Concerning the Phosphinium Radical Cation
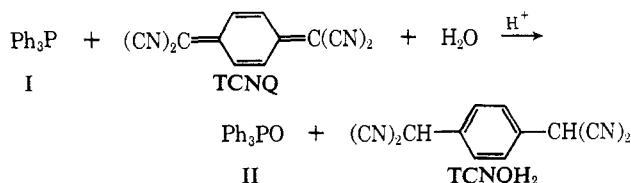
Sir:

For many years now the phosphinium radical cation ($R_3P\cdot^+$) has been suggested as an intermediate in reactions of trivalent phosphorus compounds,[1-4] but there appears to be no definitive evidence for the existence of such a species. We attempted to obtain such evidence by a study of the reactions of triarylphosphines (in particular an optically active triarylphosphine) with electron acceptor species such as 7,7,8,8-tetracyanoquinodimethane[5] (TCNQ) and tetracyanoethylene (TCNE), and the results are reported below.

Triphenylphosphine (I) reacts with TCNQ in $CHCl_3$ or CH_3CN in the presence of water and a catalytic quantity of HCl to give quantitative yields of 7,8-dihydro-7,7,8,8-tetracyanoquinodimethane[5] ($TCNQH_2$) and triphenylphosphine oxide (II), both products being identi-

$$Ph_3P + (CN)_2C=\!\!\bigcirc\!\!=C(CN)_2 + H_2O \xrightarrow{H^+}$$

I   TCNQ

$$Ph_3PO + (CN)_2CH-\!\!\bigcirc\!\!-CH(CN)_2$$

II   TCNQH_2

fied by melting point, mixture melting point, and ir spectra. The green color of the TCNQ radical anion[6] (λ_{max} 840 and 756 mμ) was observed for a few seconds after mixing the reagents.

Optically active 4-biphenyl-α-naphthylphenylphosphine[7] (III) reacts with TCNQ under identical conditions to give quantitative yields of $TCNQH_2$ and racemic-4-biphenyl-α-naphthylphenylphosphine oxide (IV). It was demonstrated that IV was racemic prior to isolation and that optically active IV (prepared by the oxidation of optically active III by H_2O_2 in glacial acetic acid) did not racemize in the presence of HCl or $TCNQH_2$.

In completely anhydrous, acid-free medium, dilute solutions of III reacted slowly with TCNQ to give 2:1 (TCNQ-phosphine) adducts. Attempts to isolate the latter led to formation of intractable polymeric material, but solutions of the adducts gave no phosphine oxide on treatment with aqueous HCl. This behavior contrasts sharply with the reaction in the presence of acid but resembles the reaction of triphenylphosphine with TCNE (*vide infra*).

The kinetics of the reaction of III with TCNQ in 80% CH_3CN-20% C_6H_6 in the presence of aqueous HCl were studied by following the disappearance of the TCNQ absorption, λ 422 mμ, when pseudo-first-order behavior was observed for at least 75% of the total reaction. The reaction was over-all third-order (k_3 = 1.18 $\times$ 10^4 l.^{2} mol^{-2} sec^{-1} at 28.6°), being first order in TCNQ, III, and acid concentration, respectively, but

independent of the water concentration over a range of 4×10^{-3} to 6×10^{-1} M.

We consider that these facts are best interpreted by the mechanism shown in eq 1-3. It seems likely that the

$$Ar_3P + TCNQ \longrightarrow Ar_3P\cdots TCNQ \rightleftharpoons$$

I or III   EDA complex

$$Ar_3P\cdot^+\cdots TCNQ\cdot^- \quad (1)$$
"ion pair"

EDA complex $\xrightarrow{\text{HCl, rate determining}}$
or
ion pair

$$Ar_3P\cdot^+ + TCNQH\cdot + Cl^- \quad (2)$$

$$Ar_3P\cdot^+ + H_2O + TCNQH\cdot \xrightarrow{\text{fast}}$$

$$Ar_3P(O) + TCNQH_2 + H^+ \quad (3)$$
II or IV

rate-determining step involves the acid-catalyzed dissociation of the EDA complex or ion pair.[8a] The resultant phosphinium radical cation (V) is rapidly attacked by water to give the final products. The formation of racemic phosphine oxide from optically active III demonstrates that V is either planar or possesses a very low energy barrier to inversion about phosphorus. Reaction 3 must be representative of at least two steps.

Under identical conditions the rate of the reaction varied considerably with the substituents on the aryl groups of the phosphine used,[8b] and it is interesting to note that the rates increased with the electron-donating ability of the substituents, indicating a parallel increase in stability of the phosphinium radical cation.

It may be argued that racemic phosphine oxide could be formed by hydrolysis of an intermediate betaine (VI) or its phosphonium salt (VII) *via* a five-covalent inter-

$$Ar_3P + TCNQ \rightleftharpoons Ar_3P^+C(CN)_2-\!\!\bigcirc\!\!-\bar{C}(CN)_2 \xrightarrow{HCl}$$

VI

$$Ar_3PC(CN)_2-\!\!\bigcirc\!\!-CH(CN)_2 \xrightarrow{H_2O}$$
$$Cl^-$$

VII

$$Ar_3PC(CN)_2-\!\!\bigcirc\!\!-CH(CN)_2 \longrightarrow$$
$$|$$
$$OH$$

$$Ar_3P(O) + TCNQH_2$$

mediate. Such a mechanism seems extremely unlikely since hydrolysis of phosphonium salts is normally only achieved under basic conditions[9] and then proceeds with inversion of configuration about phosphorus.[10] There are no reports of phosphonium salts undergoing facile hydrolysis under acid conditions, and dicyanomethylene or cyanocarboalkoxymethylenetriarylphosphoranes are stable to aqueous acid.[11]

Further evidence for the phosphinium radical cation was obtained by allowing a 50 M excess of optically active III, $[\alpha]^{25}_{436}$ $-8.8°$, to react with TCNQ in anhydrous acetonitrile-20% benzene over 18 hr at 28.8°. The recovered phosphine had $[\alpha]^{25}_{436}$ $-7.1°$, equivalent

(1) F. Ramirez and S. Dershowitz, *J. Amer. Chem. Soc.*, **78**, 5614 (1956).

(2) E. A. C. Lucken, F. Ramirez, V. P. Catto, D. Rhum, and S. Dershowitz, *Tetrahedron*, **22**, 637 (1966).

(3) P. D. Bartlett, E. F. Cox, and R. E. Davies, *J. Amer. Chem. Soc.*, **83**, 103 (1961).

(4) O. A. Ptitsyna, M. E. Pudeeva, and A. O. Reutov, *Dokl. Akad. Nauk SSSR*, **165**, 838 (1965).
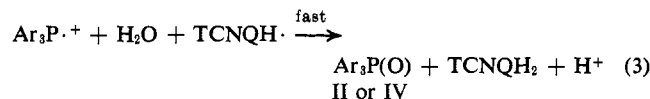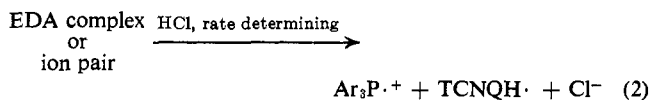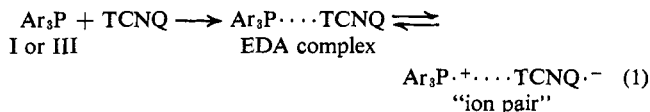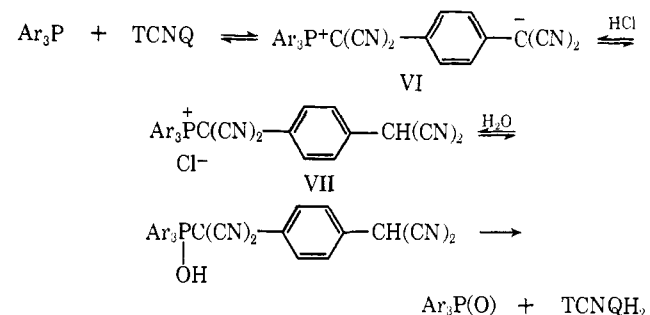
(5) D. S. Acker and W. R. Hertler, *J. Amer. Chem. Soc.*, **84**, 3370 (1962).

(6) L. R. Melby, R. I. Harder, W. R. Hertler, W. Mahler, R. E. Benson, and W. E. Mockel, *ibid.*, **84**, 3374 (1962).

(7) G. Wittig, H. J. Cristau, and H. Braun, *Angew. Chem.*, **79**, 721 (1967).

(8) (a) Nucleophilic attack on cyano olefins has been show to be acid catalyzed: E. Lord, Ph.D. Thesis, University of London, 1968; (b) details to be reported in the full paper.

(9) M. Zanger, C. A. Vander Werf, and W. E. McEwen, *J. Amer. Chem., Soc.*, **81**, 3806 (1959).

(10) K. F. Kumli, W. E. McEwen, and C. A. Vander Werf, *ibid.*, **81**, 3805 (1959).

(11) L. Horner and H. Oediger, *Chem. Ber.*, **91**, 437 (1958).

to racemization of 10 mol of phosphine per mol of TCNQ; this must involve an equilibrium process. The best explanation of this observation is a slow dissociation of the ion pair to free-radical ions.

The reaction of I with TCNE has been reported to give 1,1,1-triphenyl-2,3,4,5-octacyanophosphole (VIII),[12] and we confirm that in anhydrous medium the reaction proceeds with a 2:1 stoichiometry.[13] However, in CH_3CN in the presence of aqueous HCl, I reacts with TCNE in a 1:1 molar ratio to give a quantitative yield of II and 1,1,2,2-tetracyanoethane. In 30% CH_3CN-70% $CHCl_3$, containing 5% concentrated HCl, optically active III reacted with TCNE to give *racemic* IV (49%) and 1,1,2,2-tetracyanoethane (43%), the remaining TCNE being recovered as the 2:1 adduct with III identical with that obtained under anhydrous conditions. It is clear that the formation of racemic oxide may also be explained in terms of an intermediate phosphinium radical cation.

Since Ramirez[2] suggested that V was a possible intermediate in the reactions of triarylphosphines with chloranil we attempted to verify this by using optically active III. Racemic IV was obtained on hydrolysis of the phosphine–chloranil adduct, but the experiment was frustrated by the observation that optically active IV racemized in the presence of tetrachloroquinol probably *via* formation of a five-covalent phosphorus structure in solution.

There was no evidence for any complex formation between $TCNEH_2$ or $TCNQH_2$ and IV, and solutions of optically active IV did not racemize in the presence of $TCNEH_2$ or $TCNQH_2$.

(12) G. S. Reddy and C. D. Weiss, *J. Org. Chem.*, **28**, 1822 (1963).

(13) A recent publication[14] suggested that the structure proposed for VIII was probably incorrect. The ³¹P chemical shift (−22 ppm from H_3PO_4) is not consistent with a pentacovalent structure and we find that, under anhydrous conditions, optically active III gives a similar product which retains optical activity, thus providing further evidence against the phosphole structure.

(14) M. A. Shaw, J. C. Tebby, R. S. Ward, and D. H. Williams, *J. Chem. Soc., C*, 1611 (1968).

(15) Address correspondence to Department of Chemistry, Ralph G. Wright Laboratory, Rutgers University, New Brunswick, N. J.

R. L. Powell,[15] **C. D. Hall**[15]

Department of Chemistry
Kings College, University of London
Strand, London W.C. 2

Stereospecific Photochemical Fragmentation of Cyclobutenes in Solution

Sir:

Orbital-symmetry considerations predict that formation of four-membered rings by concerted *cis,cis* cycloaddition has a prohibitively large activation energy for ground-state reactants, but is favored when one of the reactants is electronically excited.[1,2] In accord with these expectations thermal "1,2" cycloadditions have been shown to involve diradical intermediates,[3] whereas

(1) R. Hoffmann and R. B. Woodward, *Accounts Chem. Res.*, **1**, 17 (1968), and references cited therein.

(2) L. Salem, *J. Amer. Chem. Soc.*, **90**, 543, 553 (1968).

(3) P. D. Bartlett and G. E. H. Wallbillich, *ibid.*, **91**, 409 (1969), and previous papers in this series.

complete stereospecificity in the photochemical dimerization of the 2-butenes strongly suggests a concerted process.[4] For the reverse reactions, the same orbital-symmetry considerations predict that concerted *cis,cis* cleavage of four-membered rings is the favored path photochemically but not thermally. Recent observations on the thermal cleavage of cyclobutanes indicate a diradical intermediate, substantiating, in part, these predictions.[5]

Photochemical fragmentation of cyclobutenes to ethylene and acetylenes has been reported,[6,7] but no information has been available concerning the stereochemistry of the reaction. The following deals with the photochemical cleavage of cyclobutenes **1** and **2**.

1   2

cis-Cyclobutene (**1**) was prepared from 1,1'-bicyclohexenyl (**3**) using 2-acetonaphthone as photosensitizer,[8] and *trans*-cyclobutene (**2**) was prepared using Moore and Moser's procedure.[9] Pentane solutions (0.03–0.06 *M*) of **1** and **2** were irradiated under nitrogen using a 550-W Hanovia mercury lamp and a Hanovia quartz immersion probe. Reaction mixtures were analyzed by glpc using a 15 ft × ¹/₈ in. column packed with 15% Carbowax 20M on Chromosorb W.

Direct irradiation of **1** gives 1,1'-bicyclohexenyl (**3**) as the major initial photoproduct. Formation of **3** was kept to less than 1% of the product mixture by irradiating **1** in the presence of triphenylene ($\sim 10^{-5}$ *M*). It was shown that triphenylene functions as photosensitizer for the conversion of **3** to **1**, but does not sensitize reactions of **1**. Prolonged irradiation of **1** in the presence of triphenylene yields one major photoproduct (**4**) which was isolated in 25% yield by chromatography on alumina impregnated with 33% silver nitrate. The nmr spectrum of **4** in CCl_4 with TMS as reference consists of two broad peaks centered at 1.51 and 2.15 ppm and a symmetrical multiplet centered at 5.29 ppm (relative areas 4:4:1, respectively). The ir spectrum shows bands of interest at 1450 (m) and 710 cm⁻¹ (m). The Raman spectrum of the neat product shows bands at 2290, 2240, and 1656 cm⁻¹. The mass spectrum has a parent ion peak at *m/e* 162. The observations indicate that **4** is *cis*-cyclododeca-1-en-7-yne. Chemical con-

4
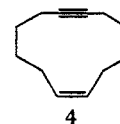
firmation of this assignment was obtained by partial reduction of the triple bond in methanol using 5% Pd on $BaSO_4$ poisoned with quinoline as catalyst.[10] The nmr of the hydrogenation product in CCl_4 is very similar

(4) Y. Yamazaki and R. J. Cvetanović, *ibid.*, **91**, 520 (1969).

(5) A. T. Cocks and H. M. Frey, *Chem. Commun.*, 458 (1969).

(6) E. H. White and J. P. Anhalt, *Tetrahedron Lett.*, 3937 (1965).

(7) I. Haller and R. Srinivasan, *J. Amer. Chem. Soc.*, **88**, 3694 (1966).

(8) W. G. Dauben, R. L. Cargill, R. M. Coates, and J. Saltiel, *ibid.*, **88**, 2742 (1966).

(9) We thank Professor W. R. Moore for sending us a detailed description of the synthesis. *Cf.* W. Moser, Ph.D. Thesis, Massachusetts Institute of Technology, 1963.

(10) D. J. Cram and N. L. Allinger, *J. Amer. Chem. Soc.*, **78**, 2518 (1956).