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.

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Received July 8, 1972

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[9] F. A. Cotton, *Accounts Chem. Res.*, **2**, 240 (1969).

[10] N. I. G. Gapotchenko, N. V. Alekseev, N. E. Kolobova, K. N. Anisimov, I. A. Ronova, and A. A. Johansson, *J. Organometal. Chem.*, **35**, 319 (1972).

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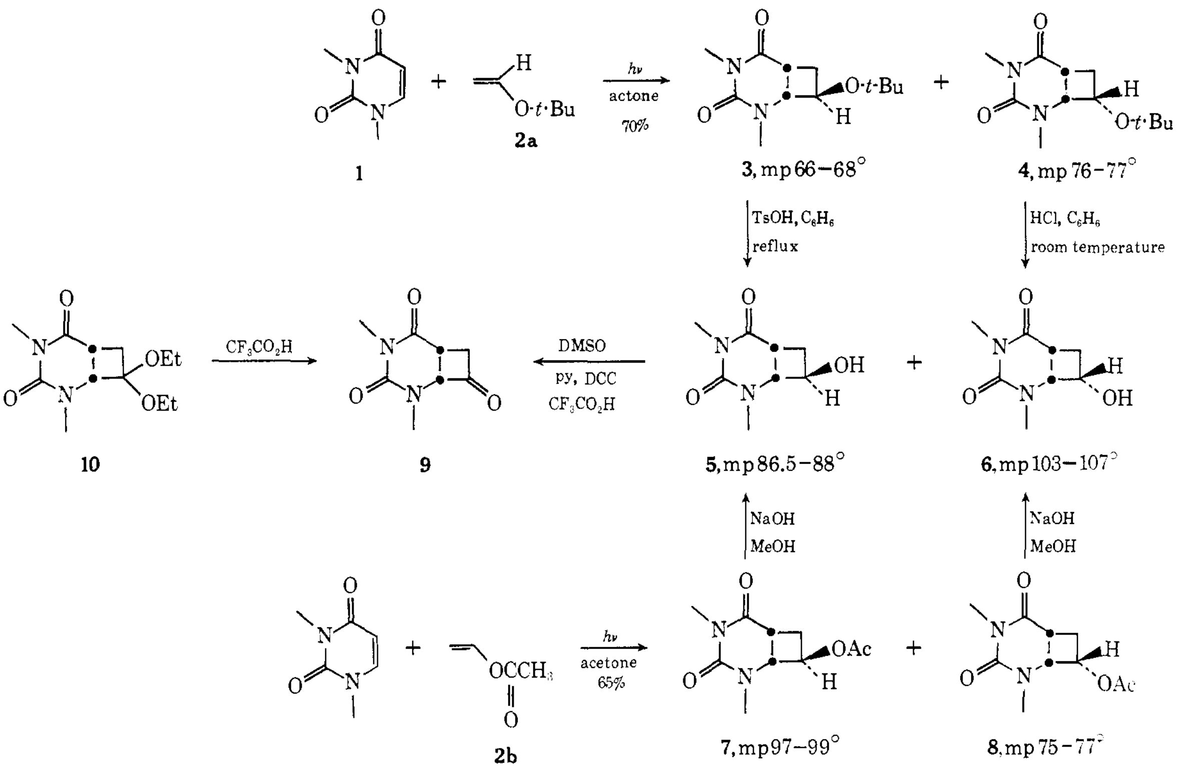
(1) For reviews in this area see: (a) J. R. Burr, *Advan. Photochem.*, **6**, 193 (1968); (b) A. D. McLaren and D. Shugar, "Photochemistry of Proteins and Nucleic Acids," Macmillan, New York, N. Y., 1964, pp 162–220; (c) E. Fahr, *Angew. Chem., Int. Ed. Engl.*, **8**, 578 (1969); (d) *Photochem. Photobiol.*,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

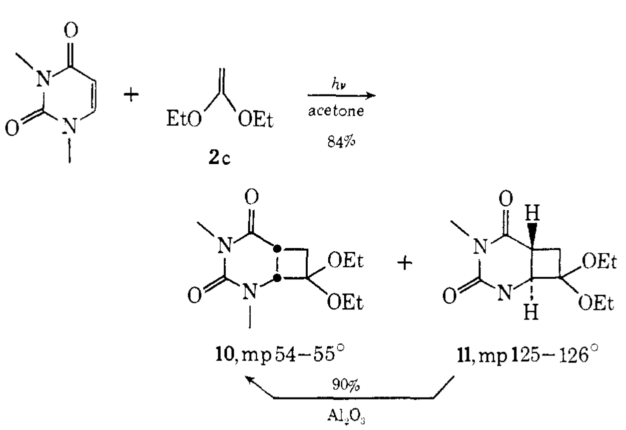
(4) For leading references see E. Hayan, *J. Amer. Chem. Soc.*, **91**, 5397 (1969).



tion of the *tert*-butoxy group of **3** and **4** with respect to the uracil 5,6 bond rests on the base stability of the alcohols **5** and **6** derived from acid cleavage of **3** and **4**. Had the opposite orientation been correct, the respective alcohol would readily undergo reactions analogous to the reverse aldol process.[5] The same alcohols could be obtained more conveniently by hydrolysis of the cycloadducts **7** and **8** obtained from photosensitized addition of **1** to **2b**. The epimeric nature of these adducts was confirmed by oxidation of alcohols **5** and **6** to a common cyclobutanone **9**. The same cyclobutanone was obtained by trifluoroacetic acid hydrolysis of the major adduct from 1,3-dimethyluracil and ketene diethyl acetal (*vide infra*). Thus, the results demonstrate that the major cycloadducts from acetone-sensitized addition of **1** to **2a–c** are formed in a similar regioselective manner.

While the orientation of the cycloadducts seems secure, the stereochemistry of the adducts can be only tenatively assigned. The *tert*-butyl ethers **3** and **4** cleave to alcohols with markedly different rates and it appears reasonable that the higher reactivity of **4** is related to relief of some nonbonded interactions present in the starting ether. The stereochemical assignments are further supported by the mass spectra of alcohols **5** and **6**. While **5** shows an M − 18 peak in its mass spectrum (0.8% of base, seven times as intense as parent ion), **6** shows an M − 18 peak of <2% of the parent ion. Since studies on loss of water in the mass spectra from simple alcohols have been shown to involve a cis 1,3 elimination,[6] **5** would be assigned as the exo alcohol in agreement with the assignment from the rate of acid cleavage of the ether. We emphasize that these assignments are tentative and X-ray studies may be necessary to rigorously establish this point.

In the cycloadditions of **1** to **2a** and **2b** there were detected two minor products, which have not as yet been obtained pure. However, from **1** and **2c** the ratio



of the major:minor adduct was 73:11 and the latter was obtained as a crystalline solid which could be isomerized on basic alumina to **10**. On the basis of spectroscopic data and its isomerization to **10**, the minor adduct is assigned as the trans-fused cyclobutane **11**.[7] Thus, the comments by Wang[5] that the absence of trans-fused cyclobutane dimers from uracils may be related to their isomerization under isolation conditions gain added significance.

The high regioselectivity of the cycloadditions noted here indicates some degree of charge polarization in the 1,3-dimethyluracil excited state, while the formation of trans-fused cyclobutanes suggests the importance of a geometrically distorted species at least for the formation

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(5) For analogy for this process in these systems see M. N. Khattak and S. Y. Wang, *Tetrahedron*, 28, 945 (1972).

(6) (a) C. G. Macdonald, J. S. Shannon, and G. Sugowdz, *Tetrahedron Lett.*, 807 (1963); (b) S. R. Shrader, "Introductory Mass Spectrometry," Allyn and Bacon, Boston, Mass., 1971, pp 52–57.

(7) The minor adducts of **1** with **2a** and **2b** disappear (vpc) when the crude reaction mixtures are treated with base. This suggests these compounds too may be trans-fused cyclobutanes.

of the trans-fused products. Although sufficient evidence is not available as yet to define the charge distribution or mechanism for these cycloadditions, the results presented here add some support to the proposal that the widely studied α,β-unsaturated ketone cycloadditions[8] are reasonable models for related reactions of the uracils, and presumably thymines.[5,9]

In contrast to the photoadducts of cyclic α,β-unsaturated ketones, the cycloadducts from uracil possess a hydrolyzable urea function. The high yields of cycloadducts and potential degradation of the urea portion of the molecule open a new and versatile method for the synthesis of four-membered rings (cyclobutanes, cyclobutenes, and perhaps cyclobutadienes). Aspects of this chemistry are currently under study.[10]

Acknowledgment. We wish to thank Dr. M. Logue and Dr. N. Leonard for helpful comments.

[8] O. L. Chapman and G. Lenz, *Org. Photochem.*, **1**, 294 (1967).

[9] (a) A. A. Lamola, *Photochem. Photobiol.*, **7**, 619 (1968); (b) P. J. Wagner and D. J. Bucheck, *J. Amer. Chem. Soc.*, **92**, 181 (1970).

[10] All compounds noted gave acceptable combustion analyses, and, except for **9**, were obtained as crystalline solids. All yields reported are isolated yields. All structures were consistent with 100-MHz nmr spectra. Due to space limitations and the complexity of these spectra they have not been described in the text. The spectra as well as decoupling studies will be discussed thoroughly in our full paper.

[11] Alfred P. Sloan Fellow (1970–1972); Camille and Henry Dreyfus Teacher–Scholar Awardee (1971–1976).

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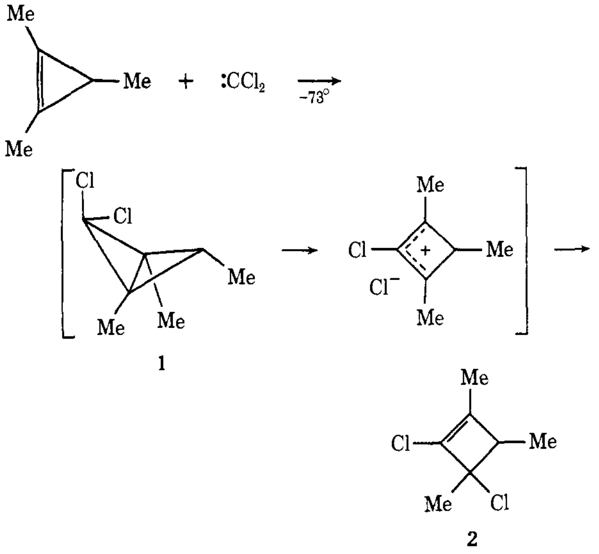
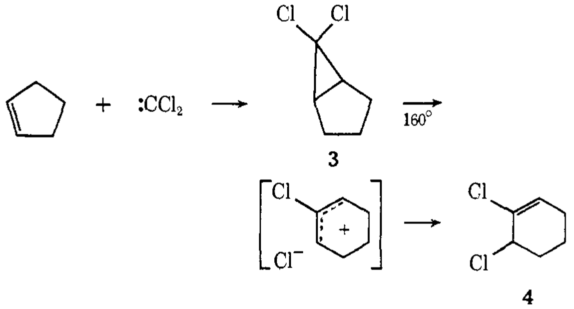
Spontaneous Generation of a Bridgehead Double Bond in a Seven-Membered Ring

Sir:

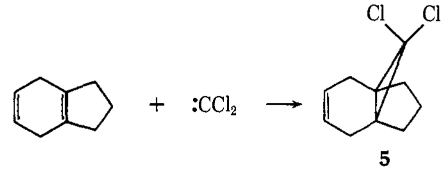
As is well known, addition of dihalocarbene (or its equivalent) to the double bond of small cyclic olefins can result in ring opening of the initial adduct[1] to yield a vinyl, allylic dihalide, *via* the intermediate haloallylic cation (*e.g.*, eq 1[2] and 2[1]). However, when the olefin is internal to two rings, the initial cyclopropane adduct is stable (*e.g.*, eq 3[3] and 4[4]).



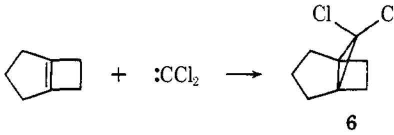
(1)

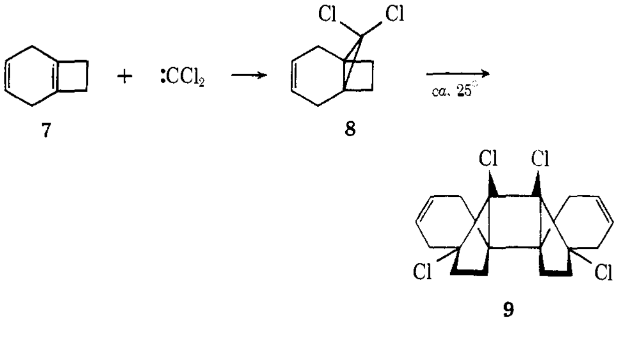


(2)



(3)





We wish to report that when dichlorocarbene (generated *via* the $CHCl_3 + KO$-*t*-Bu in pentane route) is added to 3,6-dihydrobenzcyclobutene (**7**),[5] the initial adduct **8**[6] is thermally labile when neat or when dissolved in a dipolar aprotic solvent (*e.g.*, DMSO, DMF, acetone, acetonitrile). Thus when the neat liquid **8** was allowed to warm to room temperature, an exothermic reaction occurred, whereupon crystals were deposited in the reaction flask. The crystals could be isolated in 50–60% yield, and melted sharply (mp 228° dec). Both mass spectrometry and elemental analysis indicated a formula of $C_{18}H_{20}Cl_4$, *i.e.*, a dimer of **8**. The remainder of the material in the reaction flask (*i.e.*, that which did not crystallize) proved isomeric with the crystalline dimer **9**.

Since the nmr (τ 4.53, 4 H, olefinics; τ 6.68–8.21, 16 H, aliphatics) was relatively uninformative, an X-ray analysis of the crystalline dimer was undertaken. Single crystals of **9** were grown by slow evaporation of a CH_2Cl_2 solution. Preliminary photographs displayed $2/m$ Laue symmetry and systematic extinctions for $h0l$ ($h + l = 2n + 1$ missing) and $0k0$ ($k = 2n + 1$ missing) required the monoclinic space group $P2_1/n$ (C_{2h}^5 alternate setting). Diffractometer measured cell constants were $a = 7.484$ (3), $b = 16.787$ (4), and $c =$

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[1] For a general review, see R. Barlet and Y. Vo-Quang, *Bull. Soc. Chim. Fr.*, 3729 (1969).

[2] B. M. Trost and R. C. Atkins, *Chem. Commun.*, 1254 (1971).

[3] The addition of dichlorocarbene to 4,7-dihydroindene was carried out and gave results analogously to the dibromocarbene addition already described [E. Vogel, W. Wiedemann, H. Kiefer, and W. Harrison, *Tetrahedron Lett.*, 673 (1963)].

[4] K. B. Wiberg and G. J. Burgmaier, *ibid.*, 317 (1969).

[5] J. M. Garrett and G. J. Fonken, *ibid.*, 191 (1969).

[6] P. Warner and R. LaRose, *ibid.*, 2141 (1972).