of UV-vis spectra before and at the completion of reaction) at a catalyst turnover number of 200, $[(Br_8TPP)Fe^{III}(Cl)] = 4.5 \times 10^{-5}$ M, C_6F_5IO to TME is 1.0:1.1.

Computer graphics show that alkenes can approach the iron bound oxygen only from the top (Figure 1). TME requires a large value of α (I), while smaller values of α suffice for norbornene and *cis*-stilbene. Clean epoxidation of *cis*-stilbene (the substrate prone to rearrangements[3d]) indicates that the distances between the double bond and the orbitals on iron or porphyrin nitrogen are too large for the interactions which would lead to rearrangement products[3d] and that the only interaction possible is that between the alkene orbitals and orbitals on iron bound oxygen. Thus, the only interaction required for epoxidation is between the alkene double bond and oxygen.[3d] Due to severe steric hindrance *trans*-stilbene virtually does not epoxidize at all.

Taken alone, the requirement for alkene to approach the iron bound oxygen with a modest value of α allows several mechanisms. These are as follows: (i) direct oxene insertion into the alkene double bond; (ii) initial $1e^-$ oxidation of the alkene followed by collapse of the alkene π-cation radical and iron(IV)–oxo porphyrin to epoxide plus iron(III) porphyrin; and (iii) formation of a $Fe^{(IV)}$–O–C–C^+ transient species which gives way to epoxide plus iron(III) porphyrin. Disfavored are mechanisms requiring the approach of alkene to iron(IV)–oxo prophyrin π-cation radical from the side and with small values of α and the obligatory formation of a metallaoxetane (see figure legend).

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Photo-Arbuzov Rearrangements of Benzyl Phosphites

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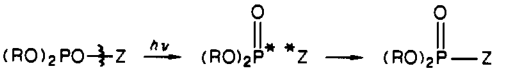
The *thermal* Arbuzov rearrangement is a widely known[1] reaction of organophosphorus molecules, eq 1. It classically occurs via a two-step mechanism catalyzed by R-X (X = halide, tosylate, etc.) and in certain instances can be autocatalytic.[1c] Intermolecular free-radical Arbuzov reactions are known as well.[2]

$$(RO)_3P \xrightarrow[\Delta]{R\text{-}X} (RO)_2P(O)R \qquad \Delta H° \geq -40 \text{ kcal/mol}^3 \qquad (1)$$

It seemed to us possible that absorption of UV light could result in reaction 2, a *photochemical* Arbuzov rearrangement.[4] With

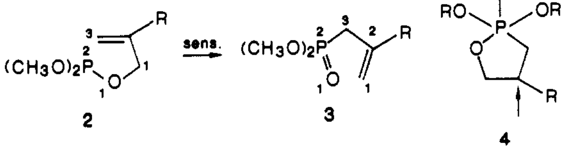


$$(RO)_2PO\text{-}\!\!\!\wr\!\text{-}Z \xrightarrow{h\nu} (RO)_2\overset{O}{\overset{\|}{P}}{}^{*}\ {}^{*}Z \longrightarrow (RO)_2\overset{O}{\overset{\|}{P}}\text{—}Z \qquad (2)$$

1

Z = UV chromophore

a sufficiently weak O–Z bond, useful regiospecificity might result. Radical or ion-pair intermediates (1) potentially could be produced. We showed recently that under conditions of triplet sensitization allyl phosphites, 2, are photorearranged in an *intramolecular* Arbuzov-like process which is formally a cyclic 2,3-sigmatropic rearrangement, 2 → 3, eq 3.[5] A cyclic triplet phosphoranyl 1,3-biradical (4) was suggested as a likely intermediate.

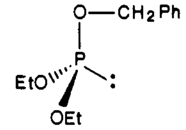


2 3 4 (3)

We report here the photorearrangement of benzyl dialkyl phosphites to the corresponding dialkyl benzylphosphonates, reaction 4. The specific processes examined are clean, regiospecific, and largely intramolecular. The rearrangements occur with a variety of benzylic phosphites to give potentially useful phosphonates.

$$(R^1O)_2POCHR^2Ph \xrightarrow{h\nu} (R^1O)_2P(O)CHR^2Ph \qquad (4)$$

Irradiations of 0.1–0.2 M solutions of phosphite 5 in deoxygenated benzene in quartz tubes (450-W medium pressure Hg lamp) gave $PhCH_2P(O)(OEt)_2$ in 85–95% yield at 90–100% conversion (^{31}P NMR, ^1H coupled; or ^1H NMR). Evidence for free-radical formation was found in the GLC detection, at nearly complete consumption of 5, of 0.5–1% of bibenzyl (equivalent to 1–2% of cage-free $PhCH_2\cdot$) and 0.5–1% of phosphite 6. Irradiation of a 1:1 mixture of 5 and 7 in benzene gave only minor amounts (1–2%) of the crossover phosphonates (^{31}P NMR). Chain reaction sequence 5 or more than minor reaction via combination of *cage-free* radical pairs is thereby excluded.



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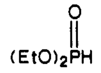
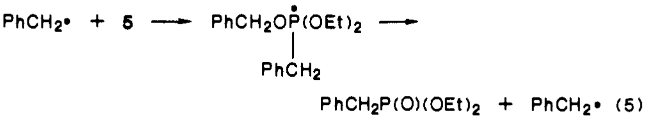


$$(EtO)_2\overset{O}{\overset{\|}{P}}H$$

6

$(MeO)_2POCH_2C_6H_4Me$-*m*

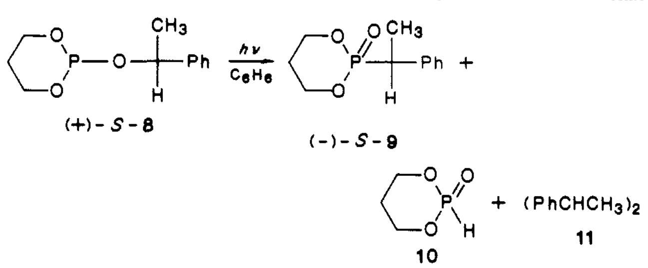
7



$$PhCH_2\cdot + 5 \longrightarrow PhCH_2O\underset{PhCH_2}{\underset{|}{\dot{P}}}(OEt)_2 \longrightarrow PhCH_2P(O)(OEt)_2 + PhCH_2\cdot \qquad (5)$$

Reaction 2 ($Z^* = PhCH_2\cdot$, R = Et) gives a reasonable interpretation of these results. Initial radical pair 1 is short-lived and *undergoes very predominantly cage recombination* to product benzylphosphonate, i.e., $k_{comb} \gg k_{diff}$. Cage-free radicals in minor amounts also recombine to form $(EtO)_2P(O)CH_2Ph$ and bibenzyl. (The possible formation of the dimer of $(EtO)_2P(O)\cdot$ has not been investigated.) Added MeOH failed to produce so much as 1% of $MeOCH_2Ph$ or any toluene, the trapping products of diffusive separation of $PhCH_2^+$ or $PhCH_2^-$ from potential ion-pair intermediate 1.

The rearrangement of 8 in C_6H_6 proceeds in 84–92% yield (GLC) at 72–98% conversion with *close to complete retention of configuration of stereochemistry at the chiral carbon* (8 → 9). Dimer 11, 0.2–1% yield, also is seen by GLC. Again k_{comb}



(+)-*S*-8

(−)-*S*-9

10

11

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[1] (a) Bhattacharya, A. K.; Thyagarajan, G. *Chem. Rev.* **1981**, *81*, 415. (b) Brill, T. S.; Landon, S. J. *Ibid.* **1984**, *84*, 577. (c) Lewis, E. S.; Hamp, D. *J. Org. Chem.* **1983**, *48*, 2025.

[2] (a) Bentrude, W. G.; Alley, W. D.; Johnson, N. A.; Murakami, M.; Nishikida, K.; Tan, H. W. *J. Am. Chem. Soc.* **1977**, *99*, 4383. (b) For references to other radical Arbuzovs, see: Bentrude, W. G. *Acc. Chem. Res.* **1982**, *15*, 117. Davies, A. G.; Griller, D.; Roberts, B. P. *J. Chem. Soc., Perkin Trans 2* **1972**, 2224. Bentrude, W. G.; Fu, J. J. L.; Rogers, P. E. *J. Am. Chem. Soc.* **1973**, *95*, 3625 and references therein.

[3] Mark, V. *Mech. Mol. Mgr.* **1969**, *2*, 319 and ref given in ref 1a and 1b. Fu, J. J. L.; Bentrude, W. G. *J. Am. Chem. Soc.* **1972**, *94*, 7710.

[4] Trialkyl phosphites undergo photo-Arbuzov rearrangements under the conditions of this report extremely slowly if at all. (See, however: LaCount, R. B.; Griffin, C. E. *Tetrahedron Lett.* **1965**, 3071).

[5] Bentrude, W. G.; Lee, S. G.; Akutagawa, K.; Ye, W.; Charbonnel, Y. *J. Am. Chem. Soc.* **1987**, *109*, 1577.

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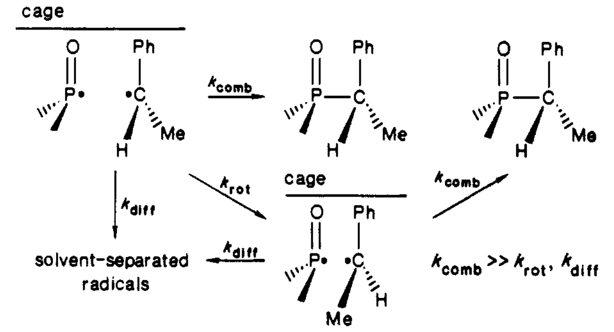
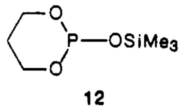
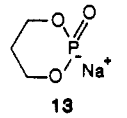
Scheme I



≫ k_{diff}. The enantiomeric composition of **8** was determined following stereospecific, retentive oxidation at 0 °C with AIBN/O_2.[6] After addition of optically pure *t*-Bu(Ph)P(S)OH,[7] a 400 MHz spectrum of **8**-oxide showed the methyls of the enantiomers of **8**-oxide as well-separated doublets of doublets (76 ± 2% ee). The enantiomeric purity of product **9** (74 ± 2% ee) was similarly assessed ($\Delta\delta$ = 13.1 Hz, $^3J_{HH}$ = 7.6 Hz, $^3J_{HP}$ = 19.1 Hz). The stereoselectivity of process **8** → **9** was thereby conservatively estimated to be >90% (C_6H_6).

The absolute stereochemistry of **8** → **9** was determined from the reactions of **12** and **13** with optically active **14**, processes of


12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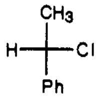
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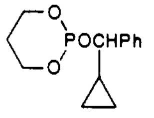
known stereochemistry.[8] The stereoselectivity of the reaction of **12** (neat at 140–150 °C) was 95% while that of **13** (70–80 °C in DMF/C_6H_6) was about 50%. The latter reaction may involve a combination of S_N2 and S_N1 processes,

Scheme I expresses the mechanistic implications of the crossover and stereochemical results. For geminate pair **15**, *combination is decidedly more rapid than either rotation or diffusion* ($k_{comb} \gg k_{rot}, k_{diff}$).

The high stereospecificity and low percentage of diffusion products noted for the photo-Arbuzov process is similar to the findings for the thermal Stevens 1,2-rearrangement ($R_2\bar{C}$—$^+NR'_3$ → $R_2R'C$—NR'_2). Quantitative CIDNP[9] and stereochemical[10] studies led to the conclusion[9] that the major portion of the Stevens rearrangement of a series of *p*-X-C_6H_4CO-$\bar{C}H$—$^+NMe_2CH_2C_6H_4$-Y-*p* in $CHCl_3$ is either concerted or proceeds via radical pairs ($R_2\dot{C}$—NR'_2 + R'·), generated in very close proximity, which combine unusually rapidly. If the depicted P-O-CH_2Ph conformation for **5** undergoes reaction, the close proximity of the benzyl carbon to the odd electron of **1** or **15** (or the lone pair of **5**) is evident. *Alternatively*, a four-electron 1,2-sigmatropic shift with retention of configuration at both migrating carbon and phosphorus terminus is in accord with the Woodward–Hoffman rules[11] for the excited singlet of such systems. Rapid combination[12] of the singlet pair **15**, with the same stereochemical consequences, is hard to distinguish from the truly concerted process or mixture of the two. Resolution of this issue may come from work now in progress on the stereochemistry at phosphorus of the photo-Arbuzov rearrangement as well as from future investigations of rearrangements involving stereochemically restricted molecules and quantitative CIDNP studies.

The generality, regiospecificity, and potential usefulness of these photo-Arbuzov rearrangements are shown by the very clean formation of benzylphosphonates from **5**, **8**, and **16**–**20**.[13] By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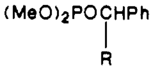
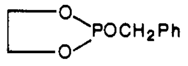

$(MeO)_2PO\underset{R}{\underset{|}{C}}HPh$

17; R = Me
18; R = cyclopropyl
19; R = H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contrast, secondary halides (RX, eq 1) react sluggishly with phosphites like **5**, **9**, and **18** and give several products because of the side reactions of CH_3X and EtX formed and attack by X^- at more than one carbon. Silyl phosphites such as **12**, useful in the Arbuzov reactions of secondary RX, are less easily obtained than are the corresponding $(RO)_2PCl$ precursors to the benzyl phosphites. The value of benzylphosphonates in alkene synthesis is well-known.[14]

Acknowledgment. This work was supported by grants from the National Science Foundation and Public Health Service, N.C.I. (CA 11045) which are gratefully acknowledged.

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(11) Woodward, R. B.; Hoffman, R. *The Conservation of Orbital Symmetry*; Verlag Chemie: Weinheim, 1970.

(12) (a) From studies of singlet pairs of $PhCH_3CH$·, *formed with a N_2 molecule between them* from the corresponding azo compounds, it was estimated that k_{rot}:k_{diff}:k_{comb} = 15:2.4:1.0. Greene, F. D.; Berwick, M. A.; Stowell, J. C. *J. Am. Chem. Soc.* **1970**, *92*, 867. (b) Kopecky, K. R.; Gillan, T. *Can. J. Chem.* **1969**, *47*, 2371.

(13) For example, a 0.1 M solution of 50 mg of **8** in C_6H_6 is >95% rearranged to **9** in 2 h on irradiation through quartz.

(14) Wadsworth, W. S., Jr. *Organic Reactions*; John Wiley and Sons: New York, 1977; Vol. 25, Chapter 2.

Synthesis of (*R*)-(+)- and (*S*)-(−)-α-Damascone by Tandem Grignard Reaction–Enantioselective Protonation: Evidence for the Intermediacy of a Chiral Complex

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Since its discovery in 1970, (±)-α-damascone **5**[1] with its typical fruity flowery scent and exceptional odor strength has become an important perfume component, and numerous syntheses of (±)-**5** have been published.[2] The conversion of (*R*)-(+)-α-ionone into (*R*)-(+)-**5** (66% ee) by Ohloff and Uhde[1b] established the absolute configuration; however, enantiomerically pure (*R*)-(+)-**5** and (*S*)-(−)-**5** have not been prepared.[3]

We herein report the efficient synthesis of enantiomerically pure (*R*)-(+)-**5** and (*S*)-(−)-**5**[4] by regio- and diastereoselective Grignard reaction on ester enolate **2**[2a] or ketene **3**[2ac,5] followed by the highly

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(1) (a) Ohloff, G. In *Progress in the Chemistry of Organic Natural Products*; Herz, W., Grisebach, H., Kirby, G. W., Eds.; Springer: Wien, 1978; Vol. 35, p 431. Demole, E.; Enggist, P.; Säuberli, U.; Stoll, M.; sz. Kovats, E. *Helv. Chim. Acta* **1970**, *53*, 541. (b) Ohloff, G.; Uhde, G. *Helv. Chim. Acta* **1970**, *53*, 531.

(2) (a) For recent syntheses, see: Fehr, C.; Galindo, J. *J. Org. Chem.* **1988**, *53*, 1828. (b) Snowden, R. L.; Linder, S. M.; Muller, B. L.; Schulte-Elte, K. H. *Helv. Chim. Acta* **1987**, *70*, 1858. Zaidlewicz, M. *Tetrahedron Lett.* **1986**, *27*, 5135. (c) Naef, F.; Decorzant, R. *Tetrahedron* **1986**, *42*, 3245. (d) Fehr, C.; Galindo, J. *Helv. Chim. Acta* **1986**, *69*, 228.

(3) The absolute configuration of natural **5** is unknown. For another preparation of (*R*)-(+)-**5** (17% ee), see: Shibasaki, M.; Terashima, S.; Yamada, S. *Chem. Pharm. Bull.* **1975**, *23*, 279.

(4) (*S*)-(−)-**5** is by far the more precious and powerful fragrance, see: Fehr, C.; Galindo, J. Swiss Patent application 5.2.1988. In addition, (*R*)-(+)-**5** opens a route to the diterpene (−)-forskolin, following Baraldi et al. (Baraldi, P. G.; Barco, A.; Benetti, S.; Pollini, G. P.; Polo, E.; Simoni, D. *J. Chem. Soc., Chem. Commun.* **1986**, 757.

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