Scheme I

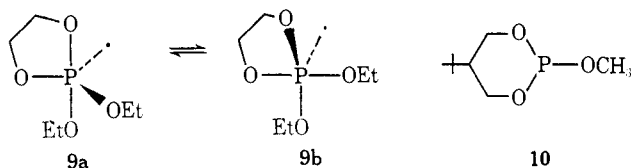Thus $\Delta G^{\pm}$ for the isomerization **5** → **6** appears to be >11 kcal/mol since it is unable to compete with β-scission.

These findings may be compared with earlier studies[13] of the t-BuO· oxidation of **10** which also proceeded

with retention at phosphorus. With **10** it could be argued, however, that the six-membered ring favors formation of **4** as is sometimes proposed[14] in pentacovalent phosphorus systems. Similarly the t-BuO· oxidation of chiral n-PrPMePh was retentive in stereochemistry.[13] However, the rate of β-scission is not known in this system. *In none of these cases is there any evidence for permutational isomerization prior to or in competition with product formation.*

If a direct analogy is drawn between phosphoranyl radical systems and truly pentacovalent systems, then it is surprising that the apparent barrier to the process **5** → **6** is so high. It is quite certain that for **11** the permutation analogous to **5** → **6** has $\Delta G^{\pm}$ several kilocalories per mole below 10 kcal/mol.[11]

The comparisons of barriers to permutational isomerizations for $(RO)_4P\cdot$ and $(RO)_5P$ should be of theoretical interest. It has been suggested to us by Professor Martin[15] that a better representation of **2** might be **12** in which the odd electron is in the apical
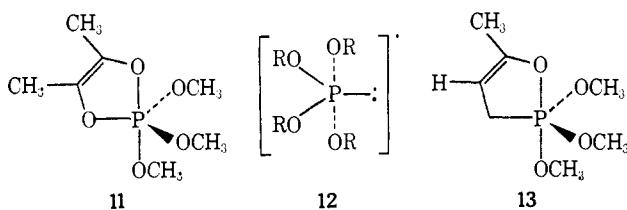
portion of an electron-deficient bonding system (three electrons), and a lone pair is equatorial. Such a bonding description would likely influence considerations of barriers for permutational isomerization of $(RO)_4P\cdot$.

(13) W. G. Bentrude, J. H. Hargis, and P. E. Rusek, Jr., *Chem. Commun.*, 296 (1969).
(14) P. Gillespie, P. Hoffman, H. Khusacek, D. Marquarding, S. Pfohl, F. Ramirez, E. A. Tsolis, and I. Ugi, *Angew. Chem., Int. Ed. Engl.*, 10, 687 (1971).
(15) J. C. Martin, University of Illinois, private communication.

Han-Wan Tan, Wesley G. Bentrude*
Department of Chemistry, University of Utah
Salt Lake City, Utah 84112
Received June 21, 1974

Photorearrangement of α-Allylbutyrophenone to 2-Phenyl-2-norbornanol. A Determination of 1,4-Diradical Lifetimes

Sir:

Two years ago we reported[1] that alkyl thiols can trap the 1,4-diradicals involved in Norrish type II photoelimination[2] without significantly quenching the reactive ketone triplet state.[3] The trapping measurements were sufficiently quantitative that diradical lifetimes could have been assigned unambiguously, except for serious discrepancies in literature values for the rate constants for reactions of alkyl radicals with thiols. Since diradicals are such important reaction intermediates in chemistry,[4] better estimates of their lifetimes seem highly desirable. Consequently we have prepared and irradiated α-allylbutyrophenone, hoping first that γ-hydrogen abstraction would compete with intramolecular oxetane formation and second, that if the diradical formed by γ-hydrogen abstraction lived at least 1 μsec, it might undergo measurable intramolecular cyclization to a cyclopentylmethyl structure.
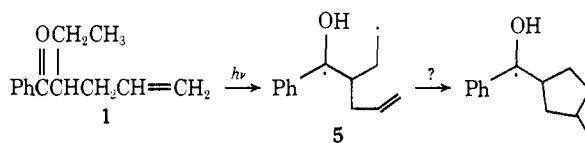
Ketone **1** was prepared by treatment of the cyclohexylenamine of butyrophenone with ethyl magnesium bromide and then with allyl bromide.[5] Upon irradia-

(1) P. J. Wagner and R. G. Zepp, *J. Amer. Chem. Soc.*, 94, 287 (1972).
(2) R. G. W. Norrish, *Trans. Faraday Soc.*, 33, 1521 (1937); P. J. Wagner, *Accounts Chem. Res.*, 4, 168 (1971).
(3) R. G. Zepp and P. J. Wagner, *J. Chem. Soc., Chem. Commun.*, 167 (1972).
(4) (a) G. Jones II, *J. Chem. Educ.*, 51, 175 (1974); (b) L. Salem and C. Rowland, *Angew. Chem. Int. Ed. Engl.*, 11, 92 (1972); (c) L. M. Stephenson and J. I. Brauman, *J. Amer. Chem. Soc.*, 93, 1988 (1971); (d) R. Hoffmann, S. Swaminathau, B. G. Odell, and R. Gleiter, *ibid.*, 92, 7081 (1970).
(5) G. Stork and S. R. Dowd, *J. Amer. Chem. Soc.*, 85, 2178 (1963).

tion at 313 nm, benzene solutions of **1** yield six products as determined by gas chromatography (vpc). Five of these products were formed in comparable yields, the sixth in less than 1% yield. Three products which comprise together 78% of the products were identified as arising from the expected[6] intramolecular oxetane formation. Two other products were formed in sufficiently high yields to be isolated and proved to be α-allylacetophenone (**2**) and 2-allyl-1-phenylcyclobutanol (**3**), the products expected[2] from type II photoelimination and cyclization. The sixth product was identified by its mass spectrum and vpc retention times on different columns, which all proved to be identical with those of the readily available 2-phenyl-2-norbornanol (**4**).[7] The relative yields of **2**:**3**:**4** were 1.4:1.0:0.1. The comparable yields of **2** and **3** are expected for α-alkylated ketones.[8]

The competition between oxetane formation and γ-hydrogen abstraction will be discussed in a separate paper. We wish to focus here on the significance of the formation of **4**. The only obvious mechanism to explain its formation incorporates the hoped for internal radical cyclization, followed by coupling of the new diradical. The cyclization would be expected to proceed about equally in the cis and trans modes; only the former could couple to a stable product.

Since roughly only half of the 5-hexenyl to cyclopentylmethyl radical cyclizations in diradical **5** could yield **4**, the observed ratio of **4**/(**2** + **3**), 0.04, indicates that the 1,4-diradical cleaves or cyclizes some 12 times more rapidly than it rearranges. Any unnoticed reactions of the cyclic diradical **6** would *lower* the rate ratio.
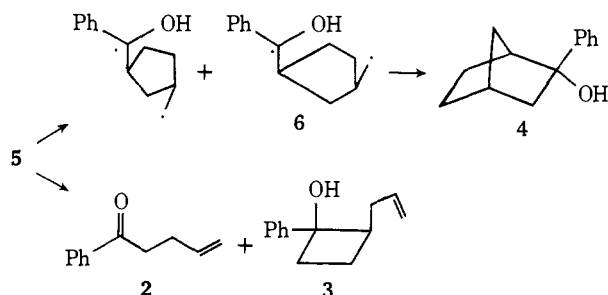
Although *cis*-3-methyl-1-benzoylcyclopentane might have been produced by disproportionation of **6**, none was observed. The accepted rate for cyclization of the 5-hexenyl radical is 10^5 sec^{-1} [9] and is little affected by alkyl substituents.[9,10] On the critical assumption that each radical site in 1,4-diradicals can react independently of and unaffected by the other, we conclude that cyclization and cleavage of **5** each occur with rate constants on the order of 6×10^5 sec^{-1}. Since some 60% of the diradicals formed from α-methylbutyrophenone undergo disproportionation back to ground state ketone,[8] we estimate the rate of the analogous process in diradical **5** to be $\sim 3 \times 10^6$ sec^{-1}. These rate constants for 1,4-diradical reactions are similar to

(6) N. C. Yang, M. Nussim, and D. R. Coulson, *Tetrahedron Lett.*, 1525 (1965); S. R. Kurowsky and H. Morrison, *J. Amer. Chem. Soc.*, **94**, 507 (1972).

(7) We thank Professor D. G. Farnum of MSU for an authentic sample.

(8) F. D. Lewis and T. A. Hilliard, *J. Amer. Chem. Soc.*, **92**, 6672 (1970).

(9) D. J. Carlsson and K. U. Ingold, *J. Amer. Chem. Soc.*, **90**, 7047 (1968); C. Walling and A. Cioffari, *ibid.*, **94**, 6059 (1972).

(10) A. L. J. Beckwith, I. Blair, and G. Phillipou, *J. Amer. Chem. Soc.*, **96**, 1613 (1974).

those we first suggested[1] but are now based on much firmer grounds. O'Neal has just estimated an even longer lifetime of 10^{-5} sec for the 1,4-diradical formed from 2-pentanone.[11]

It is important to point out that these diradicals are all triplet-derived, such that their lifetimes *could* be dominated by rates of spin inversion.[12] Whether or not this particular *caveat* is necessary awaits successful trapping of singlet diradicals. Meanwhile, we can conclude that spin inversion is surprisingly slow if it is rate determining in the reactions of triplet-derived 1,4-diradicals.

(11) H. E. O'Neal, R. G. Miller, and E. Gunderson, *J. Amer. Chem. Soc.*, **96**, 3351 (1974).

(12) P. D. Bartlett and N. A. Porter, *J. Amer. Chem. Soc.*, **90**, 5317 (1968).

P. J. Wagner,* K.-C. Liu
Chemistry Department, Michigan State University
East Lansing, Michigan 48824
Received June 27, 1974

Coupled Products from Low-Temperature Decomposition of Hydronium Dodecahydrododecaborate(2−), $(H_3O)_2B_{12}H_{12}$

Sir:

We wish to report the isolation of some rather unexpected products from two old reactions. The unusual hydrolytic stability of the $B_{12}H_{12}^{2-}$ ion is well known, so it was not surprising that when $(H_3O)_2B_{12}H_{12}(aq)$ was heated in a sealed tube, even at 200°, only a small amount of $B_{12}H_{11}OH^{2-}$ was reportedly formed.[1] The same product is formed in somewhat higher yields when a concentrated solution of $(H_3O)_2B_{12}H_{12}$ is treated with oxalic acid.[2] We have found that if the same two reactions are carried out under conditions favoring dehydration, even at moderate temperatures, $(H_3O)_2$-$B_{12}H_{12}(aq)$ undergoes decomposition of the type shown below.

$$H_3O^+ + 2B_{12}H_{12}^{2-} = B_{24}H_{23}^{3-} + H_2 + H_2O \qquad (1)$$

$$H_3O^+ + 2B_{12}H_{12}^{2-} = B_{24}H_{22}OH^{3-} + 2H_2 \qquad (2)$$

In addition to the two dimeric species, we have also isolated a tetramer, $B_{48}H_{45}^{5-}$, and, of course, the anticipated $B_{12}H_{11}OH^{2-}$ and $B_{12}H_{10}(OH)_2^{2-}$. The oxidative coupling is somewhat surprising in the absence of any strong oxidizing agents, considering that 1.45 V were required in the electrochemical oxidation.[3] This suggests that the oxidative stability of $B_{12}H_{12}^{2-}$ may owe more to kinetic than thermodynamic factors.

The synthesis and separation of the coupled products are relatively easy due to considerable differences in the solubilities of the respective tetramethylammonium salts. A 10-g sample of $Na_2B_{12}H_{12} \cdot 2H_2O$ was passed through an acid ion exchange column (Dowex 50W-X8), and the effluent was concentrated by rotary evaporation until a white precipitate appeared. Addition of 8 g of oxalic acid resulted in a very vigorous reaction with

(1) E. L. Muetterties, J. H. Balthis, Y. T. Chia, W. H. Knoth, and H. C. Miller, *Inorg. Chem.*, **3**, 444 (1964).

(2) W. H. Knoth, J. C. Sauer, D. C. England, W. R. Hertler, and E. L. Muetterties, *J. Amer. Chem. Soc.*, **86**, 3973 (1964).

(3) R. J. Wiersema and R. L. Middaugh, *Inorg. Chem.*, **8**, 2074 (1969).