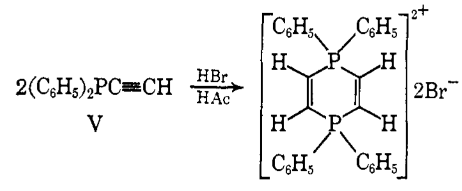
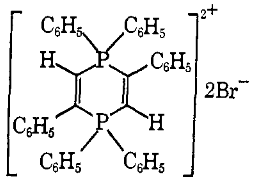


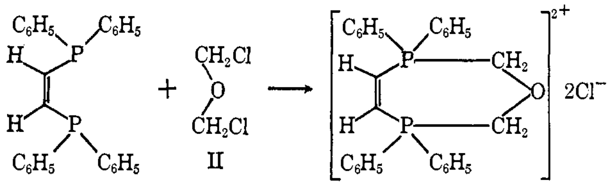
IIIc (2)

better yield of IIIc, mp 306-308° dec (from acetonitrile-methanol), was obtained by this method. Identical infrared and proton nmr spectra were obtained for IIIa and IIIc. Both gave the same picrate (IIIb), as shown by melting point and mixture melting point determinations. Simple phosphonium salts exhibit ^{31}P nmr shifts (relative to an external standard of 85% H_3PO_4) of between −20 and −40 ppm.[6] Vinylphosphonium salts, on the other hand, display increased shielding of the phosphorus nucleus.[2] The first example of a phosphonium salt displaying a positive ^{31}P nmr shift was reported recently[3] (VI).



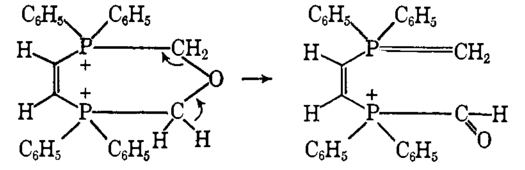
VI, +3.5 ppm

Methanol solutions of IIIa exhibited a ^{31}P nmr shift of +16.0 ppm, relative to an external standard of 85% H_3PO_4. This result is consistent, as in the case of VI, with delocalization of the four π electrons over the phosphorus 3d orbitals. Preliminary X-ray crystallographic studies of IIIa showed that it belongs to the tetragonal crystal system. Further crystallographic work is being carried out at Tulane University by Professor Charles J. Fritchie, Jr., to verify the expected planarity of the system. A silicon analog, 1,1,4,4-tetramethyl-2,3,5,6-tetraphenyl-1,4-disilacyclohexadiene-2,5, has been shown to be planar.[7] Although the mechanism of formation of IIIa has not been established, it may involve initial formation of the expected oxadiphosphoniacycloheptene (IV) (eq 3).

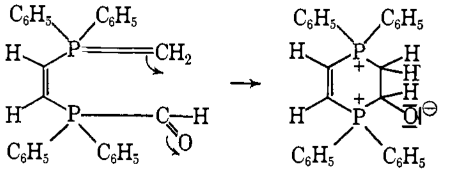


I II IV (3)

Loss of one of the acidic methylene protons[2] would lead to an ylide which would decompose into an open ylide aldehyde (eq 4). Intramolecular reaction of these functional groups would give a betaine structure which, due to steric constraint, could not undergo decomposition to an olefin and phosphine oxide typical of the Wittig reaction (eq 5). After protonation, the resultant

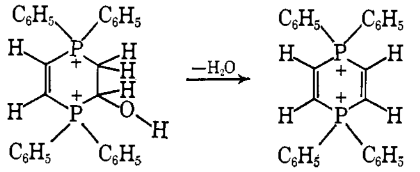


(4)



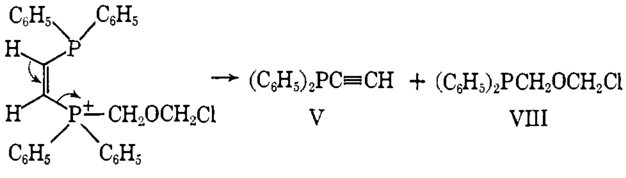
(5)

alcohol would be expected to lose water due to the acidity of the methylene protons[2] (eq 6).



III (6)

There is also the possibility that the monophosphonium salt VII undergoes elimination to give diphenylethynylphosphine (eq 7). Reaction of diphenyl-



VII (7)

ethynylphosphine with hydrogen chloride (produced by decomposition of II or VIII) would lead to III. Formation of IIIc, as in the case of VI, probably involves a series of acid-catalyzed Michael-type additions of a tertiary phosphine to an alkynylphosphine.[8]

Acknowledgment. This work was supported in part by National Science Foundation Grant GP-3823 and Petroleum Research Fund Grant 2326-A1,4. We also wish to thank Dr. G. S. Reddy of E. I. du Pont de Nemours & Co., Inc., for the ^{31}P nmr data.

---

(6) S. O. Grim, W. McFarlane, E. F. Davidoff, and T. J. Marks, *J. Phys. Chem.*, 70, 581 (1966).

(7) N. G. Bokij and J. T. S. Truchkov, *Zh. Struckt. Khim. SSSR*, **6**, 571 (1965).

(8) L. Horner and H. Hoffmann, *Angew. Chem.*, **68**, 473 (1956); H. Hoffman and H. J. Diehr, *Chem. Ber.*, **98**, 364 (1965); D. Allen, J. C. Tebby, and D. H. Williams, *Tetrahedron Letters*, 2361 (1965).

(9) NASA Fellow, 1964–1967.

Adam M. Aguiar, Keith C. Hansen[9]
Department of Chemistry, Tulane University
New Orleans, Louisiana 70118

Received May 11, 1967

The Photolysis of Bullvalene[1]

Sir:

Current interest in $C_{10}H_{10}$ hydrocarbons[2] and in the class of compounds $(CH)_{10}$ in particular[3] prompts us to

---

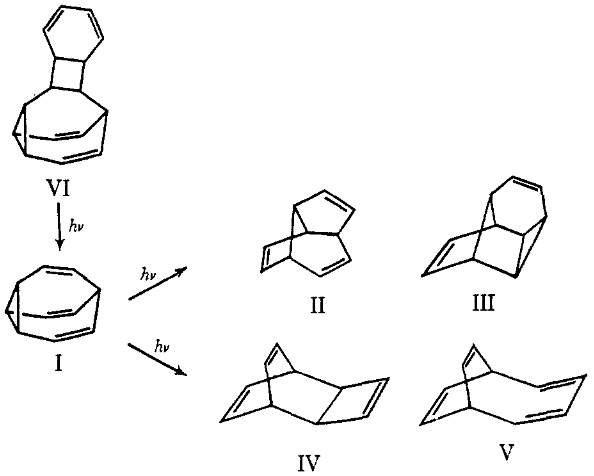
(1) Thanks are due the Lilly Research Laboratories for their generous support of this work.

(2) (a) M. Pomerantz, *J. Am. Chem. Soc.*, **88**, 5349 (1966); (b) M. Pomerantz, *ibid.*, **89**, 694 (1967); (c) J. Meinwald and P. H. Mazzocchi, *ibid.*, **89**, 696 (1967); (d) J. A. Elix, M. V. Sargent, and F. Sondheimer, *ibid.*, **89**, 180 (1967).

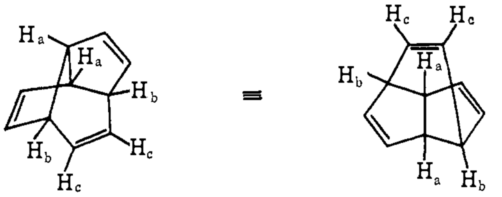
(3) (a) G. Schröder, *Angew. Chem.*, 77, 774 (1965); (b) S. Masamune, H. Cuts, and M. G. Hogben, *Tetrahedron Letters*, 1017 (1966); (c) W. von E. Doering and J. W. Rosenthal, *J. Am. Chem. Soc.*, **88**, 2078 (1966); (d) M. Jones, Jr., and L. T. Scott, *ibid.*, **89**, 150 (1967); (e)

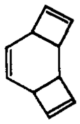
report our observation that bullvalene (I) is converted to a variety of compounds on irradiation with a Vycor-shielded Hanovia mercury arc. Two of the products, tricyclo[5.3.0.0^{4,8}]deca-2,5,9-triene (II) and tetracyclo-[4.4.0.0^{2,8}.0^{5,7}]deca-3,9-diene (III), are new and may be added to the other (CH)$_{10}$'s on a single energy surface.

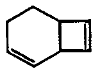
Other, easily identified products of this photolysis are Nenitzescu's hydrocarbon,[4] tricyclo[4.2.2.0^{2,5}]deca-3,7,-9-triene (IV, relative retention time[5] 1.00), and bicyclo-[4.2.2]deca-2,4,7,9-tetraene (V, relative retention time 2.92). Determination of the structures of II (relative retention time 1.11) and III (relative retention time 1.21) presents more difficulty and will be described below. Compound II is itself not stable to ultraviolet light, and varying conditions must be employed to maximize yields of the different products. After a short time many species are present, and several direct and possibly some photosensitized decompositions are taking place. Initially II is the major product of low retention time of either the photolysis of bullvalene or the prolonged irradiation of Schröder's dimer[3a] (VI). At longer times the amount of II relative to III and IV decreases. Careful monitoring of the reaction by gas chromatography allows isolation of substantial amounts of most products. Thus irradiation of 330 mg of bullvalene for 10 hr (roughly 90% decomposition) yields 28 mg of IV and 33 mg of III. Irradiation of 1.9 g of VI for 15 hr leads to 41 mg of IV (3.4%), 225 mg of bullvalene (18.6%, relative retention time 5.45), 120 mg of II (10.4%), and small amounts of III, V, and *cis*-9,10-dihydronaphthalene (VII, relative retention time 1.82).

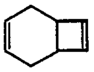


The structure of II follows from inspection of its spectra. The ultraviolet spectrum which exhibits only a shoulder at 238 mμ (ε ~1400) above 225 mμ eliminates cyclic structures with conjugated double bonds. The 100-MHz nmr spectrum[6] consists of five signals of equal area: a doublet of doublets (J = 5.9, 3.0 Hz) at τ 3.43, a triplet (J = 3.0 Hz) at τ 4.19, a doublet of doublets (J = 5.9, 2.0 Hz) at τ 4.49, and two broad singlets at τ 6.90 and 7.62. The spectrum is not simple to analyze, but decoupling experiments[6] permit the conclusion that either the singly allylic pair of hydrogens H_a appears downfield of the doubly allylic pair H_b or a long-range coupling of 3 Hz exists between H_a and H_c. Without further experiments it is not possible to decide between these alternatives; the geometrical requirements for long-range coupling[7] are satisfied and there is precedent for a reversal of chemical shifts.[8] A similar problem has been encountered by Meinwald and Kaplan.[9] The only structures permitted by the data discussed so far are II and VIII, compounds 10-3-11 and 10-3-6, respectively, in Balaban's notation.[10] Cyclobutenes generally show singlets in the vinyl region of the nmr, but the best analogy available for VIII, bicyclo[4.2.0]-octa-2,7-diene (IX), has a distressingly complex vinyl absorption.[11] While no distinction is thus possible on the basis of the nmr spectrum, the infrared is more helpful. Both IX and X have two strong bands in the 1500–1700-cm^{-1} region,[11] IX at 1640 and 1561 cm^{-1} and X at 1640 and 1554 cm^{-1}. Although both IX and X show bands little changed from the normal cyclohexene position[12] of 1646 cm^{-1}, the photoisomer of bullvalene has no strong absorption above 1575 cm^{-1} in the infrared or 1587 cm^{-1} (weak band at 1610 cm^{-1}) in the Raman.[13] These data are consistent only with structure II. Work is in progress leading to a definitive X-ray analysis.




VIII


IX


X

Compound III is the parent of two substituted molecules synthesized by Zimmerman from barrelene.[14] The nmr spectrum consists of a triplet (J = 2 Hz) of area 2 at τ 3.41, multiplets of area 1 at τ 3.67, 4.16, 7.52, and 7.78, a broad singlet of area 2 at τ 8.21, and a doublet (J = 6.3 Hz) of area 2 at τ 8.62. This spectrum, which is most strikingly similar to those reported by Zimmerman,[14] implies that one of the two double bonds is of the symmetrical norbornyl type and the other unsymmetrical. The only (CH)$_{10}$ fitting this description is III.[10]

The most attractive pathway leading to II is the vinylcyclopropane rearrangement of bullvalene. Photo-

---

W. von E. Doering and J. W. Rosenthal, *Tetrahedron Letters*, 349 (1967); (f) E. E. van Tamelen and T. L. Burkoth, *J. Am. Chem. Soc.*, **89**, 151 (1967); (g) W. von E. Doering, B. M. Ferrier, E. T. Fossel, J. H. Hartenstein, M. Jones, Jr., G. Klumpp, R. M. Rubin, and M. Saunders, *Tetrahedron*, in press.

(4) M. Avram, E. Sliam, and C. D. Nenitzescu, *Ann.*, **636**, 184 (1960).

(5) Retention times refer to a 3.5 m, 10% Carbowax 20M on 45–60 Chromosorb P column operated at 130° with 100-cc/min flow rate. Nenitzescu's hydrocarbon is used as reference.

(6) We thank Professor M. R. Willcott and B. J. Fairless of the University of Houston for measuring these spectra and for stimulating discussions.

(7) A. Rassat, C. W. Jefford, J. M. Lehn, and B. Waegell, *Tetrahedron Letters*, 233 (1964).

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

(9) J. Meinwald and B. E. Kaplan, *ibid.*, **89**, 2611 (1967).

(10) A. T. Balaban, *Rev. Rom. Chim.*, **11**, 1097 (1966).

(11) W. R. Roth, Habilitationsschrift, Köln, 1964.

(12) R. C. Lord and R. W. Walker, *J. Am. Chem. Soc.*, **76**, 2518 (1954).

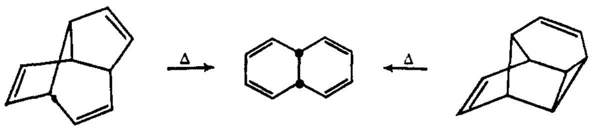
(13) We thank V. A. Maroni and Professor G. E. Leroi for measuring the Raman spectrum.

(14) H. E. Zimmerman and G. L. Grunewald, *J. Am. Chem. Soc.*, **86**, 1434 (1964).

chemical rearrangements of this type are known,[15] and the rules of Woodward and Hoffmann[16] permit a concerted suprafacial shift of order [1,3]. Numerous possible paths for the production of III exist, none of them, it seems to us, attractive enough to warrent its selection over others. We will defer comment until later.

The assignment of structure to II allows identification of the last of the four photoproducts of *cis*-9,10-dihydronaphthalene reported by Doering and Rosenthal.[3c,e] These are bullvalene, naphthalene, V, and II.[17] The isolation of II from this reaction is perhaps best rationalized as the result of further photolysis of bullvalene, itself formed by irradiation of V.[3d,18,19] The primary product of the photolysis of *cis*-9,10-dihydronaphthalene seems to be V.[3e] Compound II is rapidly destroyed when it is irradiated, but small amounts of a pentacyclic hydrocarbon can be isolated.[20]

Both II and III can be added to the list of compounds (I–V) which are thermally converted to *cis*-9,10-dihydronaphthalene (VII). The conversion of III to VII is especially facile; heating at 120° for a few minutes suffices to complete the reaction. This finds analogy in the observation of Zimmerman[14] and others[21] that disubstituted III is rapidly converted to disubstituted naphthalenes. The reaction of II is slower, but pyrolysis in a flow system at greater than 280° yields VII cleanly. Pyrolysis of II in pentane at 100° serves to slowly destroy II, the products being naphthalene (from dehydrogenation of VII) and di- and tetrahydro-II. This provides a clue to the question posed by Doering[3c] as to the fate of the hydrogen in the conversion of VII to naphthalene.[22]



II VII III

---

(15) R. N. Warrener and J. B. Bremner, *Rev. Pure Appl. Chem.*, **16**, 117 (1966).

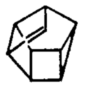
(16) R. B. Woodward and R. Hoffmann, *J. Am. Chem. Soc.*, **87**, 2511 (1965).

(17) We thank these authors for spectra of the photoproducts of VII.

(18) U. Krüerke, *Angew. Chem.*, **79**, 55 (1967).

(19) P. Radlick, private communication.

(20) An indirect clue as to the structure of II appears as the pentacyclic hydrocarbon has two different vinyl hydrogens. All possible products of internal cyclization of VIII have but one kind of vinyl hydrogen. On the other hand, such a closure in II leads to XI, a structure fitting the nmr and tentatively suggested as that of the pentacyclic hydrocarbon.



XI

(21) C. G. Krespan, B. C. McKusick, and T. L. Cairns, *J. Am. Chem. Soc.*, **83**, 3428 (1961).

(22) Note Added in Proof. Professor J. Meinwald and J. Labows have kindly informed us that they have found II to be one of the products formed on debromination of a mixture of dibromides obtained from the bromination of bullvalene.

Maitland Jones, Jr.

Department of Chemistry, Princeton University
Princeton, New Jersey 08540

Received June 9, 1967

Comparison of Solvated Electron Rates in Water and in Ice

Sir:

In a recent communication the temperature dependence of solvated electron reactions with a variety of compounds was measured.[1] Although the specific rates for the different compounds varied over a range of 10^5, the activation energy was found to be constant at 3.5 ± 0.4 kcal/mole, which is the activation energy for diffusion in water. Thus, entropic effects are responsible for the rate differences. We wish to report measurements on relative reaction rates of mobile electrons produced by γ irradiation of ice at 77°K. The relative reaction rates in ice at 77°K quantitatively parallel those in water at 300°K and support the conclusion that entropic effects are responsible for the rate differences.

We have previously shown[2] that radiation-produced mobile electrons, e_m^-, react with HSO_4^- and $H_2PO_4^-$ in 1 *M* frozen solutions at 77°K to yield trapped hydrogen atoms which can be measured by epr (eq 1). If a second

$$e_m^- + HX^- \xrightarrow{k_1} H_t + X^{2-} \tag{1}$$

solute, S, which acts as an electron scavenger and which does not yield H_t is added to the frozen solution a competition is set up (eq 2). A steady-state approximation

$$e_m^- + S \xrightarrow{k_2} \text{products not including } H_t \tag{2}$$

applied to $[e_m^-]$ yields the expression

$$\frac{G^0(H_t) - G(H_t)}{G(H_t)} = \frac{k_2[S]}{k_1[HX^-]} \tag{3}$$

where $G^0(H_t)$ and $G(H_t)$ are H_t yields per 100 ev of radiation energy absorbed in the absence and presence of the scavenger. By plotting the left side of eq 3 against $[S]/[HX^-]$, a straight line through the origin is obtained with slope equal to k_2/k_1. A variety of electron scavengers, S, has been studied in this manner, and a consistent set of values is summarized in Table I. The rates are relative to the arbitrary value of $k = 10$ for $X = NO_3^-$. Liquid-phase rates directly measured

Table I. Relative Rates of e_m^- Reactions with Solutes as Measured by Competition Kinetics of H_t Yields in H_2PO^{4-} or HSO^{4-} Ices

Solute (S)	Relative rates[a] $k(e_m^- + S)$, 77°K	$k(e_{aq}^- + S)$, 300°K
Cd^{2+}	38	52[b]
Cu^{2+}	26	27[b]
CrO_4^{3-}	17	16[b]
NO_3^-	(10)	(10)[c]
NO_2^-	5	4.2[c]
CH_3COCH_3	3	5.3[c]
Zn^{2+}	1	1.5[b]
$ClCH_2COO^-$	1	1.1[d]

[a] All rates normalized to NO_3^- rate = 10. [b] J. H. Baxendale, E. M. Fielden, and J. P. Keene, *Proc. Chem. Soc.*, 242 (1963). [c] E. J. Hart, S. Gordon, and J. K. Thomas, *J. Phys. Chem.*, **68**, 1271, 1524 (1964). [d] M. Anbar and E. J. Hart, *ibid.*, **69**, 271 (1965).

---

(1) M. Anbar, Z. B. Alfassi, and H. Bregman-Reisler, *J. Am. Chem. Soc.*, **89**, 1263 (1967).

(2) L. Kevan, P. N. Moorthy, and J. J. Weiss, *ibid.*, **86**, 771 (1964); L. Kevan and C. Fine, *ibid.*, **88**, 869 (1965).