

THERMAL DECOMPOSITION OF PHENYLAZOTRIPHENYLMETHANE

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In a recent communication Eliel, Eberhardt, Simamura and Myerson discussed the mechanism of aromatic phenylation which occurs when phenylazotriphenylmethane (PAT) is decomposed in an aromatic solvent.<sup>1</sup> They concluded that substitution occurs at a diffusion controlled rate with little activation energy. They pictured phenylation as occurring in a caged reaction between aromatic substrate and the phenyl-triphenylmethyl pair of radicals.

We possess a large amount of data not in accord with this concept.<sup>2</sup> The decomposition of PAT in a number of solvent combinations has been studied in hopes of establishing a comprehensive reactivity scale of carbon-hydrogen bonds toward the phenyl radical. We have so far established the hydrogen-transfer ability of 112 different alkanes, alkenes, alkynes, dienes, aralkyls, heterocyclics and functionally substituted alkanes toward the phenyl radical without any indication of the cage process referred to by Eliel and coworkers. Our study has shown that in hydrogen abstraction the phenyl radical has a reactivity rather similar to

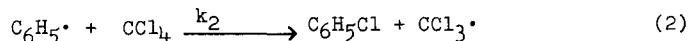
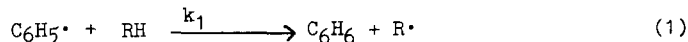
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<sup>1</sup> E. L. Eliel, M. Eberhardt, O. Simamura and S. Meyerson, Tetrahedron Letters 749 (1962).

<sup>2</sup> Eliel et. al. discussed aromatic phenylation using PAT and N-nitrosoacetanilide. Our comments do not necessarily apply to the nitroso compound.

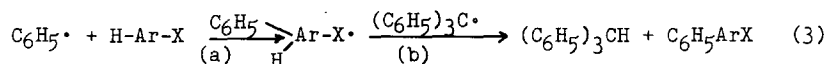
the methyl radical.

In general this study has involved the competition of a hydrogen donor ( $k_1$ ) and carbon tetrachloride ( $k_2$ ) with the phenyl radical formed in the decomposition of PAT. In pure carbon tetra-



chloride a 0.1 M solution of PAT yields 5.4 mole per cent of benzene and 72 mole per cent of chlorobenzene at 60°. The benzene yield decreases and the chlorobenzene yield increases linearly with a decrease in the initial concentration of PAT to give extrapolated yields at zero PAT concentration of 3 per cent of benzene and 90 per cent of chlorobenzene.<sup>3</sup> We feel the 3 per cent of benzene, and the 7 per cent of phenyl radicals unaccounted for represents some cage decomposition of PAT possibly to give tetraphenylmethane and/or 9-phenylfluorene. For the calculation of relative reactivities we have corrected our benzene yields by subtracting the amount of benzene (3 per cent) which would have been formed by this process in the decomposition of PAT in pure carbon tetrachloride. In mixtures of diphenyl ether, triphenylamine, biphenyl or pyrrole with carbon tetrachloride (mole ratio of aromatic/CCl<sub>4</sub>=1.0, 0.12, 0.33, 0.45, respectively) the yield of benzene is not much greater than 3 per cent (C<sub>6</sub>H<sub>6</sub>=6.0, 5.6, 6.1, 3.5 per cent, respectively) and an appreciable fraction of the phenyl radicals are captured by the carbon tetrachloride (C<sub>6</sub>H<sub>5</sub>Cl= 49, 63, 62, 54 per cent, respectively). These results are consistent with the conclusion that the only aromatic substitution process occurring is

<sup>3</sup> The PAT was prepared by oxidizing the corresponding hydrazo compound (S. G. Cohen and C. H. Wang, *J. Am. Chem. Soc.* **75**, 5504 (1953)). The yields of decomposition products were not changed by further oxidation with a wide variety of inorganic reagents and the formation of benzene cannot be explained as being due to an impurity in the PAT.



If the activation energy for reaction 3a is essentially zero and 3a is irreversible, then competing reactions 1 and 2 would also have to occur upon every collision. We do not believe this to be the case because when aralkyl hydrocarbons and carbon tetrachloride are allowed to compete for phenyl radicals the yield of benzene plus chlorobenzene is in the range of 60-90 per cent and a predictable reactivity series emerges. Such would not be the case if diffusion were controlling the rate of an irreversible reaction of the phenyl radical.<sup>4</sup> Table 1 gives some representative results.

TABLE 1

Products of the Decomposition of 0.10 M PAT in the Mixed Solvents at 60°

Hydrocarbon (RH)	$\frac{\text{CCl}_4}{\text{RH}}$	Yield, per cent		$(k_1/k_2)^a$
		$\text{C}_6\text{H}_6$	$\text{C}_6\text{H}_5\text{Cl}$	
cyclohexane	0.75	47.1	29.0	1.1
toluene	0.55	21.6	32.8	0.31
toluene- $-\text{d}_3$	0.37	11.0	31.9	.09
ethylbenzene	1.27	33.7	42.9	.91
cumene	1.16	37.5	39.0	1.0
diphenylmethane	1.21	39.7	30.5	1.5
triphenylmethane	2.51	41.7	26.2	3.7
p-xylene	1.03	32.9	36.8	0.84
mesitylene	0.96	29.6	28.0	.91
hexamethylbenzene	6.67	29.7	55.0	3.2
3-picoline	1.01	11.5	50.8	0.17
s-collidine	1.10	21.2	47.2	.42
thioanisole	2.46	13.5	56.1	.46
anisole	1.02	10.1	54.1	.13
diphenylamine	10.00	18.6	56.7	2.8
diphenylsilane	1.53	61.3	11.0	8.1
diphenylphosphine	10.40	25.8	4.6	52

$$^a \text{Rel. React.} = \frac{[\text{C}_6\text{H}_6 - .003] [\text{CCl}_4]}{[\text{C}_6\text{H}_5\text{Cl}] [\text{RH}]}$$

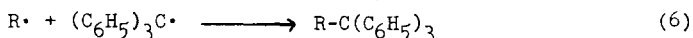
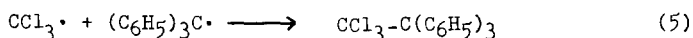
<sup>4</sup> Our results demand that either 3a has a significant  $E_a$  or 3a represents a dynamic equilibrium. We prefer the first explanation. This conclusion applies only to the free phenyl radical and is not applicable to possible concerted cage reactions occurring in the decomposition of N-nitroacetanilide.

Side reactions in these decompositions, as in the reactions described by Eliel *et. al.*,<sup>1</sup> are relatively unimportant. We believe this to be due to the stability of the trityl radical. This leads to a situation wherein phenyl radicals are generated in the presence of a concentration of trityl radicals which is not high enough to trap a significant number of phenyl radicals (i.e. to compete with reaction 1 or 2) but does effectively trap R· and CCl<sub>3</sub>· radicals. In the case of aromatic substitution described by Eliel *et. al.* the trityl radical apparently does not interfere with the addition of phenyl radicals to the aromatic nucleus but does readily remove a hydrogen atom from the resulting cyclohexadienyl radical.

We have also measured the yield of chloroalkanes formed as a side product under our reaction conditions.



When peroxides are decomposed in cyclohexane and carbon tetrachloride mixtures up to 20 molecules of chlorocyclohexane can be formed per radical generated.<sup>5</sup> However, in a typical decomposition of PAT in cyclohexane—carbon tetrachloride solution only 0.22 mole of chlorocyclohexane was formed per mole of PAT decomposed although the combined yield of benzene and chlorobenzene was 76 mole per cent (see Table 1). We feel this must be ascribed to the intervention of trityl radicals in reactions 5 and 6,



rather than due to a cage reaction of the radicals resulting from the homolysis of PAT.

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<sup>5</sup> G. A. Russell, *J. Org. Chem.* 24, 300 (1959).