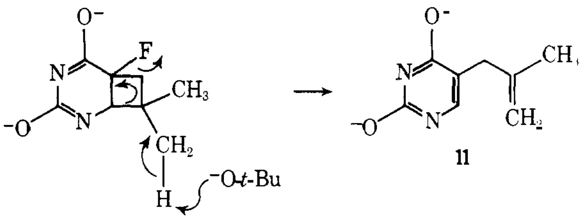

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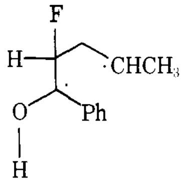
The origin of the regioselectivity could reasonably result from the effect of fluorine in altering the relative rates of: (1) formation of isomeric exiplexes[1a] or (2) ring closure vs. fragmentation for the 1,4-biradicals produced from collapse of the isomeric exiplexes.[9] Interestingly, Wagner[10] has recently shown that the ratio of ring closure to fragmentation in valerophenone photochemistry is markedly increased by an α-fluorosubstituent and has proposed fluorine hyperconjugation as an important factor in the increased amount of ring closure. The structural similarity of the biradical from α-fluorovalerophenone, **12**, and the presumed biradical intermediate in these cycloadditions, **13**, warrants consideration of a similar explanation here. While we wish to defer a thorough discussion of this question until completion of mechanistic studies, it is interesting that the acetone photosensitized cycloaddition of 5-trifluoromethyluracil (**14**) to isobutylene affords in 72% isolated yield and with >95% regioselectivity the adduct **15**.[11] Thus, the high electronegativity of the substituent may also play a role in the regioselectivity noted here.



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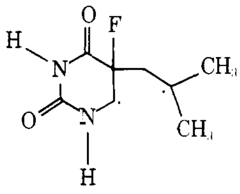

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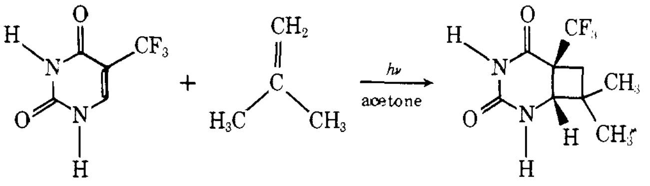

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The photostability of the vinylic fluorine under cycloaddition conditions coupled with the powerful effect of fluorine on regioselectivity and the unique fragmentation processes observed here suggest further utility of fluorinated substrates in organic photochemistry. We are currently studying the cycloaddition reactions of α- and β-fluoro-α,β-unsaturated ketones.[12]

References and Notes

(1) (a) E. J. Corey, R. B. Mitra, and H. Uda, *J. Am. Chem. Soc.*, **85**, 362 (1963), **86**, 485 (1964); (b) E. J. Corey and S. Nozoe, *ibid.*, **86**, 5570 (1964); (c) B. D. Challand, H. Hikino, G. Kornis, G. Lange, and P. deMayo, *J. Org. Chem.*, **34**, 794 (1969); (d) J. D. White and D. N. Gupta, *J. Am. Chem. Soc.*, **88**, 5364 (1966); (e) G. Büchi, J. A. Carlson, J. E. Powell, and L. F. Fietze, *ibid.*, **92**, 2165 (1970); (f) N. R. Hunter, G. A. MacAlpine, H. J. Liu, and Z. Valenta, *Can. J. Chem.*, **48**, 1440 (1970).

(2) For representative examples see (a) P. E. Eaton, *Acc. Chem. Res.*, **1**, 50 (1967); (b) T. S. Cantrell, *J. Org. Chem.*, **34**, 509 (1969).

(3) For leading references see A. Wexler, R. J. Balchunis, and J. S. Swenton, *J. Chem. Soc., Chem. Commun.*, 601 (1975).

(4) No ene-products have been observed in any of the reactions of uracils with olefins.

(5) The demanding evidence for the indicated orientation derived from the appearance of H_1 as a simple doublet of doublets due to a large coupling to fluorine (J = 23–24 Hz) and a small coupling to the N-H group (J = ~3 Hz). This latter coupling was completely removed by washing the sample with deuterium oxide.

(6) The observed regioselectivity appears somewhat solvent dependent; a higher regioselectivity has been noted in neat acetone vs. acetone-water mixtures.

(7) For **8**: uv (CH_3OH) 265 nm, ϵ 7200, thymine 265 nm, ϵ 7800; NMR (Me_2SO-d_6) δ 7.13 (s, 1 H, β-uracil hydrogen), 4.67 (br s, 2 H, vinyl), 2.87 (br s, 2 H, methylene), and 2.87 (s, 3 H, methyl).

(8) Mp: **8**, 272–274°; **9a**, 265–267°; **9b**, 277–279°; **9c**, 282–283°.

(9) P. G. Bauslaugh, *Synthesis*, **2**, 287 (1970).

(10) P. J. Wagner and M. J. Thomas, *J. Am. Chem. Soc.*, **98**, 241 (1976). We wish to thank Professor Wagner for making available a copy of this article prior to publication.

(11) **13** had mp 238–239°, NMR (Me_2SO-d_6) 60 MHz δ 1.02 (s, 3 H), 1.08 (s, 3 H), 2.10 (s, 2 H), 3.76 (d, J = 4.5 Hz which collapses to a singlet on addition of D_2O, 1 H), 7.95 (br s, 1 H), and 10.6 (br s, 1 H). The crude ^{19}F NMR of the reaction mixture showed ~ 4–5% of a second fluorine compound which we have not been able to isolate as yet.

(12) All new compounds reported here gave acceptable (±0.3%) C, H, and N combustion analyses.

(13) Camille and Henry Dreyfus Teacher-Scholar, 1970–1975.

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Carbon-13 Nuclear Magnetic Resonance Spectra of Zinc(II) Coproporphyrins. A Modus Operandi for Reproducible Measurement of Porphyrin Spectra

Sir:

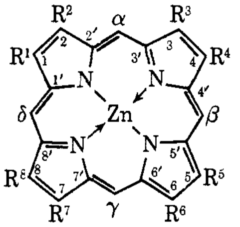
The use of carbon-13 NMR spectroscopy for the characterization of porphyrins[1] (particularly the identification of type isomers[2]), and in the delineation of the biosynthetic pathway to the type-III porphyrin skeleton[3] is now well established. Insofar as the elegant techniques employed revolve around unambiguous assignment of natural abundance spectra prior to comparison with those of pigments produced enzymically from carbon-13 labeled precursors, it is surprising that only a paucity of systematic work aimed at assignment of porphyrin spectra has been published.[4] We now report a basic method by which reproducible "monomeric" shifts of porphyrin carbons can be simply and easily obtained.

The carbon-13 spectra of virtually all free-base porphyrins show the effects of N-H tautomerism;[5] thus, the α-pyrrole carbons are always broad and unresolved (cf. Figure 1a), and in some cases they are so broad that they escape observation altogether. This exchange process can also effect the β-pyrrole and possibly the meso carbon atoms. Thus, unambiguous assignment of the individual skeletal carbon atoms becomes virtually impossible.

Incorporation of zinc(II) into the porphyrin removes the effects of the tautomeric exchange process. Zinc(II) is diamagnetic and its insertion and removal is a facile undertaking. The resultant carbon-13 NMR spectra give sharp lines for the α (and β) pyrrole carbons (Figure 1b). However, in the course of our study it became clear that the carbon-13 shifts were dependent upon the precise operating conditions (e.g., concentration, temperature, etc.). Moreover, the nature of the fine structure changed markedly with concentration. We ascribe this to the formation of highly structured aggregates in solution.[6]

Despite the generally held view that carbon-13 shifts are not concentration dependent, we have observed shifts of several parts per million in the zinc(II) porphyrins.[7] The carbon-13 shifts of the quaternary skeletal carbons of various porphyrins, even at the same concentration in $CDCl_3$, are quite inconsistent and inexplicable in terms of substituent effects. In retrospect this is not surprising since the observed shifts are a function not only of the isolated molecule

Table I. Carbon-13 Chemical Shifts (δ, ppm downfield from internal Me_4Si) of Porphyrin Skeletal Carbons in $CDCl_3$ Containing Excess Pyrrolidine



1, $R^{1,3,5,7}$ = Me; $R^{2,4,6,8}$ = pMe
2, $R^{1,4,5,8}$ = Me; $R^{2,3,6,7}$ = pMe
3, $R^{1,3,5,8}$ = Me; $R^{2,4,6,7}$ = pMe
4, $R^{1,4,6,7}$ = Me; $R^{2,3,5,8}$ = pMe

pMe = $CH_2CH_2CO_2Me$

Compound[a]	α-Pyrrole carbons[b]		β-Pyrrole carbons		Meso carbons
Zinc(II) Copro-I (**1**)	148.08 (1′,3′,5′,7′)	147.09 (2′,4′,6′,8′)	136.62 (1,3,5,7)	138.46 (2,4,6,8)	96.54 (α,β,γ,δ)
Zinc(II) Copro-II (**2**)	148.14 (1′,4′,5′,8′)	147.17 (2′,3′,6′,7′)	136.53 (1,4,5,8)	138.62 (2,3,6,7)	96.84 (β,δ) 96.43 (α,γ)
Zinc(II) Copro-III (**3**)	148.18 148.09 (1′,3′,5′,8′)	147.21 147.10 (2′,4′,6′,7′)	136.63 136.49 (1,3,5,8)	138.62 138.50 (2,4,6,7)	96.89 (δ) 96.64 96.54 (α,β) 96.38 (γ)
Zinc(II) Copro-IV (**4**)	148.09 148.00 (1′,4′,6′,7′)	147.20 147.11 (2′,3′,5′,8′)	136.63 136.52 (1,4,6,7)	138.58 138.43 (2,3,5,8)	96.94 (γ) 96.55 (β,δ) 96.27 (α)

[a] All samples used as tetramethyl esters. [b] Numbers and Greek letters in parentheses refer to carbons in structural formula.

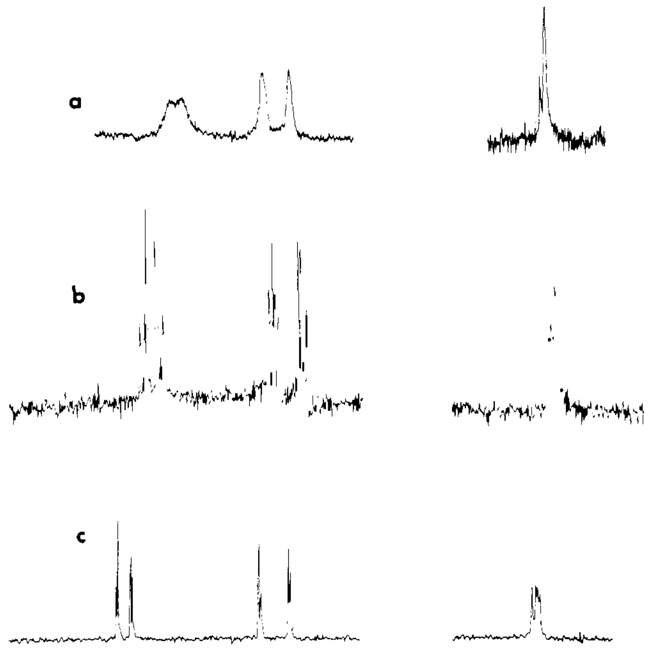


Figure 1. Carbon-13 spectra (Varian XL-100) of skeletal carbons in (a) coproporphyrin-III tetramethyl ester ($CDCl_3$ solution); (b) zinc(II) coproporphyrin-III tetramethyl ester (**3**) ($CDCl_3$); (c) zinc(II) coproporphyrin-III tetramethyl ester(**3**) (in $CDCl_3$ plus approximately 2 equiv of added pyrrolidine).

but also the degree *and the specificity* of aggregation which will vary from porphyrin to porphyrin.

Addition of a donor molecule, such as pyrrolidine, circumvents these problems because any aggregates are immediately sundered to afford simpler spectra (Figure 1c). An additional benefit is that pyrrolidine dramatically increases the solubility of such metalloporphyrins even when they are almost insoluble in $CDCl_3$ alone.[8] The chemical shifts in the presence of excess pyrrolidine are independent of concentration. Furthermore, *the chemical shifts are now capable of simple and consistent interpretation in terms of substituent effects.*

In Table I we present the δ-values for the tetramethyl esters of the four coproporphyrin-type isomers. Perusal of the meso carbon shifts alone allows the unequivocal identification of each isomer. Such an identification could not be made[2] with the metal-free compounds; in Copro-III, for example, three of the signals are isochronous (Figure 1a). Further, the remarkable consistency of the shifts allows specific assignment of almost all peaks. For example, in zinc(II) Copro-IV the three meso signals are in the ratio of 1:2:1; thus, from symmetry the line at 96.55 ppm is assigned to the β and δ meso carbons, i.e., to the meso carbons flanked by a methyl group and a propionate group. This assignment is supported by the meso carbon shift in zinc(II) Copro-I (96.54 ppm). Further consideration of the shifts in the type-II, -III, and -IV isomers shows that there is consistently a low-field peak (96.84, 96.98, and 96.94 ppm, respectively) and a high-field peak (96.43, 96.38, and 96.27 ppm, respectively). Analogy with a host of model porphyrins[9] allows us to assign the high-field line to those meso carbons flanked by two propionate side-chains, and the low-field resonance is assigned to a meso carbon between two peripheral methyl groups. These assignments are further confirmed in the spectrum of zinc(II) αγ-dideuterio-Copro-II.[10] The only signals which we are unable to assign specifically are the α and β meso carbons in zinc(II) Copro-III because both meso positions are flanked by a methyl and a propionate substituent.[11]

The quaternary pyrrole resonances are also totally consistent. We assign the α and β-pyrrole carbons as shown in Table I by analogy with the effects of methyl and propionate groups on a benzene ring. Only in zinc(II) Copro-III is there any loss of information due to isochronous signals. We do not yet feel confident in further specific assignment of the α- and β-pyrrole carbons bearing methyl or propionate groups in the type-III and -IV isomers. The substituent effects themselves are unremarkable and will be considered further, along with the side chain assignments, in a future publication.[9]

In conclusion we would suggest that all porphyrin carbon-13 spectra should be obtained under the conditions outlined herein. Only when these conditions are met does total assignment of spectra and unambiguous identification of porphyrin type-isomers become a feasible task. In principle, this procedure is applicable to all divalent diamagnetic metalloporphyrins other than those which become paramagnetic upon coordination with bases.[12]

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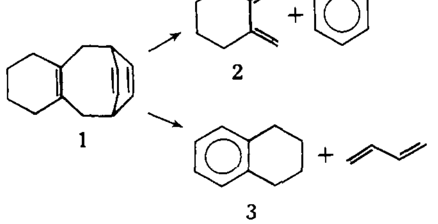
Thermal Decomposition of Tricyclo[6.4.0.2^{3,6}]tetradeca-1(8),4,13-triene. A Process Involving a Series of Intramolecular and Retro-Diels–Alder Reactions

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.

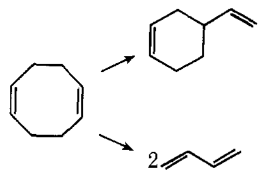
Scheme I

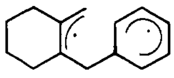


The reaction was made the subject of a brief kinetic study using the sealed ampoule technique; 6.8-μmol portions of the reactant[2] were sealed under vacuum in 2.7 cm^3, base-washed Pyrex tubes and heated (stirred salt thermostat) for periods of up to 4.5 h at 453.6 ± 0.1 K. The product mixture (up to 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. Although we offer no firm conclusion as to the detailed mechanism of these processes, we note that the biradical, **5**, is an 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.

Scheme II





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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-