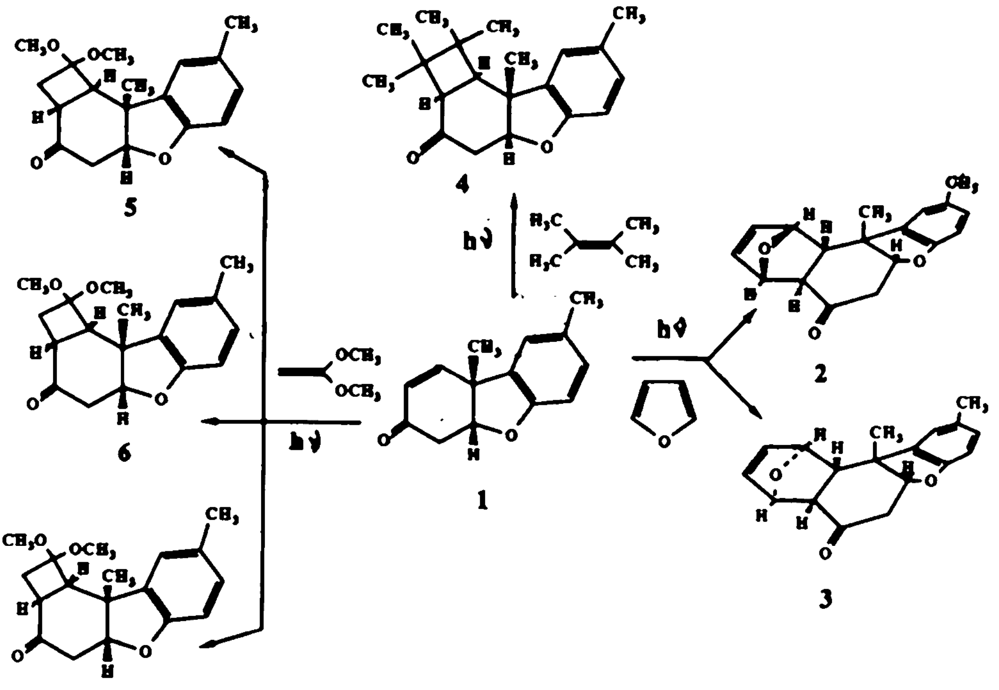
Abstract - Irradiation of Pummerer's ketone (PK) in furan gave the trans-fused [4 + 2] cycloadducts **2** and **3**, whose structures were determined by their ^1H NMR spectra and confirmed by X-ray crystallography. Irradiation of PK in the presence of tetramethylethylene (TME) gave cycloadduct **4** and with 1,1-dimethoxyethylene (DME) gave [2 + 2] cycloadducts **5**, **6** and **7**, respectively. The X-ray crystal structures of **4** - **7** show that the four- and six-membered rings of **4** and **7** are trans-fused, and **5** and **6** are cis-fused, respectively. Differential quenching of the formation of cycloadducts **2**-**5** and **7** by the free radical TEMPO was observed. Formation of cycloadducts **2**-**4** was also quenched differentially by O_2. A short lived (15 nsec) transient observed on nanosecond flash photolysis of PK is suggested to be a highly twisted triplet excited state, which is the likely precursor of both [4 + 2] and [2 + 2] adducts. It is proposed that stepwise addition of furan and alkenes to PK triplets gives triplet biradicals, which can be intercepted by TEMPO and O_2, and that these reactions probably do not involve a ground state trans-cyclohexenone intermediate.

INTRODUCTION

Previous studies by Hart, Dunkelblum and Jeffares[1] on photoinduced addition of methanol to Pummerer's ketone (PK, **1**) led to the suggestion that "an excited state or intermediate in which the C=C bond is twisted more than 90^0" might be the chemically reactive intermediate, in order to account for the observed stereospecificity (overall anti addition) of this reaction. In connection with studies in this laboratory on photocycloaddition of alkenes to cyclohexenones and the possible role of ground state trans-cyclohexenones in these reactions,[2] we have studied photocycloaddition of dienes and alkenes to PK. The initial aim of this research was to determine the stereochemistry of [2 + 2] and [4 + 2] photocycloaddition to PK and the nature of the reactive intermediates which are precursors of the cycloadducts. The [4 + 2] photocycloaddition of furan to PK has precedent in the photoaddition of acetylcycloalkenes to cyclopentadiene studied by Eaton,[3] which in the case of acetylcyclooctene was shown to involve a ground state transoid enone intermediate.

RESULTS

Irradiation of PK in neat furan gave the trans-fused [4 + 2] adducts **2** and **3**, whose structures, given in Scheme 1, were proven by ^1H-NMR spectra and confirmed by X-ray crystallography.[4] Irradiation of PK in the presence of tetramethylethylene (TME) gave cycloadduct **4** and with 1,1-dimethoxyethylene



SCHEME 1

(DME) gave [2 + 2] cycloadducts **5**, **6**, and **7**, respectively (see Scheme 1). The X-ray crystal structure of **4** shows that the four- and six-membered rings of **4** are *trans*-fused (Fig. 1), while **5** and **6** possess *cis*-fused bicyclo[4.2.0]hexan-2-one ring systems. In **6** the ring juncture protons are on the same side and in **5** on the opposite side of the ring system with respect to the angular methyl group (see Figures 2 and 3 for the crystal structures of **5** and **6**). Treatment of **7** with sodium methoxide resulted in isomerization to **6**, indicating that the two compounds are epimeric at the carbon adjacent to the carbonyl group, which immediately suggested that **7** is *trans*-fused.[5] This stereochemistry was confirmed by X-ray analysis of **7** (Fig. 4).

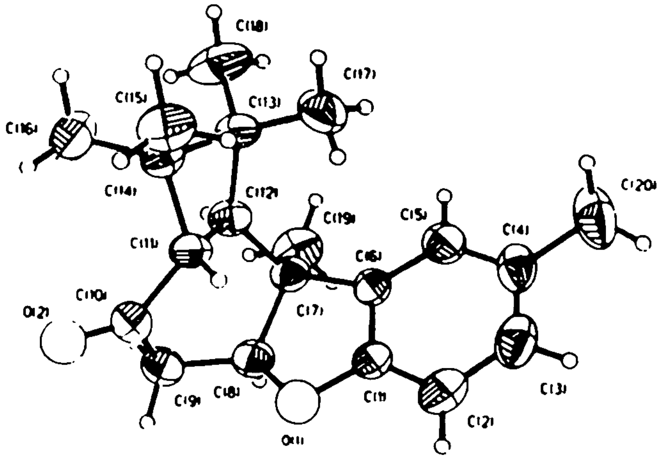


Figure 1. X-ray crystal structure of the cycloadduct **4**

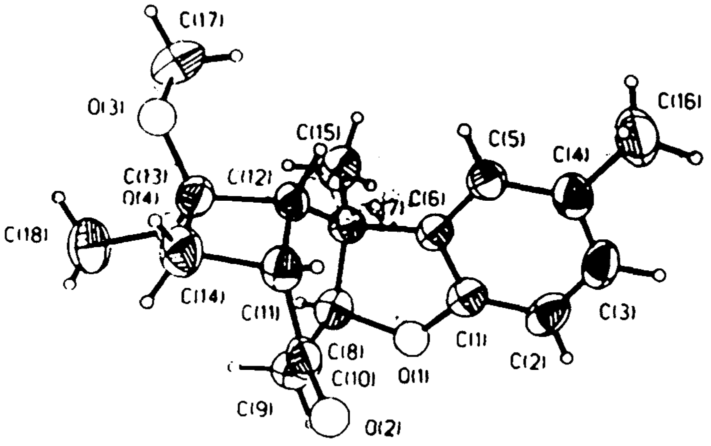


Figure 2. X-ray crystal structure of the cycloadduct **5**

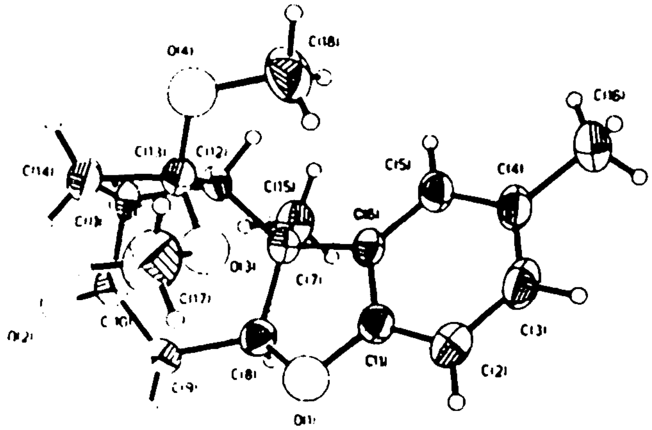


Figure 3. X-ray crystal structure of the cycloadduct **6**

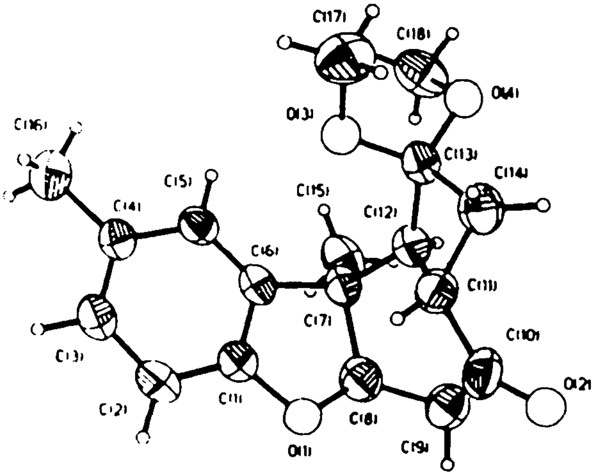
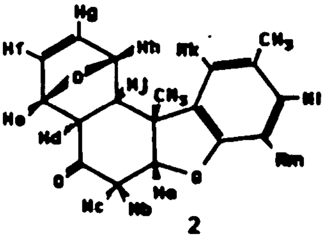


Figure 4. X-ray crystal structure of the cycloadduct **7**

Table 1. The ^{1}H-NMR Chemical Shifts (ppm) and Coupling Constants (Hz) in $CDCl_3$[a,b]



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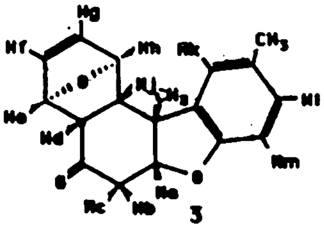

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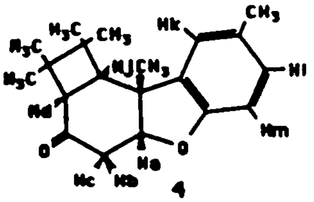

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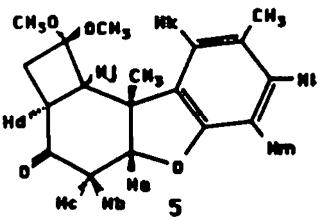

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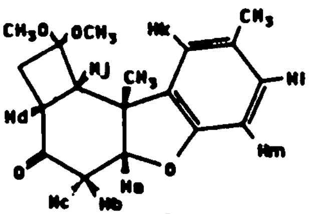

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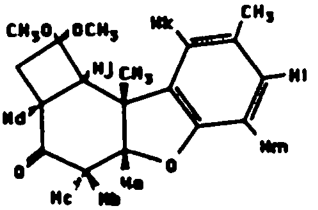

7

	2	3	4	5	6	7
H^a	4.68(dd) J=2.3 J=3.6	4.72(dd) J=2.1 J=3.6	4.49(t) J=2.9	4.96(dd) J=6.9 J=2.4	4.64(t) J=7.5	4.64(t) J=3
H^b	2.76(dd) J=18.9 J=3.6	2.57(dd) J=19.5 J=3.6	2.64(dd) J=18.3 J=2.7	2.42(dt) J=15 J=2.1	2.87- 2.95(m)	2.71(dd) J=18.6 J=3.1
H^c	2.88(dd) J=19.1 J=2.3	2.86(dd) J=18.9 J=2.1	2.74(dd) J=18.3 J=3	3.19- 3.26(m)	3.53(dd) J=13.8 J=7.2	2.84(dd) J=18.6 J=2.5
H^d	2.22(dd) J=11 J=3.3	2.51(dd) J=10 J=3.3	2.3(d) J=14.7	2.59- 2.68(m)	2.87- 2.95(m)	1.98(dd) J=11.7 J=9.6
H^j	1.81(d) J=11	1.61(d) J=10.5	2.1(d) J=14.7	3.29(d) J=9.6	3.05(d) J=9.6	2.45(d) J=9.6
H^e	5.02[c]	4.9[c]				
H^h	5.02[c]	4.95[c]				
H^g	5.79(dd) J=5.7 J=1.5	6.29(dd) J=5.7 J=1.5				
H^f	6.14(dd) J=5.7 J=1.8	6.6(dd) J=5.7 J=1.5				
H^k	6.75(s)	7.02(s) J=6	6.98(s)	6.83(s)	6.94(s)	7.11(s)
H^l	6.95(d) J=8.1	7.01(d) J=8.4	6.94(d) J=7.8	6.91(d) J=8.1	6.93(d) J=8.1	6.96(d) J=8.1
H^m	6.62(d) J=8.1	6.71(d) J=8.4	6.65(d) J=7.8	6.64(d) J=8.1	6.64(d) J=8.1	6.65(d) J=8.1
CH_2				2.26- 2.36(m)	2.3- 2.39(m)	2.22- 2.31(m)
OCH_3				3.22(s) 3.33(s)	2.73(s) 2.96(s)	2.97(s) 3.33(s)

Table 1 (continued)

CH_3			0.63(s) 0.81(s) 1.01(s) 1.02(s)			
$CH_3^{(ang)}$	1.61(s)	1.58(s)	1.47(s)	1.44(s)	1.32(s)	1.57(s)
$CH_3^{(aro)}$	2.3(s)	2.33(s)	2.29(s)	2.16(s)	2.25(s)	2.32(s)

[a] Peak multiplicities are represented by s(singlet), d(doublet), and t(triplet)

[b] All chemical shift assignments were confirmed by spin decoupling experiments.

[c] H^e and H^h appear as broad unresolved singlets; decoupling studies indicate coupling ($J \sim 1.5$ Hz) to neighboring vinyl H and coupling of H^e to H^d ($J \sim 3$ Hz) but not of H^j to H^h.

^{1}H-NMR studies of cycloadducts

In order to establish the stereochemistry of the isolated cycloadducts, their ^{1}H-NMR spectra were examined in detail to see if a correlation of coupling constants with stereochemistry would be apparent, especially for the two ring juncture protons H^d and H^j. The spectral assignments are given in Table 1. The spectra of the two stereoisomers **2** and **3** showed the following features: H^d (δ 2.22 and 2.51 in **2** and **3**, respectively) occurs at appreciably lower field than H^j (δ 1.81 and 1.61 in **2** and **3**, respectively) owing to the proximity of H^d to the carbonyl oxygen. The coupling constants between H^d and H^j were 11 and 10.5 Hz in **2** and **3**, respectively. The coupling constants between *trans* vicinal ring juncture protons in furan cycloadducts to benzo-2,4-cycloheptadienone were $J_{trans} = 6$ Hz;[6] corresponding *cis* coupling constants should be larger than this value.[7] The fact that in both **2** and **3** only one of the two ring junction protons (H^d) is additionally coupled to an adjacent bridghead proton ($J_{de} = 3.3$ Hz in **2** and **3**) is consistent with the *trans* relationship of protons H^d and H^j. If the ring-fusion in either adduct had been *cis*, the coupling of H^d and H^j to adjacent bridgehead protons would have been nearly the same. Proton H^d (exo*) in **3** occurs at lower field than H^d (endo*) in **2** due to the deshielding effect of the adjacent oxygen bridge, whereas the reverse is true for H^j. In addition, H^g and H^f appear at lower field in **3** than in **2**, which may be explained by the deshielding effect of the carbonyl oxygen, which is closer to these protons in **3** than in **2**; H^e and H^h also appear at slightly lower field in **2** than in **3**. These facts allow one to distinguish isomers **2** from **3**. Comparison with the spectra of the methanol adduct to PK[1] and other furan adducts[6,8,9] is consistent with this assignment.

For simple cyclobutane derivatives, coupling constants between *cis* vicinal protons are generally found to be larger than *trans* vicinal protons, $J_{cis} = 4.6 - 12$ Hz, $J_{trans} = 2.8 - 8.7$ Hz.[10] However, in 2,4-diazabicyclo[4.2.0]octa-3,4-diones J_{cis} is smaller than J_{trans}.[10] Examination of ^{1}H-NMR spectra of the [2 + 2] cycloadducts (Table 1) shows that the coupling constant J_{dj} in *cis*- fused (**5** and **6**) and *trans*- fused (**7**) cycloadducts is the same, namely 9.6 Hz. Thus, the assignment of *trans*/*cis* configuration purely on the basis of vicinal coupling constants would be very difficult if not impossible in these systems.

PHOTOPHYSICAL STUDIES

The quantum yields for the formation of the adducts **2** and **3** from PK (0.049 M) at 313 nm in furan solvent were 0.062 and 0.065, respectively. The formation

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*H^d and H[illegible] are designated as exo and endo depending on their relationship to the oxygen bridge.

of an intermediate with a lifetime of ca. 15 nsec with absorption centered at 270-277 nm was observed on laser flash photolysis of PK at 308 nm. By analogy with previous laser flash studies of cyclohexenones[11] and other cyclic enones,[12] this absorption is assigned to a highly twisted triplet excited state of PK.[4] Consistent with these findings is the fact that methylnaphthalene (MN) (E_T 61 kcal/mol) in concentrations up to 0.86 M (PK 0.013 M, furan 0.05 M) does not quench formation of **2** and **3**. However, the free radical tetramethyl-1-pyperidinyloxy (TEMPO) quenches formation of cycloadducts **2-5** and **7** to different extents (Table 2). Differential quenching of formation of cycloadduct **2**, **3** and **4** by oxygen was also observed. Competitive irradiation of acetonitrile solutions of **1** containing furan and varying amounts of TME and DME showed quenching by these alkenes of the formation of cycloadducts **2** and **3** (Table 2). This result suggests that a common precursor exists for both [4 + 2] and [2 + 2] cycloaddition processes.

Table 2. Stern-Volmer Quenching slopes in Acetonitrile[a]

QUENCHER	Adduct quenching slopes, $k_q\tau$, M^{-1} [b]				
	2	**3**	**4**	**5**	**7**
Tempo	12.5 ± 0.6	6.6 ± 3	36.3 ± 0.7	130 ± 1	57 ± 2
Oxygen	438.0 ± 8	132.0 ± 5	43 ± 1		
TME	2.2 ± 0.3	2.2 ± 0.3			
DME	0.7 ± 0.2				

[a] PK concentration = 0.02 M

[b] Least-squares fit to data

DISCUSSION

This study was initiated in hopes of obtaining experimental evidence for a photochemically-generated reactive transoid isomer of Pummerer's ketone **1**, which would be the first demonstrated "trans"-cyclohexenone. A number of trans-cyclohexenes have been generated photochemically,[13] beginning with acetylcyclo-

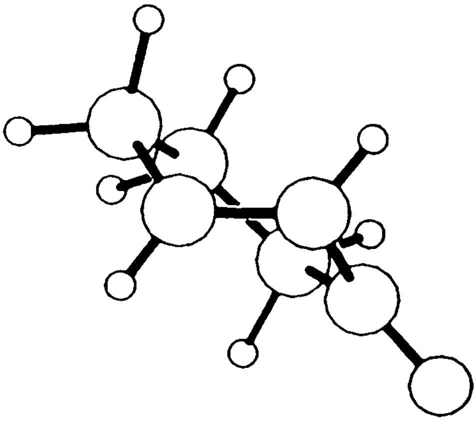
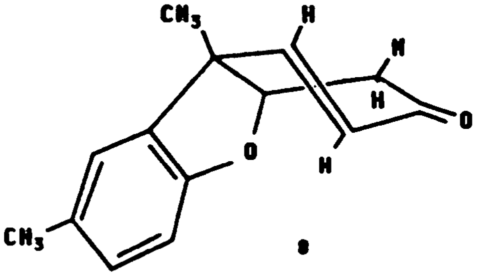


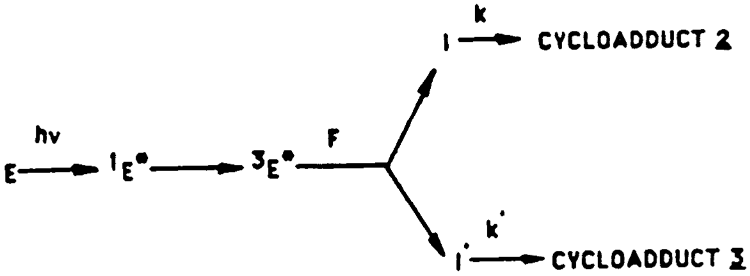
Figure 5. MNDO optimized structure for trans-cyclohexenone

hexene[14] and phenylcyclohexene,[15] but no ground state trans-cyclohexene with additional trigonal atoms in the 6-ring has been characterized. Independent unpublished theoretical calculations by Johnson[16] (using both MNDO and Dewar's new AM1 method[17]) and by Saunders[18] (using molecular mechanics) indicate that a trans isomer of cis-cyclohexenone (see Fig. 5) is in a minimum on the ground state potential surface *ca*. 60 kcal/mol above the cis isomer. However, the depth of this potential well, and most importantly the barrier for reversion of trans- to cis-cyclohexenone, is not available from these calculations. The experimental difference in the energies of cis- and trans-1-phenylcyclohexene from time-resolved photoacoustic calorimetric data is 44.7 ± 5.0 kcal/mole,[19] and the activation energy for isomerization of trans to cis in this case was found by Caldwell et al. to be 12.1 ± 0.12 kcal/mol,[20] which is in good agreement with activation energies determined by Bonneau for isomerization of a number of trans-cyclohexenes back to their more stable cis isomers.[13] Given the predicted higher energy of "trans"-cyclohexenone, which is close to the maximum on the ground state potential surface for cyclohexenes lacking an additional trigonal center,[13,20] the activation energy for thermal isomerization back to the cis isomer is expected to be considerably less than that observed for the trans-cyclohexenes studied to date. Thus, the potential minimum corresponding to "trans"-cyclohexenone may be so shallow that direct detection or isolation, even at low temperatures, may prove to be highly problematic.

We were therefore encouraged by the observation that irradiation of PK (1) in furan gave two trans-fused [4 + 2] adducts, in which addition of furan had clearly occurred on only one side of PK, consistent with addition to a twisted "trans" isomer of PK shown in structure 8. Note that this is not the structure invoked by Hart[1] to rationalize the course of photoaddition of MeOH to 1; in fact, structure 8 was considered to be of much higher energy than the alternative twist structure due to non-bonded interactions. However, Diels-Alder addition of furan to 8 should occur in a single concerted step, although the process may well be non-synchronous, that is, the two new sigma bonds may be formed to different extents at the transition state, according to Dewar's calculations and rate data.[21] Unless Diels-Alder additions to molecules such as 8 proceed in two stages via a discrete biradical *intermediate*, as distinguished from a transition state with biradical character,[21] interception by radical traps is not expected. Therefore, the observation that both TEMPO and oxygen differentially quench formation of [4 + 2] adducts 2 and 3 appears to be inconsistent with formation of these two adducts directly from 8. Rather, we prefer the alternative mechanism shown in Scheme 2, in which a twisted triplet excited state of 1 interacts directly with furan to give isomeric triplet biradical intermediates I and I' which, after an electron spin flip to



8



Scheme 2

give short-lived singlet biradicals, close to give 2 and 3, respectively. TEMPO and oxygen are expected to intercept I and I' to differing extents, according to the quenching constants $K_q = k_q \tau_{BR}$. The relatively small quantum yields are consistent with this mechanism, since reversion directly to ground state may occur from I and I' as well as the short-lived triplet of 1.

As for the [2 + 2] photocycloadditions of 1 to TME, it is not surprising that only a trans-fused adduct is formed (it is possible that cis-fused isomers are also formed in trace quantities) as the major if not exclusive adduct, since a similar observation was reported for photoaddition of TME to 4,4-dimethylcyclohexenone 9;[22] in more recent work,[23] a cis-fused adduct of TME to 9 has been isolated in small yields in certain solvents. This observation neither requires nor excludes a trans-cyclohexenone intermediate, since it can be rationalized in terms of preferred conformations of 1,4-biradical intermediates,[24] especially if formed from a highly twisted enone triplet excited state. Since laser flash data indicate neither DME or TME directly intercepts the triplet state of 9 (lifetime 25-40 ns in different solvents) which is the precursor to the cycloadducts, it is questionable whether TME or DME intercept the even shorter-lived triplet state of PK (1), given that second order rate constants for interaction of olefins and enone triplets in favorable cases are typically less than 10^7 M^{-1} s^{-1}.[25] The question can be directly answered by picosecond flash measurements.

Photocycloaddition of 1 to DME gives three [2 + 2] adducts, two cis-fused adducts (5 and 6) and one trans-fused adduct (7), whose structures were determined by x-ray crystallography. Base-catalyzed epimerization of 7 to 6 further demonstrates the stereochemical relationship of these adducts. As long ago as 1964, Corey and co-workers[5] observed formation of trans- as well as cis-fused photoadducts of cyclohexenones to alkenes; the assignment of stereochemistry has generally been made on the base of an epimerization experiment such as that mentioned above,[26] on the assumption that the thermodynamically more stable isomer has a cis ring fusion. In some cases, the assignment has been substantiated by synthetic elaboration to target molecules of known stereochemistry.[26] However, examination of models indicates that the trans-fused stereoisomer of the bicyclo[4.2.0]hexane ring system with diequatorial attachment of the cyclobutane ring may be thermodynamically more stable than the cis-fused (axial-equatorial) isomer in some cases. Thus, assignments of stereochemistry based solely upon epimerization experiments should be viewed with some skepticism.[27] Also, it is important to note that the cis-fused adducts 5 and 6 result from attack of DME on opposite faces of the reactive intermediate derived from 1, whether it be a triplet or a ground state "transoid" isomer.

CONCLUSION

Pummerer's ketone 1 undergoes [4 + 2] photocycloaddition to furan and [2 + 2] photocycloaddition to dimethoxyethylene and tetramethylethylene via a common intermediate, which is the short-lived twisted triplet excited state of 1. Trans-fused cycloadducts of both types are formed as major and sometimes exclusive products, consistent with a ground state trans-isomer of 1 as a reactive intermediate; however, such a mechanism is inconsistent with the observation of differential quenching of adduct formation by O_2 and TEMPO. It is proposed that these photocycloadditions occur stepwise via triplet biradical intermediates, which are formed directly from the twisted triplet excited state of 1.

EXPERIMENTAL SECTION

Melting points were determined on a Thomas-Hoover capillary melting point apparatus and were uncorrected. ^{1}H-NMR spectra were measured in $CDCl_3$ relative to tetramethylsilane as an internal standard on a GE-QE Nicolet 300 MHz FT-NMR spectrometer. Infrared spectra were measured on a Mattson Polaris FT-IR spectrophotometer. The spectra were recorded as solutions in carbon tetrachloride (Aldrich Spectrophotometric grade, gold label) in matched sodium chloride cells. Mass spectra were obtained with a Hewlett Packard model 5992 combined gas chromatography-mass spectrometer utilizing Hewlett Packard "peakfinder" software. A Hanovia Type L 450-W high pressure mercury lamp was used as a light source for preparative scale reactions. A Rayonet RPR 100 Photochemical Reactor (Southern New England Ultraviolet Company) equipped with a Rayonet MGR-100 merry-go-round apparatus and interchangeable ultraviolet lamps with maximum emission at 300 nm (30 nm halfwidth) was used for competitive quenching studies. Quantum yields were measured on a Photon Technology International-Amko Quantacount Apparatus. Preparative thin layer chromatography was carried out on a Chromatothron Model 7924 T (Harrison research, Palo Alto, California). Preparative plates (2 mm) were prepared using silica gel 60 P F_{254} with $CaSO_4$ 1/2 H_2O (EM Reagents, W. Germany).

Analyses by gas chromatography (GC) were made using a Hewlett-Packard model 5710 A gas chromatograph equipped with a model 3390 A integrator and 30 M x 0.25 mm Heliflex RSL-150 capillary column (Alltech). High performance liquid chromatography (HPLC) was carried out on Waters instrument Model 440 using a 25 cm x 4.6 mm econosil silica 10 column. Compound 1 was synthesized according to the procedure given in the literature[28] and purified by vacuum distillation, bp 135-140°/0.07 Torr, and repeated recrystallization of the solidified product after trituration with ether from ethanol.[29] White crystals, mp 123-4° (lit[28] mp 124°) were obtained.

Irradiation of Pummerer's Ketone 1 in Furan. A solution containing 0.526 g (0.0025 mole) of 1 in 50 mL of freshly distilled furan was degassed with argon and irradiated through a pyrex glass for 18 hours. GC analysis of the reaction product showed disappearance of initial PK. After evaporation of the furan, a crystalline product mixture was obtained which was purified by recrystallization from ethanol. The two stereoisomers, **2** and **3**, were isolated by preparative thin layer chromatography on a silica plate using methylene chloride - hexane in volume ratio 3:1 as the solvent. Recrystallization of the separated isomers from ethyl acetate : ethanol (1:5) gave colorless crystals: **2** (68%) mp 219-20°, and **3** (22%) mp 208-9°. For ^{1}H-NMR data see text and Table 1. Other spectral data for **2** are as follows. Mass spectrum, m/z (rel. intensity): 282 (31) M^+, 215 (16), 214 (94), 200 (14), 199 (100), 197 (16), 158 (8), 172 (12), 171 (31), 160 (10), 159 (48), 152 (8), 146 (37), 145 (56), 136 (54), 131 (9), 129 (10), 185 (25), 127 (9), 122 (9), 118 (19), 116 (11), 115 (37), 108 (10), 107 (22), 95 (8), 94 (17), 91 (24), 79 (11), 77 (20), 68 (16), 66 (12), 65 (22). **IR**: 1735 (C=O strech), 1720, 1700, 1650, 1560, 1540, 1505, 1480, 1455, 1220, 1030 and 980 cm^{-1}. For **3**: Mass spectrum, m/z (rel. intensity): 282 (28) M^+, 214 (92), 200 (18), 199 (100), 197 (16), 172 (17), 171 (40), 159 (50), 146 (35), 145 (55), 136 (58), 128 (33), 118 (19), 115 (36), 107 (22), 94 (21), 91 (32), 79 (15), 77 (27), 68 (25), 65 (25), 55 (20), 51 (19), 44 (33), 41 (17). **IR**: 1740 (C=O stretch), 1650, 1620, 1560, 1545, 1525, 1510, 1485, 1475, 1460, 1365, 1230, 1130 and 1030 cm^{-1}.

Formation of cycloadducts **2** and **3** was not observed upon heating 0.095 g (0.004 mole) of 1 in 7 mL of furan. The reaction was performed in a sealed ampoule at 150 - 155° for 48 hours.

Irradiation of 1 in Tetramethylethylene (TME). A solution containing 0.5 g (0.0024 mole) of 1 and 3.8 g (0.045 mole) of TME in 1 mL of acetonitrile was irradiated through Pyrex under argon for 136 hours. After removing the solvent by bubbling nitrogen through the solution, an oily product separated which crystallized from ethyl acetate-ethanol (1:5) at low temperature. Three recrystallizations from ethyl acetate-ethanol (1:5) gave colorless crystals, mp 145-146°. Adduct **4** (38 %) crystallized in the centrosymmetric, monoclinic space group P $2_1/c$ with unit cell parameters as follows: a = 13.120 (2), b = 7.110 (1), c = 18.5871 (4) Å. The final agreement factor was R = 0.066.[30] For ^{1}H-NMR data see text and Table 1. Mass spectrum m/z (rel. intensity): 298 (63) M^+, 200 (71), 185 (11), 181 (12), 160 (59), 159 (100), 146 (79), 145 (60), 139 (14), 123 (12), 117 (10), 115 (21), 111 (70), 110 (48), 97 (13), 95 (45), 91 (17), 83 (65), 79 (12), 77 (14), 69 (38), 67 (19), 55 (37), 44 (11), 43 (33), 41 (38). **IR**: 1730 (C=O stretch), 1700, 1560, 1540, 1485, 1460, 1245, 1225, 1030, 1010, 980 and 970 cm^{-1}.

Two additional adducts with M^+ m/z 298 (11 % and 14 %) were detected by GC - Mass spectrometry. These adducts were not isolated from the reaction mixture.

Irradiation of **1** in 1,1-Dimethoxyethylene (DME). A solution containing 0.483 g (0.0023 mole) of **1** and 3.69 g (0.0439 mole) of DME in 7 mL of acetonitrile was degassed with argon and irradiated through Pyrex for 43 hours. After removing the solvent by bubbling nitrogen through the solution, an oily residue formed which crystallized from ethyl acetate-ethanol (1:5) in the refrigerator. Three recrystallizations from ethyl acetate-ethanol (1:5) gave colourless crystals of **5** (38 %) m.p. 157°, which were suitable for X-ray analysis. Compound **5** crystallized in the centrosymmetric, monoclinic space group P $2_1/n$ with unit cell parameters as follows: a = 7.891 (3), b = 10.034 (5), c = 20.241 (9) Å. The final agreement factor was R = 0.0592.[29] For ^{1}H-NMR see text. Mass spectrum, m/z (rel. intensity): 302 (7) M^+, 217 (13), 215 (10), 214 (55), 200 (8), 199 (59), 197 (13), 185 (11), 172 (8), 171 (19), 160 (13), 159 (7), 158 (9), 157 (17), 156 (100), 146 (21), 145 (31), 143 (10), 142 (8), 141 (34), 131 (7), 129 (13), 128 (33), 127 (10), 126 (8), 125 (42), 117 (7), 116 (10), 115 (31), 109 (11), 105 (10), 101 (13), 97 (10), 91 (23), 89 (11), 88 (87), 83 (23), 81 (8), 79 (9), 77 (18), 75 (8), 69 (11), 68 (20), 65 (11), 59, (14), 58 (32), 55 (31), 53 (13), 51 (13), 44 (25), 43 (73), 42 (10), 41 (20). **IR**: 1710 (C=O stretch), 1480, 1450, 1365, 1310, 1250, 1180, 1150, 1120, 1030 and 960 cm^{-1}.

GC/MS analysis of the mother liquor showed the presence of **5** together with two additional isomers. Diastereomers **6** and **7** could not be separated by preparative thin layer chromatography on silica gel with ethyl acetate-methylene chloride-hexane (0.2 : 0.7 : 7), but partial enrichment of isomers could be achieved. Final purification was effected by HPLC of thus enriched mixture (ethyl acetate-hexane; 5 : 95) and recrystallization of the separated crystalline products from ethyl acetate-hexane (1 : 4) to give **6** (32 %) mp 137-8° and **7** (13 %) mp 124-5°. Compound **6** crystallized in the centrosymmetric, monoclinic space group C2/c with unit cell parameters as follows: a = 33.430 (6), b = 6.384 (1), c = 15.127 (2) Å. The final agreement factor was R = 0.050.[30] Spectral data for **6**: For ^{1}H-NMR data see text and Table 1. Mass spectrum, m/z (rel. intensity): 302 (16) M^+, 270 (14), 227 (9), 217 (22), 215 (20), 214 (100), 199 (62), 197 (13), 185 (9), 171 (17), 160(13), 159 (65), 146 (11), 145 (24), 141 (10), 128 (19), 115 (23), 91 (17), 89 (9), 88 (65), 84 (14), 83 (14), 77 (13), 68 (11), 58 (30), 55 (22), 44 (10), 43 (44), 41 (15). **IR**: 1720 (C=O stretch), 1490, 1460, 1260, 1220, 1160, 1120, 1045 and 990 cm^{-1}.

Compound **7** crystallized in the centrosymmetric, monoclinic space group P $2_1/c$ with unit cell parameters as follows: a = 14.513 (4), b = 7.427 (3), c = 15.318 (6) Å. The final agreement factor was R = 0.052.[30] Spectral data for **7**: For ^{1}H-NMR see text. Mass spectrum, m/z (rel. intensity): 302 (13) M^+ , 271 (8), 277 (10), 217 (34), 215 (18), 214 (89), 213 (17), 200 (11), 199 (73), 197 (15), 186 (8), 185 (17), 172 (9), 171 (19), 160 (9), 159 (70), 158 (7), 157 (15), 156 (100), 146 (17), 145 (26), 143 (10), 142 (8), 141 (27), 129 (11), 128 (21), 127 (8), 125 (34), 116 (8), 115 (28), 114 (8), 101 (9), 91 (15), 88 (38), 77 (10), 68 (8), 59 (9), 58 (13), 55 (15), 43 (28), 41 (9). **IR**: 1730 (C=O stretch), 1490, 1270, 1250, 1230, 1175, 1120, 1050 and 970 cm^{-1}.

Base catalysed isomerization of **7** to **6**. A solution of 3 mg of **7** containing 2 mL of approximately 15 % sodium methoxide solution in methanol was stirred overnight at room temperature. After removal of the methanol, the residue was dissolved in diethyl ether, washed with water, saturated with sodium chloride solution and dried. Removal of the solvent gave a solid whose G.C. retention time and ^{1}H NMR spectra were identical to those of isomer **6**.

Quantum yields measurements. The Quantacount apparatus (Photon Technology International) was initially calibrated and the system was balanced in the dark to zero with empty cell compartments. This procedure was repeated with two quartz cells containing furan as the solvent. The solution of PK (0.049 M) in furan (4 mL) was added to the UV cell, sealed with a rubber septum and copper wire, and then degassed with argon (oxygen free grade) for 10 min. This cell was placed in the sample compartment of the Quantacount apparatus (furan was used as a reference), and then was irradiated until 2% of the enone had been consumed. The amount of the adducts **2** and **3** formed was determined by GC using the method of standard additions[31] with the standard solution of **2** and **3** in furan respectively which were added after irradiation. Since two adducts are formed, which are well separated upon GC analysis, one of these adducts in each determination was used as an internal standard. The temperature program used in the GC analysis of adducts **2** and **3** was 200°, 0 min; 8°/min; 270°, 0 min. The number of Einsteins absorbed by the PK-furan solution was determined by multiplying the number of counts recorded on the Quantacount apparatus by the value obtained in the calibration experiment (1 count = 2.08×10^{-12} Einsteins). Quantum yields were calculated by dividing the number of moles of adducts formed by the number of Einsteins absorbed. Two measurements under identical irradiation conditions gave for quantum yield formation of **2** from PK at 313 nm in furan 0.060 and 0.063. The agreement between the set of two measurements for quantum yield formation of **3** from PK at 313 nm in furan was also satisfactory, yielding the values 0.060 and 0.070.

Quenching experiments. A stock solution of PK and furan or alkene in appropriate relative concentrations was prepared in acetonitrile. Stock solutions of the quencher (1-methylnaphtalene or TEMPO) in acetonitrile of various concentrations were also prepared. One milliliter of the PK-furan or PK-alkene stock solution was added to each of 6 pyrex test tubes, to which was added 1 mL of the quencher solution at various concentrations. After these solutions were degassed with argon, they were irradiated in the Rayonet Photochemical Reactor equipped with a merry-go-round apparatus for 3.5 hours. n-Pentadecane as an internal standard was added after irradiation to each test tube, and solutions were analyzed for adducts formed by GC. The temperature program used in the GC analysis of adducts was 200°, 0 min; 8°/min; 270°, 0 min.

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Supplementary Material Available.

X-ray crystallographic data: details of the structure determination, tables of atomic coordinates, bond lengths and angles, and anisotropic thermal parameters along with a computer generated plot with atom labels (73 pages).

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