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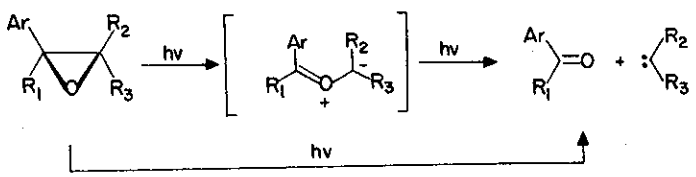
PHOTOCHEMISTRY OF BRIDGED STILBENE OXIDES

Kazuyoshi Nishiyama, Kiyoyasu Ishikawa, Ila Sarkar, David C. Lankin, and Gary W. Griffin*

Department of Chemistry, University of New Orleans, New Orleans, Louisiana 70122

The photochemistry of a pair of stilbene oxides in which the 2,3-positions are bridged by three and four methylene groups has been studied and compared with a lower homolog. Evidence is provided that cyclic ylides are produced upon photolysis of these oxiranes in solution at 254 nm. The primary photoproducts derived from the ylides in turn are β-styrylpropio- and β-styrylbutyrophenones, respectively. In the latter case Norrish type II cleavage then occurs to give as final products, 1-phenylbutadiene and acetophenone. The bridged oxiranes were shown to be more photostable than their open chain analogs and on the basis of double irradiation experiments it was established that a carbene rather than a conventional diradical process is operative or competes in the ylide photocleavage and ketone formation.

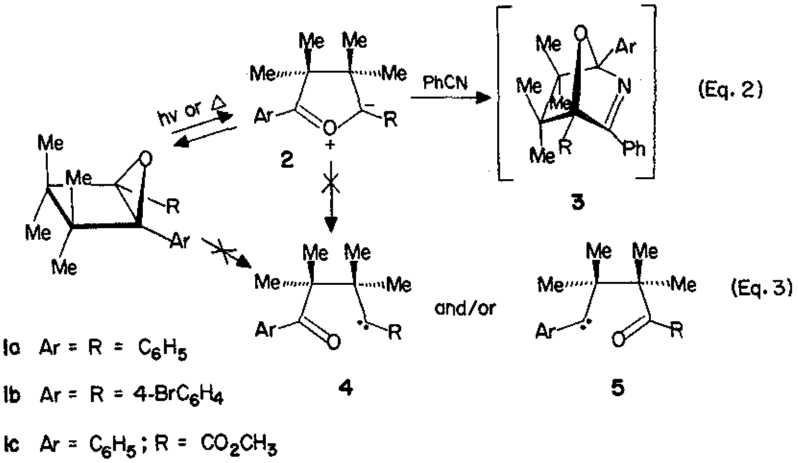
The photochemistry of aryl (1) and arene oxides (2) has been the subject of extensive study in our laboratories. Among common reactions of the former are [3→2+1]cycloeliminations to give carbonyl compounds and carbenes (1a-c) presumably through carbonyl ylides which have been intercepted in several cases with alkenes (1c-e, 1g-h) and nucleophiles (1d) (Eq. 1). Recently, we have observed that epoxydiphenylmaleic anhydride,



(Eq. 1)

which forms a remarkably stable cyclic ylide, does not photofragment in the conventional manner (1f). In contrast carbon dioxide is lost upon photolysis in solution (25°) and, unlike the closely related dicarboxy- or dicarbomethoxystilbene oxide analogs, no carbenes are detected as primary photoproducts (3,4). This observation rekindled our interest in the photochemical behavior of bridged stilbene oxides and we wish to summarize our previously unpublished as well as supplementary work in this area.

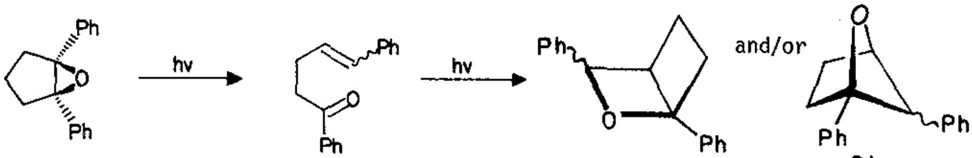
While our investigations in this area were in progress it was established that the bridged oxides 1,4-diphenyl-2,2,3,3-tetramethyl-5-oxabicyclo-[2.1.0]pentane (1a) (as well as the 4,4'-dibromodiphenyl analog 1b) and the related monoaryl glycidic ester 1c undergo thermolysis to give stable ylides 2 which, at least in the case of 1a and 1c, may be trapped by dipolarophiles *including benzonitrile which gives the unstable adducts 3 (Eq. 2)* which in turn undergo retrograde cleavage to oxazoles and 2,3-dimethyl-2-butene (5).



While ylide formation is also observed upon photolysis of 1a-c (254 nm)no evidence for photocleavage of the oxiranes 1 or ylides 2 to give ketocarbenes 4 and/or 5 is presented. In fact, reportedly, the oxide 1a is remarkably stable. Repetitive cycles of thermolysis (or photolysis) and constrained recyclization in the disrotatory fashion (dictated by steric factors) leads only to limited decomposition (5,6).

Although the photostability of the higher homologs of 1a, namely 6 and 7 exceeds that of *cis*-dimethylstilbene oxide (1j), which photolyzes to an acyclic ylide (*vide infra*), the dramatic photostability attributed to 1a is absent although in both cases photochromic behavior is observed at 77°K. Typically a benzene solution (0.1 *M*) of the oxide 6 (mp 104°C) (7) prepared by peracetic acid oxidation of 1,2-diphenylcyclopentene was irradiated

(254 nm)(8) in a quartz vessel for 5 h. The major products formed and isolated by preparative glc were identified as *cis*- and *trans*-1,5-diphenyl-4-penten-1-one (8a and 8b, 2:1, respectively) (Eq. 4). The identity of 8b [nmr CCl_4) τ 2.0-2.8 (m, aromatic and vinyl protons), 3.75 (t, vinyl protons), and 6.8-7.5 (m, methylene protons)]was confirmed by comparison of spectral data with that of an authentic sample (mp 58-59°C) prepared in an alternate fashion (9).

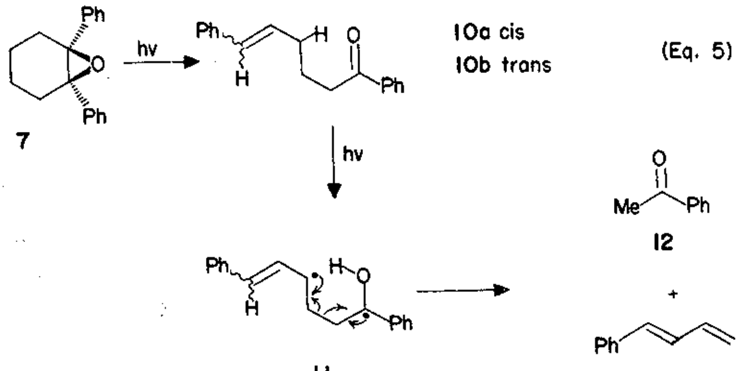


6   8a cis / 8b trans   9a   9b

(Eq. 4)

In addition, ozonolysis of 8a [nmr (CCl_4) τ 2.0-2.7 (m, aromatic protons), 3.58 (d, vinyl protons), 4.1-4.6 (m, vinyl protons), 7.0-7.4 (m, methylene protons)] and subsequent sequential treatment of the products with hydrogen peroxide and diazomethane gave as expected, dimethyl succinate and methyl 3-benzoylpropionate. Finally, the thermodynamically less stable cis isomer 8a was converted, as expected, to the trans isomer 8b upon treatment with iodine in benzene at the reflux temperature (80°C). A minor (> 1%) crystalline photoproduct (mp 280°C) is formed upon prolonged irradiation of 6 (26 h) which was assigned structure 9a or 9b on the basis of ultraviolet and infrared spectral as well as combustion analytical data (10,11). That the thermodynamically less stable isomer 8a is the predominant photoproduct may only reflect the fact that secondary photoequilibration of the primary products is relatively rapid. This contention is supported by the observation that direct irradiation of a benzene solution of 8b under conditions simulating those employed with 6 gives rise to the same product mixture of 8a and 8b (2:1, respectively).

Photolysis (254 nm) (8) of the oxide 7 (mp 77-78°C) prepared by peracetic acid oxidation of 1,2-diphenylcyclohexene (12), under conditions identical to those employed for preparation of 6, gives four products (10a, 10b, 12, and 13), which were separated and isolated by preparative glc (Eqs.5 and 6). In addition to the isomeric unsaturated ketones 10a and 10b [10a, nmr (CCl_4) τ 2.5-2.7 (m, aromatic and vinyl protons), 3.69 (t, vinyl protons) and 7.0-8.0 (m, methylene protons)] the secondary photoproducts acetophenone (12) and *trans*-1-phenylbutadiene (13) prepared independently (14) are also formed and were identified by comparison with authentic samples. It is reasonable to assume that these products arise by Norrish Type II cleavage *via* the

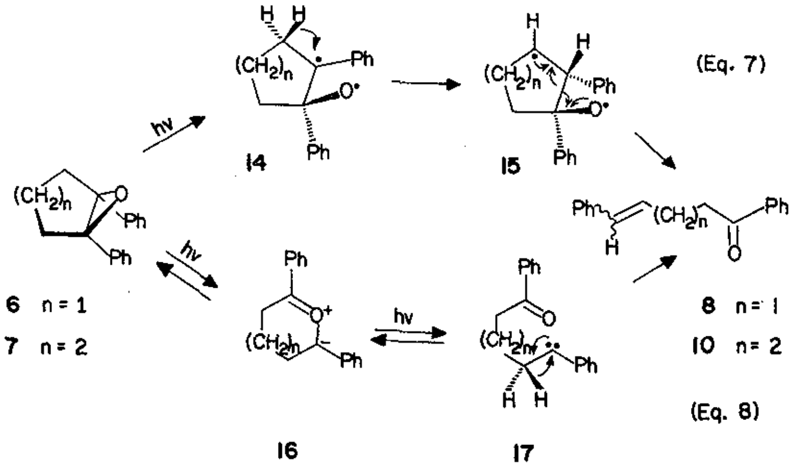


7 10a cis 10b trans (Eq. 5)

11 12 13 (Eq. 6)

diradical intermediate 11, derived from 10a and/or 10b, which have allylic gamma hydrogens (Eq.6) (15). In the case of 8a and 8b much less reactive vinylic hydrogens appear at the γ-position and only a trace of the fragmentation product 12 was detected by glc.

A priori at least two viable mechanisms may be invoked to rationalize the conversion of 6 and 7 to the isomeric pairs of unsaturated ketones 8 and 10, respectively. Extensive precedent may be found in the literature (2d) (16) for C-O bond photolysis to give diradical(s) such as 14. 1,2-Migration is also recognized as a reaction characteristic of excited state processes (17a) if not their ground state counterparts (17b) and in the case of 14 would afford the 1,4-diradical 15 which in turn would undergo fragmentation to the observed products 8 and 10 (Eq. 7). This mechanism, it is true, suffers from the disadvantage that a less stable diradical 15 must be formed from 14 although the intramolecular transfer of hydrogen from even methyl substituents is a well-documented photoreaction first recognized in our laboratories (17a).



An alternative mechanistic pathway in which the photogenerated carbonyl ylides 16 are implicated may be operative. Subsequent photocleavage to the ketocarbene 17 (1c) followed by 1,2-hydrogen migration (17) (Eq. 8) would also account for the observed conversion. If, in fact, the ylide mechanism is operative (despite our inability to observe luminescence and epr spectra anticipated for 17), then enhancement of the conversion should be observed upon simultaneous irradiation of 6 and 7 with radiation in the visible and ultraviolet regions [i.e., through double irradiation studies (1c) *vide infra*]. This assertion is dependent upon the validity of our contention that the ylide 16 will absorb in the visible and the reasonable assumption while the 1,4-diradical 15 should be transparent in this spectral region. A comparison of the absorption spectral data for the intermediates (presumed to be carbonyl ylides) (1) formed upon irradiation of 6 and 7 with those formed from *cis*-dimethylstilbene oxide are presented in Table 1 and attest to the fact that bridging does not greatly affect the nature of the intermediate.

Table 1

Spectral Properties of the Species Generated Upon Photolysis of the Oxides 6 and 7[a)]

	λ_{max}	405,	456,	528
 6	λ_{max}	399,	418 (shoulder)	525
 7	λ_{max}	405,	457	537

[a)]Photolyses (254 nm) (8) were conducted in 2-methyltetrahydrofuran at 77°K.

That the proposed ylides 16 are formed upon photolysis of oxides 6 and 7 was confirmed by interception to give the expected cycloadducts 18, 19, 20, and 21 among the photoproducts obtained from 6 and 7 using the dipolarophiles fumaronitrile (Eqs. 9 and 10) and maleonitrile in acetonitrile. The results of the photocycloaddition of 6 and 7 to fumaro- and maleonitrile are presented in Table 2. Structures 18 and 20 may be assigned to the major photoadducts obtained from fumaronitrile and the oxides 6 and 7, respectively. On the other hand, while the

Table 2

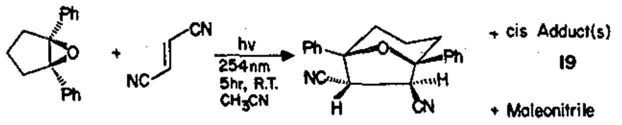
Cycloadducts Obtained from 6 and 7 and Maleo- and Fumaronitrile

Oxide	Dipolarophile	% Cycloadduct[a,b]			
		18	20	19	21
6	Fumaronitrile	40.5		4.7	
	Maleonitrile	5.6		33.0	
7	Fumaronitrile		38.1		4.5
	Maleonitrile		9.1		34.3

[a)]Irradiation (254 nm) (8) for 5 h at 40° in acetonitrile as a solvent.

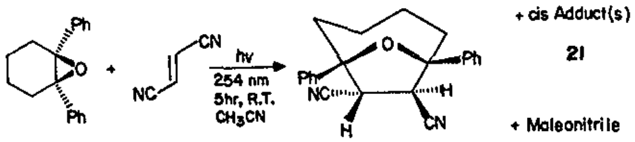
[b)]The values reported were determined by actual isolation using thick-layer and column chromatographic techniques.

cis adducts 19 and 21, like the trans adducts 18 and 20, have been characterized spectroscopically (Table 3), the structures of the former pair remain to be elucidated. Clearly, however, the stereospecificity of the cycloaddition



6 18 (Eq. 9)

reactions of 6 and 7 is high although precisely how high must yet be established and is complicated by competitive photoisomerization of the dipolarophile. *Furthermore, it should not be overlooked that these cycloaddition* reactions, although photoinitiated, generally occur in the ground state (1c-h).



7 20 (Eq. 10)

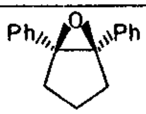
The utility of frontier orbital theory in selecting the most favorable dipolarophiles (electron-rich or electron-poor) should be noted. On the basis of frontier orbital energies, Houk (18) suggested that ylides substituted with alkyl or conjugating substituents should react readily with electron-deficient dipolarophiles and less readily or not at all with electron-rich adducts. The reaction of electron-deficient dipolarophiles with carbonyl ylides of the conjugated type 16 described herein are classified as *HOMO* controlled; i.e., the lowest unoccupied orbitals of the dipolarophiles interact with the highest occupied orbitals (HOMO) of the ylide. Our inability as well as that of others (1g) to detect adducts of 6 with those of electron-rich dipolarophiles and *cis*- and *trans*-butene-2 supports the predictions.

Table 3
Spectral Data and Physical Properties of Adducts from 18 - 21

Adduct	mp	
18 (trans)	178°C	Mass Spectrum M^+ 314 IR (Nujol) 2250 cm^{-1}(-CN) NMR ($CDCl_3$) τ 2.2-2.8 (m, aromatic, protons) 6.37 (q, methine protons), 7.2-8.4 (m, methylene protons)
19 (cis)	176°C	Mass Spectrum M^+ 314 IR (Nujol) 2240 cm^{-1} (-CN) NMR ($CDCl_3$) τ 2.2-2.8 (m, aromatic, protons) 6.46 (s, methine protons), 7.2-8.4 (m, methylene protons)
20 (trans)	182°C	Mass Spectrum M^+ 328 IR (Nujol) 2245 cm^{-1} (-CN) NMR ($CDCl_3$) τ 2.2-2.8 (m, aromatic protons) 6.27 (q, methine protons), 7.1-8.4 (m, methylene protons)
21 (cis)	183°C	Mass Spectrum M^+ 328 IR (Nujol) 2245 cm^{-1} (-CN) NMR ($CDCl_3$) τ 2.4-2.8 (m, aromatic protons) 6.23 (s, methine protons), 6.9-8.3 (m, methylene protons

While spectral and chemical evidence has been provided for the generation of the cyclic carbonyl ylides 16 under photolytic conditions where conversion of 6 and 7 to 8 and 10, respectively, occurs, additional evidence is required to confirm that the ylides are indeed intermediates. To this end a comparison of the stabilities of 6 and 7 relative to that of *cis*-dimethylstilbene oxide was conducted (Table 4).

Table 4
The Photostability of the Oxides 6 and 7 Relative to that of *cis*-Dimethyl-Stilbene Oxide

Oxide	Reaction Time (h)	% Recovery of Starting Material[a]
	1	72
	3	41
 6	1	80
	3	61
 7	1	84
	3	68

[a]Irradiations (254 nm) (8) were conducted under similar conditions (40°) in cyclohexane as a solvent and the residual oxide was isolated by tlc.

Inspection of the data shown in Table 4 indicates that the cyclic ylides 16 are indeed somewhat more stable under the conditions utilized than the corresponding open chain ylide derived from *cis*-dimethylstilbene oxide; however the marked photostability reported for 1a (5a) is not an intrinsic property of the next higher homologs 6 and 7. The significant feature, however, is that simultaneous irradiation with visible light (double irradiation)accelerates the conversion of starting material in the case of 6 and 7. For example, when the substrate 7 was subjected to double irradiation (1c) only 34% was recovered relative to 44% upon direct irradiation for 3 h (40°) in cyclohexane. This result supports the contention that the conversion of 6 and 7 to 8 and 10 may occur at least in part, according to the ketocarbene mechanism depicted in Eq. 8.

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