Table II. Comparison of Di-*t*-butylcarbinyl (I), 2-Adamantyl (III), and Isopropyl (II) Systems

Characteristic	Di-*t*-butylcarbinyl (I)	2-Adamantyl (III)	Isopropyl (II)
	Relative Rates		
Chlorides, 25°			
80% ethanol	$10^{-0.3}$		1
Tosylates, 25°			
80% ethanol	$10^{0.9}$	$10^{-2.1}$	1
CH_3COOH	$10^{1.9}$	$10^{-1.1}$	1
HCOOH	$10^{2.6}$	$10^{-0.5}$	1
97% TFE	$10^{2.8}$	$10^{-0.2}$	1
CF_3COOH	$\sim 10^{5.1}$ [a]	$10^{2.1}$	1
	Derived Data[b]		
Apparent *m* values	0.88 (25°)	0.91 (25°)	0.40 (70°)[c]
α-CH_3/H, halides, 80% ethanol, 25°	$10^{5.3}$ (chlorides)	$10^{7.5}$ (bromides)	$10^{3.8}$ (bromides)
$(k_{\text{aq alc}}/k_{\text{HOAc}})_Y$	0.34 (25°)	0.18 (25°)	6 (70°)

[a] Estimated assuming the nearly constant I/III = $10^{3.0}$ ratio observed in other solvents. [b] See ref 7b for pertinent discussion. [c] S. Winstein, E. Grunwald, and H. W. Jones, *J. Amer. Chem. Soc.*, **73**, 2700 (1951).

of the I/III rate ratio (Table II) establishes this point.[13] The 10^3 magnitude of this ratio shows that the di-*t*-butylcarbinyl system does indeed exhibit enhanced reactivity.

It would be of interest to compare the behavior of I (X = OTs) with isopropyl tosylate in the very weakly nucleophilic solvent trifluoroacetic acid. Unfortunately, I (X = OTs) is too reactive ($k_1 \approx 10^1$ sec^{-1} at 25°) to be measured using regular techniques. However, if the constancy of the I/III ratio observed for other solvents (Table II) is assumed for CF_3COOH, a rate constant can be estimated. On this basis a lower limit estimate of the "inherent" (k_c *vs.* k_c) di-*t*-butylcarbinyl (I)/isopropyl (II) ratio, $\geq 10^{5.1}$, can be made. This large value confirms theoretical expectations. The acceleration is very much greater than that observed in the corresponding tertiary series. Shiner and Meier found that methyl di-*t*-butylcarbinyl chloride solvolyzed in 80% ethanol only 18.4 times faster than did *t*-butyl chloride; only a low percentage of products with a rearranged skeleton were formed.[4] Under comparable conditions (80% ethanol, 25°), the α-methyl/hydrogen ratio (methyl di-*t*-butylcarbinyl chloride/di-*t*-butylcarbinyl chloride) was $10^{5.3}$. Although this value would formerly have been considered to be rather high (especially in 80% ethanol!), it is less than our provisional estimate of α-CH_3/H = 10^8 for limiting solvolysis.[7b] The reduction from 10^8 to $10^{5.3}$ indicates that the secondary system is assisted to a greater extent than is the tertiary. This is also shown by comparison of the estimated limiting I/II ratio ($10^{5.1}$) with the methyl di-*t*-butylcarbinyl/*t*-butyl value ($10^{1.3}$). It seems probable that the chief factor responsible for the difference in secondary *vs.* tertiary di-*t*-butylcarbinyl behavior is methyl participation. This is consistent with the observation that the products in the tertiary series are largely unrearranged while solvolysis of secondary substrate (I) gives rearrangement exclusively.

Inductive and "B strain" effects would be somewhat different in secondary and tertiary series. Using the Peterson $\Sigma\sigma$ plot for trifluoroacetolysis,[9] an estimated acceleration of $10^{4.2}$ for I (X = OTs) over isopropyl tosylate is obtained. The actual difference is $10^{0.9}$ greater. It is difficult to estimate quantitatively the difference in "B strain" effects (or even their direction!)

We conclude that the solvolyses of di-*t*-butylcarbinyl derivatives are probably assisted to a modest extent by methyl participation ($k_\Delta/k_c \approx 10^1$–$10^2$).[14] Steric ("B strain") and inductive factors also contribute to an inherently greater reactivity over isopropyl. This inherently greater reactivity is masked in many solvents by nucleophilic solvent assistance in isopropyl solvolysis, thus reducing the observed I/III ratios, sometimes to very low values.

Acknowledgment. This work was supported at the University of Vermont and at Princeton University by grants from the National Science Foundation and at Princeton by the National Institutes of Health (AI-07766) and by the Petroleum Research Fund, administered by The American Chemical Society.

Samuel H. Liggero,[15] Jon J. Harper,[6] Paul v. R. Schleyer
Department of Chemistry, Princeton University
Princeton, New Jersey 08540

A. Paul Krapcho, David E. Horn
Department of Chemistry, University of Vermont
Burlington, Vermont 05401

Received January 13, 1970

---

[13] This constancy is due to the similarity in "apparent *m*" values of I and III (Table II).[7b] Limiting (k_c) and anchimerically assisted (k_Δ) substrates do not necessarily have constant rate ratios, but their response to solvent changes should exhibit proportionality especially with the same leaving groups.

[14] We have no evidence to exclude the possibility suggested by a referee that this participation may be occurring after intimate ion pair formation. See V. J. Shiner, Jr., and W. Dowd, *J. Amer. Chem. Soc.*, **91**, 6528 (1969); V. J. Shiner, Jr., R. D. Fisher, and W. Dowd, *ibid.*, **91**, 7748 (1969).

[15] National Institutes of Health Postdoctoral Fellow, 1969–1970.

Stereochemistry of Alkaline Cleavage of *cis*- and *trans*-1-Benzyl-4-methyl-1-phenylphosphorinanium Bromide

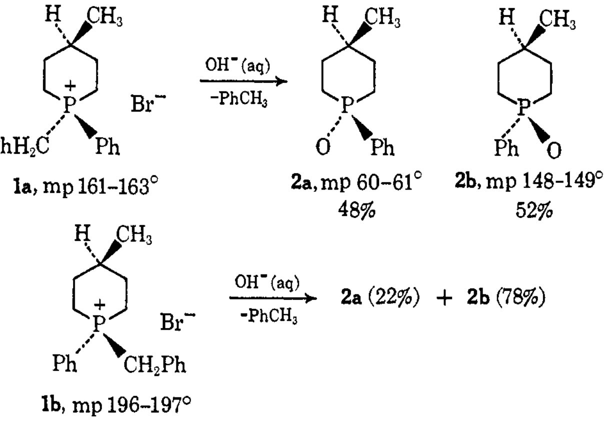
Sir:

Recently there has been considerable interest shown in the stereochemical behavior of phosphorus in cyclic systems in which phosphorus is the only heterocyclic atom.[1] Ordinarily, cleavage of acyclic phosphonium

---

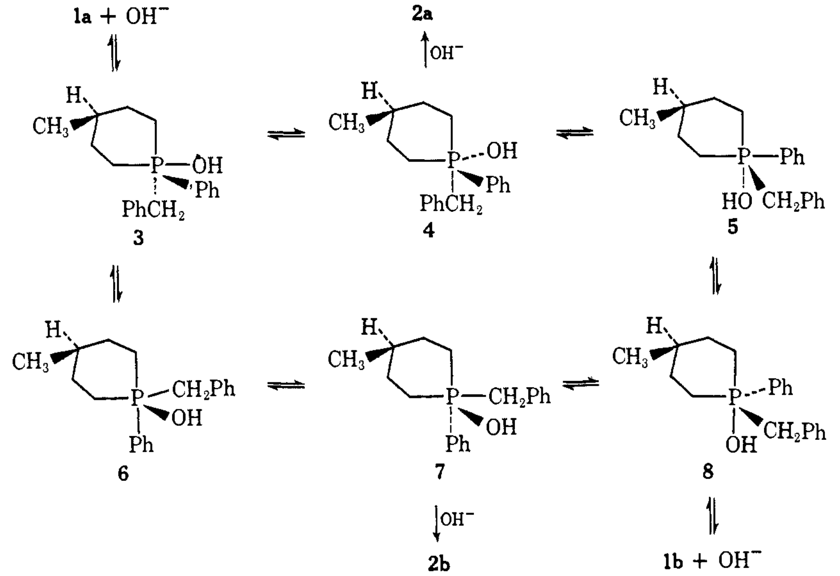
[1] (a) I. M. Campbell and J. K. Way, *J. Chem. Soc.*, 2133 (1961); S. E. Cremer and R. J. Chorvat, *J. Org. Chem.*, **32**, 4066 (1967); K. Bergesen, *Acta Chem. Scand.*, **21**, 1587 (1967); S. E. Cremer, R. J. Chorvat, C. H. Chang, and D. W. Davis, *Tetrahedron Lett.*, 5799 (1968); K. E. DeBruin and K. Mislow, *J. Amer. Chem. Soc.*, **91**, 7393

salts by aqueous hydroxide occurs with inversion of configuration at phosphorus.[2,3] Depending upon the specific compound, phosphetanium salts are observed to cleave with complete retention[1c,d] or to produce mixtures of stereoisomers.[1b,c] Stereochemical arguments have been advanced to explain these differences.[1i] Phospholanium salts have been shown to be converted to the corresponding phosphine oxides with complete retention of configuration at phosphorus.[1e,f] We now wish to report that the pure *cis* and *trans* isomers (phenyl and methyl *cis* or *trans*) of 1-benzyl-4-methyl-1-phenylphosphorinanium bromide (**1a** and **1b**) are decomposed under *identical* conditions with 1 *N* aqueous sodium hydroxide to mixtures of *different* proportions of *cis*- and *trans*-4-methyl-1-phenylphosphorinane 1-oxide (**2a** and **2b**). Although traces of hydroxide ion are observed by nmr to catalyze rapid exchange of benzyl protons of **1** in D_2O, no isomerization at phosphorus occurs under these conditions.



Product mixtures of **2a** (R_f 0.11) and **2b** (R_f 0.26) were separated by thin layer chromatography (silica gel G and acetone), the spots eluted with water, and quantitatively analyzed by ultraviolet spectroscopy; uv max (water) 218 nm (ϵ 8840) for both isomers. These quantitative results checked well with those obtained from mixtures prepared from pure **2a** and **2b** and analyzed by identical procedures. The error limit is within ±2%.

We favor the following mechanistic interpretation of our results. Apical attack at the tetrahedral phosphorus atom of **1a** or **1b** leads to the phosphorane **3** or **8**, respectively.[4] One pseudorotation,[5] **3** → **4** or **8** → **7**, places the benzyl group in an apical position, presumed to be the preferred orientation for expulsion of the leaving group,[6] to yield **2a** or **2b** with *retention* of configuration. Two pseudorotations, **3** → **6** → **7** or **8** → **5** → **4**, result in *inversion* of configuration at phosphorus. It is proposed that pseudorotation of **8** → **7** is favored over **8** → **5** → **4** since **8** → **7** places methyl and hydroxyl *cis* and avoids steric interaction of the larger benzyl or phenyl groups with methyl. For the same reason **3** → **6** → **7** would be expected to compete favorably with **3** → **4**. This explanation is consistent with observed net inversion for the cleavage of **1a** and net retention for cleavage of **1b**. We suggest that the *trans*:*cis* ratio for retention (3.5) exceeds the *cis*:*trans*



(1969); B. R. Ezzell and L. D. Freedman, *J. Org. Chem.*, **34**, 1777 (1969); D. W. Allen and I. T. Millar, *J. Chem. Soc., C*, 252 (1969); *ibid.*, *B*, 263 (1969); K. Mislow, plenary lecture presented at the International Symposium on Conformational Analysis, Brussels, Sept 8–12, 1969; (b) S. E. Cremer, R. J. Chorvat, and B. C. Trivedi, *Chem. Commun.*, 769 (1969); (c) J. R. Corfield, J. R. Shutt, and S. Trippett, *ibid.*, 789 (1969); (d) W. Hawes and S. Trippett, *ibid.*, 295 (1968); K. E. DeBruin, G. Zon, K. Naumann, and K. Mislow, *J. Amer. Chem. Soc.*, **91**, 7027 (1969); (e) K. L. Marsi, *Chem. Commun.*, 846 (1968); (f) K. L. Marsi, *J. Amer. Chem. Soc.*, **91**, 4724 (1969); (g) K. E. DeBruin, K. Naumann, G. Zon, and K. Mislow, *ibid.*, **91**, 7031 (1969); (h) S. E. Cremer and B. C. Trivedi, *ibid.*, **91**, 7200 (1969); (i) K. E. DeBruin and K. Mislow, *ibid.*, **91**, 7393 (1969).

(2) W. E. McEwen, K. F. Kumli, A. Blade-Font, M. Zanger, and C. A. VanderWerf, *ibid.*, **86**, 2378 (1964). The only reported case where this does not occur is in the alkaline cleavage of benzyl-*t*-butylmethylphenylphosphonium iodide which takes place with predominant retention of configuration (N. J. De'ath and S. Trippett, *Chem. Commun.*, 172 (1969)). This is attributed to steric factors.

(3) However, see R. A. Lewis, K. Naumann, K. E. DeBruin, and K. Mislow, *ibid.*, 1010 (1969).

(4) Another set of phosphoranes enantiomeric with structures **3** and **8** is generated by attack of hydroxide ion at a different enantiotopic face of the phosphorus tetrahedron. Dreiding models show that there is considerably more ring strain if the phosphorane ring lies in the equatorial plane than if it occupies an apical–equatorial position at phosphorus. Therefore, only conformers of the latter geometry are considered to be participating in the pseudorotational process. See also J. J. Brophy and M. J. Gallagher, *Aust. J. Chem.*, **22**, 1385 (1969).

(5) For excellent discussions of this concept see (a) F. H. Westheimer, *Accounts Chem. Res.*, **1**, 70 (1968); (b) F. Ramirez, *ibid.*, **1**, 168 (1968); P. C. Lauterbur and F. Ramirez, *J. Amer. Chem. Soc.*, **90**, 6722 (1968); ref 1g.

(6) (a) S. I. Miller, *Advan. Phys. Org. Chem.*, **6**, 253 (1968); N. K. Hamer, *J. Chem. Soc., C*, 404 (1966); (b) M. J. Gallagher and I. D. Jenkins, *Top. Stereochem.*, **3**, 61, 75 (1968).

ratio for inversion (1.1) because the most efficient retention process requires only *one* pseudorotation, whereas the most efficient inversion process requires *two*. The configurational assignments for **2a** and **2b** are tentatively determined by their ^{1}H nmr spectroscopic behavior. The methyl protons of the *trans* isomer (**2b**) would be expected to be deshielded by the oxide oxygen [found: for **2b** δ 0.99 (J = 4.5 Hz); for **2a** δ 0.89 (J = 1.0 Hz).[7] Such nmr evidence has been used to assign configurations for cyclic phosphorus[8] and sulfur[9] systems and is consistent with X-ray data.[1h] Additionally, of known geometrically isomeric pairs of phosphine oxides, the melting points of the *trans* isomers are almost always observed to be higher than those of the *cis*.[10] Our melting point data are therefore consistent with the nmr assignment, as are the solubility and chromatographic characteristics of the oxides. The configurations of phosphonium salts **1a** and **1b** and the oxides **2a** and **2b** were related by the Wittig reaction.[2] Isomers **1a** and **1b** were prepared by stereospecific reduction (retention of configuration)[11] of the corresponding oxides with phenylsilane[1f,12] and quaternization of the resulting configurationally stable phosphine with benzyl bromide.[13] Both **2a** and **2b** are configurationally stable under conditions of base cleavage.

Acknowledgment. This work was supported by National Science Foundation Grant No. GP-7407.

(7) The ^{1}H nmr spectra were measured at 60 MHz in methylene chloride with a JEOL C-60H spectrometer, using tetramethylsilane as an internal standard.

(8) D. Z. Denney and D. B. Denney, *J. Amer. Chem. Soc.*, **88**, 1830 (1966); H. E. Shook, Jr., and L. D. Quin, *ibid.*, **89**, 1841 (1967); C. Bodkin, *Chem. Commun.*, 829 (1969).

(9) J. G. Pritchard and P. C. Lauterbur, *J. Amer. Chem. Soc.*, **83**, 2105 (1961); E. Jonsson, *Ark. Kemi*, **26**, 357 (1967); P. B. Sollman, R. Nagarajan, and R. M. Dodson, *Chem. Commun.*, 552 (1967); K. W. Buck, A. B. Foster, W. D. Pardoe, M. H. Qadir, and J. M. Webber, *ibid.*, 759 (1966); A. B. Foster, J. M. Druxbury, T. D. Inch, and J. M. Webber, *ibid.*, 881 (1967); E. Jonsson and S. Holmquist, *Ark. Kemi*, **29**, 301 (1968); A. B. Foster, T. D. Inch, M. H. Qadir, and J. M. Webber, *Chem. Commun.*, 1086 (1968); K. Kondo, *Tetrahedron Lett.*, 2461 (1969); C. R. Johnson and W. O. Siegl, *J. Amer. Chem. Soc.*, **91**, 2796 (1969).

(10) See ref 6b, p 6.

(11) Reoxidation of the phosphine with *t*-butyl hydroperoxide in each case regenerated the original oxide. *t*-Butyl hydroperoxide oxidations of phosphines are known to occur with retention of configuration (D. B. Denney and J. W. Hanifin, Jr., *Tetrahedron Lett.*, 2177 (1963)).

(12) H. Fritzsche, U. Hasserodt, and F. Korte, *Chem. Ber.*, **97**, 1988 (1964).

(13) The results of elemental analyses of all new compounds were within acceptable limits.

Kenneth L. Marsi, Roger T. Clark
Department of Chemistry, California State College, Long Beach
Long Beach, California 90801

Received January 22, 1970

Absorption Spectrum and Decay Rate of the Ascorbic Acid Radical

Sir:

The autoxidation and enzymatic oxidation of ascorbic acid have been found to proceed through a free radical, the electron spin resonance spectrum of which has been observed.[1-3] Ascorbic acid has been found to be oxidized very rapidly by OH radicals formed in aqueous solutions by radiolysis.[4,5] We have observed the optical absorption spectrum of a radical formed by pulse radiolysis of an aqueous solution of ascorbic acid and have determined its rate of decay.

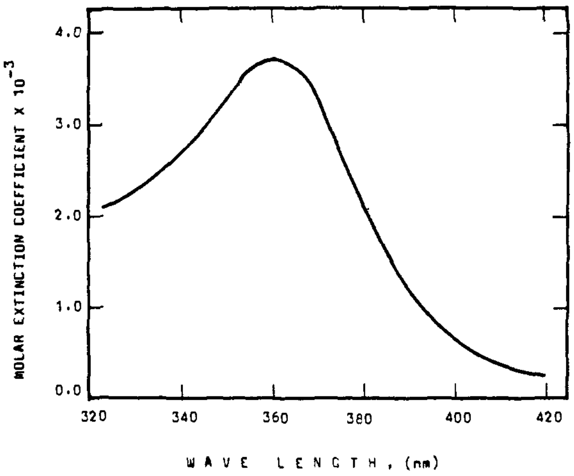


Figure 1. Absorption spectrum of the ascorbic acid radical.

Pulses of 1.9-MeV electrons of 20–30-μsec duration were delivered from a Van de Graaff generator to a 5 mM solution of ascorbic acid at the natural pH 3.3, saturated with nitrous oxide to convert solvated electrons to OH radicals. A transient absorption was found at wavelengths greater than those at which the ascorbic acid and its permanent reaction products absorb. With doses of about 800 rads, the optical densities observed at the end of the pulse were determined at a series of wavelengths, and the resulting spectrum is shown in Figure 1. The same spectrum was obtained in an argon-saturated solution containing equal concentrations (1 mM) of ascorbic and dehydroascorbic acids (pH 3.6). We see no reason to doubt that this transient is a radical intermediate in oxidation level between ascorbic and dehydroascorbic acids.

In order to determine more precisely the maximum extinction coefficient and decay kinetics of the radical N_2O-saturated solutions, 10 mM in ascorbic acid, adjusted to pH 4.1 with NaOH, were pulsed at 23° with doses ranging from 280 to 1310 rads. For each run the optical density per centimeter light path was determined as a function of time, and in every case plots of the reciprocal of the optical density against time were linear, showing good second-order decay of the radical. Setting the rate of disappearance of the radical $-d(R)/dt$ equal to $2k(R)^2$ the slope of these plots equals $2k/\epsilon$, where ϵ is the molar extinction coefficient at the wavelength used, 360 nm. From five runs, $k/\epsilon = 2.58 \pm 0.13 \times 10^4$ cm sec^{-1}. To determine ϵ, it was necessary to estimate the specific yield for formation of the radical. We assumed that every radical formed by irradiation of the water, whether e_{aq}^-, OH, or H, would result in formation of one oxidized ascorbic acid radical. The solvated electrons would, of course, react with the N_2O to form O^-, which would be converted into OH and would react

(1) I. Yamasaki, H. S. Mason, and L. Piette, *J. Biol. Chem.*, **235**, 2444 (1960).

(2) I. Yamasaki and L. H. Piette, *Biochem. Biophys. Acta*, **50**, 62 (1961).

(3) C. Lagercrantz, *Acta Chem. Scand.*, **18**, 562 (1964).

(4) N. F. Barr and C. G. King, *J. Amer. Chem. Soc.*, **78**, 303 (1956).

(5) G. E. Adams, J. W. Boag, J. Currant, and B. D. Michael in "Pulse Radiolysis," M. Ebert, J. P. Keene, A. J. Swallow, and J. H. Baxendale, Ed., Academic Press, New York, N. Y., 1965, p 131.