oxygen bond lengths are equal to within the estimated standard deviations, averaging 2.605 (0.011) Å, while the two metal–nitrogen bond distances are 2.665 (0.016) Å (N_1) and 2.648 (0.015) Å (N_2), respectively.

While the exact geometry of the coordination polyhedron in the molecule is to a certain extent controlled by the bite of the chelating ligands, we feel that it can be meaningfully described in terms of one of the possible models for the preferred ground-state geometry for decacoordination, *viz.*, the bicapped dodecahedron of D_2 symmetry.[3] In fact, reference to the eight-coordinate polyhedron is very useful since several features of this geometry are retained here. Thus, the oxygen and nitrogen atoms, O_3 and N_1, together with their symmetry-related pair and the lanthanum atom, are coplanar to within the esd's and correspond quite closely to one of the trapezoidal planes of the dodecahedron. The angular parameters θ_A and θ_B are 37.3 and 69.5°, respectively.[4] In addition, the nitrate ligand, bisected by the crystallographic twofold axis, spans the *a* edge of the second trapezoidal plane defined by La, O_1 and O_1', and N_2 and N_2'. However, these five atoms are far from coplanarity, N_2 and N_2' being *ca.* 1.10 Å from the plane defined by the metal atom, O_1, and O_1'. The dihedral angle between this latter plane and the first trapezoidal plane is 89.5° at the present level of refinement.

The arrangement of the four coordinating atoms O_2, O_2', N_2, and N_2' is primarily governed by the steric requirements of the nitrate groups and the rings of the bipyridyl molecules constituting the "equatorial" plane. However, if, as mentioned earlier, we consider the nitrogen atoms N_2 and N_2' as defining (together with O_1 and O_1') one of the trapezoidal planes of the dodecahedron, then the bipyridyl ligands span the g-type edges of this polyhedron while the ninth and tenth bonds, to the nitrate oxygen atoms, O_2 and O_2', pass approximately through the midpoints of the edges of type b, since the group of atoms La, N_2, O_2, and O_3 are almost coplanar. Allowing for the constraints of the chelating ligands, therefore, the approximation to an idealized bicapped dodecahedron is reasonably close.

The relevant nonbonded intramolecular distances defining the basic eight-coordinate polyhedron and also its extension to the ten-coordinate polyhedron are as follows: N_1N_1' (a) 3.23; N_1N_2 (g), 2.66; N_1N_2' (g), 3.81; N_1O_3' (m), 3.14; N_2O_3 (b), 4.60; N_2O_3' (b), 3.04; O_3O_1 (g), 2.96; O_3O_1' (g), 3.04; O_1N_2 (m) 3.49; O_1O_2, 2.87; N_2O_2 3.18; and N_1O_2, 3.05.

Investigation of a species with all ligands identical should throw further light on this coordination geometry, and to this end we are currently investigating the stereochemistry of the $Ce(NO_3)_5^{2-}$ complex ion.

Acknowledgment. We are grateful to the Iraqi Government for support of this research, in the form of a postgraduate fellowship to A. R. A.

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(4) J. L. Hoard and J. V. Silverton, *Inorg. Chem.*, **2**, 235 (1963). See this paper for a definition of the nomenclature used here.

A. R. Al-Karaghouli, John S. Wood
Department of Chemistry, The University
Southampton, England

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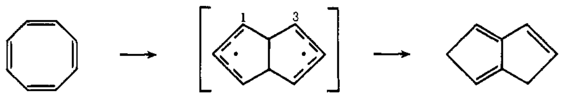
The Cyclooctatetraene–Dihydropentalene Rearrangement[1,2]

Sir:

It is becoming increasingly clear that a number of compounds of the empirical formula $(CH)_8$ share an energy surface quite as complex as that inhabited by the $(CH)_{10}$'s. Zimmerman[3a–c] has discovered the photochemical interconversions of barrelene, semibullvalene, and cyclooctatetraene. Recently Criegee and Askani[4] described the thermal conversion of octamethylcyclooctatetraene to octamethylsemibullvalene. We are prompted by this interest to report in preliminary form on the thermal rearrangement of cyclooctatetraene and to describe one new exit from the $(CH)_8$ energy surface.

Some years ago, Tanaka[5] investigated the gas- and liquid-phase pyrolysis of cyclooctatetraene. He found ethylene, acetylene, benzene, and styrene, and mentioned unidentified products. Like Tanaka we find benzene and styrene, but under some conditions the major product is the dihydropentalene I. Identification of this product was easy as it had been synthesized previously by Katz.[6] Although our route to I lacks the style of Katz' design, it is remarkably simple and rather large quantities of I can be obtained. Cyclooctatetraene was pyrolyzed in a flow system at 400–665° and the products were collected in a trap maintained at −78°. Figure 1 shows the product composition as a function of temperature. The residence time was kept at *ca.* 7.5 sec.



II I

Two mechanistic extremes suggest themselves, each leading to the diradical II. This in turn suffers a series of 1,5 hydrogen shifts, ultimately arriving at I. One pathway leads through semibullvalene to II and draws on the report of Criegee[4] for analogy. Alternatively, II may be formed directly from cyclooctatetraene.[7] These are only extremes, of course, and merge into each other as the extent of bonding between carbons 1 and 3 in II increases.

A question unanswered by this work is whether other, degenerate rearrangements of lower activation energy are rendered invisible in the absence of a label. Indications that this may be so exist in the work of

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(1) This work was supported by a grant from the Research Corporation, to whom we express our appreciation. We are also grateful to the Badische Anilin und Soda-Fabrik for a generous gift of cyclooctatetraene.

(2) Taken from the B.A. Thesis of L. O. S., Princeton University, 1968.

(3) (a) H. E. Zimmerman and G. L. Grunewald, *J. Am. Chem. Soc.*, **88**, 183 (1966); (b) H. E. Zimmerman, R. W. Binkley, R. S. Givens, and M. A. Sherwin, *ibid.*, **89**, 3932 (1967); (c) H. E. Zimmerman and H. Iwamura, *ibid.*, **90**, 4763 (1968).

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(5) I. Tanaka, *J. Chem. Soc. Japan, Pure Chem. Sec.*, **75**, 212 (1954); *Chem. Abstr.*, **48**, 4984*b* (1954).

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(7) M. Stiles and U. Burckhardt, *ibid.*, **86**, 3396 (1964). We thank Professor Stiles for discussions of unpublished work bearing on this point.

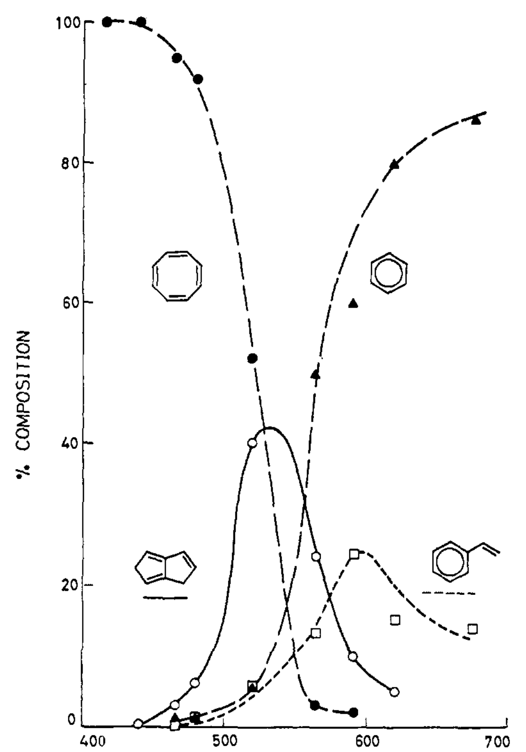

Figure 1. Cyclooctatetraene pyrolysis: product composition as a function of temperature.

Stiles[7] on diphenyldibenzocyclooctatetraenes and of Schwab[8] on 1,8-dicarbomethoxycyclooctatetraene.

(8) L. O. Schwab, unpublished work.

(9) Alfred P. Sloan Research Fellow, 1967–1969.

Maitland Jones, Jr.,[9] Lawrence O. Schwab
Department of Chemistry, Princeton University
Princeton, New Jersey 08540

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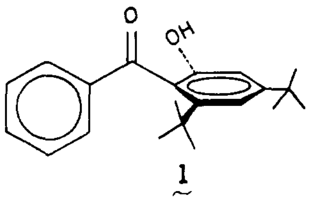
2-Hydroxy-4,6-di-*t*-butylbenzophenone Photoreactivity

Sir:

The steric requirements of the *t*-butyl groups in **1**[1] force the molecule to exist predominantly in a conformation in which the planes of the two aromatic rings are essentially perpendicular to one another.[2] As



1

is evidenced by its infrared and ultraviolet spectra, this geometrical restriction precludes the existence of both intramolecular hydrogen bonding[3] and low-energy charge-transfer transitions (<40,000 cm^{-1}) in **1**. Since both conditions are believed to provide mechanisms for rapid deactivation of excited states of 2- and 4-hydroxybenzophenone (**2** and **3**),[4,5] and other series of compounds,[6] it was of interest to determine the effect, if any, of the 2-hydroxy group on the photoreactivity of **1** relative to **2**, **3**, and benzophenone (**4**).

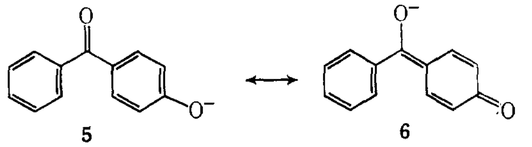
The electronic absorption and emission spectra of **1** indicate both its lowest singlet and triplet excited states to have an n,π* configuration. The former exhibits a broad maximum at λ ~3100 Å (ε ~100),[1] while the phosphorescence of **1** (0–0 band ~25,600 cm^{-1}) in an EPA glass at 77°K is bright with a mean lifetime of 2×10^{-4} sec. The singlet–triplet splitting for **1** (~5000 cm^{-1}) is also characteristic of that for n,π* states. On the basis of these spectral data one would predict efficient intersystem crossing from the lowest excited singlet state of **1**, generating a reactive n,π* triplet state. The observed photoreactivity of **1** is not in accord with this simple picture. Quantum yields measured for the total loss of **1** subsequent to irradiation[7] in 2-propanol and in methylcyclohexane are compared with those reported for **2**–**4** in Table I.

Table I. Comparison of Photoreactivity of **1**–**4**

Compd	Φ_{ROH}	Φ_{RH}
1	2×10^{-3}	1.3×10^{-3}
2[a]	7×10^{-3}	*c*
3[b]	2×10^{-2}	0.9
4[b]	1.0	0.5

[a] Taken from ref 8. [b] Taken from ref 5. [c] Not reported.

Porter[8] has related the low photoreactivity of **3** in alcoholic media to the high acidity of its charge-transfer excited singlet state (pK_a* = −3). He proposed that proton transfer to the solvent competes favorably with intersystem crossing from this state. The phenolate anion (**5**) thus generated is unreactive with respect to hydrogen abstraction due to contribution of structure **6** to its resonance hybrid. *Structures of the type* **6** *are sterically inhibited in* **1**. In hydrocarbon media, the energies of the charge-transfer singlet and triplet states of **3** are raised, and a reactive n,π* triplet is populated.



5 **6**

The low photoreactivity of **2** has been related to reversible enolization[9,10] and to the charge-transfer

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(1) R. A. Finnegan and D. Knutson, *Chem. Ind.* (London), 1837 (1965).

(2) A. T. Shulgin and H. O. Kerlinger, *Chem. Commun.*, 249 (1966).

(3) The O–H stretching vibration of **1** has been reported[2] to be a partially resolved doublet ($\bar{\nu}_{OH}^{CCl_4}$ 3609, 3588 cm^{-1}). The authors assign the 3588-cm^{-1} band to a conformer of **1** in which there is a weak intramolecular hydrogen bond between the phenolic hydrogen and the π bond of the adjacent carbonyl group. The frequency interval between the free O–H and the bonded O–H in **1** corresponds to an energy separation of ~0.05 kcal. Nonbonded interactions in *ortho*-substituted phenols are known to result in splittings of the O–H stretching frequency of this order of magnitude. In the context of this paper, intramolecular hydrogen bonding refers to bonding interactions of the order of 1 kcal or greater.

(4) A. Beckett and G. Porter, *Trans. Faraday Soc.*, **59**, 2051 (1963).

(5) G. Porter and P. Suppan, *ibid.*, **61**, 1664 (1965).

(6) J. R. Merrill and R. G. Bennett, *J. Chem. Phys.*, **43**, 1410 (1965).

(7) All photolyses were carried out in the absence of oxygen with a 1000-W xenon arc filtered to transmit light of wavelengths 2400–3400 Å. Analyses were carried out by glpc. Quantum yields are accurate to ±30%.

(8) T. S. Godfrey, G. Porter, and P. Suppan, *Discussions Faraday Soc.*, 194 (1965).