of UV-vis spectra before and at the completion of reaction) at a catalyst turnover numer of 200, $[(Br_8TPP)Fe^{III}(Cl)] = 4.5 \times$ 10^{-5} M, C₆F₅IO 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 known¹ 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

$$(RO)_{3}P \xrightarrow{R-X} (RO)_{2}P(O)R \qquad \Delta H^{\circ} \geq -40 \text{ kcal/mol}^{3} \qquad (1)$$

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

$$(\mathrm{RO})_{2}\mathrm{PO}\xrightarrow{3} Z \xrightarrow{\hbar\nu} (\mathrm{RO})_{2}\mathrm{P} \xrightarrow{*} Z \xrightarrow{} (\mathrm{RO})_{2}\mathrm{P} \xrightarrow{} Z \qquad (2)$$

Z = UV chromophore

a sufficiently weak O-Z bond, useful regiospecificity might result. Radical or ion-pair intermediates (1) potentially could be pro-

(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).

duced. 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, $2 \rightarrow 3$, eq 3.⁵ A cyclic triplet phosphoranyl 1,3-biradical (4) was suggested as a likely intermediate.



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.

$$(R^1O)_2 POCHR^2 Ph \xrightarrow{\mu\nu} (R^1O)_2 P(O)CHR^2 Ph$$
 (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 PhCH₂P(O)(OEt)₂ in 85-95% yield at 90-100% conversion (³¹P 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 PhCH₂·) 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 (³¹P NMR). Chain reaction sequence 5 or more than minor reaction via combination of cage-free radical pairs is thereby excluded.

PhCH₂• + 5
$$\longrightarrow$$
 PhCH₂OP(OEt)₂ \longrightarrow
|
PhCH₂
PhCH₂PhCH₂PhCH₂• (5)

Reaction 2 ($Z^* = PhCH_2$, 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., $k_{\rm comb} \gg k_{\rm diff}$. Cage-free radicals in minor amounts also recombine to form (EtO)₂P(O)CH₂Ph and bibenzyl. (The possible formation of the dimer of $(EtO)_2P(O)$ has not been investigated.) Added MeOH failed to produce so much as 1%of MeOCH₂Ph or any toluene, the trapping products of diffusive separation of PhCH₂⁺ or PhCH₂⁻ from potential ion-pair intermediate 1.

The rearrangement of 8 in C₆H₆ proceeds in 84-92% yield (GLC) at 72-98% conversion with close to complete retention of configuration of stereochemistry at the chiral carbon (8 \rightarrow 9). Dimer 11, 0.2–1% yield, also is seen by GLC. Again k_{comb}



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≫ k_{diff} . The enantiomeric composition of 8 was determined following stereospecific, retentive oxidation at 0 °C with AIBN/O₂.⁶ 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% (C₆H₄).

servatively estimated to be >90% (C_6H_6). The absolute stereochemistry of $8 \rightarrow 9$ was determined from the reactions of 12 and 13 with optically active 14, processes of



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/C₆H₆) 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 ($R_2\bar{C}$ — $^+NR'_3$ $\rightarrow R_2R'C$ — NR'_2). Quantitative CIDNP⁹ and stereochemical¹⁰ studies led to the conclusion⁹ that the major portion of the Stevens rearrangement of a series of p-X-C₆H₄CO-CH- $^{+}NMe_{2}CH_{2}C_{6}H_{4}$ -Y-p in CHCl₃ 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-CH₂Ph 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 rules¹¹ for the excited singlet of such systems. Rapid combination¹² 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



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 CH₃X 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

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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, (\pm) - α -damascone 5¹ with its typical fruity flowery scent and exceptional odor strength has become an important perfume component, and numerous syntheses of (\pm) -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)-(-)-5⁴ by regio- and diastereoselective Grignard reaction on ester enolate 2^{2a} or ketene $3^{2ac,5}$ followed by the highly

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