

for technical assistance in the preparation of the compounds.

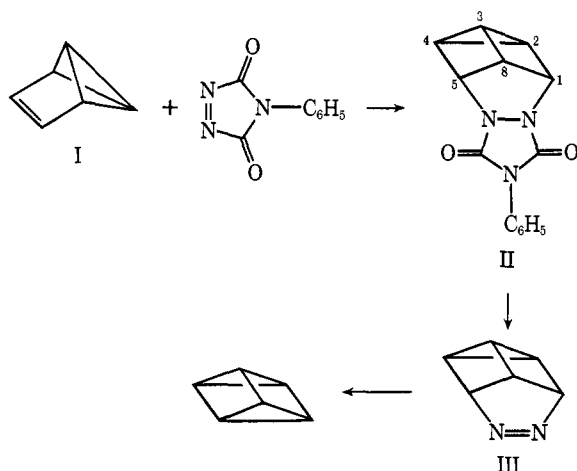
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Synthesis of Prismane

Sir:

Although derivatives have been prepared,¹ the simple molecule C₆H₆ known as prismane,² in which six carbon-hydrogen units are disposed at the corners of a triangular prism, has never been synthesized and only rarely theorized upon³ since Ladenburg first proposed its structure for benzene 104 years ago.⁴ We have now prepared pure samples of prismane by the procedure indicated in Scheme I. The last step of the synthesis is

Scheme I



an adaptation of a method tried by Trost and Cory in a previous attempt to prepare prismane^{5,6} and has been used to make other hydrocarbons.⁷⁻¹⁴ The steps

(1) (a) H. G. Viehe, R. Merényi, J. F. M. Oth, J. R. Senders, and P. Valange, *Angew. Chem., Int. Ed. Engl.*, **3**, 755 (1964); (b) K. E. Wilzbach and L. Kaplan, *J. Amer. Chem. Soc.*, **87**, 4004 (1965); (c) R. Criegee and R. Askani, *Angew. Chem., Int. Ed. Engl.*, **5**, 519 (1966); (d) D. M. Lemal and J. P. Lokensgard, *J. Amer. Chem. Soc.*, **88**, 5934 (1966); (e) W. Schäfer, R. Criegee, R. Askani, and H. Grüner, *Angew. Chem., Int. Ed. Engl.*, **6**, 78 (1967); (f) M. G. Barlow, R. N. Haszeldine, and R. Hubbard, *J. Chem. Soc. C*, 1232 (1970); (g) D. M. Lemal, J. V. Staros, and V. Austel, *J. Amer. Chem. Soc.*, **91**, 3373 (1969); (h) M. G. Barlow, J. G. Dingwall, and R. N. Haszeldine, *Chem. Commun.*, 1580 (1970).

(2) Tetracyclo[2.2.0.0^{2,6}.0^{3,5}]hexane.

(3) (a) M. Randić and Z. Majerski, *J. Chem. Soc. B*, 1289 (1968); (b) Y. Teijiro, K. Simizu, and H. Kato, *Bull. Chem. Soc. Jap.*, **41**, 2336 (1968); (c) N. C. Baird and M. J. S. Dewar, *J. Amer. Chem. Soc.*, **91**, 352 (1969); (d) R. B. Woodward and R. Hoffmann, *Angew. Chem., Int. Ed. Engl.*, **8**, 781 (1969).

(4) A. Ladenburg, *Chem. Ber.*, **2**, 140 (1869).

(5) B. M. Trost and R. M. Cory, *J. Amer. Chem. Soc.*, **93**, 5573 (1971).

(6) Both pyrolysis and photolysis were tried.

(7) The cleavage of nitrogen from an azo compound was first used to prepare a strained hydrocarbon by Criegee and Rimmelin.⁸ The use of light to effect the reaction was introduced subsequently.⁹

(8) R. Criegee and A. Rimmelin, *Chem. Ber.*, **90**, 414 (1957).

(9) (a) T. V. Van Auken and K. L. Rinehart, Jr., *J. Amer. Chem. Soc.*, **84**, 3736 (1962); (b) K. Kocsis, P. G. Ferrini, D. Arigoni, and O. Jeger, *Helv. Chim. Acta*, **43**, 2178 (1960); (c) C. Steel, *J. Phys. Chem.*, **67**, 1779 (1963).

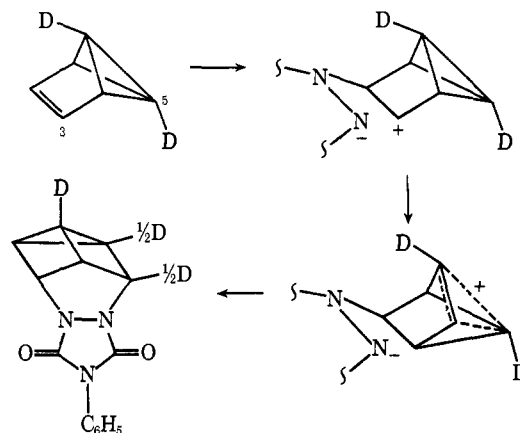
(10) (a) E. L. Allred and J. C. Hinshaw, *J. Amer. Chem. Soc.*, **90**, 6885 (1968); (b) H. Tanida, S. Teratake, Y. Hata, and M. Watanabe, *Tetrahedron Lett.*, 5341, 5345 (1969); (c) L. A. Paquette and L. M. Leichter, *J. Amer. Chem. Soc.*, **92**, 1765 (1970).

leading to the azo precursor III¹⁵ are unorthodox.

Combining benzvalene (I)¹⁸ in ether-dioxane with the powerful dienophile¹⁹ 4-phenyltriazolinedione^{13,20} (ice cooled, then set at room temperature for 1 hr) gives, after passage through silica gel using CHCl₃ eluent, in 50-60% yield, a 1:1 adduct, mp 173-175°, of structure II.²¹ Refluxing with KOH in CH₃OH-H₂O (85:15, v/v) for 24 hr, extraction, and treatment with acidic CuCl₂ then yields a cuprous chloride derivative, which with aqueous NaOH²² gives azo compound III (65% yield after crystallization from pentane and sublimation).^{16,23}

The mechanism by which II forms is revealed by 5,6-dideuterated benzvalene²⁴ with 4-phenyltriazolinedione giving adduct labeled as indicated in Scheme II.²⁶ The

Scheme II



favored path therefore is analogous to that followed by bromine in adding to benzvalene^{24,27} and once thought to be followed by azodicarboxylic esters in adding to

(11) The method was once reported to have given quadricyclane,¹² but the experiment could not be repeated.¹³ Attempts to use it to make cubane failed.¹⁴

(12) R. M. Moriarty, *J. Org. Chem.*, **28**, 2385 (1963).

(13) R. C. Cookson, S. S. H. Gilani, and I. D. R. Stevens, *J. Chem. Soc. C*, 1905 (1967).

(14) J. P. Snyder and D. G. Farnum, quoted in D. W. McNeil, M. E. Kent, E. Hedaya, P. F. D'Angelo, and P. O. Schissel, *J. Amer. Chem. Soc.*, **93**, 3817 (1971).

(15) The previous synthesis¹⁶ follows a path similar to one leading to prostaglandins.¹⁷

(16) B. M. Trost and R. M. Cory, *J. Amer. Chem. Soc.*, **93**, 5572 (1971).

(17) E. J. Corey, N. M. Weinshenker, T. K. Schaaf, and W. Huber, *J. Amer. Chem. Soc.*, **91**, 5675 (1969).

(18) T. J. Katz, E. J. Wang, and N. Acton, *J. Amer. Chem. Soc.*, **93**, 3782 (1971). The average yield now is 45%.

(19) J. Sauer and B. Schröder, *Chem. Ber.*, **100**, 678 (1967).

(20) R. C. Cookson, S. S. Gupte, I. D. R. Stevens, and C. T. Watts, *Org. Syn.*, **51**, 121 (1971).

(21) Mass spectrum: *m/e* 253 (parent, 4%), 119 (base peak, C₆H₅NCO). Pmr (CDCl₂): τ 2.55 (m, 5.00 H, phenyl), 4.98 (d of t, *J* = 4.5, 1.3 Hz, 1.93 H, H_{1,5}), 6.86 (quintet of d, *J* = 4.5, 0.95, 1.02 Hz, H₃), 7.37 (t of d, *J* = 3.4, 0.95 Hz, 1.03 H, H₂), 7.66 (m, 2.02 H, H_{2,4}); cf. similar spectrum in ref 16.

(22) O. Diels, J. H. Blom, and W. Koll, *Justus Liebigs Ann. Chem.*, **443**, 242 (1925).

(23) Explosive.

(24) R. J. Roth, Dissertation, Columbia University, 1972. The deuteration was achieved by combining benzvalene in ether with *n*-butyllithium and then adding D₂O.²⁵ 92% of the 5,6 hydrogens were replaced by deuteriums.

(25) (a) G. L. Closs and L. E. Closs, *J. Amer. Chem. Soc.*, **85**, 2022 (1963); (b) J. Meinwald, C. Swithenbank, and A. Lewis, *ibid.*, **85**, 1880 (1963); (c) E. Galantay, N. Paolella, S. Barcza, R. V. Coombs, and H. P. Weber, *ibid.*, **92**, 5771 (1970).

(26) The ratio of the intensities of the resonances at τ 2.55, 4.98, 6.86, 7.37, and 7.66 is 5.04:1.48:0.99:<0.05:1.48. The resonance at 6.82 is now a quartet with no fine splitting and that at 7.66 is a doublet of doublets.

(27) R. J. Roth and T. J. Katz, *J. Amer. Chem. Soc.*, **94**, 4770 (1972).

norborene.^{12,28} A plausible alternative,²⁹ addition to the 5 and then to the 3 position of benzvalene, does not compete.

On photolysis through Pyrex, 0.8 M solutions of III in CD₂Cl₂ at ca. 30° or in CD₃CN at 78° give mainly benzene and some 1,2-diazacyclooctatetraene.⁵ There are small amounts of other products that have not yet been isolated and there is 4–6% prismane. Except for prismane, the products were identified only by pmr analysis and accounted for 70–80% of the starting azo compound, which was consumed.

Prismane was isolated in 1.8% yield after photolyzing 3.2 g of III as a 0.19 M solution in isobutane at 35° (sealed tubes), evaporating solvent, distilling at 10⁻⁶ Torr, and purifying by glpc.³⁰ It is an explosive colorless liquid: pmr (CCl₄) singlet at τ 7.72 ($J_{\text{C-H}} = 180$ Hz);³² ¹³C nmr (in C₆D₆) δ +30.6 ppm (from TMS, d, $J_{\text{C-H}} = 179.7 \pm 2$ Hz);³⁵ ir (CS₂, cm⁻¹) 3066 (s), 1765 (w), 1640 (w), 1223 (s), 950 (m), 881 (w), 798 (s), 733 (w), 670 (m); mass spectrum (75 eV) m/e 78 (100%, parent), 77 (20%), 52 (22%), 39 (13%), no others more than 10% of base; uv (isopentane), inadequately measured because of benzene contamination, but $\epsilon_{223\text{nm}} \leq 90$.³⁷

Prismane is stable at room temperature. At 90° in toluene-*d*₈ it decomposes with a half-life of 11 hr, giving 61 mol % of benzene and no other product detectable by pmr spectroscopy.³⁸ It is therefore unnecessary to cool the reaction mixture in which prismane is prepared. In fact it is essential for the success of the synthesis that during the photolysis the azo compound III be heated.^{39,40} Thus, in toluene-*d*₈ at -65° after 5 hr of photolysis, pmr analysis shows the consumed starting material converted 92% into 1,2-diazacyclooctatetraene, 14% into benzene, and 0% into prismane, while after similar photolysis at 30° these products are observed in 6, 47, and 8% yields. To mitigate prismane's assumed instability by cooling the reaction mix-

ture is therefore a mistake, for prismane is a stable molecule.

Acknowledgments. It was N. J. Turro who first suggested to us that photolyses be tried at high temperatures. We are grateful to Thomas Rago for assistance and to the National Institutes of Health (GM-19173) and the National Science Foundation (NSF-GP-30669) for support.

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Anion Radical of Bacteriochlorophyll

Sir:

Investigations on the redox chemistry of intact photosynthesizing systems, extracted photosynthetic units, and chlorophylls have led to a general recognition¹⁻⁷ that the primary photochemical step involves electron donation from chlorophyll (Chl) in green plants and algae and from bacteriochlorophyll (BChl) in purple bacteria. Those chlorophyll molecules undergoing photooxidation appear to be in a specialized environment, perhaps a bridged dimer configuration,¹ and following electron donation the π -cation radicals of Chl or BChl are observed.^{1-3,7-10} In contrast, the identity of the primary electron acceptor is unknown,^{6,11} and its spectral and chemical properties only now are being elucidated.^{2,10-18} Among the suggested candidates in the case of bacterial photosynthesis are iron,^{6,15} ferridoxin,¹⁶ pteridines,¹⁹ flavines,¹⁸ and ubiquinone.^{6,15,17} Due to the expected similarity in optical and epr characteristics of its anion and cation, BChl itself could not be ruled out as a primary acceptor,^{3,6} and thus a source for the observed light-induced signals. However, we have prepared the anion radical of BChl

(28) J. J. Tufariello, T. F. Mich, and P. S. Miller, *Tetrahedron Lett.*, 2293 (1966).

(29) (a) C. D. Smith, *J. Amer. Chem. Soc.*, **88**, 4273 (1966); (b) P. G. Gassman and G. D. Richmond, *ibid.*, **92**, 2090 (1970); (c) M. Pomerantz, G. W. Gruber, and R. N. Wilke, *ibid.*, **90**, 5040 (1968); (d) P. G. Gassman, K. T. Mansfield, and T. J. Murphy, *ibid.*, **91**, 1684 (1969); (e) W. R. Roth and M. Martin, *Tetrahedron Lett.*, 4695 (1967); (f) A. B. Evin and D. R. Arnold, *J. Amer. Chem. Soc.*, **90**, 5330 (1968); (g) L. A. Paquette, G. R. Allen, Jr., and M. J. Broadhurst, *ibid.*, **93**, 4503 (1971).

(30) Chromosorb G (5 ft \times 1/4 in.) with 5% didecyl phthalate and 1.25% triethanolamine.³¹

(31) K. E. Wilzbach, J. S. Ritscher, and L. Kaplan, *J. Amer. Chem. Soc.*, **89**, 1031 (1967).

(32) As expected,³³ this is larger than the 160 Hz in a cubane derivative.³⁴

(33) (a) N. Muller and D. E. Pritchard, *J. Chem. Phys.*, **31**, 147, 768 (1959); (b) J. N. Shoolery, *ibid.*, **31**, 1427 (1959); (c) K. B. Wiberg, *et al.*, *Tetrahedron*, **21**, 2749 (1965).

(34) P. E. Eaton and T. W. Cole, Jr., *J. Amer. Chem. Soc.*, **86**, 962 (1964).

(35) *Cf.* cuneane's carbon shared between three- and four-membered rings: δ +31.8 ($J = 175$ Hz).³⁶

(36) L. Cassar, P. E. Eaton, and J. Halpern, *J. Amer. Chem. Soc.*, **92**, 6366 (1970).

(37) In hexamethylprismane the corresponding extinction is ca. 1000.^{14,e} If the uv of prismane is similar in shape⁶ to that of its hexamethyl derivative, the spectrum is hypsochromically shifted by at least 35 nm.

(38) There was an initial short burst of decomposition at twice this rate yielding a full mole of benzene. This may be due to catalysis by impurities that are then consumed.

(39) For a similar effect on photodecarbonylation see C. H. Bamford and R. G. W. Norrish, *J. Chem. Soc.*, 1544 (1938).

(40) It is possible that similar syntheses of cubane¹⁴ and quadricyclane¹¹ that failed would succeed at higher temperatures.

(1) J. R. Norris, R. A. Uphaus, H. L. Crespi, and J. J. Katz, *Proc. Nat. Acad. Sci. U. S.*, **68**, 625 (1971).

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