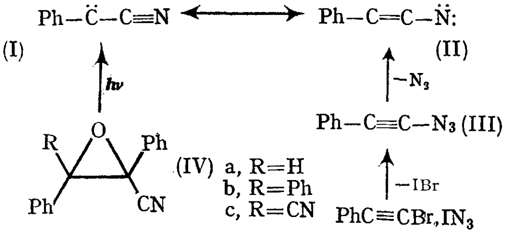
Photolysis of 1,3,2-Dioxaphosph(V)olans: Two-step Deoxygenation of Benzoyl Cyanide to Phenylcyanocarbene

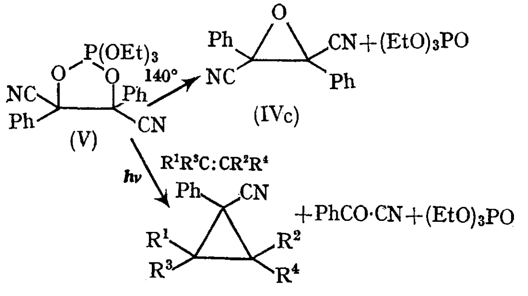
By P. PETRELLIS and G. W. GRIFFIN*

(*Department of Chemistry, Louisiana State University in New Orleans, New Orleans, Louisiana* 70122)

EXTENSIVE synthetic and theoretical interest has been expressed in the chemistry of phenylcyanocarbene (I);[1,2] it has been suggested that (I) might even exhibit properties characteristic of phenylethynyl nitrene (II).[1] We have established that phenylcyanocarbene may be generated from a variety of epoxides[3,4] including (IVa), (IVb), and (IVc) which may be prepared more conveniently than the conventional precursor phenylcyanodiazomethane. Typical arylcarbene properties were observed for phenylcyanocarbene generated from (IVa) and the related precursors, (IVb) and (IVc), which behave in a chemically equivalent manner.[3,4†] It remains to be established, however, that these results are general in nature and independent of structure of the precursor and mode of generation.[‡]

We report an alternative, simpler, and more efficient preparation of (I). 1,3,2-Dioxaphosph(V)olan (V) was previously prepared from benzoyl cyanide and triethyl phosphite.[5] Thermolysis of (V) had been shown to give *trans*-2,3-dicyano-2,3-diphenyloxiran (IVc). In view of the thermal instability and convenient preparation of (V) and the photolability of (IVc), it was of interest to investigate the photolytic behaviour of the phospholan (V). Irradiation[§] of a solution (0·3M) of (V) in 2-methylbut-2-ene or 2,3-dimethylbut-2-ene provided the corresponding phenylcyanocyclopropanes (VIa and b) and (VIc), respectively, in yields comparable to those obtained from the oxirans (IV) (60—70%).[6] The products were isolated gas chromatographically and identified by comparison of i.r. and n.m.r. spectra with those of authentic samples.[3,4] Benzoyl cyanide and triethyl phosphate were detected among the reaction products. The former is photolabile, however, and undergoes considerable resinification. Oxetan formation, a reaction which is generally observed when carbonyl derivatives are photogenerated in the presence of alkenes was not observed in this case.[7]





(VI) a, R^1=H; R^2=R^3=R^4=Me
b, R^3=H; R^1=R^2=R^4=Me
c, R^1=R^2=R^3=R^4=Me

The mechanism by which phenylcyanocarbene (I) is produced from (V) is of some interest. A plausible two-step process involves initial conversion of (V) into (IVc) which is known to photolyse to (I). This appeared to be an attractive alternative in view of the thermal properties of (V) which have already been described. From preliminary competitive rate studies employing an internal standard (hexadecane) it was evident that 1-cyano-2,2,3,3-tetramethyl-1-phenylcyclopropane (VIc) is formed faster from the phosphorane (V) than the

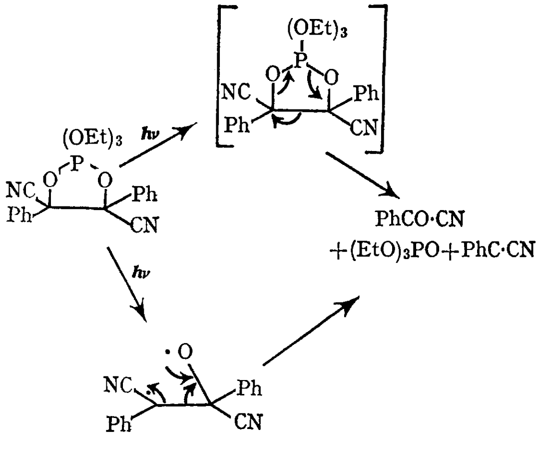
---

[†] It is apparent from the e.p.r. spectrum of (I)⟷(II) generated from (IVa) that spin density is distributed on nitrogen. Furthermore, the triplet spin parameters observed for (I) ⟷ (II) produced from the oxiran (IVa) and from phenylcyanodiazomethane are equivalent. E. Wasserman and A. Trozzolo, personal communication.

[‡] Boyer and Selvarajan (ref. 1) attempted to generate the nitrene (II) by using the adduct from iodine azide and phenylethynyl bromide, presumably (III), as a precursor. They did not detect phenylethynyl nitrene as an intermediate. The major product isolated is *trans*-dicyanostilbene. This product was not detected among the photolysis products of (IVa), (IVb), or (IVc): this may be attributed to concentration levels or to differences in energetics or spin state.

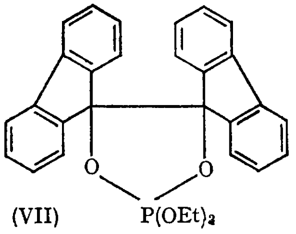
[§] An air cooled Rayonet Chamber Reactor (The Southern New England Ultraviolet Co., Middletown, Conn.) equipped with sixteen 8 w RPR-2537A low-pressure mercury lamps was used as a light source. Solutions were degassed and irradiations conducted in serum-capped quartz test tubes at 40°.

oxiran (IVc). Secondary reactions of unknown character complicate the rate studies in the case of (V) when irradiation times are extended beyond a 6 hr. period. However, we were unable to detect even traces of the oxiran (IVc) by t.l.c. among the photolysis products of (V). In view of these results a two-step mechanism involving (IVc) as an intermediate may be rejected. Alternative possibilities include concerted (Path *a*) or homolytic (Path *b*) fragmentation.

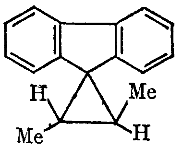


In an attempt to determine the generality and utility of phosphorane photofragmentations we have investigated the photolysis of (VII)[8] which by analogy with (V) should fragment to fluorenylidene, fluorenone, and triethyl phosphate.

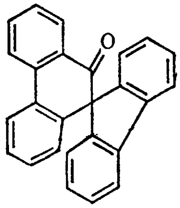
In a typical experiment a solution (0·1M) of (VII) in *trans*-but-2-ene was irradiated (24 hr.). Products characterized by t.l.c. include fluorenone, bifluorenylidene and (VIII), the expected fluorenylidene alkene adduct;[9] the major product, however, was the spiro-ketone (IX) which is also the primary thermolysis product obtained from (VII).[8] A previous report indicates that fluorenone and triethylphosphite react at elevated temperatures with formation of (IX) in addition to small amounts of bisfluorenylidene.[8b]



(VII)



(VIII)



(IX)

We thank the National Institutes of Health and the Army Research Office (Durham, N.C.), for support of this research.

(*Received, June 24th,* 1968; *Com.* 828.)

---

[1] J. Boyer and R. Selvarajan, Abstracts of 154th Meeting of the American Chemical Society, Chicago, Illinois, September, 1967, p. S 111.

[2] R. Breslow and C. Juan, *J. Amer. Chem. Soc.*, 1958, **80**, 5991, and more recent papers.

[3] P. Petrellis, H. Dietrich, E. Meyer, and G. W. Griffin, *J. Amer. Chem. Soc.*, 1967, **89**, 1967.

[4] P. Petrellis and G. W. Griffin, *Chem. Comm.*, 1967, 691.

[5] J. Mukaiyama, I. Kuwajima, and K. Ohno, *Bull. Chem. Soc. Japan*, 1965, **38**, 1954. We have modified Mukaiyama's procedure for the preparation of (V). An exothermic reaction ensues upon addition of neat triethyl phosphite to neat benzoyl cyanide which may be controlled by cooling in an ice–salt bath. Trituration of the resulting mixture yields a semisolid which upon recrystallization from ligroin affords crystals (m.p. 115—117°; lit. 117°).

[6] It should be noted that the photochemistry of 1,3,2-dioxaphosph(v)oles has been studied by Bentrude. Photofragmentation occurs to give "1,2 diones", trimethylphosphite and phosphate. See W. G. Bentrude, *Chem. Comm.*, 1967, 174.

[7] Recently Temnikova and his co-workers reported their results concerning the photofragmentation of (IVc). (See T. I. Temnikova, I. P. Stepanov, and L. O. Semenova, *Zhur. org. Khim*, 1967, **3**, 1708). Their results corroborate our observations and they too encountered problems as a result of the photolability of benzoyl cyanide.

[8] (a) F. Ramirez and C. P. Smith, *Chem. Comm.*, 1967, 662. We are indebted to Prof. Ramirez (State University of New York at Stony Brook) for providing us with a sample of the phosphorane (VII) which was used for comparative purposes; (b) I. J. Borowitz and M. Anschel, *Tetrahedron Letters*, 1967, 1517. We extend our thanks to Prof. Borowitz (Yeshiva University), for providing us with the experimental details concerning the preparation of the phosphorane (VII).

[9] W. von E. Doering and M. Jones, jun., *Tetrahedron Letters*, 1963, 791.