The determination of stoichiometry as a function of time should also be of help in resolving some of the problems concerning cleavage reactions which occur during chromic acid oxidation. The oxidation of cyclobutanol[5] under the above conditions is now being studied.

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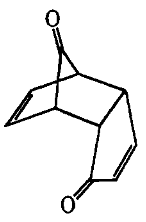
Photochemical Transformations of Substituted Cyclopentadienone Dimers[1]

Sir:

The photochemistry of the norbornen-7-one system has been the subject of sustained interest in recent years.[2] The primary photochemical reaction has been shown to be decarbonylation to the corresponding cyclohexadienes, the subsequent fate of which depended upon its substitution pattern.

Since cyclopentadienone dimers constitute a large class of the norbornen-7-one system, the investigation of their photochemical behavior is of obvious interest, the more so since their structure contains additional features which might open up alternate reaction paths. The two five-membered rings in such dimers occupy nonequivalent positions and in certain derivatives have been shown to be interconvertible[3] in what is, by now, well known as thermally allowed, suprafacial [3,3] sigmatropic rearrangements.[4] Another feature in these compounds is the juxtaposition of two olefinic bonds in an alignment permitting intramolecular cycloaddition which has, indeed, been found to occur in the parent *endo*-dicyclopentadiene and certain derivatives.[5,6] In the initial stage of this work, Schaffner and coworkers reported[7] that the irradiation of tricyclo[4.3.1^{2,5}.0]deca-3,8-diene-7,10-dione (**1**) resulted in the formation of the expected cage compound **2** accompanied by another isomer, **3**. We have therefore confined our investigation to substituted derivatives of **1** and wish to report at this stage some novel results and interpretations.



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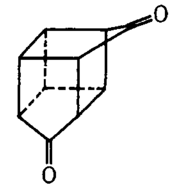

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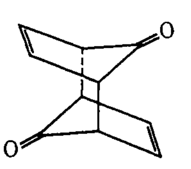

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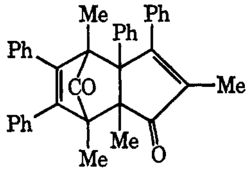

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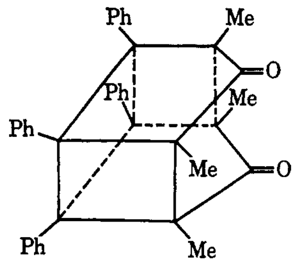

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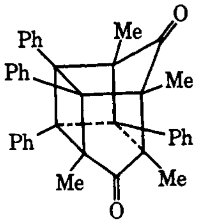

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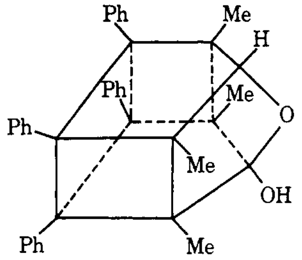

7

The Diels–Alder dimer **4** of 1,4-dimethyl-2,3-diphenylcyclopentadienone[8] (mp 183–184°; uv max (dioxane) 235 (ϵ 3×10^4), 280 nm (ϵ 4×10^4); ir (KBr) 1760, 1680 cm^{-1}; nmr (CDCl$_3$) τ 3.0 (m, 20, C$_6$H$_5$), 7.9 (s, 3, CH$_3$), 8.36 (s, 3, CH$_3$), 8.75 (s, 3, CH$_3$), 9.42 (s, 3, CH$_3$); mass spectrum (70 eV) *m/e* 520 (M$^+$)) gave upon irradiation at $\lambda > 300$ nm[9] a product **5** in excellent yield (75%) (mp 272°; uv max (dioxane) 240 nm (ϵ 2×10^4); ir (KBr) 1750 cm^{-1}; nmr (C$_6$H$_5$Cl) τ 8.8 (s, CH$_3$); mass spectrum (70 eV) *m/e* 520 (M$^+$)[10]) accompanied by minute ammounts ($\leqslant$0.25%) of a second product **6** (mp 318°; uv max (dioxane) 230 nm (ϵ 2×10^4); ir (KBr) 1750 cm^{-1}; nmr (C$_6$H$_5$Cl) τ 8.2 (s, 6, CH$_3$), 9.5 (s, 6, CH$_3$); mass spectrum (70 eV) 520 (M$^+$)).[10] The structural assignments are based on the above spectral properties as well as on chemical reactivity. The uv spectra indicate the absence of unsaturation in the cage skeletons and the ir spectra indicate the presence of strained five-membered ring ketones. The nmr spectra allow differentiation between **5** and **6** by the signals of the methyl groups and indicate their complete equivalency in **5** (point group C_{2v}) but only pair equivalency in **6** (point group C_2). The fact that the relative disposition of the two five-membered rings in **5** is as shown was proven by LiAlH$_4$ reduction (boiling THF) whereby a cyclic hemiketal **7**, mp 320°, was obtained.[10] The latter gives a monotrimethylsilyl derivative, mp 310°.

Structure **5** is novel and its formation can be rationalized only if one assigns an exo configuration to the dimer **4**. The achievement of this apparent thermodynamically more stable configuration may be understood on the basis of the known reversibility of the

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[1] V. Photochemical Behavior of Bridged Compounds. Part IV: B. Fuchs, *Israel J. Chem.*, **6**, 517 (1968).

[2] (a) Reference 1 and earlier publications in the series and references cited therein; (b) D. I. Schuster, H. F. T. Lee, A. Padwa, and P. G. Gassman, *J. Org. Chem.*, **30**, 2262 (1965).

[3] (a) R. B. Woodward and T. J. Katz, *Tetrahedron*, **5**, 70 (1959); (b) R. C. Cookson, J. Hudec, and R. O. Williams, *Tetrahedron Lett.*, **22**, 29 (1960); (c) P. Yates and P. Eaton, *Tetrahedron*, **12**, 13 (1961); (d) E. Vogel and E. G. Wyes, *Angew. Chem.*, **14**, 489 (1962); (e) K. N. Houk, *Tetrahedron Lett.*, 2621 (1970).

[4] R. B. Woodward and R. Hoffmann, *Angew. Chem.*, **81**, 888 (1969).

[5] G. O. Schenck and R. Steinmetz, *Chem. Ber.*, **96**, 520 (1963).

[6] W. G. Dilling, *Chem. Rev.*, **66**, 373 (1966).

[7] E. Baggiolini, E. G. Herzog, S. Iwasaki, R. Schorta, and K. Schaffner, *Helv. Chim. Acta*, **50**, 297 (1967).

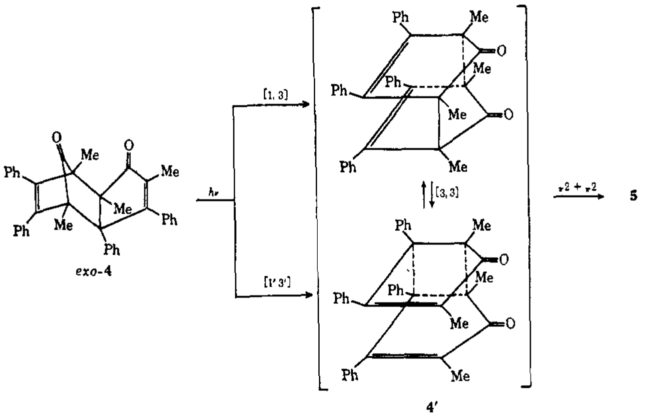
[8] (a) C. F. H. Allen and J. A. Van Allan, *J. Amer. Chem. Soc.*, **64**, 1260 (1942); (b) C. F. H. Allen and J. A. Van Allan, *ibid.*, **72**, 5165 (1950). These authors established the gross structure of **4** excluding its stereochemistry.

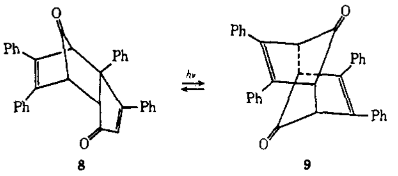
[9] Preparative irradiations were carried out in Rayonet reactors using Sylvania F8T5 Black ray lamps or in immersion reactors using Hanovia 450-W high-pressure mercury lamps. Dioxane solutions in Pyrex vessels were purged with nitrogen prior to and during irradiations. Quantitative, time-dependent, and monitored irradiations were performed on a Jasco-CRM-FA spectro irradiator at 311 nm.

[10] (a) Satisfactory elemental analyses were obtained. (b) The products are unusually resistant to chemical attack and of exceedingly low solubility in all organic solvents.

monomer–dimer structures in tetrasubstituted cyclopentadienones.[8,11,12]

The photochemical transformation of **4** to **5** can then be formulated as a [1,3] sigmatropic rearrangement, *exo*-**4** → **4′**, followed by intramolecular $_{\pi}2 + {}_{\pi}2$ cycloaddition **4′** → **5**. An alternative and, to this author's knowledge, unprecedented, completely concerted rearrangement, *exo*-**4** → **5**, cannot be excluded but is also difficult to prove. It would imply a six-center electron redistribution process with two conceivable bonding interactions between the two allylic counterparts, between the lowest bonding or highest antibonding orbitals. The latter would obtain in our case.





The small yields of **6** in the above photochemical experiment are tentatively attributed to internal cycloaddition of contaminating *endo*-**4** isomers in the starting material.

Turning to another instance, the tetraphenyl derivative **8**[13] (mp 206°; uv max 233 (ϵ 1.4 × 10^4), 287 nm (ϵ 2 × 10^4); ir (KBr) 1780, 1690 cm^{-1}; nmr ($CDCl_3$) τ 7 (m, 21), 5.6 (d, 1), 6.2 (dd, 1), 6.9 (d, 1); mass spectrum (70 eV) *m/e* 464 (M^+)) was irradiated at $\lambda >$ 310 nm,[9] yielding (20%) exclusively **9** (mp 257°; uv max (dioxane) 238 (ϵ 4.4 × 10^4), 280 nm (ϵ 2.4 × 10^4); ir (KBr) 1770 cm^{-1}; mass spectrum (70 eV) *m/e* 464 (M^+)).[10]

Continual spectrophotometric scanning of the irradiation mixture revealed two isosbestic points at 268 and 318 nm.[9] Moreover, irradiation of pure **9** under identical conditions gave a similar mixture of **8** and **9**. The transformation is thus shown to be reversible and to involve no long-lived intermediates.

Sensitization and quenching experiments[9] were performed. Irradiation of **7** in the presence of acetophenone (E_T = 74 kcal/mol) almost entirely suppressed the formation of **9**; naphthalene (E_T = 61 kcal/mol) slightly enhanced its formation, whereas piperylene (E_T = 56 kcal/mol) reduced it appreciably. These preliminary results indicate the intermediacy of triplet excited states at least in the transformation **9** → **8** if not also in the reverse process. Should the latter situation obtain, one would be led to the conclusion that $E_T{}^9 > E_T{}^8$. Surprisingly, no internal cycloaddition product analogous to **2** was detected. In all other respects, however, the situation is similar to that now found for the unsubstituted dimer,[7,14] the process consisting apparently of a [1,3] sigmatropic transformation in an undissociating dimer **8**, of endo configuration.

The above results permit the formulation of a unified picture of light-induced sigmatropic rearrangements[4,15] in cyclopentadienone dimers. The outcome depends upon the configuration of the tricyclic starting material; endo dimers undergo internal cycloaddition to type **2** cages and/or rearrangements to diketones of type **3** whereas exo dimers photoisomerize to cages of type **5** possibly *via* intramolecular cycloaddition in unsaturated rearranged intermediates. To be sure, these are not the only available modes for photoisomerization and, therefore, the scope and generality of these processes as well as their driving forces are problems still demanding elucidation.[16]

Quantitative photochemical measurements, further transformations of the photoproducts, and additional instances of light-induced isomerizations in these systems are now under investigation.

Acknowledgments. Mrs. Sarah Weinman and Mr. Shimon Hauptman rendered skillful technical assistance. The mass spectrometric measurements were kindly performed at the Chemistry Departments of Bar-Ilan University, Ramat Gan, and/or Israel Institute of Technology, Haifa, courtesy of Drs. B. Sklarcz and A. Mandelbaum, respectively.

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[11] M. A. Ogliaruso, M. G. Romanelli, and E. I. Becker, *Chem. Rev.*, **65**, 261 (1965).

[12] For pertinent discussion and references on this subject, *cf.* ref 3e.

[13] C. F. H. Allen and J. W. Gates, Jr., *J. Amer. Chem. Soc.*, **64**, 2120, 2123 (1942).

[14] J. Gauthier, K. Schaffner, M. Pasternak, and B. Fuchs, in preparation.

[15] The general photochemical [1,3] sigmatropic suprafacial rearrangement is well documented;[4] *cf.* also D. I. Schuster and D. H. Sussman, *Tetrahedron Lett.*, 1661, 1657 (1970), and references therein.

[16] The significance of these findings is, in this author's opinion, well beyond the specific cases treated here. Indeed, a variety of related literature cases, the results of which appear equivocal if not unfounded, demand reinterpretation or further investigation. Some such cases are now being investigated in this laboratory and will be reported in due course.

Magnetic Circular Dichroism Studies. XII.[1] The Determination of Tryptophan in Proteins

Sir:

In spite of extensive studies[2–7] the quantitative and in several cases[8] even qualitative determination of tryptophan in proteins remains difficult. Because of the

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[1] For part XI see: D. L. Elder, E. Bunnenberg, C. Djerassi, M. Ikehara, and W. Voelter, *Tetrahedron Lett.*, 727 (1970).

[2] J. R. Spies and D. C. Chambers, *Anal. Chem.*, **21**, 1949 (1949).

[3] T. W. Goodwin and R. A. Morton, *Biochem. J.*, **40**, 628 (1946).

[4] F. W. J. Teale, *ibid.*, **76**, 381 (1960).

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[8] U. Henning, D. R. Helinski, F. C. Chao, and C. Yanofsky, *J. Biol. Chem.*, **237**, 1523 (1962).