Search for Electron-Transfer Decomposition and the Production of Electronically Excited State Species in the Thermolysis of *p*-(Dimethylamino)phenyl-Substituted Dialkyl Peroxides

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Kinetic, product, and chemiluminescence (CL) studies were made with 1-[4-(dimethylamino)phenyl]ethyl *tert*-butyl peroxide (1), 2-[4-(dimethylamino)phenyl]propyl *tert*-butyl peroxide (2), and 1-phenylethyl *tert*-butyl peroxide (3). Activation parameters for 1 in chlorobenzene are as follows: E_a = 36.2 ± 0.6 kcal/mol, log A = 15.45 ± 0.32, $\Delta H^{\ddagger}$ = 35.4 ± 0.6 kcal/mol, $\Delta S^{\ddagger}$ = 9.66 + 1.35 eu. These activation parameters are within the range expected for simple peroxide bond homolysis. The small rate acceleration by the *p*-dimethylamino group (k_1/k_3 = 2.07 at 129 °C) is reasonable, again for the simple peroxide bond homolysis. Product studies with 1 and 2 in comparison to 3, indicate that the dimethylamino group serves as a good hydrogen atom donor. This was further substantiated by the thermolysis of 3 in the presence of *N,N*-dimethylaniline and 2,6-di-*tert*-butyl-*p*-cresol. CL was observed in the thermolysis of 1 and 2 in aerated *o*-dichlorobenzene solutions at 140 °C. The CL quantum yield decreased significantly when solutions of 1 and 3 were purged with nitrogen or argon. No CL was observed in the thermolysis of 3, but CL was observed when *N,N*-dimethylaniline was added to the aerated solution. These results suggest that the CL from 1 and 2 is due primarily or entirely to autoxidation processes involving the dimethylamino group and not to electron-transfer processes involving this group and the peroxide bond.

Recently, the amino group has played an interesting role in the thermolysis of dioxetanes and dioxetanones. Evidence has been presented for a dramatic change in mechanism from a biradical process[1-4] to an electron-transfer (CIEEL)[5] process when an amino group is incorporated with these cyclic peroxides.[6-10] Accompanying the change in mechanism is a striking change in the singlet (S_1)/triplet (α_S/α_T) carbonyl efficiencies, where the CIEEL mechanism is characterized by a dramatically higher α_S/α_T ratio. The effect of the amino substituent upon the decomposition of dioxetanones is also of particular interest to certain bioluminescent systems.[11]

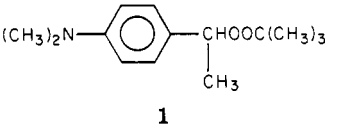
The role of the amino group in changing the course of reaction and chemiluminescence (CL) characteristics has been noted with peresters as well. In a study of acyl ring substituted 1-phenylethyl peroxybenzoates by Schuster and co-workers, the *p*-dimethylamino substituent was unique in lowering $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ as well as increasing the yield of excited-state singlet-substituted benzoic acid.[12]

Table I. Products from the Thermolysis of 1 in Chlorobenzene at 129 °C under Nitrogen and Air[a]

product	yield, mmol/100 mmol of 1	
	N_2	air
CH_3COCH_3	15.2	18.3
t-C_4H_9OH	70.1	78.0
p-$(CH_3)_2NC_6H_4CH(OH)CH_3$ (4)	45.0	40.2
p-$(CH_3)_2NC_6H_4CHO$	14.0	13.9
p-$(CH_3)_2NC_6H_4COCH_3$ (5)	14.0	11.2

[a] $[1]_0 = 4.03 \times 10^{-2}$ M.

Considering the pivotal importance of the amino group in changing the mechanism and altering efficiencies of excited-state products in these peroxides, we were interested in pursuing the effect of a *p*-(dimethylamino)phenyl group on the thermolysis of a dialkyl peroxides. dialkyl peroxides, without amino substituents, containing at least one tertiary alkyl group undergo thermolysis by an initial homolysis of the peroxide bond,[13] and they are not known to produce excited-state products. The dialkyl peroxides selected for this study are 1-[4-(dimethylamino)phenyl]-ethyl *tert*-butyl peroxide (1), 2-[4-(dimethylamino)-



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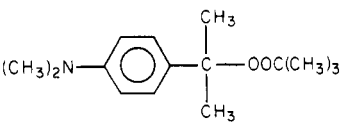

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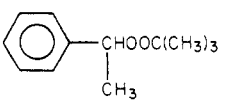

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Table II. Product Yields[a] from the Thermolysis of 3 in Chlorobenzene at 129 °C under an Air Atmosphere

product	additive: none[b]	$C_6H_5N(CH_3)_2$[c]	BHT[d]
CH_3COCH_3	78.8	10.2	42.8
t-C_4H_9OH	3.12	97.3	50.5
$C_6H_5CH(OH)CH_3$	1.1	64.4	33.2
C_6H_5CHO	26.2	e	23.8
$C_6H_5COCH_3$	49.4	31.7	37.1

[a] In mmol/100 mmol of 3. [b] $[3]_0 = 3.86 \times 10^{-2}$ M. [c] $[3]_0 = 3.45 \times 10^{-2}$ M and $[C_6H_5N(CH_3)_2] = 7.85 \times 10^{-2}$ M. [d] $[3]_0 = 4.04 \times 10^{-2}$ M and [BHT] = 4.46×10^{-2} M (BHT = 2,6-di-*tert*-butyl-*p*-cresol). [e] $C_6H_5N(CH_3)_2$ interfered with the analysis for C_6H_5CHO.

phenyl]propyl *tert*-butyl peroxide (**2**), and 1-phenylethyl *tert*-butyl peroxide (**3**) as a model compound for **1**. By analogy to the 1-phenylethyl peroxybenzoates, both **1** and **3** could undergo hydrogen atom abstraction from the caged alkoxy radicals to give the acetophenone and *tert*-butyl alcohol. With **1**, the possibility of an electron-transfer process to accelerate the rate of decomposition as well as to generate excited-state *p*-(dimethylamino)acetophenone can be considered, analogous to that observed with the secondary perester.[12] With **2**, an electron-transfer process to accelerate the rate is possible, but a CL process analogous to the secondary perester[12] is not possible. Since dialkyl peroxides may be viewed as the simplest of the peroxides, the results with **1** and **2** can form a basis from which to evaluate CIEEL processes with other peroxides.

Results

Products. Decomposition of **1** was carried out in chlorobenzene for about 10 half-lives under air and nitrogen atmospheres. The results are given in Table I. Product balances for the *tert*-butyl portion of **1** are 85–96% and about 65% for the arylalkyl portion. The presence of oxygen does not cause a significant change in the yields of the analyzed products. The relatively high yield of **4** compared to that of **5** is notable, since chlorobenzene is a poor hydrogen atom donor. In addition, the product balance of the aryl alkyl portion of **1** compared to the *tert*-butyl portion is markedly lower. Products (and yields) from the thermolysis of **2** in chlorobenzene (6.40×10^{-2} M) at 129 °C in an air atmosphere were acetone (21%), *tert*-butyl alcohol (66%), and p-$(CH_3)_2NC_6H_4C(OH)(CH_3)_2$ (57%). No p-$(CH_3)_2NC_6H_4COCH_3$ was observed. As was observed with **1**, the arylalkyl product balance (57%) with **2** is also low compared to the *tert*-butyl portion (87%).

For comparison to **1** and **2**, product studies with **3** were carried out in chlorobenzene and in this solvent with *N,N*-dimethylaniline (DMA) and the radical trap 2,6-di-*tert*-butyl-*p*-cresol (BHT). The results are shown in Table II. Indeed, in the absence of the dimethylamino group and additives, **3** produces the arylmethylcarbinol and *tert*-butyl alcohol in low yield as expected in the poor hydrogen atom donor solvent. Both the radical trap BHT and DMA serve as hydrogen atom donors to increase the yields of the alcohol products.

Kinetics. Rate data for the thermolysis of **1–3** in chlorobenzene and with this solvent containing styrene are given in Table III. Activation parameters for **1** in the absence of styrene are as follows: $E_a = 36.2 \pm 0.6$ kcal/mol, $\log A = 15.45 \pm 0.32$, $\Delta H^{\ddagger} = 35.4 \pm 0.6$ kcal/mol, $\Delta S^{\ddagger} = 9.66 \pm 1.35$ eu. Styrene retards the rate of decomposition of **1** and **3** by about the same factor, 0.84 and 0.82, respectively, which indicates some induced decomposition.

Table III. Rates of Thermolysis of 1-3 in Chlorobenzene under an Air Atmosphere[a]

peroxide	temp, °C	10^5k,[b] s^{-1}
1[c]	100.4	0.182 ± 0.010
1[c]	110.8	0.697 ± 0.031
1[c]	120.9	2.18 ± 0.08
1[c]	129.2	6.18 ± 0.19
1[d]	129.2	5.22 ± 0.17
2[e]	129.2	79.1 ± 8.0
2[f]	129.2	15.1 ± 0.7
3[g]	129.2	3.09 ± 0.09
3[h]	129.2	2.52 ± 0.06

[a] Rates were measured by following the disappearance of the *tert*-butyl protons in **1–3** by NMR. [b] Least-squares fit with standard error. [c] $[1]_0 = 2.36 \times 10^{-2}$ M. [d] $[1]_0 = 2.27 \times 10^{-2}$ M and [styrene] = 0.424 M. [e] $[2]_0 = 3.50 \times 10^{-2}$ M. [f] $[2]_0 = 3.50 \times 10^{-2}$ M and [styrene] = 0.400 M. [g] $[3]_0 = 3.86 \times 10^{-2}$ M. [h] $[3]_0 = 3.72 \times 10^{-2}$ M and [styrene] = 0.376 M.

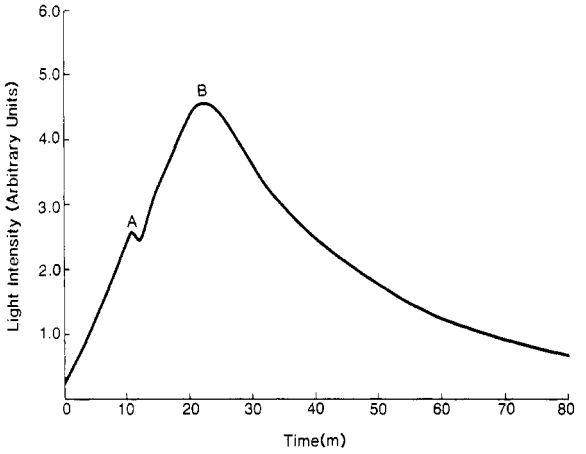

Figure 1. A typical light emission profile, which shows the two intensity maxima (A and B), with $[1]_0 = 0.116$ M in aerated *o*-dichlorobenzene at 140 °C.

Considerably more styrene had undergone polymerization with **3** than with **1**. After about 70% reaction, NMR analysis indicated about 90% loss of styrene with **3**, while **1** showed a 5% loss of styrene after about 60% reaction. Apparently the *p*-dimethylamino group of **1** acts as an efficient chain-transfer agent to inhibit the polymerization of styrene. The effect of styrene on **2** is much more pronounced, where the rate is reduced by a factor of about 0.2 with the radical trap.

Light Emission Measurements. Chemiluminescence (CL) from amino peroxides **1** and **2** was noted in *o*-dichlorobenzene at 140 °C in aerated solutions. A representative CL intensity–time plot is shown in Figure 1, where two intensity maxima are observed. The time required to reach maximum intensity for the first peak (t_{max}(A)) corresponds closely to the time required to reach thermal equilibrium after innoculation of the thermally equilibrated solent with peroxide and rapid shaking. That is, the t_{max}(A) values are similar to those expected from prompt emitters such as dioxetanes. Emission associated with peak B is delayed relative to where prompt emission is expected. In some instances, when peak B was located closer to the origin, we were unable to detect peak A.

A survey of the CL from peroxides **1–3** with various additives is given in Table IV. Aerated and nitrogen-purged solutions were compared to see if autooxidation processes were responsible for the CL. To ascertain the relative amounts of triplet- and singlet-state CL from **1**, 9,10-dimbromoanthracene (DBA) and 9,10-diphenylanthracene (DPA) were used as additives.[14] Since this

Table IV. Light Emission Studies with Peroxides 1-3 and Additives in *o*-Dichlorobenzene at 140 °C

peroxide (concn, M)	additive (concn, M)/conditions[a]	$t_{max}(A)$[b]	$t_{max}(B)$[b]	$10^9\Phi_{App}$[c]
1 (0.116)		8	23	2.03
1 (0.116)	N_2, then Ar purge	5	48	0.657
1 (0.116)	DBA (3.45×10^{-4})	9	20	1.74
1 (0.116)	DBA (7.74×10^{-4})	N[d]	16	1.71
1 (0.116)	DBA (14.6×10^{-4})	N[d]	14	1.64
1 (0.116)	DBA (26.2×10^{-4})	10	12	1.46
1 (0.116)	DPA (4.90×10^{-4})	8	20	1.97
1 (0.116)	DPA (9.90×10^{-4})	6	21	2.69
1 (0.116)	DPA (16.2×10^{-4})	8	24	3.33
1 (0.116)	DPA (28.0×10^{-4})	7	20	3.59
1 (0.116)	rubrene (23.5×10^{-4})	N[d]	12	3.69
2 (0.126)		4.5	20	2.08
2 (0.126)	N_2 purge	4	24	0.524
3 (0.104)				0
3 (0.104)	p-$(CH_3)_2NC_6H_5$ (0.142) + DBA (26.2×10^{-4})	3.5	9.5	2.71

[a] Unless specified, an air atmosphere was used. DBA and DPA are 9,10-dibromo- and 9,10-diphenylanthracene, respectively. [b] In minutes. [c] Φ_{App} is the apparent quantum yield (einstein/mole). [d] N means no peak was observed.

method relies on the fluorescence quantum yields of DBA and DPA (Φ_f^{DBA} and Φ_f^{DPA}) and since these values are temperature dependent, the triplet and singlet efficiency values are approximate. Values of Φ_f^{DBA} and Φ_f^{DPA} are calculated to be 0.019 and 0.34 at 140 °C from previously determined parameters.[14c] A plot of $1/\Phi_{App}$ vs. $1/[DPA]$ for 1 gives the following: intercept = $2.24 \pm 0.09 \times 10^8$, slope = $1.39 \pm 0.07 \times 10^5$, $r = 0.997$. From intercept = $1/(\alpha_S\Phi_f^{DPA})$ we calculate the singlet efficiency (α_S) to be approximately 1.3×10^{-6}%. Since added DBA causes a small decrease in Φ_{App}, the usual double-reciprocal plot method was not used to calculate the triplet efficiency (α_T). Instead, α_T was approximated by using an average value of 1.6×10^{-9} einstein/mol for Φ_{App} with 1 and DBA, along with $\Phi_{App} = \alpha_T\Phi_{ET}\Phi_f^{DBA}$, where Φ_{ET} is assumed to be 1/2.42.[14b,c] This gives $\alpha_T \simeq 3.5 \times 10^{-6}$%. The calculations indicate very low efficiencies in the production of both triplets and singlets. Due to the approximations used in treating the data, the exact values of α_T and α_S are uncertain, but they probably represent a reasonable estimate.

Discussion

The attenuated rate acceleration by amino groups, observed in the thermolysis of dioxetanes[6-10] and a perester,[12] was not observed in the thermolysis of peroxides 1 and 2. Activation parameters for the thermolysis of 1 (E_a = 36.2 kcal/mol, log A = 15.45) are in the expected range for a simple peroxide bond homolysis.[13] For example, activation parameters for cumyl *tert*-butyl peroxide in dodecane are E_a = 34.3 kcal/mol and log A = 14.36,[15] while for dicumyl peroxide E_a = 34.5 kcal/mol, and log A = 14.63 in cumene.[16] Amino peroxide 1 does undergo decomposition somewhat faster than the parent unsubstituted peroxide 3 (k_1/k_3 = 5.22/2.52 = 2.07), but this can be reasonably attributed to a normal substituent effect. Small negative ρ values are observed in peroxide bond homolyses. For example, ρ = –0.38 (σ correlation) for benzoyl peroxides,[17] and ρ = –0.22 (σ^+ correlation) for 3-(arylmethyl)-1,2-dioxetanes.[18] From the relative rate k_1/k_3, a ρ value of –0.38 is calculated with $\sigma_{p\text{-}Me_2N}$ = –0.83[19] and ρ = –0.19 with $\sigma^+_{p\text{-}Me_2N}$ = –1.7.[19] The close agreement of the calculated ρ values based on k_1/k_3 with model systems suggests a normal substituent effect by the p-$(CH_3)_3N$ group on simple peroxide bond homolysis. In the absence of styrene, amino peroxide 2 shows a rate accleration vs 1 of about 13-fold (cf. Table III). However, with 0.4 M styrene, the rate enhancement is lowered to a factor of about 3-fold. The large reduction in rate of thermolysis of 2 in the presence of 0.4 M styrene indicates a facile induced decomposition path for 2, such that the unimolecular rate for 2 may not differ significantly from 1. It appears that there is nothing unusual in the thermolysis of amino peroxides 1 or 2 as seen from kinetic data. These data then suggest simple peroxide bond homolysis for 1 and 2.

Although the kinetic data do not suggest unusual effects by the p-$(CH_3)_2N$ group in *producing* radicals from 1 and 2, the product studies indicate that the fate of these alkoxy radicals is quite different from alkoxy radicals produced from 3. Typical of alkyl peroxide decompositions in poor hydrogen atom donor solvents, 3 gives predominately products derived from β scission of *tert*-butoxy and $C_6H_5CH(O)CH_3$ radicals (cf. Table II, no additives). In contrast, alkoxy radicals generated from 1 and 2 abstract hydrogen atoms at the expense of β scission. The most reasonable explanation for increased hydrogen atom abstraction products from 1 and 2 is the presence of the dimethylamino group, which serves as a good hydrogen atom donor. This proposal is supported by the effect of *N,N*-dimethylaniline (DMA) on product yields in the thermolysis of 3. As seen from Table II, a dramatic change from predominantly β scission to hydrogen atom atbstraction products results by addition of 7.85×10^{-2} M DMA. After correction for the concentration differences between DMA and BHT given in Table II (but not the number of donor hydrogen atoms), it appears that DMA is a slightly better hydrogen atom donor than BHT on the basis of alcohol yields). Since BHT is considered to be a good hydrogen atom donor, the results emphasize the facility of the dimethylamino group in this role. The lower product balance in the arylalkyl relative to the *tert*-butyl portion of amino peroxides 1 and 2 is understandable in terms of hydrogen atom abstraction from the dimethylamino group of 1 and 2 or their products. The radicals produced by hydrogen atom abstraction from the di-

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methylamino group should be intercepted in part by oxygen in the aerated solutions. This process did not significantly effect the yields of the *observed* products as seen from Table I, when the thermolysis of **1** was carried out in aerated solution vs. a nitrogen atmosphere.

Thermochemical calculations suggest that some reactions of the amino peroxides have energy sufficient to produce excited-state products. For example, the heat of reaction ($\Delta H_r°$) corresponding to eq 1 is calculated[20] to be −64.3 kcal/mol.[21] The energy available to generate an

$$p\text{-}(CH_3)_2NC_6H_4\underset{\mathbf{1}}{CH(OOC(CH_3)_3)CH_3} \rightarrow p\text{-}(CH_3)_2NC_6H_4COCH_3 + HOC(CH_3)_3 \quad (1)$$

excited state species (E_{AVL}) is given by $E_{AVL} = -\Delta H_r° + fE_a$, where E_a is the activation energy and f is the fraction of the latter quantity that is contributed to E_{AVL}. If f = 1 and E_a = 36 kcal/mol (as observed for **1**), $E_{AVL} \simeq 90$ kcal/mol, which is sufficient to reach both the S_1 and T_1 states of *p*-(dimethylamino)acetophenone.[22] Unfortunately, neither the kinetic nor the product studies suggest a major reaction course directed to production of excited-state products.

In contrast to the negative suggestions from kinetic and product studies, light emission was observed from the thermolysis of both **1** and **2**, but not from that of **3**. The intensity/time plot for most of the measurements was unusual in that two intensity maxima (A and B) were observed (cf. Figure 1). The second and dominant emission (B) is delayed in time from where emission was expected from a compound that directly produces excited-state species. This latter prompt emission corresponds closely to the first peak A. The major amount of CL from either **1** or **2**, corresponding to peak B, must result from a reaction that occurs subsequent to peroxide bond homolysis of **1** or **2**. With a nitrogen/argon purge, the apparent CL quantum yield (Φ_{App}) shows a significant decrease for both **1** and **2** (Table IV). This suggests that an autoxidation process is responsible for the majority of the CL produced. It appears that after a 30-min nitrogen purge there is still enough oxygen present to cause some CL. The increased value of t_{max}(B), which is particularly evident with **1**, is consistent with a consecutive reaction where the velocity of the subsequent autoxidation process is reduced at lower oxygen concentration.[23] The occurrence of an autoxidation reaction is also consistent with the product studies which indicated hydrogen atom abstraction from the dimethylamino group. Trapping of the resulting radicals with oxygen would initiate the autoxidation process. We have not pursued the reaction(s) in the autoxidation process that may be responsible for CL. However, it seems likely that a Russell termination reaction of two peroxy radicals[24] may be respnsible for CL as proposed in other autoxidation reactions.[25]

Further evidence for an autoxidative CL process involving the dimethylamino group as the major source of emission from **1** and **2** is seen from the thermolysis of **3** with and without DMA. In aerated solutions, no CL is observed from the thermolysis of **3** (cf. Table IV). But with 0.142 M DMA and **3**, CL is observed where the Φ_{App} is similar to that observed with **1** and **2**. Related to these observations is the reported CL from the thermolysis of dicyclohexyl peroxydicarbonate and DMA in the presence of oxygen.[26] Here, CL was suggested to result from peroxy radical termination reactions.

Typical of autoxidative CL processes, the CL quantum yields for **1** and **2** are low.[25] Although the accuracies of the triplet and singlet efficiencies are uncertain, they represent a useful approximate calibration. The approximate triplet and singlet efficiencies for **1** were calculated to be 3.5×10^{-6}% and 1.3×10^{-6}%, respectively. By comparison, a relatively efficient dioxetane such as tetramethyl-1,2-dioxetane generates triplet and singlet acetone with efficiencies of about 36% and 0.43%, respectively.[14c] Thus, even the dominant autoxidation CL associated with **1** is trivial compared to most dioxetanes.

Although the CL associated with peak A is small compared to peak B, the former emission holds the last possibility of direct CL from **1** and **2**. This possibility seems very unlikely, since an "A" peak is also observed in the thermolysis of **3** with DMA. We do not have an explanation for the appearance of the small "A" peak.

Intermolecular electron-transfer processes with certain peroxides have resulted in CL (CIEEL).[5,12,27] The intensity of CL has been correlated with the oxidation potential of the donor in these reactions. The CL associated with **1** cannot be associated with a CIEEL process on the basis of this criterion. Both DPA and rubrene give approximately the same Φ_{App} values (Table IV), but the oxidation potentials differ considerably (DPA $\approx$ 1.22 V and rubrene $\approx$ 0.82 V vs. SCE).[12]

Intramolecular electron transfer CL has been detected where the donor is the *p*-dimethylaminophenyl group and the acceptor is a dioxetane[6] and a perester.[12] The reduction potential of the dioxetane is estimated to lie between +0.2 and −0.4 V vs. SCE,[6] while the half-wave potential of peresters is reported to lie between −0.8 and −1.0 V.[28] It appears that the p-$(CH_3)_2NC_6H_4$ group suffices as a donor for peroxides with reduction potentials as negative as −0.8 to −1.0 V. Reduction potentials for di-*tert*-butyl peroxide and other dialkyl peroxides are reported to be more negative than −2 and −1 V, respectively.[28] The lack of either rate acceleration or CL induced by the p-$(CH_3)_2NC_6H_4$ group suggests that the reduction potentials of dialkyl peroxides are too negative to allow electron-transfer processes. How much more negative than about −1 V the reduction potential of the peroxide can be and still undergo intramolecular electron transfer with the p-$(CH_3)_2NC_6H_4$ group is yet to be discovered.

Experimental Section[29]

Materials. Chlorobenzene was distilled from P_2O_5 and stored over Drierite. *o*-Dichlorobenzene was distilled and stored over

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(21) The calculated heats of formation ($\Delta H_f°$) for **1**, p-$(CH_3)_2NC_6H_4COCH_3$, and t-C_4H_9OH are −29.3, −18.5, and −75.1 kcal/mol, respectively.

(22) We estimate the E_{S_1} and E_{T_1} values of p-$(CH_3)_2NC_6H_4COCH_3$ to be approximately 84 and 69 kcal/mol, respectively.

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(29) Melting points are corrected, and boiling points are uncorrected. Temperatures reported with kinetic data are corrected. NMR spectra were obtained with a Varian EM-390 spectrometer and IR spectra with a Perkin-Elmer 337 spectrometer. GLC analyses were performed on a Varian-1200 (FID) chromatograph equipped with a Hewlett-Packard 3390A reporting integrator.

Drierite. *p*-(Dimethylamino)benzaldehyde (Aldrich) was used as supplied as a GLC standard.

1-[4-(Dimethylamino)phenyl]ethanol. This carbinol was prepared from methylmagnesium iodide and *p*-(dimethylamino)benzaldehyde[30] (Aldrich) in 79% yield and was recrystallized from about 8:1 hexane/benzene: mp 61–62 °C (lit.[30] mp 60 °C); IR (CCl_4) 3600, 3450, 3080, 3050, 3020, 2960, 2860, 2780, 1340 cm^{-1}; NMR (CCl_4) δ 6.96 (AB, J = 8 Hz, 2 H), 6.43 (AB, J = 8 Hz, 2 H), 4.64 (q, J = 7 Hz, 1 H), 1.29 (d, J = 7 Hz, 3 H), 2.83 (s, 6 H), 1.37 (s, 1 H).

2-[4-(Dimethylamino)phenyl]-2-propanol. The reaction of methylmagnesium iodide with ethyl *p*-(dimethylamino)benzoate (Aldrich) was used to prepare this carbinol: 89% yield; IR (CCl_4) 3400 (br), 3090, 3060, 3030, 2960, 2850, 1650, 1510, 1480, 1445, 1345, 1280, 1265, 1060 cm^{-1}; NMR (CCl_4) δ 7.17 (AB, J = 9 Hz, 2 H), 6.49 (AB, J = 9 Hz, 2 H), 2.85 (s, 6 H), 2.18 (s, 1 H), 1.48 (s, 6 H). This carbinol was used without further purification to prepare peroxide **2**.

***p*-(Dimethylamino)acetophenone.** A procedure similar to that previously reported[31] was used to prepare this compound from *N,N*-dimethylaniline and acetic anhydride, with zinc chloride catalysis, in about 2% yield: mp 103.5–105.5 °C (lit.[31] mp 105 °C); IR (CCl_4) 3030, 2970, 2920, 2860, 2785, 1653 cm^{-1}; NMR (CCl_4) δ 7.65 (AB, J = 9 Hz, 2 H), 6.48 (AB, J = 9 Hz, 2 H), 3.03 (s, 6 H), 2.40 (s, 3 H).

1-[4-(Dimethylamino)phenyl]ethyl *tert*-Butyl Peroxide (1). To a magnetically stirred solution of 0.545 g (6.06 mmol) of *tert*-butyl hydroperoxide (Lucidol, purified by azeotropic distillation[32]) in 20 mL of methylene chloride was added 0.100 g (0.581 mmol) of *p*-toluenesulfonic acid (*p*-TsOH, MCB), followed by the addition of 1.00 g (6.06 mmol) of 1-[4-(dimethylamino)-phenyl]ethanol. The reaction mixture was protected from moisture with a calcium chloride drying tube. Stirring was continued at room temperature for 7 h, and the mixture was washed with four 2-mL portions of 10% sodium bicarbonate solution. The methylene chloride phase was dried over magnesium sulfate and then concentrated with a rotary evaporator (bath temperature ~30 °C) to give 1.55 g of a brown liquid. The crude product was distilled through a micromolecular still at a 0.05-mm pressure (bath temperature ~85 °C) to give 1 in 77% yield as a light tan semisolid: IR (CCl_4) 3080, 3030, 3020, 2970, 2910, 2870, 1605, 1505, 1440, 1360, 1340, and 1065 (possible C–N stretching), 870 cm^{-1} (possible 0–0 stretch); NMR (CCl_4) δ 6.93 (AB, J = 9 Hz, 2 H), 6.42 (AB, J = 9 Hz, 2 H), 4.66 (q, J = 6 Hz, 1 H), 1.33 (d, J = 6 Hz, 3 H), 2.86 (s, 6 H), 1.11 (s, 9 H); MS, m/e (relative intensity) 237 (M^+, 3.9), 164 (2.7), 163 (6.3), 148 (100), 120 (7.1), 57 (2.5).

2-[4-(Dimethylamino)phenyl]propyl *tert*-Butyl Peroxide (2). To a stirred solution of 1.00 g (11.1 mmol) of *tert*-butyl hydroperoxide (Lucidol, purified[32]) in 20 mL of methylene chloride, was added 75 mg (0.44 mmol) of *p*-TsOH followed by 2.00 g (11.1 mmol) of 2-[4-(dimethylamino)phenyl]-2-propanol. After stirring 1 h at room temperature, an additional 20 mg (0.12 mmol) of *p*-TsOH was added, and after 1.5 h an additional 25 mg (0.15 mmol) of *p*-TsOH was added. The reaction mixture was stirred for a total of 2.5 h, and then it was washed with five 10-mL portions of 10% sodium bicarbonate solution. After drying over magnesium sulfate, the solvent was removed under reduced pressure to give 1.24 g of a dark brown visious liquid. This crude product was purified by distillation through a micromolecular still at 0.005 mm pressure (bath 85–92 °C) to give **2** in 28% yield as a clear colorless liquid: IR (CCl_4) 3090, 2980–2700, 1605, 1510, 1360, 1285, 1190, 1110, 1010, 870 cm^{-1} (w); NMR (CCl_4) δ 6.98 (AB, J = 8.5 Hz, 2 H), 6.34 (AB, J = 8.5 Hz, 2 H), 2.81 (s, 6 H), 1.44 (s, 6 H), 1.13 (s, 9 H); MS, m/e (relative intensity) 251 (M^+, 3.7), 194 (8.2), 177 (12), 162 (100).

1-Phenylethyl *tert*-Butyl Peroxide (3). To a magnetically stirred solution of 0.900 g (10.0 mmol) of *tert*-butyl hydroperoxide (Lucidol, purified[32]) in 2 mL of propionic acid (MCB), which was cooled in an ice-bath, was carefully added 0.18 mL (3.2 mmol) of concentrated sulfuric acid dropwise down the wall of the flask. Now 1.22 g (10.0 mmol) of α-phenylethyl alcohol (MCB) was slowly added in 1 mL of propionic acid. The ice bath was removed, stirring was continued for 7.7 h, and then 10 mL of water was added. The mixture was extracted with three 5-mL portions of methylene chloride, and the combined organic phases were washed with six 2-mL portions of 10% sodium bicarbonate solution, followed by three 2-mL water washes. The organic extract was dried over magnesium sulfate and concentrated on a rotary evaporator (bath temperature ~35 °C) to give 2.72 g of a light yellow liquid. This liquid was distilled through a micro spinning annular (Teflon) band column to give two fractions: (1) bp 53–55 °C (1.0 mm) [lit.[33] bp 56–57 °C (1 mm)], 0.243 g; (2) bp 63–67 °C (1.0 mm) [lit.[34] bp 91–92 °C (5 mm)], 0.698 g. Fraction 1 corresponded to **3**: 12.5% yield; IR (CCl_4) 3080, 3055, 3025, 2975, 2920, 872, 696 cm^{-1}; NMR (CCl_4) δ 7.12 (s, 5 H), 4.78 (q, J = 6 Hz, 1 H), 1.38 (d, J = 6 Hz, 3 H), 1.17 (s, 9 H). Fraction 2 corresponded to 1-phenylethyl propionate: 39% yield; IR (CCl_4) 3080, 3060, 3030, 2980, 2930, 1740, 1188, 1060, 696 cm^{-1}; NMR (CCl_4) δ 7.14 (s, 5 H), 5.69 (q, J = 6 Hz, 1 H), 1.46 (d, J = Hz, 3 H), 2.23 (q, J = 8 Hz, 2 H), 1.07 (t, J = 8 Hz, 3 H).

Kinetic Measurements. Chlorobenzene solutions of **1–3** (with or without additives) were sealed in 5-mm NMR tubes and immersed in a thermostated oil bath. The tubes were periodically removed and quenched in cold water at recorded times. NMR spectra were measured, the tubes were returned to the bath, and the timer was again started. Rate coefficients were determined from first-order plots by using absorption area ratios relative to the total aromatic area (primarily chlorobenzene) and the least-squares method. Reasonably good agreement was obtained by using the α-methyl, methine, or *tert*-butyl protons in **1** or **2** to determine the rate coefficient, since all these absorptions proceeded to zero after 10 half-lives. The appearance of the *tert*-butyl alcohol C–H protons occurred at higher field by about 0.1 ppm from the *tert*-butyl peroxy protons and did not interfere. The *tert*-butyl group, with more protons, typically gave a higher correlation coefficient, and the reported rate coefficients are based on the disappear of this group in **1–3**.

Product Studies. Solutions of **1–3** in chlorobenzene were heated in sealed 1-mm capillary tubes for about 10 half-lives at 129 °C in a thermostated oil bath with an internal standard. A 9 ft × $^1/_8$ in. 5% Carbowax 20M on Varaport 30 column (column 60 °C, detector and injector 220 °C, flow rate 33 mL of nitrogen/min) was used for the analysis of acetone (t_R = 2.9 min) and *tert*-butyl alcohol (t_R = 3.7 min). The column temperature was programmed to 120 °C in order to obtain the chlorobenzene peak ($t_R \simeq$ 10 min). A 5 ft. × $^1/_8$ in. 5% OV-17 on Varaport 30 column (column 190 °C, detector and injector 220 °C, flow rate 33 mL of nitrogen/min) was used to analyze the products from **1**: 1-[4-(dimethylamino)phenyl]ethanol (t_R = 2.7 min),[35] *p*-(dimethylamino)benzaldehyde (t_R = 7.1 min), *p*-(dimethylamino)-acetophenone (t_R = 8.7 min) [chlorobenzene (t_R = 0.96 min)]. Analysis of the products from **2** was carried out under the same conditions as for **1**. The yield of 2-[4-(dimethylamino)-phenyl]-2-propanol was determined from the *p*-(dimethylamino)-α-methylstyrene peak (t_R = 3.37 min), which resulted from dehydration of the carbinol. The styrene peak was confirmed by comparison of t_r values with an authentic sample. A 5 ft × $^1/_8$ in. 7% Carbowax 20 M on Varaport 30 column (column 140 °C, detector and injector 225 °C, flow rate 33 mL/min) was used to analyze products from **3**: benzaldehyde (t_R = 1.8 min), acetophenone (t_R = 2.8 min), α-phenylethyl alcohol (t_R = 4.6 min [chlorobenzene (t_R = 0.69 min)].

TLC was used to confirm the products from **1**. Merck F-254 precoated silica gel on aluminum strips were developed with 95% benzene/5% ethyl acetate and visualized with iodine. The R_f values for authentic compounds and those from the thermolysis of **1** in chlorobenzene at 129 °C were, respectively: 1-[4-(dimethylamino)phenyl]ethanol, 0.18, 0.18; *p*-(dimethylamino)-

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benzaldehyde, 0.23, 0.22; p-(dimethylaminoacetophenone, 0.08, 0.08. Additional spots appeared from the reaction mixture with R_f values of 0.02, 0.05, 0.12, 0.32, and 0.47, which were not identified.

Light Emmission Measurements. The apparatus and techniques used to measure light emission were previously described.[1e,14c,36] For the present measurements, an electrically heated thermostated aluminum block was used in place of the water bath. The o-dichlorobenzene solvent with or without additives (3.00 mL) was thermostated in a 1-cm stoppered cell at 140 °C and injected with 50 μL of a peroxide solution. The cell was rapidly removed, shaken, and returned to the instrument. The output from the PMT was traced on a strip-chart recorder, and the area was integrated with a planimeter. The system was calibrated with tetramethyl-1,2-dioxetane and DBA, where α_T = 36% is assumed.

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Registry No. 1, 83026-53-3; 2, 83026-54-4; 3, 28047-94-1; 4, 5338-94-3; 5, 2124-31-4; 2-[4-(dimethylamino)phenyl]-2-propanol, 83026-55-5; *tert*-butyl hydroperoxide, 75-91-2; α-phenylethyl alcohol, 98-85-1.

Arylation and Heteroarylation of Photochemically Generated Purinyl Radicals[1]

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Neutral purinyl radicals are new transient intermediates in nucleic acid chemistry. Photolysis of 9-substituted 6-iodopurines with ultraviolet light provides an excellent method for generating purin-6-yl radicals (or caged radical pairs), through homolysis of the weak carbon–iodine bond. The intermediacy of these radicals can be inferred from ESR data. When photolysis is carried out in the presence of benzene, the nascent purinyl radicals (or radical pairs) are intercepted and the corresponding 9-substituted 6-arylpurine is isolated. Heteroaromatic arylations also are possible. Thus, photolysis in the presence of *N*-methylpyrrole results in the formation of 9-substituted 6-(*N*-methylpyrr-2-yl)purine. Furan and thiophene derivatives also undergo photoarylation. The products are consistent with the preferred sites for radical attack upon these heteroaromatics. Reaction with diphenyl disulfide results in the formation of the corresponding purinyl thioether.

We have reported recently the use of a diazotization/deamination procedure for the conversion of 6-aminopurine precursors to various 6-halogenated purines.[2] This deamination procedure was utilized for the direct synthesis of the antibiotic nebularine, from readily available adenosine.[3] These reactions apparently proceed via diazotization of the 6-amino group to form unstable intermediate diazonium salts or azo compounds which decompose homolytically under the reaction conditions to generate purinyl radicals. We have discovered that 9-substituted purin-6-yl radicals or corresponding radical pairs can be relatively cleanly generated by the photolysis of 6-iodopurines. This paper reports on the generation and specific arylation and heteroarylation of transient purinyl radicals.

Direct attachment of aryl groups to the purine ring has not been reported to occur in nature. Few 6-arylpurines have been synthesized, although 6-phenylpurine and some *N*-alkyl derivatives have been prepared.[4,5] 6-(3-Methylpyrrol-1-yl)purine, a methylpyrrole attached to purine through the pyrrole nitrogen at position 6, has been prepared from zeatin.[6] Synthetic 2-arylpurines,[7] which have been evaluated as coronary vasodilators, as well as 8-phenylpurines,[8] are also known. The only literature method for direct 6-arylation of purines is nucleophilic displacement of chlorine from 6-chloropurines by phenyllithium. The 6-arylpurines, especially those possessing heterocyclic substituents in the 6-position, bear a structural resemblance to cytokinins such as kinetin and its riboside,[9] although the aminomethylene spacer group is absent in the arylpurines. Synthetic aryl and heteroaryl purines also may be useful as biochemical probes for the study of enzyme-catalyzed reactions.

Results and Discussion

The preparation of biaryls via photolysis of iodo aromatics such as iodobenzene has been the subject of a number of investigations.[10,11] These reactions proceed via homolysis of the weak aryl carbon–iodine bond.[12] Phenyl radicals generated in heteroaromatic solvents such as furan, thiophene, and pyrrole afford modest yields of phenyl-substituted heterocyclic products.[13,14] Preferred sites for radical attack on various heteroaromatics have been experimentally determined.[15] Photoarylations in which a heteroaryl iodide is employed generally proceed as for iodobenzene.[16-18] When shorter wavelength UV light is

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