Acknowledgment. We thank the Science Research Council for a grant to purchase the XL-100 spectrometer.

References and Notes

(1) For a general review, see H. Scheer and J. J. Katz in "Porphyrins and Metalloporphyrins", K. M. Smith, Ed., Elsevier, Amsterdam, 1975, p 482.
(2) R. J. Abraham, G. E. Hawkes, and K. M. Smith, *J. Chem. Soc., Chem. Commun.*, 401 (1973); *J. Chem. Soc., Perkin Trans. 2*, 627 (1974).
(3) A. R. Battersby and E. McDonald in "Porphyrins and Metalloporphyrins", K. M. Smith, Ed., Elsevier, Amsterdam, 1975, p 87.
(4) This is all the more surprising when one considers the great concentration dependence exhibited in the proton NMR of porphyrins and metalloporphyrins; see ref 1.
(5) R. J. Abraham, G. E. Hawkes, and K. M. Smith, *Tetrahedron Lett.*, 1483 (1974); *J. Chem. Soc., Perkin Trans. 2*, 627 (1974).
(6) Similar dramatic effects are observed in the proton NMR spectra of certain zinc(II) porphyrins (work in progress in these laboratories).
(7) Magnesium(II) and cadmium(II) porphyrins also show pronounced aggregation which is destroyed by addition of pyrrolidine. A study of other divalent metalloporphyrins is at hand.
(8) Zinc(II) porphine is almost insoluble in $CDCl_3$ but addition of a little pyrrolidine affords good solubility.
(9) R. J. Abraham, F. Eivazi, G. E. Hawkes, H. Pearson, and K. M. Smith, manuscript in preparation.
(10) Prepared by condensation of 5,5′-diformyl-3,3′-di(2-methoxycarbonylethyl)-4,4′-dimethylpyrromethane with 3,3′-di(2-methoxycarbonylethyl)-4,4′-dimethylpyrromethane-5,5′-dicarboxylic acid in deuterated *p*-toluenesulfonic acid and methanol: G. W. Kenner and K. M. Smith, *Ann. N.Y. Acad. Sci.*, **206**, 138 (1973).
(11) Prediction of "absolute" chemical shifts in porphyrins with a more complex array of substituents requires the influence of substituent effects on more distant pyrrole subunits to be considered. These considerations will be detailed in our full paper.[9]
(12) E.g., R. J. Abraham and P. F. Swinton, *J. Chem. Soc. B*, 903 (1969).
(13) I. C. I. Fellow, 1974–1976.

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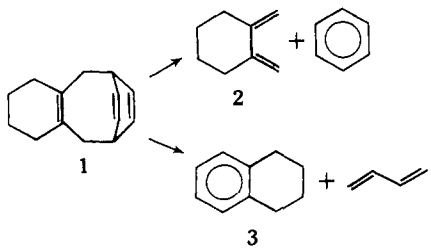
Received November 19, 1975

Thermal Decomposition of Tricyclo[6.4.0.2^{3,6}]tetradeca-1(8),4,13-triene. A Process Involving a Series of Intramolecular and Retro-Diels–Alder Reactions

Sir:

During the course of routine investigation of the thermal stability of the previously prepared[1] 1,4-1′,4′ photoadduct of 1,2-dimethylenecyclohexane and benzene, **1** (the title compound), we discovered, in addition to the thermal reversal of the photoformation reaction, a second but unexpected pathway leading to the formation of butadiene and tetralin (Scheme I). The continuing interest in valence bond isomerization processes prompts us to report this result and point out the possible mechanistic implications.

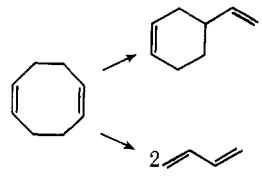
Scheme I



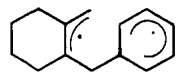
The reaction was made the subject of a brief kinetic study using the sealed ampoule technique; 6.8-μmol portions of the reactant[2] were sealed under vacuum in 2.7 cm^3, base-washed Pyrex tubes and heated (stirred salt thermostat) for periods of up to 4.5 h at 453.6 ± 0.1 K. The product mixture (up to C_{10}) was analyzed by GLC (4 m silicone oil on Chromosorb P at 100°C) using an internal standard technique. The products, viz., butadiene, benzene, 1,2-dimethylenecyclohexane, **2**, and tetralin, **3**, were identified by GLC–mass spectrometry (MS 12), and product recovery (in terms of reactant loss) was at least 86% and probably greater.[2] Analysis of the C_{14} fraction (Carbowax 20M on Universal B at 130 °C) revealed the presence of two minor products amounting to ca. 1% of the total reactant and product. These were identified as $C_{14}H_{18}$ isomers by mass spectrometry but have not as yet been further characterized. The division between major product pathways as indicated by the ratio [**3**]/[**2**] averaged at 1.55 although a slight trend was apparent with time from a low of 1.43 (at 24% conversion) to 1.72 (at 100% conversion). The products, and product mixtures, were stable under the conditions of the experiments. The reaction followed unimolecular kinetics and a rate constant, $k = (3.5 \pm 0.3) \times 10^{-4}$ s^{-1}, was obtained for total product formation.

In the delineation of the mechanism of this reaction a likely initial fate of **1** appears to us to be transformation to tricyclo[8.4.0.0^{3,8}]tetradeca-1^{10},4,6-triene (**4**), by means of a sigmatropic 1,3 carbon shift. Concomitant symmetry-forbidden [4 + 4] cycloreversion to **2** and benzene also seems probable on the analogy of the pyrolysis of cycloocta-1,5-diene[3] (Scheme II) studied by Srinivasan and Levi. Al-

Scheme II



though we offer no firm conclusion as to the detailed mechanism of these processes, we note that the biradical, **5**, is an

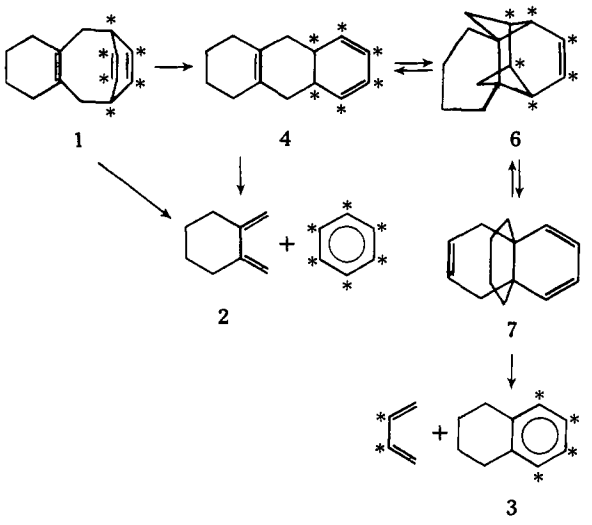


5

energetically viable intermediate in our case.[4] **4** itself may now augment the yields of **2** and benzene by symmetry allowed [4 + 2] cycloreversion, the retro-Diels–Alder reaction, but in order to lead to the other products, we propose that **4** undergoes competitive internal [4 + 2] cycloaddition, an example of the intramolecular Diels–Alder process[6-8] leading to the hitherto unknown pentacyclo[8.4.0.0^{3,8}.0^{1,4}.0^{7,10}]tetradec-5-ene (**6**). This highly strained hydrocarbon[9], by virtue of its symmetry, may now either revert to **4** or proceed to the propellatriene, tricyclo[4.4.4.0^{1,6}]tetradeca-2,4,8-triene (**7**), in both cases by retro-Diels–Alder processes. **7**, by means of a further retro-Diels–Alder reaction can now lead to the observed products tetralin, **3**, and butadiene. These proposals are summarized in Scheme III.

It remains to be shown whether either of the two minor isomeric $C_{14}H_{18}$ species observed corresponds to either of the intermediates **4** or **7**, but in any case these latter must be thermally labile to fit our scheme. The aromatization occurring during retro-Diels–Alder reaction of **4** and **7** to products undoubtedly provides a driving force but the question of whether it is sufficient will have to await a direct test. The intramolecular isomerization of **4** must also be facile to compete successfully with the decomposition. Again, this must await a direct test, but favorable omens are provided by analogous intramolecular Diels–Alder reac-

Scheme III



tions implicated in the rearrangements of annulated bicyclo[4.2.0]octatrienes[6] and the degenerate reactions of cyclooctatetraene[7] studied by Paquette and co-workers and also in the thermal behavior of several unsaturated bicyclo[4.2.2] and [4.2.1] species.[8]

In order to add weight to these proposals, the specifically labeled 3,4,5,6,13,14-hexadeuterio analogue of **1**, prepared by photoaddition of **2** to hexadeuteriobenzene, was also pyrolyzed, and the products were analyzed for deuterium content. The mass spectra of **2** and of benzene were in accord with complete retention of all deuterium in the benzene, while those of **3** and butadiene showed that these molecules were d_4 and d_2, respectively.[12] Additionally samples of tetralin (d_4) and butadiene (d_2) were obtained by preparative GLC and their NMR spectra recorded.

The absence of absorptions (<2% of those of tetralin-H_{12}) in the aromatic region for the tetralin (d_4) indicated no aromatic protons and characterized the tetralin as the 2,3,4,5-tetradeuterio derivative. The NMR spectrum of the butadiene (d_2) consisted of two simple absorptions ($\tau(CCl_4)$ 4.90 (s, 1 H) and 4.96 (s, 1 H)) with negligible absorption in the τ 3.0–4.5 region (<4% of that for butadiene H_6). The observed signals coincide with those of the geminal protons on C_1 and C_4 in fully protonated butadiene and the absence of other absorptions characterizes the butadiene as the 2,3-dideutero derivative. Scheme III traces, by means of asterisks, the fate of the deuterium label through the various isomers in the proposed mechanism and it can be seen that the product isotopic pattern observed is just that expected.

Further investigations of this mechanism and of the thermal stability of the proposed intermediates are under way in our laboratory.

References and Notes

(1) J. C. Berridge, D. Bryce-Smith, and A. Gilbert, *Tetrahedron Lett.*, 2325 (1975).

(2) Samples were prepared by evaporating solvent from 0.50 cm^3 of a solution of **1** in *n*-pentane. The technique gave samples reproducible within ±3% but analysis suggested possible mass losses during transfer up to 14%.

(3) R. Srinivasan and A. A. Levi, *J. Am. Chem. Soc.*, **86**, 3756 (1964).

(4) Thermochemical estimates[5] place **5** about 33 (±5) kcal mol^{-1} higher in enthalpy than **1**. A possible Arrhenius equation consistent with the measured rate constant is $\log (k/s^{-1}) = 14.5 - 37.3$ kcal mol^{-1}/RT ln 10.

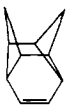
(5) Based on methods described in S. W. Benson, "Thermochemical Kinetics", Wiley, New York, N.Y., 1968.

(6) L. A. Paquette, R. E. Wingard, Jr., and J. M. Photis, *J. Am. Chem. Soc.*, **96**, 5801 (1974), and references cited therein.

(7) L. A. Paquette, M. Oku, W. E. Heyd, and R. H. Meisinger, *J. Am. Chem. Soc.*, **96**, 5815 (1974).

(8) (a) W. von Philipsborn, J. Altman, E. Babad, J. J. Bloomfield, D. Ginsburg, and M. B. Rubin, *Helv. Chim. Acta*, **53**, 725 (1970); (b) L. A. Paquette, R. H. Meisinger, and R. E. Wingard, Jr., *J. Am. Chem. Soc.*, **95**, 2230 (1973); (c) M. J. Goldstein and S. A. Kline, *Tetrahedron Lett.*, 1089 (1973), and references cited in these papers.

(9) Thermochemical estimates[5] place **6** about 21 (±6) kcal mol^{-1} above **4**. This means that **6** itself must be very kinetically labile. The prototype, nonannulated molecule, tetracyclo[4.4.0.$0^{2,9}$.$0^{5,8}$]dec-3-ene, shown below, and hereafter named felicene,[10] may well be even less stable



than the *cis*[2]-bishomobenzene intermediate implicated in analogous rearrangements.[6,7] Another polycyclic olefin which rearranges by a retro-Diels–Alder reaction is basketene[11] which has on the other hand been isolated.

(10) The winning entry in an ad hoc competition involving the authors, A. C. Clements, G. Kennedy, D. A. Penny, and D. J. Smith.

(11) H. H. Westberg, E. N. Cain, and S. Masamune, *J. Am. Chem. Soc.*, **91**, 7512 (1969); correction *ibid.*, **92**, 5291 (1970).

(12) The 70-eV spectra showed parent ions (M) at 136 amu (tetralin) and 56 amu (butadiene). Additionally the M + 1 peaks were in accord with ^{13}C natural abundance in both cases within experimental error indicating the assigned deuterium distribution to apply to at least 95% of these products.

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Oxygen Binding to Mercaptide–Heme Complexes. Models for Reduced Cytochrome P-450

Sir:

The sustained interest in studying oxygen binding to hemoproteins had led, in the past 2 years, to the preparation of model systems, for both oxymyoglobin and oxyhemoglobin.[1-7] In the majority of these systems, the presence of a nitrogen base at the fifth coordination site of the iron(II) porphyrin was found to be important for heme oxygenation. In this communication we wish to report the binding of oxygen to a heme that contains a mercaptide ion as the axial ligand.

We recently described the preparation of a model compound for reduced cytochrome P-450 as well as its CO complex, in which *n*-butyl mercaptide ion, whose reactivity was enhanced by using a crown ether cation scavenger, served as axial ligand for the protoheme.[8,9] This compound bound CO reversibly and exhibited striking spectral resemblances to those of the P-450 enzyme. However, when this compound was exposed to O_2 at ambient temperature, a drastic spectral change was observed presumably due to the following reactions: oxygenation of heme, autoxidation of heme, and oxidation of the mercaptide ion which would not only decrease the effective concentration of mercaptide available for heme coordination but could aslo result in the production of oxidation products capable of binding to the heme. Since all of these reactions could take place simultaneously spectral evidence for the oxygen binding to heme was ambiguous when the observations were made at room temperature.

It was found, nevertheless, that at lower temperatures the latter two reactions were sufficiently inhibited to allow us to observe clean, and reversible, oxygen binding. Thus at −45° addition of O_2 to the heme-mercaptide complex in dimethylacetamide (DMA) resulted in the spectral change a → b in Figure 1.[10] The spectrum of the oxygen adduct showed no deterioration after 1 h under these conditions. Addition of excess cold pyridine to this solution displaced O_2 and re-