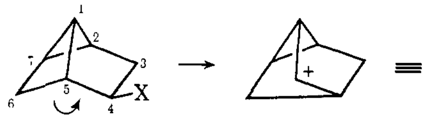
Table II. Acetolysis Products from 4-Psinortricyclyl Tosylates[a]

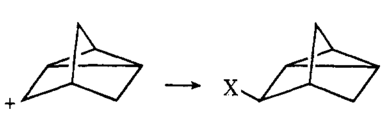
Compd	3-OTs	3-OAc + 5-norbornenyl-OAc	2-OAc	Unknown
1-OTs[b,c]	78	21.5		0.5
2-OTs[d]		3	97	Trace

[a] Relative per cent yields; solutions were 0.01–0.05 *M* in substrate and buffered with sufficient sodium acetate to neutralize liberated tosylic acid. Products were identified by spectral comparisons with authentic samples. [b] 24.5°. [c] Corrected for initial contamination by **3**-OTs. [d] 75°.

as it ionizes with participation of the 5,6 bond. Table II shows that the vastly predominant products are indeed derived mainly from the nortricyclyl cation system which is formally related to **1** by a nondegenerate Wagner–Meerwein rearrangement. The major events are ion-pair return to unreactive **3**-OTs[7] and solvolytic capture of the nortricyclyl cation.[8] Thus, **1** represents a new route to the nortricyclyl ion-pair system.[9]



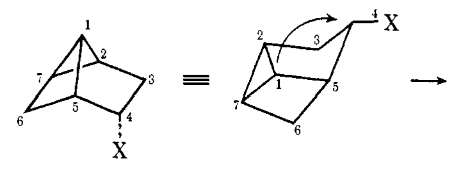
1



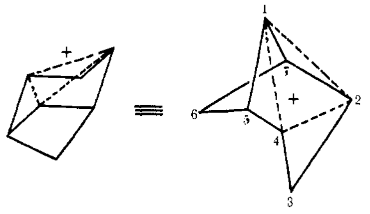
3

It might have been anticipated that **2**-OTs would be slightly less reactive than *endo*-2-norbornyl due to inductive destabilization of charge by the β-cyclopropyl ring.[10] In fact, Table I shows it to be substantially more reactive. Most striking is the finding that while there is a small amount of leakage to the nortricyclyl cation, the predominant solvolytic product is unrearranged *endo*-acetate, **2**-OAc. *exo*-Acetate **1**-OAc, which is completely stable to the reaction conditions, was not detected (<0.1%). The dichotomy between the products derived from **1**-OTs and **2**-OTs is highlighted when compared with the renowned 2-norbornyl system where there is predominant leakage from the endo epimer to that species which derives from the exo epimer.

It is proposed that **2**-OTs ionizes with anchimeric assistance of the 1,2 bond to give the trishomocyclopropenyl cation **4**. Endo directed capture of nucleophile at C_2 or C_4 would then account for net retention of configuration.[11] To test for the intermediacy of **4**,



2



4

2-OTs-*4-d* and **2**-OTs-*3,3,4-d*$_3$ were acetolyzed in separate experiments. In each case nmr analysis (250 MHz) indicated equal deuterium concentrations at C_2 and C_4 of recovered **2**-OAc. The mass and nmr spectra of **2**-OAc recovered from solvolysis of **2**-OTs in DOAc indicated that there is little or no proton exchange with solvent during the course of the reaction.

Thus, the rate, product, and scrambling data for **2**-OTs are all consistent with the formulation of **4** as the major ionic intermediate. However, the full story regarding this cation is yet to be told, since we find that the sample of **2**-OAc recovered from *either* of the two deuterium labeled precursors contains not 0.5 D at C_2 and C_4, as would be expected on the basis of statically bridged **4**, but rather 0.24 ± .02 D at each of these positions.[12a] It thus appears that cation **4** experiences a degenerate isomerization under the solvolytic conditions, probably one which scrambles four of the five methine protons.[12b]

Acknowledgments. The author is grateful to Professors W. L. Mock and R. F. Sprecher for helpful discussions, to B. Aufderheide, Dr. P. Balaram, and Dr. J. Dadok for assistance in recording nmr spectra, and to J. Boal for mass spectral determinations. Spectra (250-MHz) were recorded at the NMR Facility for Biomedical Studies, NIH Grant No. RR 00292.

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Received June 24, 1972

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(6) S. Winstein, E. Clippinger, R. Howe, and E. Vogelfanger, *J. Amer. Chem. Soc.*, **87**, 376 (1965).

(7) No olefinic hydrogens could be detected in this material, indicating the absence of *exo*-5-norbornenyl tosylate.

(8) The small amount of unknown acetolysis product appears (glpc) not to be **1**-OAc.

(9) The extent to which the relative reactivities of **1**-X and **3**-X reflect the difference in their ground-state energies is not yet clear. Clarification of this factor should lead to a more detailed description of the electron delocalization during ionization of **1**-X, and we hope to elaborate on this point in the future.

(10) (a) P. v. R. Schleyer, *J. Amer. Chem. Soc.*, **86**, 1856 (1964); (b) Y. E. Rhodes and T. Takino, *ibid.*, **92**, 5270 (1970); (c) M. J. S. Dewar and J. M. Harris, *ibid.*, **92**, 6557 (1970).

(11) (a) H. Tanida, *Accounts Chem. Res.*, **1**, 239 (1968); (b) J. S. Haywood-Farmer and R. F. Pincock, *J. Amer. Chem. Soc.*, **91**, 3020 (1969); (c) P. G. Gassman and A. F. Fentiman, Jr., *ibid.*, **92**, 2551 (1970); (d) G. D. Sargent and M. A. Herkenham, *ibid.*, **94**, 2892 (1972); (e) M. S. Baird and C. B. Reese, *Chem. Commun.*, 523 (1972).

(12) (a) The analysis is based on the acetate methyl group as internal standard. (b) More recent results indicate that it is the methine proton at C_1 which remains unique, and that the two methylene positions are scrambled equally. This raises the intriguing possibility that the intermediate is a C_{2v} bridged species, the prototype of which has recently been discussed theoretically.[13]

(13) W-D. Stohrer and R. Hoffmann, *J. Amer. Chem. Soc.*, **94**, 1661 (1972).

Unusual Metalloporphyrins. XIV. The Structure of [*meso*-Tetraphenylporphinato]bis[tricarbonylrhenium(I)]

Sir:

X-Ray structural studies have established that the metal atoms in some metalloporphyrins are 0.3–0.5 Å out of the plane of the four pyrrole nitrogen atoms of a porphyrin molecule.[1] Even greater displacements of metal atoms from the plane of four isoindole nitrogen

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(1) J. L. Hoard, *Science*, **174**, 1295 (1971).

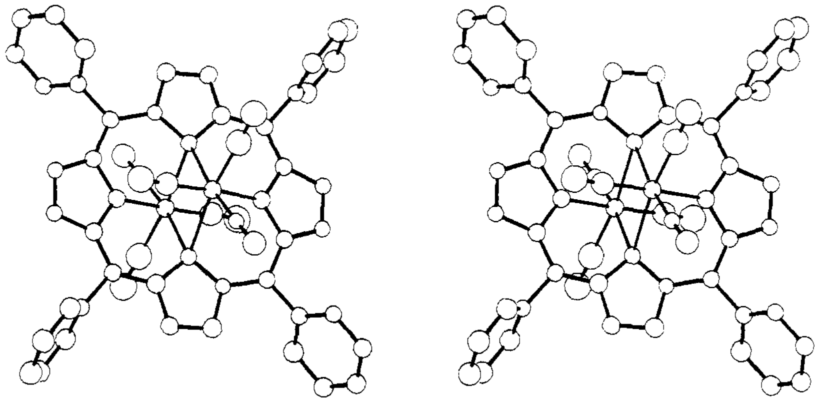

Figure 1. Stereoview of [*meso*-tetraphenylporphinato]bis[tricarbonylrhenium(I)].

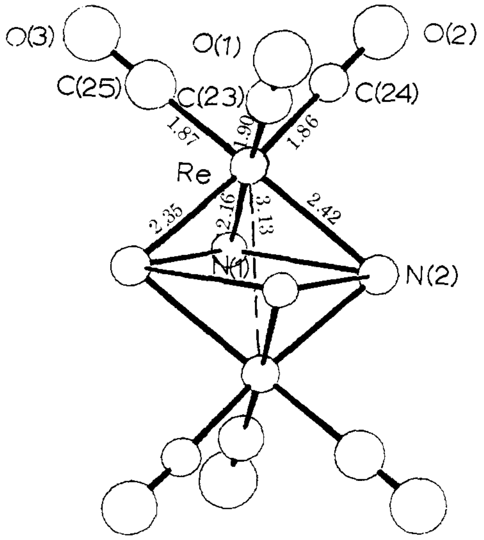

Figure 2. Coordination sphere showing bond distances around the Re atoms. The lines between nitrogens signify the plane of the macrocycle. Atoms not labeled are centrosymmetrically related to labeled atoms.

atoms of a phthalocyanine molecule have been observed in tin(II) phthalocyanine (1.11 Å),[2] tin(IV) bisphthalocyanine (1.29 and 1.32 Å),[3] and uranium(IV) bisphthalocyanine (1.40 Å).[4] In the above compounds, each metal atom is coordinated to all four of the nitrogen atoms of the macrocycles.

Recently the unusual metalloporphyrin, μ-[mesoporphyrin IX dimethyl esterato]bis[tricarbonylrhenium(I)], was reported.[5] On the basis of chemical evidence it was postulated that two rhenium atoms are bonded to one porphyrin molecule, presumably on opposite sides of the plane of the macrocycle, with a strong metal–metal bond between them. It was further postulated that each metal atom is coordinated to two opposite pyrrole nitrogen atoms. It was calculated that each rhenium atom is 1.32 Å out of the plane of the four nitrogen atoms.[6] Such a structure is of great interest since it has been theorized that intermediates in metal ion incorporation reactions (including insertion of iron(II) and magnesium(II) in protoporphyrin IX), acid-catalyzed solvolysis reactions, and metal ion exchange reactions in porphyrin systems[7] may have a similar stereochemistry.

We wish to report a single-crystal X-ray diffraction analysis on a similar compound, namely, [*meso*-tetraphenylporphinato]bis[tricarbonylrhenium(I)] (I), which has not been reported earlier.[5,6] Unlike μ-[mesoporphyrin IX dimethyl esterato]bis[tricarbonylrhenium(I)], suitable crystals of this compound were easily obtainable.

The compound I was prepared by refluxing dirhenium dodecacarbonyl (150 mg) and *meso*-tetraphenylporphine (100 mg) in 10 ml of decalin for ~13 hr. After completion of the reaction, the complex was precipitated with heptane. The precipitate was dissolved in benzene and the concentrated solution was chromatographed on a silica gel. The major middle fraction was concentrated to dryness and the solid was crystallized from a benzene and heptane mixture (mp ~200°). The visible spectrum of I in benzene shows three peaks at 411 (soret), 483 (I), and 514 (II) nm (relative intensity II > I) and the ir spectrum ($CHCl_3$) has three strong peaks at 1890, 1905, and 2011 cm^{-1} in the carbonyl-stretching region. The mass spectrum of I shows a parent peak at m/e 1150 $[(M)^{+}]$.[8] The triplet at $(M)^{+}$, $(M + 2)^{+}$, and $(M + 4)^{+}$ further supports the presence of two rhenium atoms in each molecule due to two common isotopes (^{185}Re and ^{187}Re) of naturally occurring rhenium.

The material used for the X-ray crystallographic analysis was recrystallized from dioxane. Crystal data: $C_{50}H_{28}N_4O_6Re_2$; $M = 1153.2$; space group $P2_1/c$; $a = 11.887\,(2)$ Å; $b = 16.363\,(2)$ Å; $c = 11.586\,(2)$ Å; $\beta = 117.02\,(1)°$; $V = 2007.8$ Å^3; $Z = 2$; $D_c = 1.908$ g/cm^3; linear absorption coefficient, μ, for Mo Kα radiation is 64.4 cm^{-1}.

Three-dimensional intensity data were collected on a Datex-Syntex diffractometer using pyrolytic graphite monochromatized Mo Kα radiation ($\lambda = 0.71069$ Å). A total of 2747 independent reflections were measured out to 2θ *ca.* 45°. Of these, 1970 were considered observed.

The positions of the rhenium atoms were easily found from a Patterson synthesis. The positions of the re-

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[2] M. K. Friedel, B. F. Hoskins, R. L. Martin, and S. A. Mason, *Chem. Commun.*, 400 (1970).

[3] E. B. Fleischer, *Accounts Chem. Res.*, 3, 111 (1970).

[4] A. Gieren and W. Hoppe, *Chem. Commun.*, 413 (1971).

[5] D. Ostfeld, M. Tsutsui, C. P. Hrung, and D. C. Conway, *J. Amer. Chem. Soc.*, 93, 2548 (1971).

[6] D. Ostfeld, M. Tsutsui, C. P. Hrung, and D. C. Conway, *J. Coord. Chem.*, in press.

[7] R. Khosropour and P. Hambright, *J. Chem. Soc., Chem. Commun.*, 13 (1972).

[8] $^{185}Re_2{}^{12}C_{44}{}^{1}H_{28}{}^{14}N_4(12_2 16_0)_6$.

maining 30 nonhydrogen atoms in the asymmetric unit were found from a series of ΔF Fourier maps. The structure has been refined by block-diagonal least-squares techniques to the present discrepancy indices of $R = 0.063$ (based on F) and weighted $R = 0.077$. At the present stage of refinement the thermal motion for all atoms has been assumed to be isotropic.

There are some significant features of this structure which were not predicted earlier.[5,6] A stereoview of the complex is given in Figure 1 while Figure 2 shows the bonding in the coordination sphere. It is a centrosymmetric complex having two rhenium atoms bonded to the porphyrin, one above and one below the plane of the macrocycle. Each rhenium atom is 1.42 Å out of the plane. The rhenium ions are not positioned directly over the center of the porphyrin but are set to one side so that each metal ion is bonded to three nitrogen atoms. The Re–N distance which involves the nitrogen atom to which only one metal ion is bonded (N(1)) is 2.16 (2) Å. The two Re–N distances involving the nitrogen atoms each of which is bonded to both metal ions (N(2)) are considerably longer, 2.35 (2) and 2.42 (2) Å. The fourth Re–N distance is 3.23 Å. This is the first example in metalloporphyrin (or metallophthalocyanine) systems where three instead of four nitrogen atoms of a porphyrin molecule are involved in bonding to a metal atom.

Of particular interest is the Re–Re distance of 3.126 (3) Å. This distance is somewhat long for metal–metal bonding. Bond distances for Re–Re single bonds range from 2.7 to 3.02 Å.[9,10] Furthermore, the closed-shell electron rule is fulfilled without postulating a Re–Re bond. However, this distance is short enough that some sort of Re–Re interaction cannot be ruled out. We are at the present trying to study the Re–Re interaction using magnetic methods on similar metalloporphyrins containing two rhenium atoms, each with a formal oxidation state of 2.

The porphyrin ring is quite distorted. The two distances from the center of the ring to the pyrrole nitrogen atoms are 2.31 (2) and 1.80 (2) Å for N(1) and N(2), respectively. The distances from the center of the ring to the methine carbons are 3.42 (3) and 3.46 (3) Å. The C_α–N distances for bonds involving N(1) average 1.38 (2) Å, while for bonds involving N(2) the average distance is 1.42 (2) Å, indicating some loss of double bond character for these bonds. The average C_α–C_β distances are 1.44 (1) and 1.42 (2) Å for the rings containing N(1) and N(2), respectively. The C_β–C_β distances are 1.36 (1) and 1.37 (1) Å. The average C_α–C_m distance is 1.40 (2) Å, while the average C–C distance in the phenyl rings is 1.39 (2) Å.

Each pyrrole ring is planar, but the angle between adjacent pyrrole rings is 17.3°. The two phenyl rings are tilted from the plane of the four pyrrole nitrogen atoms by angles of 81.4 and 53.5°. Refinement will be continued assuming anisotropic thermal motion and using higher order, absorption corrected data.

Acknowledgment. This work was supported by the National Science Foundation (Grant No. G012064), institutional support (D.P.S.R. No. 00381), the Robert A. Welch Foundation (Grant No. A0328), and the Texas Agricultural Experiment Station Project H1668.

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Regioselectivity in the Photosensitized Cycloadditions of 1,3-Dimethyluracil

Sir:

The photochemistry of the nitrogen bases of nucleic acids has been actively investigated both theoretically and experimentally.[1] However, while considerable theoretical work has been directed at relating chemical reactivity and excited state electron distribution in these bases,[2] the majority of the chemical studies in these systems has been restricted to photohydration and photodimerization reactions.[3,3a] Since we felt photocycloaddition reactions of these nitrogen bases with various substrates would be not only of intrinsic interest, but also of value in assessing the electron distribution of the excited state, we have initiated studies on the photocycloaddition reactions of biologically important nitrogen bases. In this communication we wish to report the high-yield, regioselective, acetone-sensitized cycloaddition of 1,3-dimethyluracil (**1**) to *tert*-butyl vinyl ether (**2a**), vinyl acetate (**2b**), and ketene diethyl acetal (**2c**). In addition to cis-fused cyclobutanes, novel trans-fused cyclobutane adducts were detected in these studies and in one instance isolated and completely characterized.

The importance of the triplet state of uracil in these dimerizations[4] suggested that our initial studies involve the triplet uracil species as reactant. Photolysis of 2% solutions of **1** in acetonitrile containing acetone (0.5 *M*) as sensitizer and a 7–10 molar excess of *tert*-butyl vinyl ether yielded four products in the ratio of 46:50:2:2 by vpc. Chromatography on silica gel yielded crystalline **3** and **4**, whose nmr, ir, and mass spectra were suggestive of 1:1 adducts of **1** and **2a**. The orienta-

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(1) For reviews in this area see: (a) J. R. Burr, *Advan. Photochem.*, **6**, 193 (1968); (b) A. D. McLaren and D. Shugar, "Photochemistry of Proteins and Nucleic Acids," Macmillan, New York, N. Y., 1964, pp 162–220; (c) E. Fahr, *Angew. Chem., Int. Ed. Engl.*, **8**, 578 (1969); (d) *Photochem. Photobiol.*, **7**, 511 (1968).

(2) For leading references see (a) Z. Neiman, *Israel J. Chem.*, **9**, 119 (1971); (b) V. I. Danelov, Y. A. Kruglyak, V. A. Kuprievich, and V. V. Ogloblin, *Theoret. Chim. Acta*, **14**, 242 (1969); (c) B. Pullman, *Photochem. Photobiol.*, **7**, 525 (1968); (d) V. Klunwashter, J. Drobnik, and L. Augenstein, *ibid.*, **5**, 579 (1966); (e) A. Imamura, H. Fuyita, and C. Nagata, *Bull. Chem. Soc. Jap.*, **40**, 21 (1967).

(3) While additions of excited-state species to ground-state uracils are well known (P. Song, M. Harter, T. A. Moore, and W. C. Herndon, *Photochem. Photobiol.*, **14**, 521 (1971)) we have been able to find only four brief reports of excited uracil addition to olefins (E. Krajewska and D. Shugar, *Science*, **173**, 435 (1971); I. Pietrzykowska and D. Shugar, *Acta Biochim. Pol.*, **17**, 361 (1970); R. Beugelmans, J. Fourrey, S. Gero, M. LeGoff, D. Mercier, V. Ratovelomana, and M. Janot, *C. R. Acad. Sci. Paris*, **274**, 882 1972)); C. Helene and F. Brun, *Photochem. Photobiol.*, **11**, 77 (1970).

(3a) Note Added in Proof. Products arising from addition of a carbonyl group across the uracil double bond have also been characterized. For a leading reference see D. E. Bergstrom and N. J. Leonard, *Biochemistry* **11**, 1 (1972).

(4) For leading references see E. Hayan, *J. Amer. Chem. Soc.*, **91**, 5397 (1969).