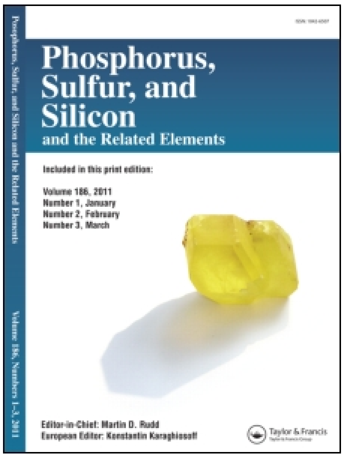

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RADICAL-PAIR INTERMEDIATES IN THE PHOTOLYSIS OF ARYLMETHOXY GROUPS ATTACHED TO THREE- COORDINATE PHOSPHORUS

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Abstract. Stereochemical and product studies of the photochemistry of the title compounds is interpreted in terms of concerted as well as singlet and triplet radical-pair mechanisms.

Key Words: Radical pairs, photo-Arbuzov rearrangements, stereochemistry

Early work from this group demonstrated the high-yield conversion of benzyl phosphite **1** to the corresponding benzylphosphonate (**3**) in a photo-Arbuzov reaction.[1,2] A yield of bibenzyl of about 1% was formed which suggested either a largely concerted process or one in which radical pair intermediates (**2**, Ar = C_6H_5) are very short lived and undergo rapid, near-exclusive combination to **3**. The synthetic utility of this process for the synthesis of acyclic nucleoside-based phosphonates has been demonstrated.[3,4]

$$\mathrm{ArCH_2OP(OMe)_2} \xrightarrow{h\nu} [\,\mathrm{(MeO)_2P(O)\cdot \quad \cdot CH_2Ar}\,] \longrightarrow \mathrm{(MeO)_2P(O)CH_2Ar}$$

1 Ar = C_6H_5
4 Ar = p-$CH_3COC_6H_4$

2

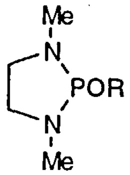
3 Ar = C_6H_5
5 Ar = p-$CH_3COC_6H_4$

We now report that direct irradiation of 0.02 M dimethyl *p*-acetylbenzyl phosphite (**4**) in benzene at 335 nm yields only 12% of the photo-Arbuzov product (**5**) (quantum yield, ϕ, = 0.07) and major amounts of the dimer of the *p*-acetylbenzyl radical (**6**) (ϕ = 0.14; chemical yield 48%, based on moles of arylmethyl radicals

6 p-$CH_3COC_6H_4CH_2\cdot$

potentially available from **4**). $(MeO)_2P(O)\cdot$ from cage escape attacks benzene to give products of trapping of the resulting cyclohexadienyl adduct with radical **6**. This result is consistent with rapid crossover, typical of ketones, of the initially formed excited singlet state of **4** to the triplet (presumably π,π^*) excited state. Triplet **4** then yields caged, triplet, radical pairs (**2**, Ar = p-$CH_3COC_6H_4$) that undergo diffusion more rapidly than intersystem crossing to singlet pairs and combination to **5**. Addition of appropriate amounts of PhSH diverts the carbon-centered radicals to p-$CH_3COC_6H_4CH_3$ and the dimethylphosphonyl radicals to $(MeO)_2P(O)H$ and greatly reduces the yield of **5**. The triplet nature of the excited state of the photoreaction of **4** also was demonstrated by CIDNP and CIDEP studies.[5] By inference, photorearrangement on direct irradiation of **1** proceeds from the singlet excited state.

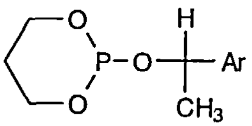
A survey of the photoreactions (254 nm) of a series of phosphoramidites, illustrated by **7**, showed that in acetonitrile or cyclohexane 65-70% yields of



7 R = $PhCH_2$, 1-naphthylmethyl

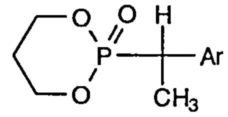
phosphonates resulted. Significantly, these photoprocesses were accompanied by the formation of 10-25% of 1,2-diarylethanes (accountability of arylmethyl radicals potentially formed) that obviously arise from dimerization of free arylmethyl radicals that diffuse out of the initial solvent cage.

Stereochemical studies of these reactions, with 2-arylethyl analogs of known configuration at the carbon stereogenic center, also are in accord with the idea that increased amounts of products of radical diffusion result from relatively long-lived radical pairs. Earlier, we reported results of a proton NMR study that employed the



R-**8** Ar = C_6H_5
R-**9** Ar = p-$CH_3COC_6H_4$

chiral shift reagent *tert*-BuPhP(S)OH to demonstrate that phosphite *R*-**8** yields nearquantitative amounts of phosphonate with at least 90% retention of configuration at the stereogenic carbon center in **10**.[1] This result has now been confirmed by HPLC on a CHIRACEL column. Photorearrangement of **8** (*R*/*S* = 97/3) in acetonitrile or cyclohexane yielded **10** with *R*/*S* = 85/15. Not surprisingly, 40% of the carbon-centered radicals potentially formed on direct irradiation (λ>320 nm) of the acetyl-substituted phosphite **9** (55 and 97% conversions) is accounted for as dimer **11**. Product phosphonate **12** was

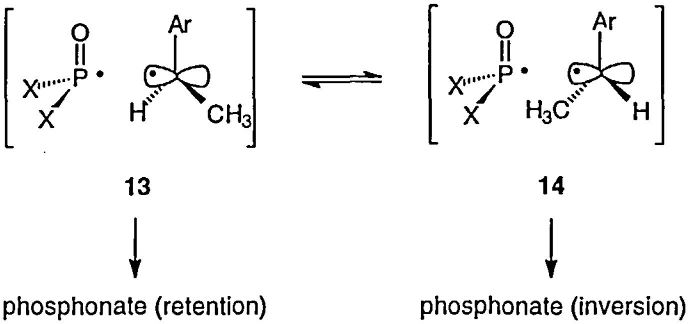


R-**10** Ar = C_6H_5
R-**12** Ar = p-$CH_3COC_6H_4$

$[p\text{-}CH_3COC_6H_4CH_2\text{-}]_2$

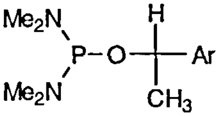
11

nearly racemic at carbon (*R*/*S* = 50/50-54/46). Clearly, the long-lived, triplet, free-radical pairs initially formed (**13**, Ar = p-$CH_3COC_6H_4$) undergo rapid stereochemical equilibration (**13** $\rightleftarrows$ **14**) on diffusion out of the initial radical cage and perhaps also within the cage. (The relative contributions of stereorandomization before and after escape from the solvent cage are currently being determined)



The stereochemistry of the phosphoramidite photorearrangements is typified by **15**. Starting with a 98/2 *R*/*S* ratio, a phosphonate ratio reduced to 65/35 (*R*/*S*) was encountered; and 20% of the potential 1-naphthylmethyl radicals appeared as dimer. This suggests that the amino substituents promote reaction via relatively long-lived free radical pairs. The most straightforward rationale is that a portion of the photoreactions of **15**, and other phosphoramidites, proceed via triplet caged

15



radical pairs (**13** and **14**, Ar = C_6H_5 or Np). Either intersystem crossing of the singlet excited state is promoted by the amino substituents or initially formed singlet radical pairs equilibrate rapidly with their triplet counterparts in competition with their coupling to product phosphonate. To help better define the origins of the increased amounts of products of radical diffusion encountered in the phosphoramidite photoreactions, experiments with appropriate triplet quenchers and sensitizers are underway, along with collaborative CIDNP and CIDEP studies with the group of Professor N.J. Turro, Columbia University.

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