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Kinetic Applications of Electron Paramagnetic Resonance Spectroscopy. XX. 2,4,6-Tri(*tert*-butyl)benzyl, -anilino, -phenoxy, and -phenylthiyl Radicals[1]

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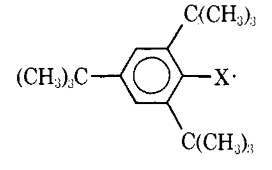
Received February 10, 1975

Abstract: The title radicals have been generated, and their kinetic behavior has been examined. The EPR parameters for the benzyl and anilino radicals indicate that the benzylic and amino hydrogens are coplanar with the aromatic rings. The benzyl radical decays rapidly with second-order kinetics ($k = (5 \pm 2) \times 10^8\ M^{-1}\ \mathrm{sec}^{-1}$ at 24°) to give the bibenzyl. The anilino radical exists in equilibrium with the hydrazine ($\Delta H = -13.1 \pm 0.5$ kcal/mol, $\Delta S = -27 \pm 2$ gibbs/mol). The rate constant for anilino decay to its dimer can be represented by $\log (k_{-1}/M^{-1}\ \mathrm{sec}^{-1}) = 6.3(\pm 1.0) - 2.5(\pm 0.8)/\theta$, where $\theta = 2.3RT$ kcal/mol, and that for decomposition of dimer to two anilino radicals by $\log (k_1/\mathrm{sec}^{-1}) = 12.2 - 15.6/\theta$. The phenylthiyl radical is also in equilibrium with its dimer at ambient temperatures ($\Delta H = -23.3$ kcal/mol), but the phenoxy radical shows no sign of dimerization even at −100°. The behavior of these four radicals is discussed in terms of the strengths of the bonds formed by head-to-head dimerization.

In several previous papers in this series, we have shown that radical lifetimes can be dramatically increased by steric protection of the radical center.[4] Each of these papers was confined to radicals of a single type. That is, each dealt with radicals in which the atom that formally bore the unpaired electron was held constant, and the size of the surrounding groups was varied.

Equally dramatic changes in radical lifetimes can be achieved by holding to the same basic molecular structure and altering the atom carrying the unpaired electron. This is because the mutual bonding capacities of different atoms are not all the same. In the present paper, we illustrate this phenomenon by reporting on the kinetic behavior of the 2,4,6-tri(*tert*-butyl)benzyl, -anilino, -phenoxy, and -phenylthiyl radicals.



X = CH_2, NH, O, S

The 2,4,6-tri(*tert*-butyl)phenoxy ($Ar\dot{O}$)[5,6] is a well-known blue-colored radical that is readily prepared by oxidation of the phenol with a variety of reagents. It can be stored at room temperature in concentrated solutions (e.g., 1 *M* in benzene) for prolonged periods of time, in the absence of air. The pink-colored 2,4,6-tri(*tert*-butyl)anilino radical ($Ar\dot{N}H$) has also been examined in some detail,[7-12] particularly with respect to its EPR[7,8,10-12] and uv-visible[7,9] spectra. In solution (at $<10^{-4}$ *M*) it "can be preserved for several days when the solvent is *n*-hexane but the stability is less in cyclohexane".[7] The isoelectronic tri(*tert*-butyl)benzyl radical ($Ar\dot{C}H_2$) has not been previously reported. It was readily obtained from tri(*tert*-butyl)toluene or tri(*tert*-butyl)benzyl chloride which have been recently synthesized.[13,14] Tri(*tert*-butyl)phenylthiyl ($Ar\dot{S}$) has been previously studied, but there are conflicting reports as to its lifetime in solution.[15-17]

Experimental Section

General. The kinetic EPR procedure has been adequately described in previous papers in this series.[1] Unless otherwise stated, all materials were prepared and handled in an argon atmosphere.

Materials. The ArOH was a (purified) commercial sample (K & K Laboratories). Standard literature procedures were used to prepare $ArCH_3$,[13] $ArNH_2$,[18] ArSH,[19] and ArNO.[20] The disulfide ArSSAr was prepared by oxidizing ArSH with silver oxide and was purified by vacuum sublimation, mp 233° (lit.[19] 233°).

Hexa(*tert*-butyl)bibenzyl ($ArCH_2CH_2Ar$) was prepared by reaction of $ArCH_2Cl$[13] (0.1 g) with finely divided sodium in paraffin wax at 120° under N_2 for 30 min.[4d,21,22] In this time, the NMR signal due to the CH_2Cl protons disappeared. Column chromatography on acidic alumina yielded 0.04 g of the crystalline hydrocarbon $ArCH_2CH_2Ar$: mp 228°; proton NMR spectrum in $CDCl_3$ (in parts per million downfield from Me_4Si) 1.20 (p-$C(CH_3)_3$) and 1.22 (o-$C(CH_3)_3$) (totalled 54 H), 3.40 (4 H, $-CH_2CH_2-$), 7.48 (4 H, aryl *m*-H). The elemental analysis was poor (Anal. Calcd for

Table I. EPR Parameters for ArX Radicals (Hyperfine Couplings Are in Gauss)

Radical	g	$a^{\mathrm{H}m}$	a^{X}	$a^{\mathrm{H}\alpha}$	$a^{\mathrm{H}p\text{-}(CH_3)_3C}$	Ref
$Ar\dot{C}H_2$	2.0025	1.78	*a*	15.34	*a*	This work[b]
$Ar\dot{N}H$	*c*	1.89	6.70 (^{14}N)	11.75	0.27	12[d]
$Ar\dot{O}$	*c*	1.70	10.23 (^{17}O)[e]		0.37	12[d]
$Ar\dot{S}$	2.0103	*a,f*	14.75 (^{33}S)		*a*	15[b]

[a] Not resolved. [b] In benzene. [c] Not reported in ref 12. [d] In hexane. [e] A. Rieker and K. Scheffler, *Tetrahedron Lett.*, 1337 (1965). [f] Failure to resolve the meta couplings may be due to the large line width (2.8 G).

$C_{38}H_{62}$: C, 87.96; H, 12.04. Found: C, 87.61, 88.28; H, 11.81, 11.69), apparently because the compound contains traces of ArOH (see below). However, the molecular weight (526 by VP osmometry in benzene; calcd mol wt, 518.9) and the mass spectrum (maximum *m/e* peak at 518) leave little doubt as to the identity of this compound. The parent ion in the mass spectrum was of relatively low intensity, but there is a major ion corresponding to the $ArCH_2^+$ fragment (*m/e* 259). The principal peaks and their relative intensities at 70 eV were: 518 (0.3), 516 (0.4), 462 (1.0), 460 (1.7), 406 (1.6), 404 (2.7), 392 (1.2), 390 (1.2), 259 (100), 246 (71), 243 (158), 231 (613), 216 (63), 201 (321). The peaks with *m/e* below 200 had intensities less than 100.

Product Studies on $Ar\dot{C}H_2$. Kinetic work on the $Ar\dot{C}H_2$ radical (see Results) indicated that this radical underwent a bimolecular self-reaction very readily. A solution of $ArCH_3$ (0.01 g) in di-*tert*-butyl peroxide (0.2 ml) was degassed and then photolyzed for 2 hr at room temperature in the cavity of the EPR spectrometer. VPC analysis showed that $ArCH_2CH_2Ar$ was formed together with an approximately equal yield of a second dimer having a somewhat longer VPC retention time. The second dimer was not identified, but we presume it is formed by combination of $Ar\dot{C}H_2$ with radicals formed by *tert*-butoxy attack on the *tert*-butyl groups of $ArCH_3$.

In a second experiment, $ArCH_2CH_2Ar$ was identified as the only product (except for Me_3SnCl) formed by photolysis of $ArCH_2Cl$ (0.04 g) and $Me_3SnSnMe_3$ (0.20 ml) in benzene (0.20 ml) in a Rayonet Reactor (2537 Å, approximately 200 W). After 3 hr of photolysis, the NMR signal due to $-CH_2Cl$ (δ 5.30 with reference to benzene at δ 7.37) disappeared, and the band for the $-CH_2CH_2-$ group of the dimer appeared at δ 3.43. Cooling the benzene solution deposited prisms of the dimer in quantitative yield, mp 228°, alone or mixed with the sample prepared by action of sodium on $ArCH_2Cl$.

We conclude that $Ar\dot{C}H_2$ radicals couple to give the head-to-head dimer.

Product Studies on $Ar\dot{N}H$. $ArNH_2$ (0.07 g) was dissolved in 3 ml of benzene and the solution degassed and then added under argon to a centrifuge tube containing 2 g of PbO_2. The tube was shaken for ca. 30 sec and centrifuged, and 1 ml of the supernatant solution was removed. The benzene was removed under vacuum, and the solid residue was then dissolved in 0.3 ml of cyclopropane and sealed under vacuum. Great care was taken to exclude air from the reaction at all stages. The proton NMR spectrum of this solution at −80° showed mainly the aniline [1.01[23] (9 H, *p*-$(CH_3)_3C$); 1.20 (18 H, *o*-$(CH_3)_3C$); 3.79 (2 H, NH_2); 6.91 (2 H, *m*-H)] together with three peaks (having about 5% of the intensity of the adjacent aniline peaks)[25] at 1.10, 1.30, and 6.94. These three peaks disappear on warming the sample to room temperature but reappear on recooling to −80°. We therefore *tentatively* assign them to the anilino dimer. From the apparent absence of vinylic protons plus the observation of just two *tert*-butyl peaks and one aromatic proton peak, we presume that the dimer is formed by head-to-head coupling of the anilino radicals, i.e., ArNHNHAr.

Attempts to Decompose $ArCH_2CH_2Ar$. The strength of the central bond was estimated to be ca. 40 kcal/mol (see Discussion) which suggested that this compound might decompose to $Ar\dot{C}H_2$ radicals at moderate temperatures. Heating a 0.1 *M* solution of $(ArCH_2)_2$ in 1,3-di(*tert*-butyl)benzene to 230° in the cavity of the EPR spectrometer did not give a detectable concentration of $Ar\dot{C}H_2$, though a strong signal due to $Ar\dot{O}$ (which presumably arises from ArOH present as an impurity in the bibenzyl) was observed from ~100 to ~180°. The compound was not appreciably decomposed by this treatment to judge from the VPC trace. (The thermal stability of $ArCH_2CH_2Ar$ is also attested to by the VPC conditions, viz., a 3-ft SE 30 silicon-gum rubber column at 250°, which gave a retention time of 45 min.)

In a second experiment, a 2×10^{-2} *M* solution of the bibenzyl was heated to 140° in the presence of 5×10^{-4} *M* of the free radical, 2,2,6,6-tetramethylpiperid-4-on-*N*-oxyl. After 3 hr, the decrease in the concentration of the nitroxide in a blank sample was somewhat greater (~20%) than in the sample containing the bibenzyl (~10%). If $Ar\dot{C}H_2$ radicals are formed, they must be too hindered to give a stable *O*-benzyloxime.

In a third experiment, a 2×10^{-2} *M* solution of $(ArCH_2)_2$ in thiophenol was heated to 207° in a sealed tube. After 5 days, there was no appreciable decompositions of the bibenzyl, but a trace (VPC analysis) of $ArCH_3$ had been formed.

Results

EPR Spectra. Of the radicals studied in this work, only $Ar\dot{C}H_2$ has not previously been reported. Good EPR spectra were obtained by reaction of $ArCH_2Cl$ with photochemically generated $Me_3\dot{S}i$ or $Me_3\dot{S}n$ radicals and by reaction of $ArCH_3$ with photochemically generated $(CH_3)_3C\dot{O}$ radicals. The EPR parameters at room temperature are compared in Table I with those of $Ar\dot{N}H$, $Ar\dot{O}$, and $Ar\dot{S}$. Two features of the $Ar\dot{C}H_2$ spectrum are notable.

(i) Despite the presence of two *o*-*tert*-butyl groups, the $\dot{C}H_2$ group must be coplanar with the aromatic ring. This follows from the similarity of these hyperfine couplings to appropriate protons in $C_6H_5\dot{C}H_2$, viz.,[26] $a^{\mathrm{H}\alpha} = 16.4$ G, $a^{\mathrm{H}m} = 1.75$ G.[27] By the same argument,[30] the $\dot{N}H$ group in $Ar\dot{N}H$ must also be coplanar with the ring. Neither conclusion is entirely unexpected since the OH group in ArOH has long been known to be coplanar.[31]

(ii) There is no resolvable hyperfine coupling with any *tert*-butyl group. This may have been due to the *relatively* low intensity of the EPR signal since a^{H}(*p*-*t*-Bu) is expected to be ~0.17 G by comparison with $Ar\dot{O}$ (~0.37 G) and $Ar\dot{N}H$ (~0.27 G).[8,10-12,32] Coupling to the *o*-*tert*-butyl protons should be very small.[34]

Kinetics and Products

$Ar\dot{C}H_2$ radicals, generated at concentrations of 1-3 × 10^{-7} *M* by photolysis of solutions of $ArCH_3$ in di-*tert*-butyl peroxide decay rapidly and with second-order kinetics. Product studies (see Experimental Section) indicate that this reaction is a head-to-head dimerization to the hindered bibenzyl.

$$2Ar\dot{C}H_2 \xrightarrow{k} ArCH_2CH_2Ar$$

The rate constant for decay, k, is $(5 \pm 2) \times 10^8\ M^{-1}\ \mathrm{sec}^{-1}$ at room temperature.

$Ar\dot{O}$ radicals are very long-lived in solvents such as di-*tert*-butyl peroxide or benzene at room temperature. Even at high concentrations, the radicals show no sign of dimerization at room temperature, nor even at −100°.

$Ar\dot{N}H$ radicals are reported to be fairly long-lived.[7] The only logical reason for the difference in behavior of $Ar\dot{C}H_2$ and $Ar\dot{O}$ would seem to be the differences in the strengths of the bonds formed by a head-to-head dimerization. Bond strengths in the respective dimers should follow the order C-C > N-N > O-O, and hence one would expect that $Ar\dot{N}H$ would exhibit behavior intermediate between

$\mathrm{Ar\dot{C}H_2}$ and $\mathrm{Ar\dot{O}}$, rather than that it would behave just like $\mathrm{Ar\dot{O}}$. This proved to be the case. That is, $\mathrm{Ar\dot{N}H}$ radicals couple rapidly to give the head-to-head hydrazine dimer (see Experimental Section) but the reaction is reversible at room temperature.

Our usual procedure for radical production for kinetic studies involves photolysis of di-*tert*-butyl peroxide solutions of the parent compound. This proved rather unsatisfactory with $\mathrm{ArNH_2}$ because the initial formation of $\mathrm{Ar\dot{N}H}$ was rapidly followed by the formation of $\mathrm{Ar\dot{N}O\text{-}\mathit{t}\text{-}Bu}$.[36] The latter radical ($a^{\mathrm{N}} = 10.21$ G, $a^{\mathrm{H_m}} = 1.91$ G, $g = 2.004$ at room temperature)[37] is remarkably long-lived and its presence prevented kinetic studies on $\mathrm{Ar\dot{N}H}$ in this system.[39]

$$\mathrm{ArNH_2} \xrightarrow{t\text{-BuO}\cdot} \mathrm{Ar\dot{N}H} \xrightarrow{t\text{-BuO}\cdot} \mathrm{ArNHO\text{-}\mathit{t}\text{-}Bu} \xrightarrow{t\text{-BuO}\cdot} \mathrm{Ar\dot{N}O\text{-}\mathit{t}\text{-}Bu}$$

Fortunately, the $\mathrm{Ar\dot{N}H}$ radical could be produced "cleanly" by oxidation of $\mathrm{ArNH_2}$ with lead dioxide in deoxygenated hydrocarbon solutions.[25] After a brief shaking, the sample was centrifuged, and the radical solution was carefully removed (under argon) for kinetic examination. The $\mathrm{Ar\dot{N}H}$ concentration was found to increase and decrease reversibly on raising and lowering the temperature, indicating that a dimer is formed reversibly.

$$\mathrm{ArNHNHAr} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} 2\mathrm{Ar\dot{N}H}$$

In pentane, the equilibrium constant, K ($= k_1/k_{-1}$), can be represented by the van't Hoff relation ($K = e^{\Delta S/R}e^{-\Delta H/RT}$) with $\Delta H = -13.1 \pm 0.5$ kcal/mol (temperature range -40 to $-65°$) and $\Delta S = -27 \pm 2$ gibbs/mol.

The rate constant for the bimolecular decay of $\mathrm{Ar\ \dot{N}H}$, k_{-1}, was obtained by measuring the rate of approach to equilibrium after a sudden change in the temperature. Under the conditions of these experiments, the concentration of dimer is much greater than the $[\mathrm{Ar\dot{N}H}]$ concentration, and the rate constant can be represented by

$$k_{-1} = \frac{2.303}{2[\mathrm{Ar\dot{N}H}]_e} \log \left\{\frac{[\mathrm{Ar\dot{N}H}] + [\mathrm{Ar\dot{N}H}]_e}{[\mathrm{Ar\dot{N}H}] - [\mathrm{Ar\dot{N}H}]_e}\right\} \Big/ t + \text{constant}/t$$

where $[\mathrm{Ar\dot{N}H}]_e$ is the radical concentration at equilibrium ($t = \infty$). The equilibrium can be approached from either side. In order for thermal equilibrium to be more rapid than chemical equilibrium, measurements were made warming cooled samples to $-40°$ and cooling warmer samples to temperatures in the range -100 to $-60°$. The rate constants so obtained could be represented by

$$\log (k_{-1}/M^{-1}\ \mathrm{sec}^{-1}) = 6.3(\pm 1.0) - 2.5(\pm 0.8)/\theta$$

where $\theta = 2.3RT$ kcal/mol. This equation yields $k_{-1} = 3 \times 10^4\ M^{-1}\ \mathrm{sec}^{-1}$ at room temperature. Thus, the head-to-head coupling of the hindered anilino radicals is slower by four orders of magnitude than the head-to-head coupling of the hindered benzyl radicals.

Combination of the Arrhenius equation for $\mathrm{Ar\dot{N}H}$ dimerization with the van't Hoff equation for the equilibrium yields:

$$\log (k_1/\mathrm{sec}^{-1}) = 12.2 - 15.6/\theta$$

The preexponential factor for decomposition of the hindered hydrazine is somewhat lower than the values found for most unimolecular bond scission reactions.[42]

The lifetime of solutions of $\mathrm{Ar\dot{N}H}$ at room temperature depends upon the solvent.[7] The radical is much more persistent in benzene ($\tau_{1/2} \sim$ 15-20 hr at 24°) than in saturated hydrocarbons such as pentane where its half-life is only a few hours.[43] Presumably $\mathrm{Ar\dot{N}H}$ can abstract hydrogen from alkanes.[44]

$$\mathrm{Ar\dot{N}H} + \mathrm{RH} \rightarrow \mathrm{ArNH_2} + \mathrm{R}\cdot \xrightarrow{\mathrm{Ar\dot{N}H}} \mathrm{ArNHR}$$

$\mathrm{Ar\dot{S}}$ radicals were generated by photolysis of ArSH and ArSSAr solutions in hydrocarbon solvents and by photolysis of ArSH in di-*tert*-butyl peroxide. None of these systems proved satisfactory for kinetic studies. On cutting off the light, the intensity of the EPR signal *increased* (by up to a factor of 2) in a few seconds[16] and then slowly decreased following approximately first-order kinetics[15,16] both at $-80°$ and at room temperature. It is possible that CIDEP effects[45] are responsible for the (apparent) increase in the $\mathrm{Ar\dot{S}}$ concentration when the light was cut off. However, since the radical dimerizes to ArSSAr[46] and since this reaction is reversible (see below), it is also possible that the unusual behavior of the $\mathrm{Ar\dot{S}}$ radicals is due to an effect of the light on the radical-dimer equilibrium. Because of these complications, we abandoned attempts to measure the rate of the $\mathrm{Ar\dot{S}}$ dimerization and concentrated instead on the equilibrium.

A $3.31 \times 10^{-3}\ M$ solution of ArSSAr in isooctane showed no detectable $\mathrm{Ar\dot{S}}$ radicals at 0° but, at 18°, the $\mathrm{Ar\dot{S}}$ concentration was $7.43 \times 10^{-8}\ M$ and, at 28°, it was $2.05 \times 10^{-7}\ M$. The radicals were in equilibrium with the dimer and did not decay irreversibly (during the length of an experiment) until the temperature was raised to 40° (at which temperature they are, we presume, reacting with the solvent). The calculated equilibrium constants are $1.7 \times 10^{-12}\ M$ at 18° and $1.3 \times 10^{-11}\ M$ at 28°. The temperature range is too small to justify the calculation of ΔH and ΔS directly from these data. However, if we *assume* that ΔS will be the same as for the $\mathrm{Ar\dot{N}H}$ equilibrium, then ΔH is calculated to be -23.5 kcal/mol at 18° and -23.1 at 28°. That is, $\Delta H = -23.3$ kcal/mol, with a probable error of less than ± 2 kcal/mol.

Discussion

The radicals $\mathrm{Ar\dot{C}H_2}$, $\mathrm{Ar\dot{N}H}$, $\mathrm{Ar\dot{O}}$, and $\mathrm{Ar\dot{S}}$ must all have a rather similar degree of steric crowding about the radical center, though the distribution of the unpaired electron in these radicals will differ because of variations in bond lengths, relative orbital energies, and overlap with the aromatic ring.[47] The differences in their kinetic behavior can be most simply attributed to differences in the strengths of the bonds formed by head-to-head dimerization. In the absence of steric hindrance, the strengths of these bonds, i.e., $DH°(\mathrm{C_6H_5X\text{-}XC_6H_5})$ can be estimated from Benson et al. compilations[48] of the heats of formation, $\Delta H_f°$, of radical and dimer:

$$\begin{array}{lll}
2\Delta H_f°(\mathrm{C_6H_5X}\cdot) - \Delta H_f°(\mathrm{C_6H_5X})_2 & & = DH°(\mathrm{C_6H_5X\ XC_6H_5}) \\
\mathrm{C_6H_5\dot{C}H_2}\ 2 \times 45 - 32.4 & & = 57.6\ \text{kcal/mol} \\
\mathrm{C_6H_5\dot{N}H}\ 2 \times 55\ - 77.9 & & = 32.1\ \text{kcal/mol} \\
\mathrm{C_6H_5\dot{S}}\ 2 \times 49.5\ - 58.4 & & = 40.6\ \text{kcal/mol} \\
\mathrm{C_6H_5\dot{O}} & & \sim 0\ \text{kcal/mol}^{49}
\end{array}$$

The corresponding sterically hindered dimers have lower bond strengths which are given by the measured enthalpy for the radical-dimer equilibrium, ΔH. That is

$$DH°(\mathrm{ArNH\text{-}NHAr}) = 13.1\ \text{kcal/mol}$$
$$DH°(\mathrm{ArS\text{-}SAr}) = 23.3\ \text{kcal/mol}$$

The hydrazine is therefore destabilized by $32.1 - 13.1 = 19.0$ kcal/mol and the disulfide by $40.6 - 23.3 = 17.3$ kcal/

mol. The extent of this destabilization by the *o-tert*-butyl groups is both remarkably similar and surprisingly small when compared with the $\sim 8 \pm 2$ kcal/mol destabilization of the O-H bond in ArOH relative to C_6H_5OH.[50]

If $ArCH_2CH_2Ar$ were destabilized by ~ 18 kcal, the strength of its central bond would be ~ 40 kcal/mol and decomposition to two $Ar\dot{C}H_2$ radicals should occur fairly readily if the preexponential factor (in the Arrhenius equation) for this scission has its "normal"[42] value of $\sim 10^{16}$ sec^{-1}. That is, if the Arrhenius equation can be represented by $k = 10^{16} \exp(-40{,}000/RT)$ sec^{-1} then, at 207° (for example), $k \sim 6 \times 10^{-3}$ sec^{-1} which corresponds to a half-life for the dimer of ~ 2 min. Since our attempts to decompose the dimer were not too successful, we suggest that the preexponential factor is appreciably less than 10^{16} sec^{-1}. Thus, a preexponential factor of about 10^{12} sec^{-1} [the magnitude found for decomposition of $(ArNH)_2$] and a bond strength of 40 kcal/mol yield a half-life at 207° of $\sim 2 \times 10^4$ min, i.e., ~ 14 days, which is quite consistent with our data. An "abnormally" small preexponential factor for a unimolecular scission is not unreasonable[42] if, in the transition state, steric hindrance still inhibits free rotation and rocking (relative to the central bond) of the separating $Ar\dot{C}H_2$ radicals.

The kinetic behavior of $Ar\dot{O}$ is quantitatively different from that of the other three radicals because there is no attractive force favoring formation of ArOOAr. Thus, the $Ar\dot{O}$ radicals do not dimerize at any temperature. The other three radicals dimerize readily and, to judge from the benzyl and anilino cases, the rate of this process increases rapidly with increasing strength of the bond being formed. This can be understood in terms of Hammond's postulate.[51] That is, the transition state for the more exothermic reaction will tend to resemble the reactants, and so bond formation will start to occur when the radicals are relatively far apart and the influence of the *tert*-butyl groups is small. For less exothermic reactions, the influence of the *tert*-butyl groups is greater because the transition state will tend to resemble the products, and the radicals must get closer together before they will react.

Acknowledgment. One of us (L.R.C.B.) thanks the NRC for support with an operating grant.

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(39) On storing solutions containing both $Ar\dot{N}H$ and $Ar\dot{N}O$-*t*-Bu radicals for a few days, the concentration of $Ar\dot{N}O$-*t*-Bu increases at the expense of $Ar\dot{N}H$.

$$Ar\dot{N}H + ArNHO\text{-}t\text{-}Bu \rightarrow ArNH_2 + Ar\dot{N}O\text{-}t\text{-}Bu$$

The $Ar\dot{N}O$-*t*-Bu radicals do not dimerize even at low temperatures, cf., $Ar\dot{N}H$ (text), $ArN(\dot{O})Me$,[40] and 3,5-*t*-$Bu_2C_6H_4\dot{N}$-*t*-Bu.[41]

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