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PHENYL RADICALS FROM PHENYLAZOTRIPHENYLMETHANE: REACTION WITH TRIMETHYL PHOSPHITE

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Several years ago Walling and Rabinowitz[1] noted the failure of t-butyl radicals generated from the reaction (1) of t-butoxy radicals with triethyl phosphite to undergo a similar reaction (2) with phosphite and suggested that polar structures might be important contributors stabilizing the transition state for t-butoxy radical attack at phosphorus (structure II)

$$(1)\quad \text{t-BuO}\cdot + \text{P(OEt)}_3 \longrightarrow \left[\begin{array}{c} \text{t-BuO}\cdot\ \ \ddot{\text{P}}\text{(OEt)}_3\ \text{I} \\ \updownarrow \\ \text{t-BuO}^-\ \ \cdot\overset{+}{\text{P}}\text{(OEt)}_3\ \text{II} \end{array}\right]^{\ddagger} \longrightarrow \text{t-BuO}\dot{\text{P}}\text{(OEt)}_3 \longrightarrow \text{t-Bu}\cdot + \text{OP(OEt)}_3$$

$$(2)\quad \text{t-Bu}\cdot + \text{P(OEt)}_3 \longrightarrow \text{t-BuP(O)(OEt)}_2 + C_2H_5\cdot$$

Such stabilization would not be expected to be so important for the relatively electropositive (nucleophilic) t-butyl radical. Thus, what should be a thermodynamically favorable reaction (2) could be rendered kinetically unfavorable. The idea that polar factors may be important finds further support in the fact that thiyl radicals (AlkS·) react in fashion like t-butoxys[1,2] and trichloromethyl radicals from CCl_4 are also readily reactive[3] (3).[‡]

$$(3)\quad Cl_3C\cdot + \text{P(OAlk)}_3 \longrightarrow Cl_3C\dot{\text{P}}\text{(OAlk)}_3 \xrightarrow[-\,CCl_3\cdot]{CCl_4} Cl_3C\overset{+}{\text{P}}\text{(OAlk)}_3Cl^- \longrightarrow Cl_3CP(O)(OAlk)_2$$

The potential reaction of the phenyl radical with trimethyl phosphite in similar manner to that suggested in (2) and (3) is of special interest, since phenyl seems to be intermediate in polar character being less electrophilic than t-butoxy but more electrophilic (less nucleophilic) than alkyl.[‡‡] Thus phenyl would be predicted to benefit less from structures like II in its

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[‡] It is conceivable that net reaction occurs here only because CCl_4 is present to trap the $Cl_3C\cdot$ - P(OAlk)_3 adduct formed in a reversible reaction which would not otherwise lead to product.

[‡‡] For example, the Hammett rho values determined from competitive abstraction experiments with substituted toluenes are -0.75 at 40° for t-butoxy radical[4] and zero to -0.4 at 60° for phenyl[5,6] two radicals of similar reactivity. The uncertainty in the latter value results from uncertainty in the correction to be made in each solvent ($ArCH_3$) for benzene formed via cage reaction. Corrections at infinite dilution give the more negative values. Partial rate factors from meta attack by phenyl on substituted benzenes show phenyl to be very slightly nucleophilic, rho = 0.05.[7] From orientation and relative rate data with monosubstituted benzenes, a nucleophilicity order cyclohexyl > methyl > phenyl has been estimated.[8] A reasonable ordering of radical electronegativities is t-butoxy > phenyl > methyl > t-butyl.[9]

reactions with trimethyl phosphite than would *t*-butoxy but more than would alkyl.

In this connection, Griffin and coworkers have reported[10] the photoreaction of aryl iodide-trialkyl phosphite mixtures to yield dialkyl arylphosphonates and have proposed the following sequence involving the phenyl radical (4). However, as pointed out by Walling and Pearson,[11]

$$C_6H_5\text{-}I \xrightarrow{h\nu} C_6H_5\cdot + I.$$

$$(4)\quad C_6H_5\cdot \xrightarrow{P(OAlk)_3} C_6H_5\overset{\bullet}{P}(OAlk)_3 \xrightarrow[I_2]{I\cdot\text{ or}} C_6H_5\overset{+}{P}(OAlk)_3I^-$$

$$C_6H_5\overset{+}{P}(OAlk)_3I^- \longrightarrow C_6H_5P(O)(OAlk)_2 + Alk\text{-}I$$

other mechanisms could account for the observed reaction. A nucleophilic photoreaction is an alternative worthy of serious consideration as evidenced by the recent paper of Barltrop *et al.*[12] concerning the apparent attack on electronically excited aryl halides by a variety of nucleophiles. Another possibility is that sequence (4) is correct but that net reaction of phenyl with phosphite depends on the presence of I_2 or I· to trap the intermediate phosphoranyl radical. A similar situation is thought to obtain in the reaction (5) of cyclohexyl radicals with PCl_3 which

$$(5)\quad R\cdot + PCl_3 \rightleftharpoons R\overset{\bullet}{P}Cl_3 \xrightarrow{O_2} RPCl_3OO.$$

appears to lead to product only if oxygen is present to prevent the reversal of the addition step.[13]

To remove the objectionable features of the phenyl iodide system, we have generated phenyl radicals in an unequivocal manner from the thermolysis of phenylazotriphenylmethane (PAT) in deoxygenated solutions of trimethyl phosphite at approximately 60°C. Products of reactions carried to 8-10 half lives are shown in Table I. That phenyl radicals are present is demonstrated by their diversion to benzene when large amounts of dimethyl phosphite are added as a hydrogen donor. We suggest the following mechanism (6). The involvement of discrete phosphoranyl

$$(6)\quad C_6H_5\cdot + P(OCH_3)_3 \longrightarrow C_6H_5\overset{\bullet}{P}(OCH_3)_3\ (III) \longrightarrow C_6H_5P(O)(OCH_3)_2 + CH_3\cdot$$

radical intermediates (III) is by no means sure. The formation of high yields of 1,1,1-triphenylethane accounts for a high percentage of the methyls thought to be formed. That trityls are involved in some type of trapping reaction (7) analogous to (5) is unlikely, since this would require a 1:1 correspondence of yields of dimethyl phenylphosphonate and 1,1,1-triphenylethane.

$$(7)\quad C_6H_5\overset{\bullet}{P}(OCH_3)_3 + \cdot C(C_6H_5)_3 \longrightarrow C_6H_5P(O)(OCH_3)_2 + CH_3C(C_6H_5)_3$$

This view is also supported by the diversion of trityls to benzophenone in air, and to 1,1,1 triphenylmethane by added dimethyl phosphite (3.13*M*) with little effect on the yield of phenylphosphonate. It should also be emphasized that if, as we propose, methyls are indeed free in solution, they fail to react with trimethyl phosphite as very little dimethyl methylphosphonate is formed. If methyls do react with phosphites under some conditions the alternatives here, such as reaction with trityl or hydrogen-abstraction, are more favorable in this instance.[‡] This is in contrast to the rapid reaction of phenyl with the phosphite. In view of the previous work with t-butyl radicals[1], it is not surprising that trityls do not give the tritylphosphonate. The constancy of the yield of phenylphosphonate with variation in PAT concentration is in contrast to the concentration dependence of the yield of chlorobenzene in the thermolysis of PAT in CCl_4 and is an indication of the high rate of reaction of phenyls with trimethyl phosphite.[‡‡][5,6]

TABLE I

PRODUCTS OF THE REACTION OF PHENYL RADICALS WITH TRIMETHYL PHOSPHITE

Conc. PAT	% Yield Products[a]					
(moles/liter)	C_6H_6	$C_6H_5P(O)(OCH_3)_2$	$(C_6H_5)_3CCH_3$	$(C_6H_5)_3CH$	p-Phenyl Triphenylmethane	9-Phenyl Fluorene
0.01	< 1	97, 98	85, 79	9, 15	< 0.5	4, 3
0.05	< 1	97, 95, 97	85, 76, 83	9, 17, 10	< 0.5	4, 3, 4
0.10	< 1	97, 98	84, 78	9, 11	< 0.5	4, 3
0.15	< 1	97, 99	83, 79	9, 12	< 0.5	4, 3
0.01[b]	< 1	99	43	16	< 0.5	0
0.05[c]	2.4	93	5.0	87	2.5	1.2
0.05[d]	29	27	0.42	60	29	0.8

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[a] Reactions run at 55-60°. Analyses by vpc, sensitivity corrected, error estimate ± 3% of reported yield. Results from independent, duplicate sets of runs. Trimethyl phosphite as solvent except in last experiment (footnote d). [b] Under one atmosphere of dry air. ~ 20% benzophenone also formed. [c] 3.13 M conc. of $(CH_3O)_2P(O)H$ added. [d] 0.31 M conc. trimethyl phosphite in $(CH_3O)_2P(O)H$ as solvent.

If the greater electrophilicity of the phenyl radical is in fact the reason for its reactivity with trimethyl phosphite and the unreactivity of the t-butyl and methyl radicals, then it might be well to examine the reactions of the p-tolyl and p-anisyl radicals as they have been shown[6,7] to be more nucleophilic (less electrophilic) than phenyl. On the other hand, it may be more correct to consider the relative stabilities of the various phosphoranyl radical intermediates which can potentially be formed in these reactions. This is especially true if addition of the radical to trivalent phosphorus is an endothermic process in which case the transition state for formation of the phosphoranyl radical would resemble that radical. The ability of a ligand

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[‡] Davidson reports in a footnote of a recent communication[14] that alkyl radicals are reactive with phosphorous esters. The specific esters were not specified.

[‡‡] Bridger and Russell noted[5] that addition of triphenylphosphine to carbontetrachloride solutions of PAT stopped the formation of chlorobenzene, presumably as a result of the preferential reactions of the phenyl radicals with the phosphine.

to stabilize a phosphorus intermediate through contraction of the phosphorus *d*-orbitals[15] may determine the reactivity of that group as a radical. Alternatively, the relative strength of the C-P bond formed may determine whether the addition step is thermodynamically favorable.

Finally, decomposition of PAT in phosphites may give some information as to the occurrence of cage processes. The invariance of the yield of dimethyl phenylphosphonate with changes of PAT concentration over the range studied might suggest that 2-3% of the phenyl radicals not accounted for in formation of phenylphosphonate react in the solvent cage. Caution should probably be employed in making such comparisons with other solvents since the phosphite may be able to interfere with what would normally be cage processes, since phosphite molecules may often be the nearest reactive neighbor molecule to the initially formed caged pair.[16]

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