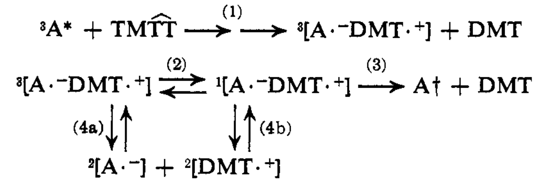
absence of the sensitizer even if the sample was irradiated with light of wavelengths which cause direct splitting of the dimer.

We explain the enhanced signals on the basis of the CKO (radical pair) theory.[6] An analysis of the signal directions is straightforward, if one assumes a polarizing encounter of quinone radical anion ($A\cdot^-$) and monomer radical cation ($DMT\cdot^+$). Kinetic studies and quenching experiments[1f,g] suggest that the triplet state of A is involved in the primary step so that the geminate radical pair should be generated as a triplet (in Kaptein's notation,[6e] +). The product-forming reaction, *i.e.*, reverse electron transfer, has to occur in the encounter cage (+); the *g* value of $DMT\cdot^+$[7] is smaller (−) than that of $A\cdot^-$.[9] Given these parameters the signal direction of a proton in the product should be opposite to the sign of the hyperfine coupling constant of the same proton in the parent radical ion; emission (−) is expected (and observed) for the methyl group ($a_{CH_3} = +20$ G),[8] absorption (+) for the olefinic proton ($a_H \approx -4$ G).[8] Additional support for the involvement of $DMT\cdot^+$ is derived from the fact that the intensity enhancement of the signals is proportional to the magnitude of the hyperfine coupling constants of $DMT\cdot^+$.

On the basis of the CIDNP results we propose the following mechanism for the A–$TM\widehat{TT}$ photoreaction (Scheme I).

Scheme I[a]



[a] A dagger denotes nuclear spin polarization; an asterisk denotes an excited state; arabic numerals indicate electron spin multiplicity.

The fate of the radical ion pairs, after their excess energy is dissipated, should be spin dependent, *i.e.*, only pairs of singlet multiplicity should undergo reverse electron transfer (3). This spin selection principle is closely analogous to the one generally accepted for pairs of neutral radicals[6] and appears equally sound energetically, at least for the system discussed here. Electron return in a triplet pair requires that either A or DMT be generated in the triplet state which appears energetically unfavorable under the reaction conditions.[10] Therefore, we assume that aside from intersystem crossing triplet pairs can only diffuse apart (4a).

If Scheme I is correct, in particular if the formation of the triplet ion pair is fast and essentially irreversible and if the combined energies of $^3A^*$ and DMT are higher than the energy of the $A\cdot^-$–$DMT\cdot^+$ pair, the identical pair should be formed in the reaction of $^3A^*$ with monomeric DMT, and subsequent electron return should yield spin-polarized DMT. Indeed, when A was irradiated in aqueous solutions containing low concentrations of DMT, CIDNP spectra were observed which showed the same features as the spectra obtained in the dimer reaction.

This result might suggest that the CIDNP spectra observed in dimer samples arise from the reaction of $^3A^*$ with DMT previously produced from the dimer. We deem this unlikely since the signals were recorded within seconds after starting the irradiation, when the concentrations of DMT were still negligible.

The CIDNP data cannot establish the detailed mechanism leading from the dimer to the $A\cdot^-$–$DMT\cdot^+$ pair. However, it appears that the cleavage sequence is essentially irreversible since a limiting quantum yield of 1 was found for this reaction.[1f,g] This observation would explain why we did not observe spin-polarized $TM\widehat{TT}$.

Further work is in progress to elucidate the photochemistry of similar systems by using the CIDNP technique.

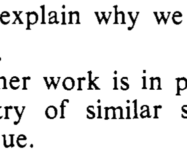
Acknowledgments. The authors are indebted to Dr. S. Meiboom and Mr. R. C. Hewitt for their help during the use of their modified pmr spectrometer, to Mr. F. Doleiden for technical assistance, and to Dr. E. A. Chandross for helpful discussions.

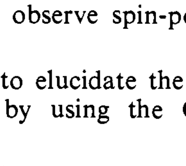
Heinz Dieter Roth, Angelo A. Lamola*
Bell Laboratories
Murray Hill, New Jersey 07974
Received October 21, 1971

The Peristylane System[1]

Sir:

We are pursuing the synthesis of dodecahedrane (**1**). For the purpose of synthetic design we view dodecahedrane as made up of two subunits, cyclopentane and the C-15 fragment **2**, as illustrated. We have named the larger fragment "peristylane" from the Greek περιστῦλον, a group of columns arranged about an open space and designed to support a roof.


1


2

We report now the preparation of the first members of the peristylane family. Our synthesis proceeds by elaboration of *cis*-bicyclo[3.3.0]octane-2,8-dione (**6**), preserving the mirror plane symmetry element. The cis ring fusion in bicyclo[3.3.0]octane is 6 kcal/mol more stable than the trans;[2] this large difference is of great help in maintaining stereochemical control while manipulating derivatives of the system.

---

(6) G. L. Closs and A. D. Trifunac, *J. Amer. Chem. Soc.*, **92**, 2183, 2186, 7227 (1970); (b) G. L. Closs, C. E. Doubleday, and D. R. Paulson, *ibid.*, **92**, 2185 (1970); (c) R. Kaptein and L. J. Oosterhoff, *Chem. Phys. Lett.*, **4**, 195, 214 (1969); (d) S. H. Glarum, Abstracts, 159th National Meeting of the American Chemical Society, Houston, Texas, Feb 1970, No. ORGN 040; (e) R. Kaptein, *Chem. Commun.*, 732 (1971).

(7) We assume that $DMT\cdot^+$ has a similar *g* value as the thymine radical cation ($g_{T\cdot^+} = 2.0038$).[8]

(8) M. D. Sevilla, *J. Phys. Chem.*, **75**, 626 (1971); *cf.* L. C. Snyder, R. G. Shulman, and D. B. Neumann, *J. Chem. Phys.*, **53**, 256 (1970).

(9) $g_{A\cdot^-} = 2.0040$; we are indebted to Mr. J. H. Marshall for determining this value.

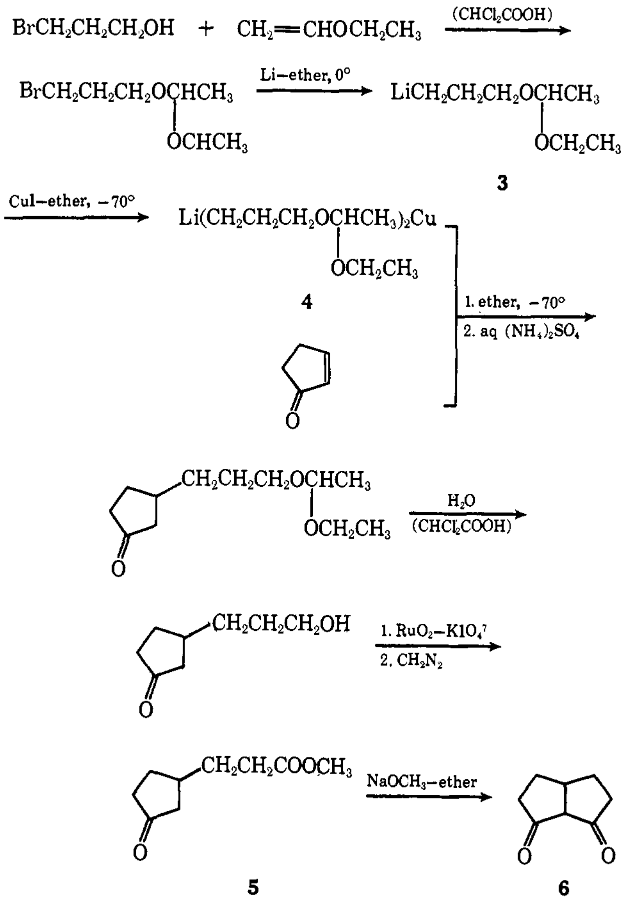
(10) The triplet state of A lies at 2.7 eV, that of DMT at 3.2 eV. We estimate the energy of the ion pair $^3[A\cdot^-DMT\cdot^+]$ to be ≤ 2.5 eV.

(1) Taken in large part from the Ph.D. Thesis of R. H. M., The University of Chicago, 1971. A referee from the American Chemical Society Nomenclature Committee has informed us that the correct systematic name for peristylane is tetradecahydro-3,4-methanocyclopenta[*cd*]pentaleno[6.1.2-*fgh*]pentalene.

(2) J. W. Barrett and R. P. Linstead, *J. Chem. Soc.*, 611 (1936).

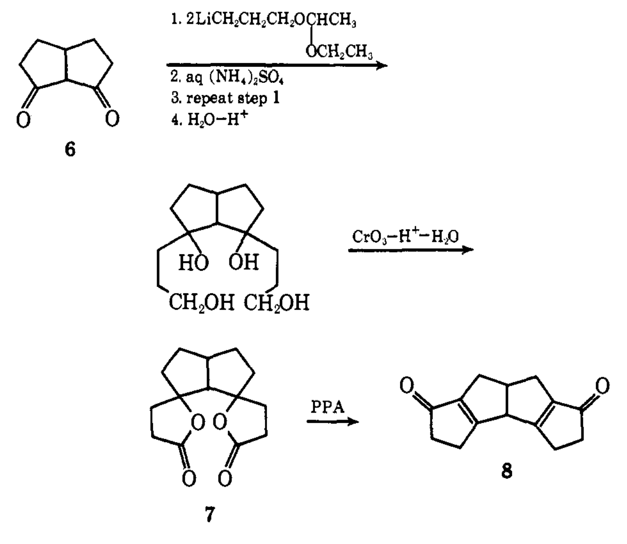
cis-Bicyclo[3.3.0]octane-2,8-dione is prepared in 80–90% yield by Claisen cyclization of the keto ester **5**.[3] Our route to **5** derives from conjugate addition to 2-cyclopentenone of the lithium organocuprate **4** prepared from the organolithium **3** (Chart I).[4] These new reagents are discussed by us in detail elsewhere.[5] The reactions can be carried out relatively readily on a 1-mole scale; **5** is obtained in 50% yield overall from cyclopentenone.[6]

Chart I



Annellation of **6** to the tetracycle **8** is accomplished by way of the dilactone **7** as illustrated in Chart II. Again good use is made of lithium reagent **3**.[5] Many reactions are involved in building the dilactone, but the sequence can be carried out readily in 45% yield overall without purification of any of the intermediates. Only a single dilactone is isolated: mp 154–155°; ir ($CHCl_3$) λ 5.64 μ.[8] The bicyclooctane ring fusion is very probably cis for thermodynamic reasons; the two spiro centers are transients in the synthesis and not of concern.

Chart II



Intramolecular Friedel–Crafts acylation within dilactone **7** is brought about by heating **7** with 50 times its weight of polyphosphoric acid at 75° for 5 days.[9] This procedure gives 65–70% of the bisenone **8**: mp 209–210° dec; ir ($CHCl_3$) λ 5.92 and 6.10 μ; uv (95% EtOH) λ shoulder 236 (ε 17,000), max 248 (20,000), and 306 mμ (230).[10] As **8** is formed under equilibrating conditions, its central ring fusion is taken to be cis.

The conversion of **7** to **8** is difficult to carry out on scale with polyphosphoric acid, an exasperating reagent, impossible to handle efficiently or stir effectively. We found recently that trifluoromethanesulfonic acid containing 5 wt % phosphorus pentoxide transforms **7** to **8** in about the same yield as polyphosphoric acid but at room temperature and in less time (2 days). This new reagent can be handled without difficulty and promises to be very useful in carrying out this and other difficult acylations and the like.[11]

Catalytic hydrogenation of **8** in ethyl acetate at −20° over standardized[12] 10% palladium-on-charcoal gives the saturated dione **9** stereospecifically (>97%): mp 89–90°; ir ($CHCl_3$) λ 5.78 μ; uv (ether) λ max 294 mμ (ε 27). This material exchanges six hydrogens on treatment with base but is not epimerized. On this basis, and in view of its origin, **9** is assigned the all-cis, all-syn configuration.

Double bonds are introduced into the terminal rings of **9** by bromination–dehydrobromination of intermediate ketals.[13] The sequence (Chart III) is run without isolation of the intermediates and provides the desired bisenone **10** in 40–55% overall yield: mp 84–85.5°; ir ($CHCl_3$) λ 5.89 and 6.31 μ; uv (95% EtOH)

---

(3) H. Stetter, I. Krüger-Hansen, and M. Rizk, *Chem. Ber.*, **94**, 2702 (1961).

(4) For examples of conjugate addition of other lithium organocuprates to other unsaturated ketones, see H. O. House and W. F. Fischer, Jr., *J. Org. Chem.*, **34**, 3615 (1969), and references cited therein.

(5) P. E. Eaton, G. F. Copper, R. C. Johnson, and R. H. Mueller, *J. Org. Chem.*, submitted for publication.

(6) The literature procedure for **5** (as the ethyl ester) requires eight steps from cyclopentenone and runs in 17% overall yield.[3]

(7) Ester formation, a common side reaction in most oxidations of primary alcohols, is not observed when this oxidant is used in aqueous acetone. We are grateful to Dr. B. W. Roberts for calling this to our attention.

(8) Satisfactory analyses (combustion and mass spectrometric) have been obtained for all new compounds for which a melting point is reported here.

(9) For earlier examples using simpler systems, see C. Rai and S. Dev, *J. Indian Chem. Soc.*, **34**, 178 (1957), and references cited therein.

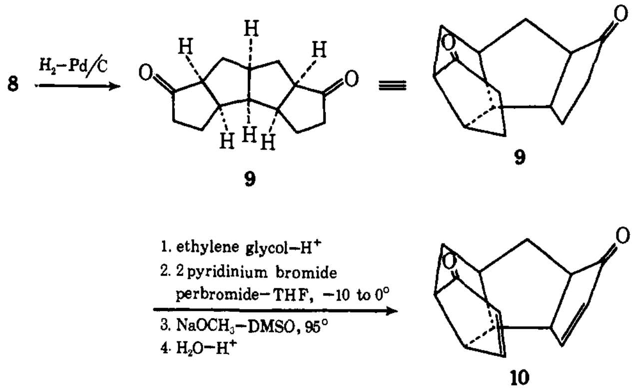
(10) *Cf.* bicyclo[3.3.0]oct-1(5)-en-2-one: ir ($CHCl_3$) λ 5.92 and 6.10 μ; uv (95% EtOH) λ max 241 (ε 11,000) and 300 mμ (70). The ultraviolet spectrum of **8** can be accounted for by invoking an interaction between the proximate enone chromophores.

(11) NOTE ADDED IN PROOF. In continuing this work, Dr. Glenn Carlson of this laboratory has found that a solution of 5–10 wt % of phosphorus pentoxide in ordinary methanesulfonic acid is yet a superior reagent. Treatment of **7** with this mixture at 35° gives an 80–85% yield of **8**. We note that methanesulfonic acid–methanesulfonic anhydride mixtures do not effect this conversion satisfactorily.

(12) Commercial catalyst is stirred with distilled water; acetic acid is added until the pH of the solution is 5–6. The catalyst is filtered, washed thoroughly with distilled water, and dried *in vacuo*.

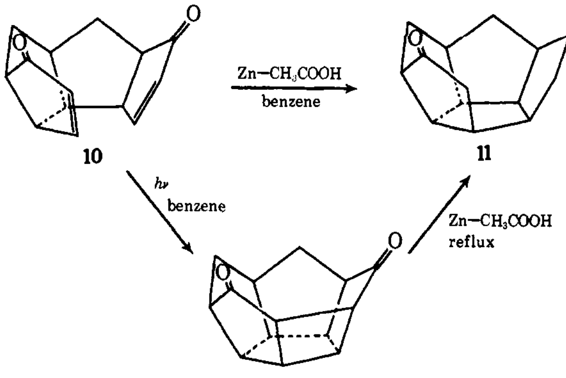
(13) P. E. Eaton, *J. Amer. Chem. Soc.*, **84**, 2344 (1962).

Chart III

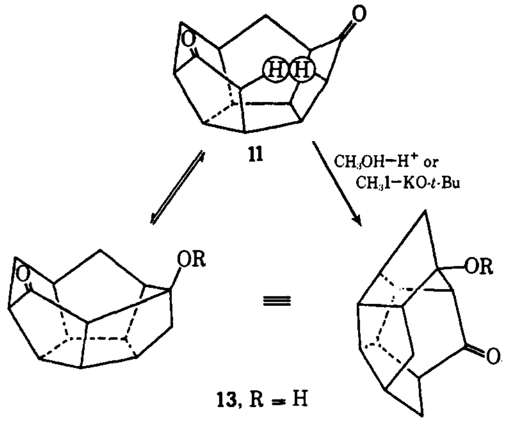


λ max 228 (ϵ 13,000) and 321 mμ (110);[14] nmr ($CDCl_3$) δ 7.85 (2 H, d of d, J = 6 and 3 Hz, $HC{=}C{-}C{=}O$), 6.03 (2 H, d of d, J = 6 and 2 Hz, $C{=}CH{-}C{=}O$), 3.7 (2 H, m), 2.9 (4 H, m), 1.9 (2 H, m), and 1.4 ppm (2 H, m). Catalytic hydrogenation of **10** regenerates **9** cleanly; thus both compounds have the same configuration at the central ring fusion.

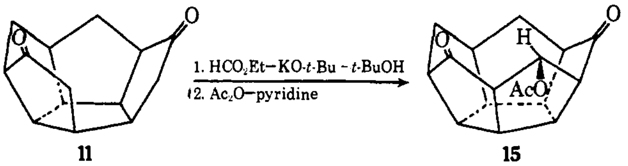
Trans-skeletal reductive coupling within **10** is brought about by treatment with zinc and acetic acid.[15] Although this is the most direct method for the conversion of **10** to **11**, for practical reasons the transformation is better carried out instead by way of photochemical closure[16] of **10** to the norperistylane **12** (90%; mp >260° dec; ir (CCl_4) λ 5.79 μ) and subsequent reductive cleavage of **12** to **11** (85%) with zinc in refluxing acetic acid.[17]



Numerous recrystallizations of **11** fail to improve its indistinct melting point (210–226° dec) or change its spectral properties [ir (CCl_4) λ 2.98 and 5.79 μ; nmr ($CDCl_3$) hydroxyl proton (exchangeable, position concentration dependent), no absorption attributable to hydrogen on carbon-bearing oxygen]. Apparently diketone **11** equilibrates readily with the isomeric hydroxy ketone **13**, the product of internal aldol cyclization. In a related process, probably *via* an intermediate hemiketal, reaction of **11** with acidic methanol gives cleanly the methoxy ketone **14**: mp 68.5–69.5°; ir (CCl_4) 5.79 μ, no hydroxyl absorption; nmr ($CDCl_3$) δ 3.33 ppm (3 H, s), no other low-field absorption. The same methoxy ketone is produced on treatment of **11** with methyl iodide and base. The driving force for these closures (to a norbornane derivative) must certainly derive from relief of crowding of the inside methylene hydrogens α to the carbonyl functions of **11**.



Completion of the synthesis of the peristylane system from **11** requires introduction of the fifteenth carbon atom and closure of the sixth ring. Both are accomplished by treating **11** with ethyl formate in *tert*-butyl alcohol containing potassium *tert*-butoxide. The hydroxyperistylane so formed is not isolated as such but is taken on directly to the corresponding acetate **15**:



mp 169–173° dec with loss of acetic acid; ir (CCl_4) λ 5.74 and 8.15 μ; nmr ($CDCl_3$) δ 5.70 (1 H, singlet, 2.5 Hz wide at half-height) and 2.02 (3 H, s). The spin coupling (*ca.* 1 Hz) of the proton on carbon-bearing acetate to the vicinal protons indicates a dihedral angle between them of about 100° and leads to the assignment of configuration shown.

Acknowledgment. We are grateful to the American Cancer Society, the National Science Foundation, and the National Institutes of Health for financial support of this work. We acknowledge with thanks the assistance of R. C. Johnson, G. F. Cooper, and I. Oelrich. R. H. M. thanks the NIH for a Predoctoral Fellowship.

Philip E. Eaton,* Richard H. Mueller
Searle Chemistry Laboratory
Department of Chemistry, The University of Chicago
Chicago, Illinois 60637

Received October 14, 1971

---

(14) *Cf. cis*-bicyclo[3.3.0]oct-2-en-4-one: ir ($CHCl_3$) λ 5.87 and 6.29 μ; uv (95% EtOH) λ max 224 (ϵ 11,400) and 319 mμ (40).

(15) See J. Wiemann, P.-F. Casals, and S. Risse (*Bull. Soc. Chim. Fr.*, 1281 (1963)) for examples of intermolecular reductive coupling of enone systems.

(16) P. E. Eaton, *Accounts Chem. Res.*, **1**, 50 (1968).

(17) For another example of a cleavage of this sort, see E. Wenkert and J. E. Yoder, *J. Org. Chem.*, **35**, 2986 (1970).

Photochemistry of Disulfides. I. Carbon–Sulfur Cleavage in the Photosensitized Decomposition of Simple Disulfides

Sir:

There is clear evidence that cystine residues are primary targets in the photochemical inactivation of enzymes.[1] In addition, the photochemistry of some

---

(1) Reviews: K. C. Smith and P. C. Hanawalt, "Molecular Photo-