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Photochemical Decarbonylation of 2,2,4,4-Tetramethyl-6-oxabicyclo[3.1.0]hexan-3-one: An Entry into the Diradical Manifold of the Novel 3-Oxa-di-π-methane Rearrangement

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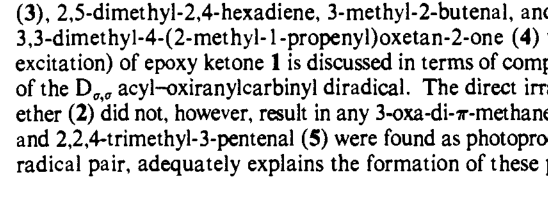
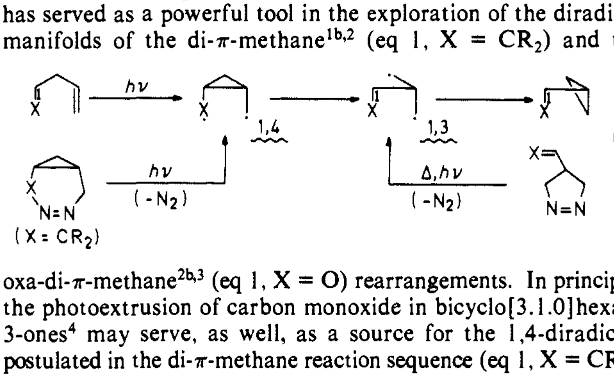
Abstract: The photochemical decarbonylation of 2,2,4,4-tetramethyl-6-oxabicyclo[3.1.0]hexan-3-one (**1**) provided a convenient entry into the diradical manifold of the novel 3-oxa-di-π-methane rearrangement. Besides the expected 3-ODPM product 2,5-dimethyl-4,5-epoxy-2-hexene (**6**), other photoproducts were bis(2-methyl-1-propenyl) ether (**2**), 2,5-dimethyl-4-hexen-3-one (**3**), 2,5-dimethyl-2,4-hexadiene, 3-methyl-2-butenal, and dimethylketene. The intermediacy of the thermally labile β-lactone 3,3-dimethyl-4-(2-methyl-1-propenyl)oxetan-2-one (**4**) was established spectroscopically. The novel photochemistry (n,π*-excitation) of epoxy ketone **1** is discussed in terms of competing $D_{\sigma,\sigma}$ vs. $D_{\sigma,\pi}$ diradical formation and subsequent decarbonylation of the $D_{\sigma,\sigma}$ acyl–oxiranylcarbinyl diradical. The direct irradiation of the 3-oxa-di-π-methane substrate bis(2-methyl-1-propenyl) ether (**2**) did not, however, result in any 3-oxa-di-π-methane reaction. 2,2,3,3-Tetramethylbutanedial, isobutyraldehyde, isobutylene, and 2,2,4-trimethyl-3-pentenal (**5**) were found as photoproducts. Initial carbon–oxygen bond cleavage, leading to a vinyl–vinyloxy radical pair, adequately explains the formation of these products. These results are rationalized in terms of Salem diagrams.

Thermal and photochemical extrusion of small, stable fragments from suitable substrates has widely been used for the generation of diradicals.[1] Especially the denitrogenation of azo compounds has served as a powerful tool in the exploration of the diradical manifolds of the di-π-methane[1b,2] (eq 1, X = CR_2) and the oxa-di-π-methane[2b,3] (eq 1, X = O) rearrangements. In principle, the photoextrusion of carbon monoxide in bicyclo[3.1.0]hexan-3-ones[4] may serve, as well, as a source for the 1,4-diradicals postulated in the di-π-methane reaction sequence (eq 1, X = CR_2). For this purpose it is essential that radical stabilizing substituents in the α-positions of the ketone are introduced to lower the activation energy[5] for decarbonylation of the initially formed acyl–cyclopropylcarbinyl diradical. In that case the formation of the cyclopropyldicarbinyl diradical can efficiently compete with the concurrent opening of the three-membered ring (eq 2).[4,5]

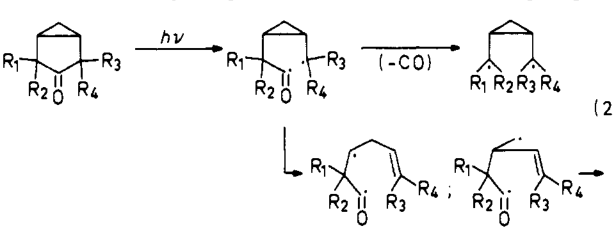


(1)



(2)

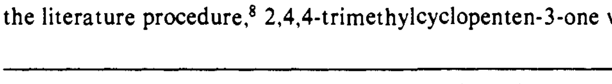
Since the literature apparently does not provide any examples of a 3-oxa-di-π-methane rearrangement, i.e., the photolysis of a divinyl ether affording a vinyloxirane (eq 3),[6] we found it worthwhile to synthesize the hitherto unknown 2,2,4,4-tetramethyl-6-oxabicyclo[3.1.0]hexan-3-one (**1**) and to examine its photochemistry in the interest of providing an entry into the diradical manifold of the hitherto unobserved 3-oxa-di-π-methane reaction (eq 3). In this context it was essential to investigate the photochemistry of the bis(2-methyl-1-propenyl)ether[7a] (**2**) as the potential 3-oxa-di-π-methane substrate.



(3)

Results

Synthesis of Substrates. 2,2,4,4-Tetramethyl-6-oxabicyclo[3.1.0]hexan-3-one (**1**) was prepared by epoxidation of 3,3,5,5-tetramethylcyclopentenone.[7b] The latter ketone was obtained by methylation of 2,4,4-trimethylcyclopenten-3-one[8] (eq 4). Unlike the literature procedure,[8] 2,4,4-trimethylcyclopenten-3-one was



(4)

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(1) (a) Dervan, P. B.; Dougherty, D. A. In *Diradicals*; Broden, W. T., Ed.; Wiley: New York, 1982; p 107. (b) Givens, R. S. In *Organic Photochemistry*; Padwa, A., Ed.; Marcel Dekker: New York, 1981; Vol. 5, p 227.

(2) (a) Zimmerman, H. E.; Boettcher, R. J.; Buehler, N. E.; Keck, G. E.; Steinmetz, M. G. *J. Am. Chem. Soc.* **1976**, *98*, 7680. (b) Adam, W.; Carballeira, N.; De Lucchi, O.; Hill, K. In *Stereochemistry and Reactivity of Systems Containing π-Electrons*; Watson, W. H., Ed.; Verlag Chemie International: Deerfield Beach, FL, 1983; p 241. (c) Zimmerman, H. E. In *Rearrangements in Ground and Excited States*; de Mayo, P., Ed.; Academic: New York, 1980; Vol. 3, p 131.

(3) (a) Adam, W.; De Lucchi, O.; Hill, K. *J. Am. Chem. Soc.* **1982**, *104*, 2934. (b) Adam, W.; De Lucchi, O.; Hill, K.; Peters, E.-M.; Peters, K.; von Schnering, H. G. *Chem. Ber.* **1985**, *118*, 3070. (c) Schuster, D. I. In *Rearrangements in Found and Excited States*; de Mayo, P., Ed.; Academic: New York, 1980; Vol. 3, p 255.

(4) Mariano, P. S.; Bay, E.; Watson, D. G.; Rose, T.; Bracken, C. *J. Org. Chem.* **1980**, *45*, 1753.

(5) Weiss, D. S. In *Organic Photochemistry*; Padwa, A., Ed.; Marcel Dekker: New York, 1981; Vol. 5, p 347.

(6) To distinguish between the various heterosubstituted di-π-methane rearrangements, we suggest to use the usual IUPAC rule for specifying the replaced carbon atom by the appropriate numeric prefix; e.g., the common oxa-di-π-methane rearrangement (ODPM) would herewith be called the 1-ODPM and the present case the 3-ODPM. This nomenclature replaces the previously defined oxy-di-π-methane designation for the present 3-ODPM rearrangement (cf.: Adam, W.; Berkessel, A.; Krimm, S. *Tetrahedron Lett.* **1985**, *26*, 619).

(7) (a) Gillis, B. T.; Schimmel, K. F. *J. Org. Chem.* **1960**, *25*, 2187. (b) Cullen, E. R.; Guziec, F. S., Jr.; Murphy, C. J. *J. Org. Chem.* **1982**, *47*, 3563.

(8) Edwards, O. E.; Lesage, M. *Can. J. Chem.* **1963**, *41*, 1592.

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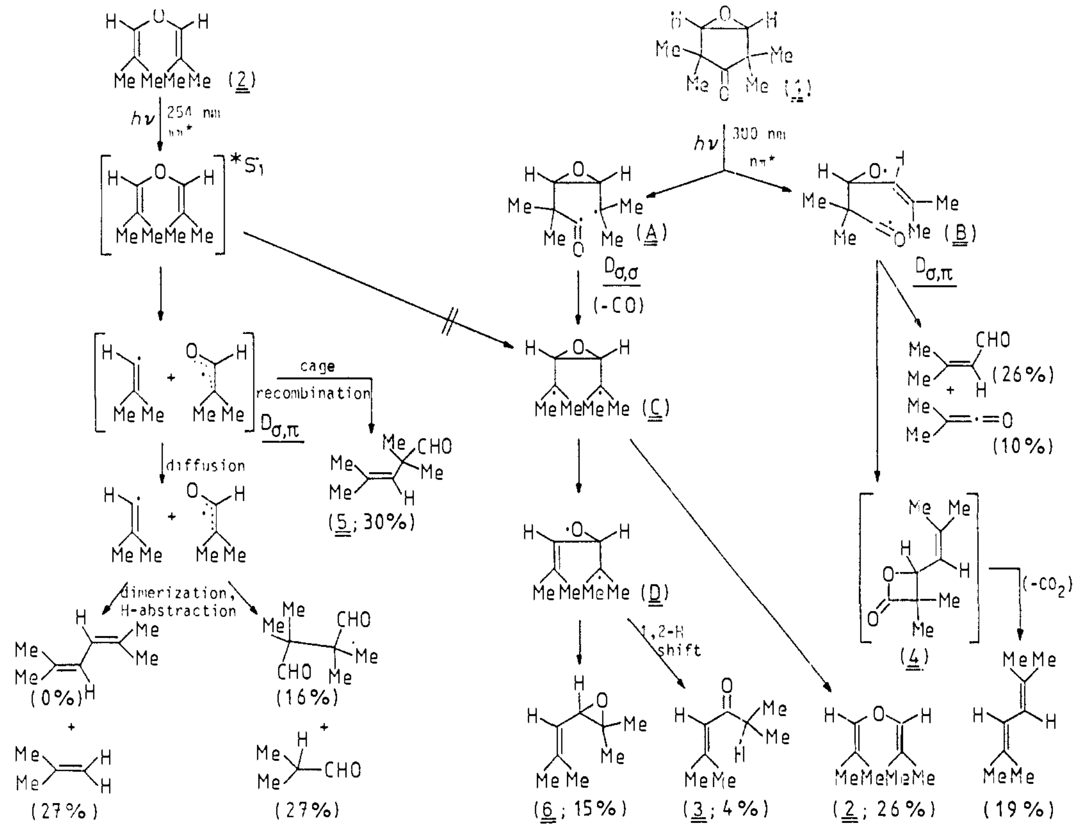
Scheme I



prepared by α-bromination, followed by dehydrobromination of the readily available 2,2,5-trimethylcyclopentanone.[9] For characterization purposes, a sample of 3,3,5,5-tetramethylcyclopentenone was converted to its 2,4-dinitrophenylhydrazone. Lithium diisopropylamide (LDA) catalyzed aldol condensation of methyl isopropyl ketone with acetone and subsequent iodine-catalyzed dehydration afforded 2,5-dimethyl-4-hexen-3-one[10] (**3**).

Photolyses. Irradiation of epoxy ketone **1** at 300 nm in *n*-pentane afforded the products shown in Scheme I. The relative yields are given in parentheses. The product balance was at least 90%. The qualitative identification of the photoproducts was achieved by comparison of capillary GC retention times and mass spectra (GC/MS) with the authentic substances. The quantitative determination of the product yields was carried out by means of capillary GC calibration with 1-hexanol as internal standard. Dimethylketene was identified in the form of *n*-hexyl isobutyrate, i.e., its adduct with 1-hexanol. The intermediacy of β-lactone **4** rests on spectral evidence (cf. Experimental Section); here it is sufficient to mention that its characteristic carbonyl band at 1832 cm^{-1} is clearly visible in the IR spectrum.

The photostability of all photoproducts in the photolysate of the epoxy ketone **1** was established by both the shape of their concentration vs. time profiles and independent irradiation of authentic samples in the presence of starting epoxy ketone **1** under the corresponding photolysis conditions.

The quantum yield of substrate consumption (ϕ_{-S}) in the photolysis of the epoxy ketone **1** was measured by comparison of its decay rate with that of cyclopentanone[11] under identical irradiation conditions. ϕ_{-S} was found to be 0.29 ± 0.03 for the epoxy ketone **1**.

The direct irradiation of the divinyl ether **2** in acetonitrile at 254 nm afforded the products shown in Scheme I. Relative yields are given in parentheses. In this photolysis only a moderate product balance (54%) could be achieved. Except for the 2,2,3,3-tetramethylbutanedial, which was isolated by preparative GC and identified by comparison of its ^{1}H NMR and IR spectra with literature data,[12] the identity of all photoproducts was established by capillary GC coinjections with authentic samples and by comparison of the ^{1}H NMR spectra of the photolysate with those of the authentic substances.

Control experiments showed that isobutylene, isobutyraldehyde, and 2,2,3,3-tetramethylbutanedial[12] were photostable during the photolysis in the photolysate of divinyl ether **2** under corresponding conditions. However, 2,2,4-trimethyl-3-pentenal[13] (**5**) underwent considerable secondary photolysis[14] to give 2,4-dimethyl-2-pentene also in the presence of excess divinyl ether **2**.

Upon prolonged irradiation, slow photodecomposition of isobutyraldehyde could be observed as well.

Co-injections with authentic materials clearly showed the absence of 2,5-dimethyl-2,4-hexadiene, 2,5-dimethyl-4,5-epoxy-2-hexene[15] (**6**), and 2,5-dimethyl-4-hexen-3-one[10] (**3**) among the photoproducts of divinyl ether **2**. To provide unequivocal evidence that ene epoxide **6** was not formed in the photolyses of divinyl ether **2**, the authentic **6** was photolyzed and the photolysate coinjected with that of divinyl ether **2**. Again no decomposition products of the expected 3-oxa-di-π-methane product **6** could be found in the photolysate of the divinyl ether **2**. Furthermore, the absence of 3,5-dimethyl-4-hexen-2-one, the isomer produced in the acetone-sensitized photolysis of ene epoxide **6**,[16] was established by GC coinjection of an authentic sample with the photolysate of divinyl ether **2**.

Acetone sensitization of the divinyl ether **2** did not yield any of the products observed upon direct irradiation. The slow consumption of the substrate led to higher molecular weight products.

Discussion

From the results of the photolysis of bis(2-methyl-1-propenyl) ether (**2**) it is evident that this divinyl ether does not represent

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[10] Balaban, A. T.; Nenitzescu, C. D. *Ann. Chem.* **1959**, *625*, 74.

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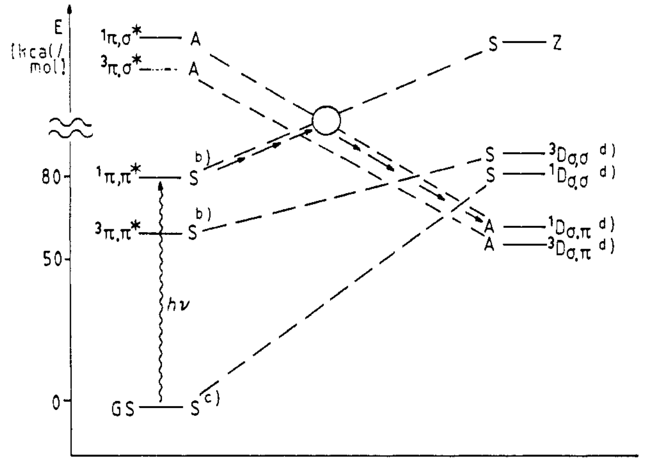
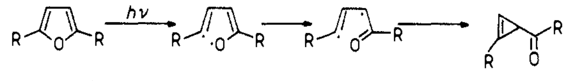


Figure 1. State correlation diagram for the photochemical homolysis of divinyl ether. The higher energy nπ*-states were not included since they correlate with higher excited states of the products.[20] (b) Excited state energies of 1,3-butadiene were used.[22] (c) $\Delta H^\circ_f = -3$ kcal/mol for the unsubstituted divinyl ether.[23] (d) The energies of these diradical states were estimated by taking a vinyl C–O bond energy of 85 kcal/mol[24] and 22 kcal/mol for the energy gap between the $D_{\sigma,\sigma}$ and the $D_{\sigma,\pi}$ states.[25]

a suitable substrate for the desired 3-oxa-di-π-methane rearrangement (eq 3). Whereas triplet sensitization by acetone of the divinyl ether **2** is ineffective, its photoreactivity upon direct irradiation can be explained by assuming the formation of a vinyl–vinyloxy radical pair as the primary product (Scheme I). Since for the unsubstituted vinyloxy radical the odd electron is mainly located at the carbon rather than at the oxygen atom,[17] it is not surprising that cage recombination of the initially formed vinyl–vinyloxy radical pair gives rise to the β,γ-unsaturated aldehyde **5** as the main product. In the case of the related bis(2,2-diphenylvinyl) ether,[18] analogous enal **5** formation could unambiguously be attributed to cage recombination by means of CIDNP and crossover experiments.

Diffusion out of the cage affords the free dimethylvinyl and vinyloxy radicals, which then display normal free-radical chemistry such as dimerization or hydrogen abstraction from the solvent. The absence of 2,5-dimethyl-2,4-hexadiene as the dimerization product of the dimethylvinyl radical is presumably due to facile abstraction of the allylic hydrogens from the starting material.

The legitimate question arises at this point: why does the divinyl ether **2** prefer to fragment a rather stable carbon–oxygen bond to give a vinyl–vinyloxy radical pair rather than to undergo the expected 3-oxa-di-π-methane rearrangement? Photoelectron spectroscopy provided some insight into this perplexing mechanistic problem. Since on the basis of the photoelectron spectrum of divinyl ether **2** it was concluded[19] that the lowest excitation is of the π,π*-type, expectedly its photochemistry should more closely resemble that of furans (eq 5). For the latter it has been shown[20]



(5)

that π,π*-excitation results in rearrangement to the isomeric cyclopropene via an initially formed vinyl–vinyloxy diradical. Therefore, the qualitative state correlation diagram, also known as a Salem diagram,[21] for the primary photoreaction of furan[20] should be useful in rationalizing the observed photochemistry of the divinyl ether **2** (Figure 1). In Salem's terminology this C–O bond fission constitutes a tritopic process[21] since it may generate either a $D_{\sigma,\sigma}$ or a $D_{\sigma,\pi}$ radical pair. In other words, the vinyloxy radical may be formed either as a σ- or as a π-radical.

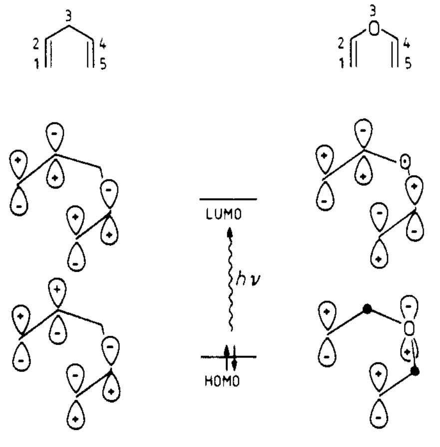


Figure 2. Orbital phases of the HOMOs and LUMOs for 1,4-pentadiene and 3-oxa-1,4-pentadiene (divinyl ether).

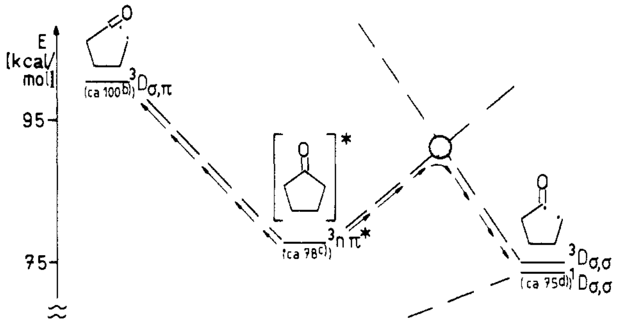
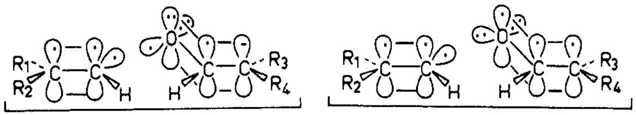


Figure 3. Salem diagram for the α-cleavage of unstrained cycloalkanones. For reasons of clarity, electronic states of the starting ketone and products not involved in the initial photoreaction are omitted. (b) ΔH_f of bent diradical plus calculated linearization energy (for acetone).[21a] (c) Reference 28. (d) Reference 29.



$D_{\sigma,\sigma}$ $D_{\sigma,\pi}$

Both experimental data and calculations[25] indicate that the π-configuration is the electronic ground state of the vinyloxy radical. Although the energetically favored $D_{\sigma,\pi}$ state correlates with a higher excited state (π,σ*) of the divinyl ether, a surface jump (encircled area, Figure 1) allows the generation of the $D_{\sigma,\pi}$ vinyl–vinyloxy radical pair from the π,π*-excited divinyl ether. Under the irradiation conditions used (254 nm), n,π*-excitation of furan[20] and divinyl ether[19] is unlikely for energy reasons.

Zimmerman's formalism of bond-order control[26] provides additional support for the reluctance of the divinyl ether **2** toward 3-oxa-di-π-methane rearrangement. Whereas the 1,4-pentadiene constitutes a four-π-electron system, the divinyl ether represents a six-π-electron system. The additional two π-electrons derive from one of the lone pairs of the central sp^2-hybridized oxygen atom. Inspection of Figure 2 reveals that HOMO–LUMO excitation of the 1,4-pentadiene reduces the antibonding interaction between C-2 and C-4,[26] whereas the same excitation in the case

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(17) Wetmore, R. W.; Schaefer, H. F., III; Hiberty, P. C.; Brauman, J. I. *J. Am. Chem. Soc.* **1980**, *102*, 5470.

(18) Similar results have been obtained for the analogous bis(2,2-diphenylvinyl) ether; cf.: Adam, W.; Berkessel, A.; Hildenbrand, K.; Peters, E.-M.; Peters, K.; von Schnering, H. G. *J. Org. Chem.* **1985**, *50*, 4899.

(19) We thank Prof. R. Gleiter (Universität Heidelberg) for measuring and interpreting the PE spectrum of divinyl ether **2**.

(20) Poquet, E.; Dargelos, A.; Chaillet, M. *Tetrahedron* **1976**, *32*, 1729.

(21) (a) Salem, J. *J. Am. Chem. Soc.* **1974**, *96*, 3486. (b) Dauben, W. G.; Salem, L.; Turro, N. J. *Acc. Chem. Res.* **1975**, *8*, 41.

(22) Murov, S. L. *Handbook of Photochemistry*; Marcel Dekker: New York, 1973.

(23) Pilcher, G.; Skinner, H. A.; Pell, A. S.; Pope, A. E. *Trans. Faraday Soc.* **1963**, *59*, 316.

(24) Egger, K. W.; Cocks, A. T. *Helv. Chim. Acta* **1973**, *56*, 1516.

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(26) Zimmerman, H. E. *Top. Curr. Chem.* **1982**, *100*, 45.

of the divinyl ether increases the antibonding interaction between C-2 and C-4. Consequently, divinyl ethers do not serve as suitable substrates for the desired 3-oxa-di-π-methane rearrangement.

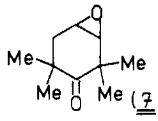
Let us now consider the results obtained in the photolysis of the epoxy ketone **1** in regard to the 3-oxa-di-π-methane rearrangement. Indeed, the synthesis and photolysis of the epoxy ketone **1** proved to be quite rewarding in this context. Upon n,π*-excitation we postulate that the epoxy ketone **1** undergoes α-cleavage to yield initially an acyl–carbinyl diradical, for which the acyl moiety may be generated as a bent σ-radical or as a linear π-radical.[5,27] A simplified Salem diagram[21] for the α-cleavage of acyclic or unstrained cyclic alkanones is given in Figure 3. Although the ^{3}n,π*-state of the alkanone correlates directly with the $D_{\sigma,\pi}$ diradical, the generation of this linear diradical species from unstrained cycloalkanones is energetically not feasible.[5] Instead, avoided surface crossing (encircled area, Figure 3) leads to the lower energy bent $D_{\sigma,\sigma}$ acyl–epoxycarbonyl diradical A (Scheme I).

In the case of n,π*-excitation of the epoxy ketone **1**, α-cleavage with concurrent oxirane ring opening to the $D_{\sigma,\pi}$ oxyl–acyl diradical B (Scheme I) can apparently compete energetically with the formation of the $D_{\sigma,\sigma}$ diradical A (Scheme I). The release of ca. 25–30 kcal/mol of strain energy of the oxirane ring presumably serves as a driving force in producing the otherwise inaccessible $D_{\sigma,\pi}$ diradical B. Decarbonylation[5] of the $D_{\sigma,\sigma}$ diradical A affords the 1,4-diradical C, which may fragment either into the divinyl ether **2** or into the 1,3-diradical D. Cyclization of the 1,3-diradical D finally affords the vinyl epoxide **6**, the searched for 3-oxa-di-π-methane product, whereas a 1,2-hydrogen shift gives enone **3**. Transformations D → **3** + **6** are well documented for oxatrimethylenes.[30]

Decarbonylation of the linear $D_{\sigma,\pi}$ diradical B appears unlikely since n,π*-excited carbon monoxide would result. Instead, diradical B is well lined up for fragmentation into dimethylketene and 3-methyl-2-butenal (Scheme I). Alternatively, cyclization of the diradical B generates the thermally labile β-lactone **4**, which decarboxylates to the 2,5-dimethyl-2,4-hexadiene (Scheme I). The formation of the β-lactone **4** fits the general course established for the photochemistry of β,γ-epoxy ketones.[31]

Since concerted cheletropic decarbonylation has been proposed in n,π*-excitation,[32] concerted loss of carbon monoxide from n,π*-excited epoxy ketone **1** might in principle also be envisaged as a pathway to the divinyl ether **2**. However, the proposed concerted cheletropic decarbonylation of cyclopenten-4-ones[32a] still lacks unambiguous experimental proof.

The high propensity of the epoxy ketone **1** toward decarbonylation, as shown in Scheme I, is in striking contrast to earlier observations on similar systems. For example, no decarbonylation products were reported for the photolysis of the epoxy ketones **7**[33] and **8**.[31a] It is known[5] that the rate of decarbonylation of acyl radical sites greatly depends on the presence of radical stabilizing substituents at the α-carbon. In addition to the two methyl groups, the oxirane ring[34] in the β-position most likely accounts for the unprecedented behavior of epoxy ketone **1**.



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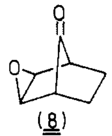

(8)

In conclusion, the difference in the photochemistry of the epoxy ketone **1** and the divinyl ether **2** is striking and could have hardly been anticipated. Thus, whereas irradiation of the divinyl ether **2** led exclusively to carbon–oxygen bond homolysis, affording a vinyl–vinyloxy radical pair as the primary photoproduct, the photolysis of the epoxy ketone **1** provided a convenient entry into the diradical manifold of the 3-oxa-di-π-methane rearrangement via the initially formed acyl–epoxycarbonyl diradical. Presumably, photochemical decarbonylation of other 6-heterosubstituted bicyclo[3.1.0]hexan-3-ones may serve as a suitable method for the generation and mechanistic exploration of the 1,4- and 1,3-diradicals postulated for hitherto unobserved 3-hetero-di-π-methane rearrangements.

Experimental Section

General. Melting points are uncorrected. Infrared spectra were taken on a Beckman Acculab 4 spectrometer; ^{1}H NMR spectra were taken at 90 MHz on a Varian EM 390 spectrometer or at 400 MHz on a Bruker WM 400 spectrometer. ^{13}C NMR spectra were measured at 22.6 MHz on a Bruker WH 90 spectrometer or at 100.61 MHz on a Bruker WM 400 spectrometer. Mass spectra were run on a Varian MAT CH7 spectrometer, and high-resolution mass spectra were run on a Finnigan MAT 8500 instrument. UV spectra were recorded on a Cary 17 instrument. The elemental analyses were kindly run for us by Prof. G. Maier's staff of the Universität Giessen. Known compounds used in this research were either purchased from standard suppliers or prepared according to literature procedures and purified to match the reported physical and spectral data. Only the experimental details of hitherto unknown compounds or procedures are provided. Photolyses were carried out in a Rayonet Model RP-100 (Southern New England Ultraviolet Co.) photochemical reactor at 254 nm and at 300 nm (quartz vessels). Capillary GC was performed on a Fractovap 2000 (Carlo Erba Co.); for preparative GC a Model 4200 (Carlo Erba Co.) was used. Compounds used for capillary GC calibrations were purified by preparative GC prior to use. GC/MS measurements were kindly run for us by Dr. H. Idstein, Institut für Pharmazie and Lebensmittelchemie, Würzburg, using a Varian Aerograph 1440, equipped with a 30-m fused-silica capillary column (Carbowax 20 M) and a Finnigan MAT 44 mass spectrometer.

Syntheses. 2,4,4-Trimethylcyclopenten-3-one.[8] To a stirred solution of 5.00 g (39.6 mmol) of 2,2,5-trimethylcyclopentanone[9] in 140 mL of chloroform, a solution of 7.03 g (44.0 mmol) of bromine in 45 mL of chloroform was added dropwise at ca. 20 °C over 1 h. The solution was then washed with saturated sodium bicarbonate and with water, dried over anhydrous magnesium sulfate, and rotavaporated at 20 °C and 15 torr. Powdered potassium hydroxide (6.06 g, 108 mmol) was dissolved in 30 mL of triethylene glycol by heating the solution to ca. 60–70 °C. To the cooled solution was added the crude brominated trimethylcyclopentanone. **Caution**: If the dehydrobromination is carried out on a larger scale, addition of the bromide may result in vigorous evolution of heat and the reaction can run out of control. The pressure was reduced to 50 torr, and the dehydrobromination product was distilled off by slowly increasing the temperature up to ca. 140 °C. The crude distillate was taken up in 30 mL of ether, dried over anhydrous sodium sulfate, and rotavaporated at 20 °C and 15 torr. The remaining colorless liquid was subjected to Kugelrohr distillation at 110–130 °C and 50 torr, affording 2.90 g (59%) of the pure 2,4,4-trimethylcyclopenten-3-one. The spectral data were identical with those reported.[8]

3,3,5,5-Tetramethylcyclopentenone. A flame-dried 100-mL, three-necked, round-bottomed flask, equipped with a magnetic spin bar, nitrogen inlet and outlet, and a rubber septum, was charged with 16 mL (30.4 mmol) of 1.9 M *n*-butyllithium in hexane added by syringe over 10 min to a stirred solution of 3.05 g (30.2 mmol) of diisopropylamine in 30 mL of absolute THF held at 0 °C. After 15 min at ca. 20 °C, the solution was cooled to −78 °C. Absolute hexamethylphosphoric triamide was added (5.40 g , 30.2 mmol), and the solution was stirred for 15 min. A solution of 2.50 g (20.2 mmol) of 2,4,4-trimethylcyclopenten-3-one in 10 mL of absolute THF was then syringed into the reaction mixture over 15 min, and the resulting yellow solution was stirred at −78 °C for 1 h. Subsequently, 5.70 g (40.3 mmol) of methyl iodide was added. The reaction mixture was allowed to warm up to ca. 20 °C over 4 h and was stirred at ca. 20 °C for 12 h. Afterwards 30 mL of hexane was added, and the mixture was washed with water, 5% hydrochloric acid, and again

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with water. The organic layer was dried over anhydrous sodium sulfate and carefully rotavaporated at 20–30 °C and 15 torr. The remaining yellow oil was taken up in 3 mL of absolute methanol and cooled to −78 °C. The mother liquor was pipetted off after completion of crystallization to afford 2.25 g (81%) of large, colorless, and highly volatile needles, mp 43–44 °C [lit.[7b] mp 44 °C]. IR (CCl_4): 3042, 2978, 2935, 2871, 1759, 1735, 1473, 1450, 1383, 1368, 1250, 1166, 1089, 1040 cm^{-1}. ^1H NMR ($CDCl_3$, 90 MHz): δ 1.08 (s, 12 H, $-CH_3$), 5.87 (s, 2 H, 1,2-H). ^{13}C NMR ($CDCl_3$, 100.61 MHz): δ 25.01 (q, $-CH_3$), 49.47 (s, C-3,5), 136.61 (d, C-1,2), 225.41 (s, C-4). MS (70 eV): *m/e* (relative intensity) 138 (9%, M^+), 110 (67%, $M^+ - CO$), 95 (100%, $M^+ - C_3H_7$). Exact mass calcd for $C_9H_{14}O$ (138.2): 138.1045. Found: 138.1048.

3,3,5,5-Tetramethylcyclopentenone 2,4-Dinitrophenylhydrazone. A sample of 400 mg (2.02 mmol) of 2,4-dinitrophenylhydrazine was treated with 2 mL of concentrated acid and then carefully with 3 mL of water. Subsequently, 10 mL of ethanol was added to the warm solution of the hydrazine, followed by a solution of 150 mg (1.09 mmol) of 3,3,5,5-tetramethylcyclopentenone in 2 mL of ethanol. The reaction mixture was kept at ca. 20 °C for 5 weeks. The red precipitate was collected by filtration to yield 50.0 mg (14%) of the crude hydrazone. Recrystallization from ethanol afforded large, red needles, mp 131 °C. IR (CCl_4): 3345, 2970, 1618, 1592, 1520, 1505, 1428, 1340, 1314, 1277, 1140, 1083 cm^{-1}. ^1H NMR ($CDCl_3$, 90 MHz): δ 1.34 (s, 6 H, $-CH_3$), 1.52 (s, 6 H, $-CH_3$), AB system (δ_A 5.62, δ_B 5.93, J = 7 Hz, 2 H, 1,2-H), 7.5–7.9 (m, 2 H, aryl H), 9.1–9.2 (m, 1 H, aryl H), 10.92 (br, s, 1 H, − NH−). ^{13}C NMR ($CDCl_3$, 100.61 MHz): δ 24.04 (q, $-CH_3$), 28.80 (q, $-CH_3$), 47.06 (s, C-3), 50.13 (s, C-5), 116.13 (d, C-6′), 123.42 (d, C-3′), 129.22 (s, C-2′), 129.87 (d, C-5′), 136.66 (d, C-2), 136.87 (d, C-1), 137.85 (s, C-4′), 145.31 (s, C-1′), 174.58 (s, C-4). MS (70 eV): *m/e* (relative intensity) 318 (44%, M^+), 303 (100%), 122 (41%), 107 (33%), 93 (32%). Anal. Calcd for $C_{15}H_{18}N_4O_4$ (318.4): C, 56.60; H, 5.70; N, 17.60. Found: C, 56.62; H, 5.67; N, 17.45.

2,2,4,4-Tetramethyl-6-oxabicyclo[3.1.0]hexan-3-one (1). A sample of 1.00 g (7.25 mmol) of 3,3,5,5-tetramethylcyclopentenone was dissolved in 50 mL of absolute chloroform. The solution was cooled to 0 °C, and 1.62 g (7.98 mmol) of 85% *m*-chloroperbenzoic acid was added. The reaction mixture was stirred at 0 °C for 30 min and then for 14 h at ca. 20 °C. Another 250 mg (1.23 mmol) of 85% *m*-chloroperbenzoic acid was added, and stirring was continued for 2 h. The reaction mixture was then washed with 5% aqueous KOH and with water, dried over anhydrous sodium sulfate, and rotavaporated at 20–30 °C and 15 torr, affording 1.00 g (89%) of the crude epoxy ketone **1** as a colorless oil. Final purification was achieved by preparative GC, using a 1.5-m × 0.8-cm glass column packed with 10% Carbowax on Volaspher A2 and operated at a carrier gas (N_2) pressure of 1.4 kg/cm^2 and column, injector, and detector temperatures of 170, 180, and 230 °C, respectively. The pure epoxy ketone **1**, 750 mg (67%), was obtained as a colorless oil. IR (CCl_4): 3019, 2969, 2939, 2878, 1760, 1474, 1450, 1389, 1370, 1039, 1008, 904 cm^{-1}. UV (*n*-pentane): λ_{max} (log ϵ) 295 (1.38), 304 (1.34), 316 (1.11). ^1H NMR (C_6D_6, 90 MHz): δ 0.79 (s, 6 H, *exo*-CH_3), 1.12 (s, 6 H, *endo*-CH_3), 2.94 (s, 2 H, 1,5-H). ^{13}C NMR ($CDCl_3$, 100.61 MHz): δ 20.11 (q, *exo*-CH_3), 22.08 (q, *endo*-CH_3), 46.83 (s, C-2,4), 60.91 (d, C-1,5), 221.82 (s, C-3). MS (70 eV): *m/e* (relative intensity) 154 (35%, M^+), 126 (22%, $M^+ - CO$), 83 (60%, $C_5H_7O^+$), 70 (100%, $C_4H_6O^+$). Anal. Calcd for $C_9H_{14}O_2$ (154.2): C, 70.10, H, 9.15. Found: C, 70.30, H, 9.26.

2,5-Dimethyl-4-hexen-3-one (3).[10] A solution of 2.35 g (23.2 mmol) of diisopropylamine in 20 mL of absolute THF in a flame-dried flask was cooled to 0 °C; 13.7 mL (25.5 mmol) of 1.86 M *n*-butyllithium in hexane was syringed into the reaction mixture. Stirring was continued at ca. 20 °C for 15 min, the solution was cooled to −78 °C, and 2.00 g (23.2 mmol) of methyl isopropyl ketone in 20 mL of absolute THF was added over 30 min. Stirring at −78 °C was continued for 1 h, and 1.35 g (23.2 mmol) of acetone in 10 mL of absolute THF was added. The reaction mixture was stirred at −78 °C for another 15 min, allowed to warm up to ca. 20 °C, and then poured into 150 mL of ice-cold 5% HCl. The mixture was extracted into ether. The organic phase was dried over anhydrous sodium sulfate and rotavaporated at 20 °C and 15 torr, affording 1.70 g of a yellow oil. A 0.5-g sample and ca. 10 mg of iodine were placed into a Kugelrohr apparatus. After the temperature was adjusted to 140 °C, slow reduction of the pressure to 100 torr produced 350 mg of a pale yellow oil. Purification was achieved by preparative GC, using a 1.5-m × 0.8-cm glass column packed with 10% Carbowax on Chromosorb W-NP (80/100) and operated at a carrier gas (N_2) pressure of 1.0 kg/cm^2 and column, injector, and detector temperatures of 120, 180, and 220 °C, respectively. Pure enone **3** (300 mg, 69%) was obtained as a colorless oil. IR (CCl_4): 2985, 2940, 2918, 2880, 1699, 1630, 1472, 1451, 1390, 1125, 1047 cm^{-1}. ^1H NMR (CCl_4, 90 MHz): δ 1.08 (d, J = 7 Hz, 6 H, − CH_3), 1.91 (br s, 3 H, *cis*-CH_3), 2.15 (br s, 3 H, *trans*-CH_3), 2.53 (sept, J = 7 Hz, 1 H, − $CHMe_2$), 6.0–6.2 (m, 1 H, vinyl H). ^{13}C NMR ($CDCl_3$, 22.6 MHz): δ 18.4 (q, − CH_3), 20.7 (q, *cis*-CH_3), 27.7 (d, − $CHMe_2$), 41.5 (q, *trans*-CH_3), 122.6 (d, vinyl CH), 155.4 (s, vinyl C), 204.7 (s, CO).

Photolyses. Quantitative Photolysis of Epoxy Ketone 1. A 2-mL aliquot of a degassed solution of epoxy ketone **1** (0.008 72 M) and 1-hexanol (0.006 88 M, internal standard) in *n*-pentane was stirred magnetically and irradiated under exclusion of air at 300 nm. The photolysate was analyzed by capillary GC on a 50-m Carbowax column, employing a temperature gradient starting with 47 °C (6 min) and increasing the temperature at 10 °C/min to 157 °C (10 min). Injector and detector temperatures of 225 and 200 °C, respectively, and a carrier gas (N_2) flow of 0.9 mL/min were used. Samples were taken before and during the irradiation in 5–30-min intervals up to a total photolysis time of 255 min. The calibrations of the starting material and of the products vs. 1-hexanol were carried out under identical GC conditions.

In each analysis, the concentration of the internal standard was corrected for the concentration of 1-hexyl isobutyrate, and the final product distribution was calculated from the initial slopes of the concentration vs. time profiles.

Low-Temperature Photolysis of Epoxy Ketone 1 and Characterization of 3,3-Dimethyl-4-(2-methyl-1-propenyl)oxetan-2-one (4). A sample of 120 mg (0.778 mmol) of epoxy ketone **1** was dissolved in 30 mL of *n*-pentane. The solution was cooled to ca. 0 °C, flushed with nitrogen for 10 min, and irradiated at 300 nm under a gentle stream of nitrogen for 2 h. Capillary GC analysis (for conditions cf. quantitative photolysis) indicated ca. 60% conversion of the starting material. The photolysate was rotavaporated at 0 °C and 15 torr, the residual oil was taken up in 1 mL of C_6D_6, and the 400-MHz ^1H and the 100.61-MHz ^{13}C NMR spectra were taken at 5 °C. The NMR solution was then heated to 60 °C for 2 h, and the spectra were retaken. NMR data of 3,3-dimethyl-4-(2-methyl-1-propenyl)oxetan-2-one (**4**).[35] ^1H NMR (C_6D_6, 400 MHz, 5 °C): δ 0.84 (s, 3 H, $-CH_3$), 0.96 (s, 3 H, $-CH_3$), 4.57 (d, J = 8.8 Hz, 1 H, oxetane H), 5.10 (d mc, J = 8.8 Hz, 1 H, vinyl H). ^{13}C NMR (C_6D_6, 100.61 MHz, 5 °C): δ 55.70 (s, C-3), 79.17 (d, C-4), 120.19 (d, vinyl CH), 141.30 (s, vinyl C), 175.42 (s, C-2).

In a second run, 30 mg (0.195 mmol) of the epoxy ketone **1** was dissolved in 2.5 mL of *n*-pentane, flushed with nitrogen for 5 min, and irradiated at 300 nm for 70 min. The photolysate was then rotavaporated at 10 °C and 15 torr. The residual oil was taken up in ca. 2 mL of carbon tetrachloride, and its IR spectrum showed a strong band at 1832 cm^{-1}. When the CCl_4 solution was kept at 60 °C, the half-life at 60 °C of the β-lactone **4** could be estimated to be ca. 30 min from the decay of its carbonyl absorption band.

Quantitative Photolysis of the Divinyl Ether 2. A sample of 44.0 mg (0.349 mmol) of divinyl ether **2** was dissolved in ca. 0.5 mL of CD_3CN and placed into a quartz NMR tube. The solution was purged for 5 min with N_2, and the tube was sealed. After 135 min of irradiation at 254 nm, the tube was cooled to 0 °C, 6.27 mg (0.0373 mmol) of 1,2-dinitrobenzene (internal standard) was added, and the 90-MHz ^1H NMR spectrum was taken. The product distribution (weight percent, normalized to 100% consumption of divinyl ether **2**) was calculated from the average of four integrations, affording 9 ± 1% 2,2,3,3-tetramethylbutanedial. 15 ± 2% isobutyraldehyde, 15 ± 2% isobutylene, and 16 ± 2% 2,2,4-trimethyl-3-pentenal (**5**).

Pentenal 5 (Capillary GC Determination). A sample of 28.0 mg (0.222 mmol) of divinyl ether **2** was dissolved in 10 mL of absolute acetonitrile. The solution was purged with nitrogen for 10 min and then irradiated at 254 nm. The concentrations of the starting material and the aldehyde **5** were monitored by capillary GC, using a 50-m Apiezon L column operated at column, injector, and detector temperatures of 70, 150, and 175 °C, respectively, with a carrier gas (N_2) flow of 1.0 mL/min. Extrapolation to 0% consumption of divinyl ether **2** afforded 15.0 ± 1.0% (weight percent, normalized to 100% consumption of divinyl ether **2**) of aldehyde **5**.

Isolation of 2,2,3,3-Tetramethylbutanedial in the Photolysis of Divinyl Ether 2. A sample of 600 mg (4.75 mmol) of divinyl ether **2** in 40 mL of absolute acetonitrile was flushed with nitrogen for 10 min and irradiated at 254 nm for 150 min. The solvent was rotavaporated at 30–40 °C and 15 torr to a volume of ca. 2 mL. By means of preparative GC 20 mg (3%) of 2,2,3,3-tetramethylbutanedial[12] was isolated, using a 1.5-m × 0.8-cm glass column packed with 10% Apiezon L on Chromosorb W-HP and operated at column, injector, and detector temperatures of 100, 150, and 150 °C, respectively, with a carrier gas (N_2) flow of 23 mL/min.

Acetone-Sensitized Photolysis of Divinyl Ether 2. A sample of 37.0 mg (0.0293 mmol) of divinyl ether **2** was dissolved in 20 mL of acetone. The solution was purged with nitrogen for 10 min and irradiated at 300

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[35] Due to the complexity of the photolysis mixture, the methyl ^1H and ^{13}C NMR resonances of the β-lactone **4** could only in part be assigned.

nm. Capillary GC monitoring on a 50-m OV 101 column, operated at column, injector, and detector temperatures of 110, 150, and 175 °C, respectively, with a carrier gas (N_2) flow of 0.8 mL/min, showed that consumption of the divinyl ether **2** was completed after 60 min, but only higher molecular weight products were formed.

Control Experiments. Photostability of the Photoproducts of Epoxy Ketone 1. Aliquots of 2 mL of 0.005–0.01 M solutions of the authentic photoproducts of the epoxy ketone **1** in *n*-pentane were irradiated independently at 300 nm for 225 min with 1-hexanol as internal standard. The concentrations of the substrates were monitored by capillary GC (for conditions cf. quantitative photolysis). A significant decrease of concentration could not be observed for any of the photoproducts of epoxy ketone **1**.

Photostability of Epoxide 6 in the Photolysate of Divinyl Ether 2. A sample of 30.0 mg (0.238 mmol) of divinyl ether **2** and 20.0 mg (0.159 mmol) of authentic epoxide **6**[15] in 10 mL of absolute acetonitrile was purged with nitrogen for 10 min and irradiated at 254 nm. The concentrations of **2** and **6** were monitored by capillary GC, using a 50-m OV 101 column operated at column, injector, and detector temperatures of 70, 150, and 175 °C, respectively, with a carrier gas (N_2) flow of 1.0 mL/min. After 100 min of irradiation, the decomposition of the divinyl ether **2** was completed, whereas only a slight decrease in the concentration of the epoxide **6** could be observed. In a second run a solution of 50.0 mg (0.396 mmol) of divinyl ether **2** in 5 mL of absolute acetonitrile was purged with nitrogen for 10 min and photolyzed to 64% consumption of the starting material (ca. 25 min). To the photolysis mixture 50.0 mg (0.396 mmol) of the epoxide **6** was added and the photolysis continued. Again a rapid decay of the divinyl ether **2** was observed, whereas epoxide **6** was inert. In a third run, 40.0 mg (0.317 mmol) of epoxide **6** in 20 mL of absolute aceonitrile was irradiated for 1 h. By means of coinjection of this solution with the photolysate of divinyl ether **2**, the absence of decomposition products of epoxide **6** was established.

Photostability of 2,5-Dimethyl-4-hexen-3-one[10] (3) in the Photolysate of Divinyl Ether 2. A sample of 7.46 mg (0.0591 mmol) of divinyl ether **2** and 11.4 mg (0.0903 mmol) of enone **3** was dissolved in 5 mL of absolute aceonitrile. An aliquot of 2 mL was purged with nitrogen for 10 min and irradiated at 254 nm. The concentrations of **2** and **3** were monitored by capillary GC (for conditions cf. above photostability experiment). After 75 min of irradiation, 61% of divinyl ether **2** was consumed, whereas the concentration of the enone **3** remained unchanged.

Photostability of 2,2,3,3-Tetramethylbutanedial, Isobutyraldehyde, and Isobutylene in the Photolysate of Divinyl Ether 2. The shapes of the concentration vs. time profiles (for recording conditions cf. yield of pentenal **5**) of these photoproducts indicated that secondary photolysis did not occur in the presence of excess divinyl ether **2**.

Formation of 3,5-Dimethyl-4-hexen-2-one. A solution of 35.0 mg (0.277 mmol) of ene epoxide **6** in 20 mL of acetone was irradiated at 300 nm for 80 min until 75% conversion of the ene epoxide **6** to its isomeric 3,5-dimethyl-4-hexen-2-one.[16] By means of capillary GC coinjection (for conditions cf. yield of pentenal **5**) of this solution with the photolysate of divinyl ether **2**, the absence of the enone as a photoproduct of divinyl ether **2** was confirmed.

Absence of 2,5-Dimethyl-2,4-hexadiene in the Photolysate of Divinyl Ether 2. Capillary GC coinjection (for conditions cf. yield of pentenal **5**) of the photolysate of divinyl ether **2** with an authentic sample of 2,5-dimethyl-2,4-hexadiene established that it was not formed as a photoproduct.

Quantum Yield (ϕ_{-S}) of Epoxy Ketone 1. Aliquots of 2.4 mL of solutions of epoxy ketone **1** (0.0340 M) and of cyclopentanone (0.0338 M) in *n*-pentane with 1-hexanol as internal standard were photolyzed at 300 nm under identical irradiation conditions, the decay of the substrates being monitored by capillary GC (for conditions cf. quantitative photolysis of epoxy ketone **1**). The relative decay rates of the two ketones were determined from the initial slopes of their concentration vs. time profiles. When the known ϕ_{-S} of cyclopentanone ($\phi_{-S} = 0.28$)[11] was employed, the ϕ_{-S} of epoxy ketone **1** was found to be 0.29 ± 0.03.

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Registry No. 1, 97455-13-5; **2**, 764-51-2; **3**, 13905-13-0; **4**, 97455-14-6; **6**, 13295-59-5; 2,4,4-trimethylcyclopenten-3-one, 71221-73-3; 2,2,5-trimethylcyclopentanone, 4573-09-5; 3,3,5,5-tetramethylcyclopentenone, 81396-36-3; 3,3,5,5-tetramethylcyclopentenone 2,4-dinitrophenylhydrazone, 102521-12-0; methyl isopropyl ketone, 563-80-4; acetone, 67-64-1.

Stereospecific Photoreduction of Polycyclic α,β-Unsaturated Ketones[1]

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Abstract: The photolysis of 4a-methyl-4,4a,9,10-tetrahydro-2(3*H*)-phenanthrone (**1**) in isopropyl alcohol (*i*-PrOH) is found to give lumiketone rearrangement product **5** and reduction product **8** via the enone triplet π,π* excited state. Other reduction products, **6**, **7**, and **9**, arise from the triplet n,π* excited state. The lower limit of the energy of the triplet state E_{n,π^*} is estimated to be ~67 kcal/mol above the ground state and that of the relaxed triplet π,π* excited state is ~61 kcal/mol. Reduction of the C=C bond on the enone chromophore from both excited states is stereospecific, with the twisted π,π* triplet leading exclusively to cis-fused bicyclic ketone and the planar n,π* triplet to the trans-fused isomer. The results from the photolysis of 4a-methyl-4,4a,5,6,7,8-hexahydro-2(3*H*)-naphthalenone (**4**) are consistent with these findings.

It is well-established[2,3] that 4,4-disubstituted α,β-unsaturated cyclohexenones rearrange to yield bicyclo[3.1.0]hexan-2-ones (lumiketones) upon UV excitation. It has been proposed[4] that this photorearrangement generally occurs via a twisted π,π* excited state of the enone. However, Zimmerman et al.[5] proposed that a triplet n,π* excited state is the reacting intermediate in the photorearrangement of 4-methyl-4,4a,9,10-tetrahydro-2(3*H*)-phenanthrone (**1**).

Two different modes of photoreduction of α,β-unsaturated cyclohexenones have been observed. Reaction directly at the C=O chromophore leads to a ketyl radical by abstraction of a hydrogen atom onto the electrophilic carbonyl oxygen of a ^{3}n,π* state. This ketyl radical can either combine with another one of its kind to

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