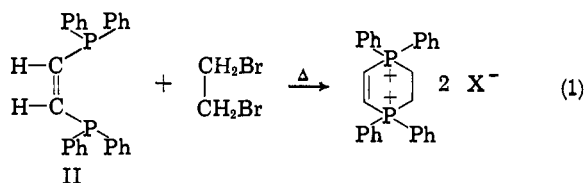


# Communications to the Editor

## 1,1,4,4-Tetraphenyl-1,4-diphosponiacyclohexene-2 Salts. Preparation, Anomalous Hydrolysis, and Proton and Phosphorus-31 Nuclear Magnetic Resonance Shifts

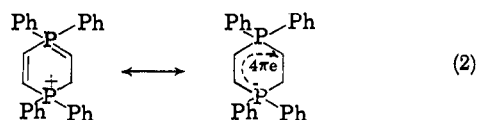
Sir:

We wish to report the preparation of 1,1,4,4-tetraphenyl-1,4-diphosponiacyclohexene-2 dibromide (Ia, X = Br) and dipicrate (Ib, X = picrate) from the reaction of *cis*-vinylenebis(diphenylphosphine) (II)<sup>1</sup> with excess refluxing 1,2-dibromoethane (eq 1).<sup>2</sup>



Compound Ia melted at 298–300° dec (MeOH-acetone). *Anal.* Calcd for C<sub>28</sub>H<sub>26</sub>P<sub>2</sub>Br<sub>2</sub>: C, 57.33; H, 4.45; P, 10.61; Br, 27.39. Found: C, 57.22; H, 4.50; P, 10.47; Br, 27.21. Treatment of an aqueous solution of Ia with sodium picrate gave an immediate yellow precipitate of Ib, mp 273–275° (CH<sub>3</sub>CN-EtOH). *Anal.* Calcd for C<sub>40</sub>H<sub>30</sub>P<sub>2</sub>N<sub>6</sub>O<sub>14</sub>: N, 9.54; Br, 0.00. Found: N, 9.32; Br, 0.00. Infrared spectra indicate a phenylphosphonium salt. Employing the method of Masterton,<sup>3</sup> the osmotic pressure of solutions of less than 10<sup>-2</sup> M concentration shows Ia to be a 2:1 electrolyte with a molecular weight of 580 (calcd 584). In more concentrated solutions Ia behaves as a 1:1 electrolyte and the effective molecular weight is 308 (half of the calculated value is 292). No evidence of a bromine to phosphorus bond has been detected in the infrared spectrum.

The 60-Mc proton nmr spectrum of a trifluoroacetic acid solution of Ia exhibits two peaks centered at  $\tau$  1.42, 51 cps apart, with a broad complex at the center, a complex centered at  $\tau$  2.15 ppm, and a sharp doublet centered at  $\tau$  6.11 ( $J_{\text{PCH}} = 8$  cps), in the ratio of 1:10:2, assigned to the *cis*-vinyl, the phenyl, and the methylene protons, respectively. Use of deuterium oxide as the solvent shifted the peaks to lower field strength with a decrease in the area of methylene protons. At 60° this decrease was considerably greater, indicating that exchange occurs between the D<sub>2</sub>O and the methylene protons. This is expected since these protons, once abstracted, leave a conjugated ylid (eq 2). The nmr in



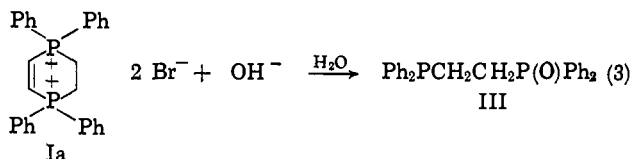
D<sub>2</sub>O shows: *cis*-vinyl,  $\tau$  1.0; phenyl,  $\tau$  1.82; and methylene protons,  $\tau$  5.83. TFA does not protonate the double bond.

(1) A. M. Aguiar and D. Daigle, *J. Am. Chem. Soc.*, **86**, 2299 (1964).

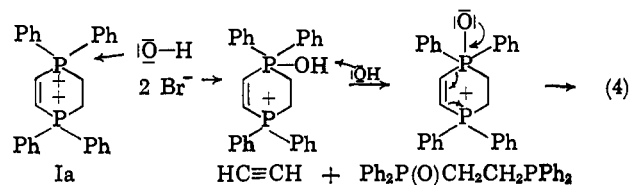
(2) G. Markl, *Angew. Chem. Intern. Ed. Engl.*, **4**, 1023 (1965).

(3) W. L. Masterton and J. A. Scola, *J. Phys. Chem.*, **68**, 14 (1964).

Reaction of Ia with hot, dilute aqueous base leads to the monoxide of ethylenebis(diphenylphosphine) (III, eq 3).

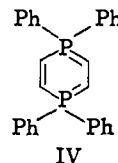


Loss of the olefinic portion indicates initial attack on the phosphorus atom, subsequent proton abstraction, and collapse of the zwitterion with loss of acetylene (eq 4).<sup>4,5</sup>  $\beta$  Elimination *via* abstraction of the vinyl



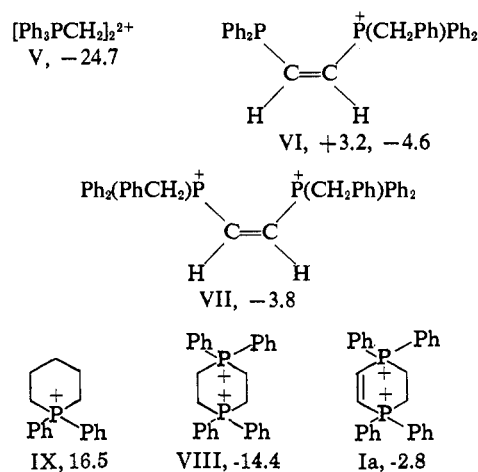
proton seems unlikely in view of the nmr data.

Attempts at production of the possibly aromatic, conjugated diylid IV by proton abstraction (butyllithium, phenyllithium) have led to ring opening.



We have found that vinylphosphonium salts have P<sup>31</sup> nuclei which are magnetically more shielded than simple phosphonium salts. Listed in Chart I are P<sup>31</sup> nmr shifts (in parts per million) relative to 85% H<sub>3</sub>PO<sub>4</sub> taken

Chart I



in methanol. Apparently there is some 2p <sub>$\pi$</sub> -3d <sub>$\pi$</sub>  delocalization in Ia, VI, and VII.

Compounds VI and VII were prepared by the reaction of II with benzyl bromide in benzene and in ex-

(4) M. Zanger, C. A. VanderWerf, and W. E. McEwen, *J. Am. Chem. Soc.*, **81**, 3806 (1959).

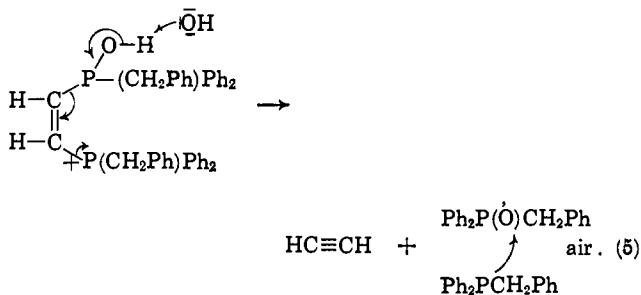
(5) A. M. Aguiar, H. Aguiar, and D. Daigle, *ibid.*, **87**, 671 (1965).

cess benzyl halide, respectively. Compound VI melted at 218–219° (MeOH–acetone). *Anal.* Calcd: Br, 14.1. Found: Br, 14.31. Compound VII melted at 333–335° (MeOH–CH<sub>3</sub>CN).

Proton nmr spectra of VI in deuteriochloroform solution at 60 Mc show a doublet centered at  $\tau$  5.01 ( $J_{\text{PCH}} = 15$  cps), two phenyl proton complexes at  $\tau$  2.9 and 2.4, and a peak at  $\tau$  1.5. In TFA the doublet is at  $\tau$  5.40. The ratio of phenyl and vinyl protons to methylene protons indicates a monophosphonium salt. The *trans* isomer of II<sup>1</sup> reacts with benzyl bromide in benzene to give an isomer of VI (mp 208–210°) with a doublet centered at  $\tau$  4.85 ( $J_{\text{PCH}} = 15$  cps) and peaks at  $\tau$  2.85, 2.5, and 2.25. In TFA the doublet appears at  $\tau$  5.4, showing that isomerization takes place in this solvent.

Compound VII is insoluble in CDCl<sub>3</sub>. A TFA solution gives a spectrum identical with that of the product from *trans*-II and excess benzyl bromide (mp 309–312°). This may be due to isomerization in the formation, but more likely, by TFA. The spectra show a doublet (separation = 14 cps) with a shallow complex in the middle centered at  $\tau$  5.25, and the phenyl–vinyl proton complex in the ratio of 1:8.

Basic hydrolysis of VII gave benzyldiphenylphosphine oxide and not the oxides of I (eq 5).



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## Photochemical Behavior of Cycloalkenes

Sir:

Numerous studies have established that transfer of triplet energy to acyclic or macrocyclic olefins from suitable photosensitizers (having  $E_T \geq 69$  kcal/mole) results in *cis-trans* isomerization of the double bond,<sup>1</sup>

(1) (a) R. B. Cundall, *Progr. Reaction Kinetics*, **2**, 165 (1964); (b) G. S. Hammond, N. J. Turro, and P. A. Leermakers, *J. Phys. Chem.*, **66**, 1144 (1962); (c) A. C. Testa, *J. Org. Chem.*, **29**, 2461 (1964); (d) H. Morrison, *Tetrahedron Letters*, 3653 (1964); *J. Am. Chem. Soc.*, **87**, 932 (1965); (e) H. Nozaki, Y. Nisikawa, Y. Kamatani, and R. Noyori, *Tetrahedron Letters*, 2161 (1965).

undoubtedly as a consequence of the preferred orthogonal conformation of triplet olefins.<sup>2</sup> By contrast, the photochemical behavior of smaller ring cyclic olefins, in which *trans* isomers are exceedingly strained,<sup>3</sup> has been little studied except for several reports of dimerization.<sup>4</sup> We wish to describe here two related light-induced reactions of cycloalkenes which appear to be widely applicable and are of both synthetic and mechanistic interest.

Irradiation of 1-alkylcycloalkenes in the presence of aromatic hydrocarbon photosensitizers (benzene, toluene, or xylene) has been found to induce isomerization to the analogous exocyclic olefins. Thus (+)-3-carene (**1**) is converted to (+)-3(10)-carene (**2**), ( $\pm$ )-1-menthene (**7a**) to ( $\pm$ )-1(7)-menthene (**8a**), and the ethyl analog **4**<sup>5</sup> to the exocyclic isomer **5**.<sup>6,7</sup> In the presence of alcohols there is a competing reaction leading to the formation of tertiary ethers. Thus in 9:1 methanol–xylene **7a** is converted to the *cis* (27% yield) and *trans* isomers (16%) of **9a**<sup>8</sup> as well as to the exocyclic olefin **8a** (36%). 1-Methylcycloheptene affords the analogous tertiary ether<sup>9</sup> (62% yield). (+)-3-Carene (**1**) gives (+)-3 $\alpha$ - (3%) and (+)-3 $\beta$ -methoxycarane (**3**, 17%), the rearranged ether **6** (12%), and the olefin **2** (23%); in aqueous *t*-butyl alcohol–benzene the corresponding alcohols<sup>10</sup> are formed in a similar ratio.<sup>11</sup>

Unsubstituted cycloalkenes also undergo ether formation, but less efficiently. In an interesting example of the synthetic potential of this reaction, the diene **10** was found to give selectively the tertiary ether **11**. By contrast, the conformationally rigid cedrene (partial structure **12**), the acyclic olefin 3,5-dimethyl-3-heptene, and the exocyclic olefins **2** and **8a** are totally inert to addition or rearrangement under these conditions.

Labeling studies with **7b** have revealed that the transformation to **8** in benzene or benzene–methanol is principally *intermolecular*, resulting in the loss of 0.8–0.9 D and giving predominantly the D<sub>2</sub> product **8b** (along with **9b** in methanol). Moreover, at least in the

(2) See, for example, the discussion in ref 1a.

(3) Chemical evidence for the formation of the highly reactive *trans*-cycloheptene has been described: E. J. Corey, F. A. Carey, and R. A. E. Winter, *J. Am. Chem. Soc.*, **87**, 934 (1965). *trans*-Cyclohexene is unknown.

(4) See, for example (a) D. Scharf and F. Korte, *Tetrahedron Letters*, 821 (1963); (b) *Chem. Ber.*, **97**, 2425 (1964); (c) D. R. Arnold, R. L. Hinman, and A. H. Glick, *Tetrahedron Letters*, 1425 (1964); (d) D. R. Arnold, D. J. Trecker, and E. B. Whipple, *J. Am. Chem. Soc.*, **87**, 2596 (1965).

(5) G. Ohloff, G. Schade, and H. Farnow, *Chem. Ber.*, **90**, 106 (1957).

(6) This isomerization was apparently first observed by F. J. McQuillin and J. D. Parrack, *J. Chem. Soc.*, 2973 (1956), in the conversion of a mixture of  $\alpha$ - and  $\beta$ -eudesmol to the pure  $\beta$  isomer by irradiation in benzene solution. However, the generality of this reaction was not recognized.

(7) Irradiations were conducted with a 450-w mercury lamp and a Vycor immersion apparatus containing 150 ml of solution and 1.00 g of olefin. Satisfactory analytical and spectral data were obtained for all new compounds.

(8) (a) W. Hueckel and P. Heinzelmann, *Ann.*, **687**, 82 (1965). (b) The formation of the isomeric ethers **9a** from **7a** was first observed by J. A. Marshall and R. D. Carroll, *J. Am. Chem. Soc.*, **88**, 4092 (1966), to whom the author is deeply indebted for discussion of their results prior to publication.

(9) W. Hueckel and J. Waechter, *Ann.*, **672**, 62 (1964).

(10) H. Kuczyński and K. Piatkowski, *Roczniki Chem.*, **31**, 59 (1957); H. Kuczyński and Z. Chabudziński, *ibid.*, **34**, 177 (1960). Several examples of rearrangement of the carane skeleton to that of bicyclo-[3.1.0]hexane resulting from the generation of positive character at C-3 have recently been observed (P. J. Kropp, *J. Am. Chem. Soc.*, in press).

(11) The ether products can also be obtained, but in lower yield, by irradiation of the various olefins under identical conditions except for the absence of a photosensitizer.