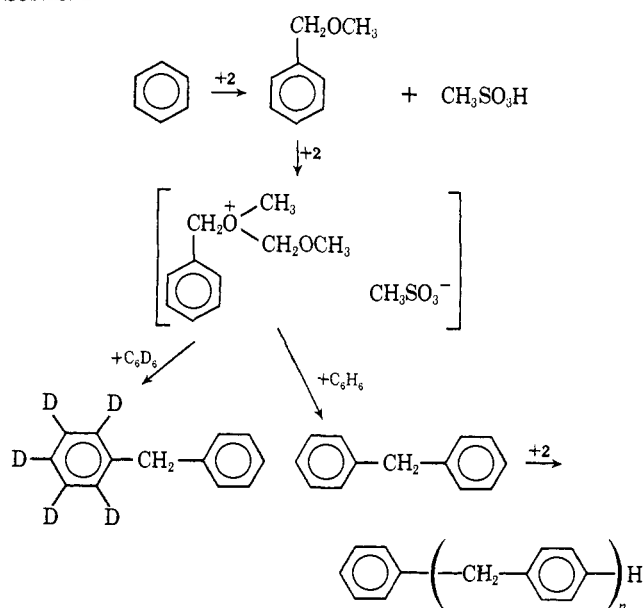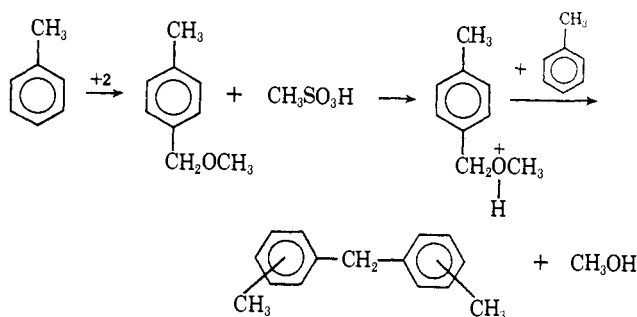**Scheme I**

Thus toluene reacted with the sulfonate **2** to give a mixture of polytolylmethanes in 80% yield together with methanol. Distillation of the mixture gave ditolylmethanes as the major (86%) products.

We have also demonstrated the ability of the sulfonate **2** to cleave a number of ethers. As well as the benzyl ethers, whose cleavage is described above, cyclic ethers are also cleaved. Thus, ethylene oxide reacts at 0° to give the methoxymethyl glycol methanesulfonate, in 41% yield, while overnight reflux of the sulfonate **2** in tetrahydrofuran gives a 30% yield of the analogous methoxymethylbutanediol methanesulfonate. Studies of this type of ether cleavage continue.
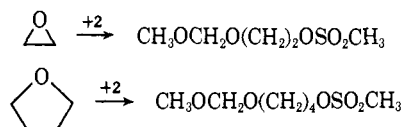
By these reactions we have demonstrated a wide range of utility for methoxymethyl methanesulfonate. This, coupled with its high reactivity, make it a potentially

(7) A similar explanation can now be advanced for the observation that reaction between benzene derivatives and chloromethyl ether gives predominantly benzyl chloride rather than the expected benzyl ether.[2] With the sulfonate **2** and benzene, diphenylmethane is the observed product, since benzyl methanesulfonate, the anticipated product, is known to spontaneously dissociate to yield methanesulfonic acid and products derived from the benzyl carbonium ion; see J. K. Kochi and G. S. Hammond, *J. Amer. Chem. Soc.*, **75**, 3443 (1953). In the chloromethyl ether–benzene reaction, however, the analogous intermediate, benzyl chloride, is stable and is the product isolated.

useful synthetic reagent whose utility is currently under further study.

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Electrocyclic Additions to Pentacyclo[4.4.0.0²,⁵.0³,⁸.0⁴,⁷]deca-9-ene[1]

Sir:

We have found that the strained hydrocarbon pentacyclo[4.4.0.0²,⁵.0³,⁸.0⁴,⁷]deca-9-ene (**1**)[2] undergoes thermal addition of maleic anhydride and tetracyanoethylene in manner similar to tetracyclo[3.2.0.0²,⁷.0⁴,⁶]-heptane.[3] Thus, maleic anhydride adds to **1** (in CCl_4 at 65° for 2 days) forming the 1:1 adduct **2** [65% yield; mp 152–155° (in preheated bath), solidifies and remelts at 220–222°; ν^{KBr} 1840, 1775 (anhydride), 1538 cm⁻¹ (olefin); τ ($DCCl_3$) 4.0 (q, 2 H), 4.39 (t, 2 H), 6.7 (m, 4 H), 7.0 (t, 2 H), 7.4 (m, 2 H)] and the 2:1 adduct **3** [32% yield; mp >300°; ν^{KBr} 1840, 1787 cm⁻¹ (anhydride)]. **3** can also be prepared in 83% yield from **1** by heating with excess maleic anhydride in chlorobenzene at 100° for 26 hr. Heating **2** (at 95° for 15 hr) opens the cyclobutene ring and affords the triene **4** [92% yield; mp 220–222°; ν^{KBr} 1850, 1775 (anhydride), 1600 cm⁻¹ (olefin); τ ($DCCl_3$) 3.6 (m, 2 H), 4.6 (m, 4 H), 6.75 (m, 4 H), 7.05 (m, 2 H)]. Heating **4** with maleic anhydride yields **3** in 81% yield.

The *exo,exo* conformation of the anhydride groups in **3** is supported by the following: first, conversion of **3** (with methanol and H_2SO_4) to a tetramethyl ester, **5** [90% yield; mp 227–228°; τ ($DCCl_3$) 4.22 (q, 4 H), 6.49 (m, 12 H), 7.30 (m, 4 H), 7.2 (m, 4 H), 7.98 (s, 2 H)]; the nmr spectrum of **5** indicates that two planes of symmetry are present; thus, the carboxyl functions are either all *exo* or all *endo;* second, bromination of **5** affords a saturated bromo five-membered-ring lactone, **6** or **7** [mp 244–245°; ν^{KBr} 1760 (lactone), 1732, 1724 (ester C=O) cm⁻¹; τ ($DCCl_3$) 5.32 (>CHBr), 5.65 (>CHO–), 6.25, 6.30, and 6.32 (–CO₂CH₃)]. Thus, only the all-*exo* conformations of the carboxyl functions will allow for lactone formation.

The close proximity of the olefinic bonds in **2**, **4**, and **5** is shown by the facile photoinduced ring closure affording the three new hexacyclics **8** [85% yield from **2;** mp 212–213°; ν^{KBr} 1845, 1780 cm⁻¹ (anhydride); τ ($DCCl_3$) 6.8 (m, 6 H), 7.1 (m, 4 H), 7.6 (m, 2 H)], **9** [63% yield from **4;** mp 174–175°; τ ($DCCl_3$) 3.49 (t, 1 H), 3.93 (t, 1 H), 6.82 (m, 4 H), 7.44 (m, 5 H), 8.08 (m, 1 H)], and **10** [80% yield from **5**; mp 181–182°; τ ($DCCl_3$) 6.42 (s, 12 H, methyl ester), 6.81 (m, 4 H), 7.28 (m, 4 H), 7.80 (m, 2 H), 8.14 (m, 4 H)]. Bis decarboxylation (lead tetraacetate in pyridine) of the diacid **11** [97% from **8**; mp 212–213°; ν^{KBr} 1720 cm⁻¹ (carboxylic acid)] affords the hexacyclic olefin **12** [48% yield; mp 122–124°; ν^{KBr} 1610, 680 cm⁻¹ (*cis*-disubstituted al-

(1) E. LeGoff, S. Oka, and W. G. Deadman, 158th National Meeting of the American Chemical Society, New York, N. Y., Sept 1969, Abstract ORGN 57.

(2) S. Masamune, H. Cuts, and M. G. Hogben, *Tetrahedron Lett.*, 1017 (1966); W. G. Dauben and D. L. Whalen, *ibid.*, 3743 (1966); R. Furstoss and J.-M. Lehn, *Bull. Soc. Chim. Fr.*, 2497 (1966).

(3) C. D. Smith, *J. Amer. Chem. Soc.*, **88**, 4273 (1966).
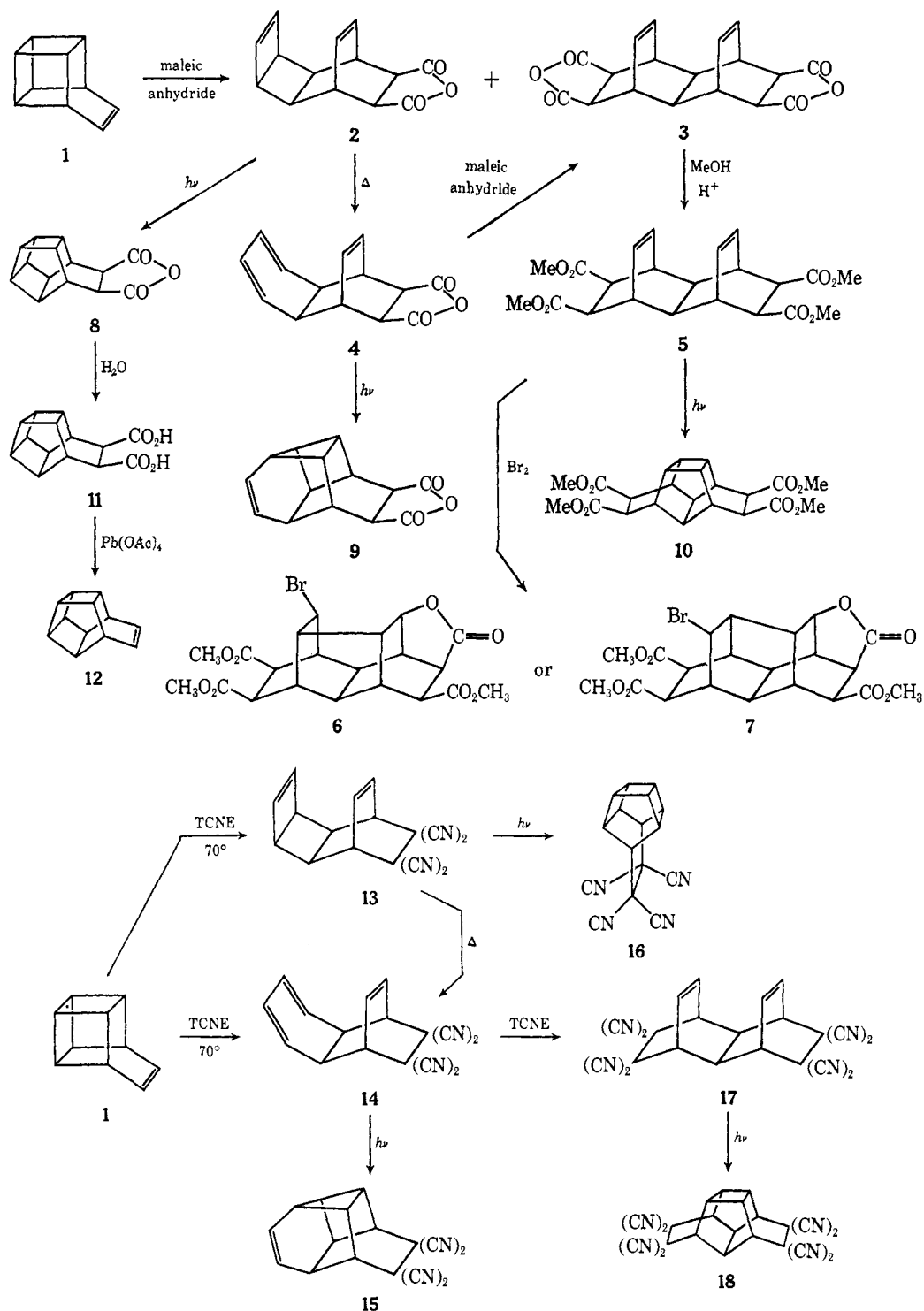
kene); τ (DCCl$_3$) 3.74 (sextet, 2 H), 6.93 (p, 4 H), 7.18 (m, 2 H), 7.39 (m, 4 H); m/e 156 (parent)].

If tetracyanoethylene is used in place of maleic anhydride in the sequence of reactions just described an analogous series of compounds can be synthesized (12–18).[4]

Of several ways a cycloaddition can occur between **1** and a dieneophile, only the concerted (thermally allowed) $2\pi + 2\sigma + 2\sigma$ addition across the 1,8 carbons of **1** provides a pathway consistent with the formation of **2**. Heating converts the 1:1 adduct **2** into **4**. This reaction probably involves a nonconcerted thermal opening of the cyclobutene moiety. A second molecule of the dieneophile can then add to the resulting diene, affording **3**. Adding further support to this mechanism is the *exo,exo* conformation of **3** which is consistent with the principle of maximum overlap of π centers in both concerted steps. The double bond in **1**, while not involved in the actual shift of electrons during the cycloaddition, appears to have a directive influence on the incoming dienophile.[5]

Acknowledgments. We wish to thank Professor Masamune for details of the "basketene" synthesis, BASF for a generous supply of cyclooctatetraene, and,

(4) *Caution!* A brisant explosion occurred when 600 mg each of tetracyanoethylene and basketene were heated together at about 120°.

(5) Elemental analyses for all new compounds were well within experimental error.

most importantly, the National Institutes of Health (Grant AI-07869) for financial support.

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The Structure of
Di-π-cyclooctatetraeneuranium (Uranocene)

Sir:

Streitwieser and Mueller-Westerhoff have recently reported the synthesis and characterization of bis(cyclo-octatetraene)uranium.[1] As the name "uranocene" implies, this compound was proposed to be a new type of sandwich metal complex homologous with ferrocene.[2] We have completed an X-ray diffraction analysis of a single crystal of this material which shows it is indeed a π sandwich compound with a molecular symmetry of D_{8h} as shown in Figure 1.

The deep green compound crystallizes in $P2_1/n$ (an alternate setting of $P2_1/c$, C_{2h}^5) with $a = 7.084$ (3),[3] $b = 8.701$ (3), $c = 10.631$ (5) Å, $\beta = 98.75°$ (3), $V = 6476$ (10) Å³. For two formula units in the cell, the calculated density of 2.29 g/cm³ is in the range expected from comparison with heavy metal compounds which have similar formulas. Several of the extremely air-sensitive crystals were sealed within thin-walled quartz capillaries (0.3 mm in diameter) under a carefully purified nitrogen atmosphere. Intensity data were collected by the stationary crystal–stationary counter method on a manually operated diffractometer using Zr-filtered Mo $K\alpha$ radiation out to a Bragg 2θ angle of 35°. These data were corrected for absorption.

With two formula units in the cell the molecule may be unambiguously placed on the origin with $\bar{1}$ (C_i) crystallographic point symmetry. The uranium atoms then contribute only to structure factors $F(h,k,l)$ for which $h + k + l$ is even. Those structure factors with $h + k + l$ odd are due entirely to the scattering of the carbon and hydrogen atoms. For this class of reflections the problem is virtually the same as a light-atom structure. Assignment of phases for these reflections is then difficult, but their magnitudes are very sensitive to the carbon atom positions.

Because of the enormous scattering power of the uranium atom, especially at large 2θ angles, a standard Patterson map was dominated by Fourier ripple peaks around the origin and no uranium–carbon vectors could be discerned. However, an origin-removed sharpened Patterson map showed very little ripple, and the strongest eight peaks in this map for vectors in the range 1.6–3.0 Å all had lengths of about 2.6 Å and clearly showed the sandwich structure of the molecule with virtually no significant distortion. The coordinates from the Patterson map were directly used in subsequent least-squares refinements. To test the correctness of the

(1) A. Streitwieser and U. Mueller-Westerhoff, *J. Amer. Chem. Soc.*, 90, 7364 (1968).

(2) Although other complexes of planar cyclooctatetraene dianion are known (see, for example, M. A. Bennett, *Advan. Organometal. Chem.*, 4, 376 (1966); H. Breil and G. Wilke, *Angew. Chem. Intern. Ed. Engl.*, 5, 899 (1968)), these compounds contain rather weakly bound C_8H_8 dianions and show chemical behavior characteristic of ionic bonding.

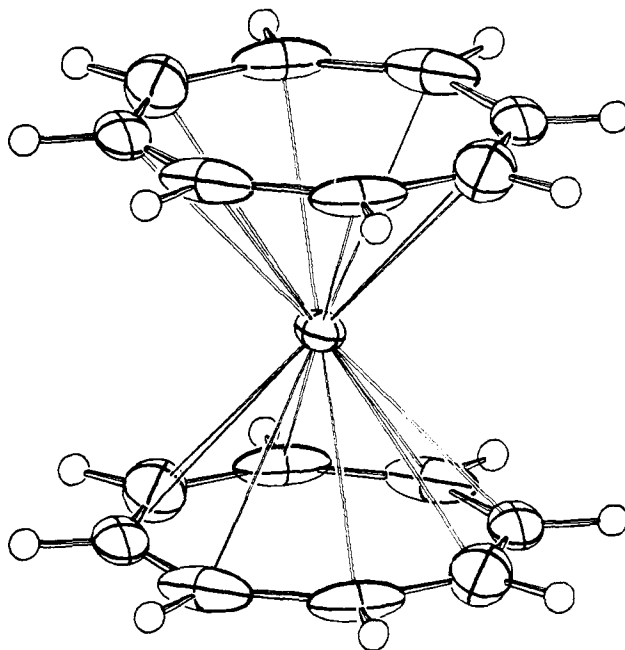(3) The standard deviation in the least significant digits is given in parentheses.

Figure 1. A perspective drawing of $(C_8H_8)_2U$, di-π-cyclooctatetraeneuranium.

carbon atom positions, refinements were carried out both for the full data set and for the class with $h + k + l$ odd (which are in general weak but due *only* to the carbon and hydrogen scattering). The standard R factor, including all data with only the uranium atom included in the structure-factor calculations, is 10.8%. The standard R factor after refinement of the carbon atom positional parameters, using only the data with $h + k + l$ odd, is 11.4%. The present level of refinement for all 540 reflections with $F^2 > \sigma(F^2)$ corrected for absorption gives R and wt R as 3.3 and 3.9%, respectively. A difference Fourier shows no peaks greater than 0.9 e/Å³. The largest of these peaks are either within 0.1 Å or so of the origin and due to uncorrected anisotropy in the uranium electron density, or are at positions corresponding to those calculated for hydrogen atoms.

Since the molecule lies on the origin with $\bar{1}$ (C_i) crystallographic point symmetry, the two planar C_8H_8 rings are then constrained to be parallel and eclipsed. The orientations of the carbon atom thermal ellipsoids (Figure 1) show a preferential oscillation of the rings about the molecular symmetry axis, as expected in a compound of this type. The rms amplitude of vibration along the major axis is approximately 0.35 Å for all of the carbon atoms in the ring. The U–C and C–C bond lengths are all equivalent to within the present level of refinement. The average U–C bond length is 2.648 (5) Å, with the assigned standard deviation estimated from the variance. The standard deviations of individual U–C and C–C bonds as determined from the variance–covariance matrix are 0.02 and 0.03 Å, respectively. The average C–C bond length is 1.395 (15) Å. The two averages for alternating sets of four bonds are 1.391 and 1.398 Å. The eight carbon atoms of an individual ring all lie within about 0.02 Å of the least-squares plane. This planarity and the equality of alternate bond lengths leave no question that this is a pseudoaromatic ring and that di-π-cyclooctatetraene-