

**Methyl Myristate.** Methyl myristate (99%, Aldrich Chemical Co.) was distilled before use: mp 19 °C (lit. mp 19 °C);  $\Delta H_{\text{fus}}$  12.0  $\pm$  0.18; no transitions other than fusion were detected in the temperature range studied.

**Dodecyl Alcohol.** Dodecyl alcohol (Eastman Kodak) was recrystallized (aqueous ethanol) before use: mp 24.5–25 °C (lit. mp 22–26 °C);  $\Delta H_{\text{fus}}$  9.6  $\pm$  0.22 kcal/mol; no transitions other than fusion were detected in the temperature range studied.

**1,3-Diphenylacetone.** 1,3-Diphenylacetone (Aldrich Chemical Co.) was distilled, recrystallized (aqueous ethanol), and sublimed before use: mp 34–34.8 °C (lit. mp 35 °C);  $\Delta H_{\text{fus}}$  4.83  $\pm$  0.2 kcal/mol; no transitions other than fusion were detected in the temperature range studied.

**Octadecyl Alcohol.** Octadecyl alcohol (Eastman Kodak) was recrystallized (95% ethanol) and sublimed: mp 57–58 °C (lit. mp 59.4–59.8 °C);  $\Delta H_{\text{fus}}$  16.75  $\pm$  0.65 kcal/mol.

**2,4,6-Tri-*tert*-butylphenol.** 2,4,6-Tri-*tert*-butylphenol (Aldrich Chemical Co.) was recrystallized (1:1 hexane–ethanol) before use: mp 129–130.2 °C (lit. mp 128–30 °C);  $\Delta H_{\text{fus}}$  4.65  $\pm$  0.1 kcal/mol; no transitions other than fusion were detected in the temperature range studied.

**Cinnamyl Alcohol.** Cinnamyl alcohol (Matheson Coleman And Bell) was recrystallized from hexane and sublimed before use: mp 33.9–35.9 °C (lit. mp 33 °C);  $\Delta H_{\text{fus}}$  3.76  $\pm$  0.2; no tran-

sitions other than fusion were detected in the temperature range studied.

**Thymol.** Thymol (Mallinckrodt) was recrystallized before use: mp 50.5–51.5 °C (lit. mp 51.5–52 °C);  $\Delta H_{\text{fus}}$  5.3  $\pm$  0.13 kcal/mol; no transitions other than fusion were detected in the temperature range studied.

**Triphenylamine.** Triphenylamine (Eastman Kodak) was recrystallized (ethyl acetate) and sublimed before use: mp 126.2–127.2 °C (lit. mp 127 °C);  $\Delta H_{\text{fus}}$  5.95  $\pm$  0.1; no transitions other than fusion were detected in the temperature range studied.

**Acknowledgment.** We are grateful to the Weldon Spring Fund of the University of Missouri and the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of portions of this work.

**Supplementary Material Available:** Tables containing the names and experimental fusion entropies and enthalpies of the 226 monosubstituted and 218 multisubstituted hydrocarbon derivatives used in this correlation as well as the values estimated by the group additivity parameters of Table II are available (44 pages). Ordering information is given on any current masthead page.

## Photoreduction of $\pi, \pi^*$ and $n, \pi^*$ Triplet Carbonyls by Amines: 2-Naphthaldehyde, 2-Acetonaphthone, *p*-Aminobenzophenone, and *p*-Cyanobenzophenone. Catalysis by Aniline and Aliphatic Thiol

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Photoexcited 2-naphthaldehyde (2-NA), 2-acetonaphthone (2-AN), and *p*-aminobenzophenone (*p*-AMB), with  $\pi, \pi^*$  triplets, do not abstract H from  $\alpha$ -C or N of a primary amine, 2-butylamine. Reductions are catalyzed by aniline plus aliphatic thiol, but not by thiol alone, to  $\phi = 0.6, 0.5,$  and  $0.35,$  respectively. These triplets abstract H from N of a secondary amine, diisopropylamine, but the resulting ketyl and alkylaminyl radicals disproportionate, regenerating starting materials; these reductions are catalyzed by thiol to  $\phi = 0.6$ – $0.5$ . Catalysis results from sequences of H atom transfers, from thiol to aminyl radicals, and from  $\alpha$ -C of amines to thiyl radical, forming  $\alpha$ -aminoalkyl radicals, which lead to final reduction products. Reduction of 2-NA by tertiary amines, triethylamine (TEA) and *N,N*-diethylethanolamine, is efficient in acetonitrile,  $\phi = 1.5,$  and less so in benzene,  $\phi = 0.5$  and  $0.7,$  respectively. Values for 2-AN are lower,  $0.5$ – $0.6$  in acetonitrile, and  $<0.1$  and  $0.4,$  respectively, in benzene. *p*-AMB is reduced by TEA in benzene,  $\phi = 0.3$ . *p*-Cyanobenzophenone, with an  $n, \pi^*$  triplet, is reduced by these amines, in benzene, with  $\phi = 0.8$  by the primary amine,  $\phi = 1.4$  by TEA, and  $\phi$  increased from  $0.3$  to  $0.5$  by thiol in reduction by the secondary amine. Relations of reactivity to carbonyl reduction potential, triplet-state energy and configuration, ionization potential of amine, and medium polarity are discussed.

### Introduction

Photoreduction of aromatic carbonyl compounds by amines is affected by excited-state configuration, degree of substitution on N, and polarity of environment.<sup>1</sup> The reactions generally proceed via initial charge-transfer interaction,  $k_{\text{ir}},$ <sup>2</sup> which may be followed, to varying degree, by (i) spin inversion and return to starting materials,  $k_{\text{e}},$ <sup>2</sup> (ii) formation of free cation and anion radicals,<sup>3</sup> or (iii)

hydrogen transfer from  $\alpha$ -C,  $k_{\text{h}},$  or from N,  $k'_{\text{h}}$  forming ketyl radical, I, and  $\alpha$ -aminoalkyl radicals II or IV, or alkylaminyl radical, III, respectively, eq 1.<sup>2,4</sup> Values of  $k_{\text{ir}}$  rise with decreasing ionization potential of donors,<sup>5–8</sup> from primary to secondary to tertiary amines of related structure, and may also be correlated with ionization potential of donor-derived radicals.<sup>9</sup>

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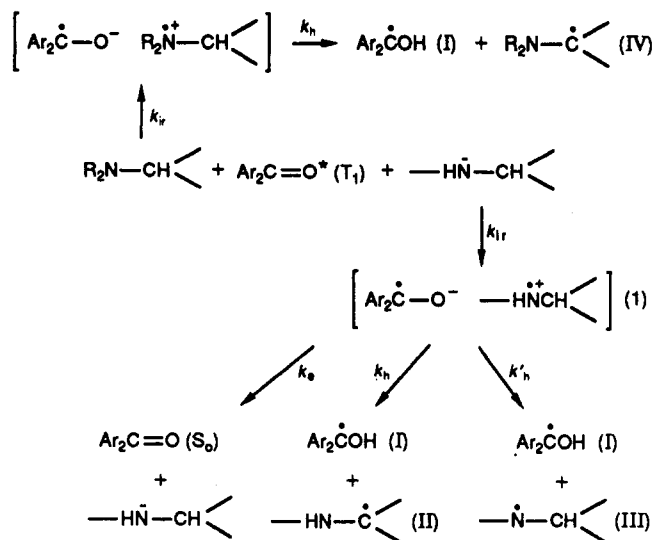
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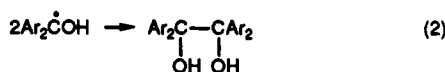
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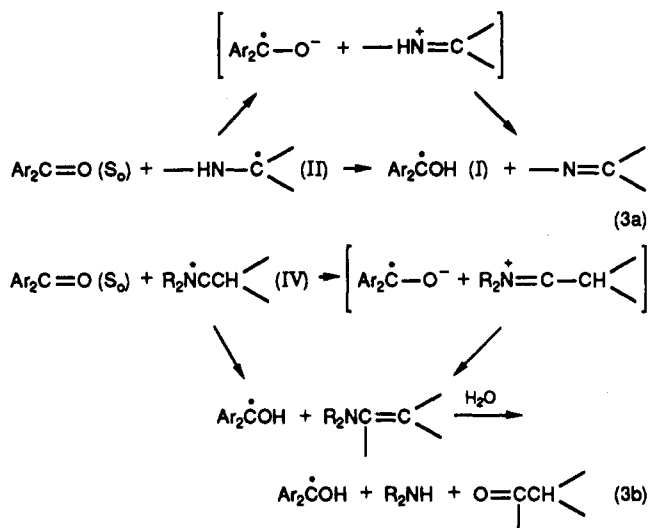
(8) Abakumov, G. A.; Chesnokov, S. A.; Cherkasov, V. K.; Razuvaev, G. A. *Chem. Abstr.* 1985, 103, 122727h.



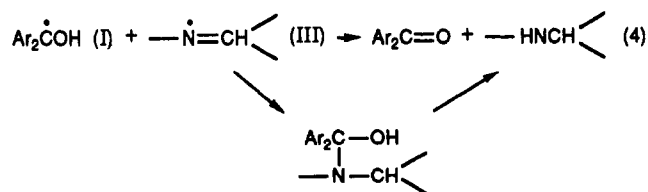
The initial reaction of the  $n, \pi^*$  triplet of benzophenone with members of the three classes of aliphatic amines in benzene leads to ketyl radical with unit quantum yield,  $\phi_{\text{ketyl}} = 1$ ,<sup>4</sup> but yields of final product,  $\phi_{\text{red}}$ , as from dimerization of ketyl radicals, eq 2, vary, less than one with



a secondary amine, and greater than one with primary and tertiary amines. Overall  $\phi_{\text{red}}$  approaches 1.6 in reduction by triethylamine (TEA) in aqueous pyridine, indicating that  $\alpha$ -aminoalkyl radicals reduce ground-state ketone, eq 3; the appropriate oxidative deamination products were

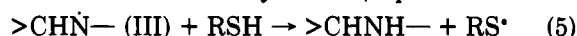


found.<sup>10</sup> This slower second step occurs with rates and yields related to ease of reduction of the ketone.<sup>11</sup> The lower reduction yields with primary and secondary amines than with tertiary are attributed to partial formation of N-centered alkylaminyl radicals, III,<sup>4,12</sup> more from secondary than from primary amines. These disproportionate with ketyl radicals, regenerating starting materials, eq 4, in competition with pinacol formation via ketyl dimerization, or reduction of ground-state ketone.

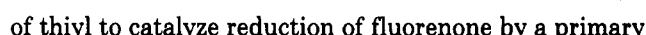


Ketones with  $\pi, \pi^*$  or charge-transfer (CT) triplets have lower reactivity. Fluorenone is reduced inefficiently by primary and secondary amines,  $\phi_{\text{red}} \leq 0.2$ , but efficiently by TEA in cyclohexane,  $\phi_{\text{red}} = 0.9$ .<sup>13</sup> Low efficiency is found in neat TEA or TEA in 2-propanol, and arises from low triplet yields.<sup>14-16</sup> Similarly, *p*-aminobenzophenone, *p*-AMB, is reduced fairly efficiently by TEA in cyclohexane, inefficiently by a secondary amine, and little if at all by primary amines and alcohols;<sup>2a</sup> its intersystem crossing is low in acetonitrile and essentially fails in 2-propanol.<sup>17</sup> 2-Naphthaldehyde, 2-NA, and 2-acetonaphthone, 2-AN, are also reduced inefficiently by a secondary and essentially not at all by a primary amine; they are reduced by TEA with high  $\phi_{\text{red}}$  in acetonitrile, and low  $\phi_{\text{red}}$  in nonpolar solvents; their triplet yields appear unaffected by solvent polarity.<sup>18</sup>

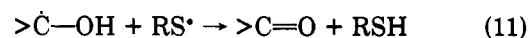
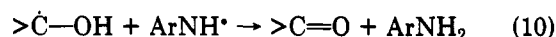
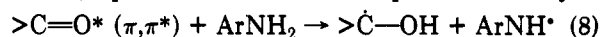
Remarkably, aliphatic thiol, a very inefficient photoreducing agent<sup>12</sup> and a retarder of photoreduction by alcohols,<sup>19</sup> effectively catalyzes the inefficient photoreduction of fluorenone by a secondary amine<sup>20</sup> and also increases quantum yields of photoreduction of benzophenone by both primary and secondary amines.<sup>12</sup> This catalysis is attributed to conversion of disproportionating N-centered radicals, III, to product forming C-centered radicals, II, by a sequence of hydrogen atom transfers from thiol to III and from  $\alpha$ -C of amine to thiyl radical, eqs 5 and 6. This



process competes effectively with the yield reducing disproportionations of ketyl radical which may occur.<sup>12</sup> Experiments with added *tert*-butylamine, an efficient source of aminyl radicals, showed that the direct conversion, analogous to eq 7, did not occur efficiently.<sup>12</sup> The failure



of thiyl to catalyze reduction of fluorenone by a primary amine was attributed to low abstraction of H from either  $\alpha$ -C or N of the primary amine. Catalysis was achieved by addition of aniline; the low energy  $\pi, \pi^*$  triplet abstracts H from N of the aromatic amine, with its weaker N-H bond, and initiates an arylaminyl-thiyl-aminoalkyl radical sequence, eqs 8, 9, and 6,<sup>20</sup> leading to photoreduction product, eq 2, in competition with possible disproportionations, eqs 10 and 11. We now report such catalysis



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in related systems. Preliminary results were published in the proceedings of a conference.<sup>21</sup>

### Experimental Section

**Materials.** 2-NA, 2-AN, and p-AMB (Aldrich) were recrystallized from ethanol, hexane, and 2-propanol-cyclohexane, respectively. *p*-Cyanobenzophenone, *p*-CNB, was prepared from *p*-cyanobenzoyl chloride, following a literature procedure.<sup>22</sup> 2-Butylamine, triethylamine, *N,N*-diethylethanolamine, DEOA, triethanolamine, TEOA, and *n*-pentanethiol (Aldrich), diisopropylamine and benzene (Eastman), and aniline (Fisher) were distilled. Acetonitrile was from Burdick and Jackson. Aberchrome-540 was from Aberchromics Ltd., Davies Chemical Labs, University College of Wales, Dyfed Wales, U.K.

**Methods.** Aliquots, 3 or 4 mL, of solutions of the required concentrations of reagents were prepared and transferred into 1 cm square quartz photolysis cells. Equipment and degassing procedure were as previously described;<sup>20</sup> irradiation and quantum yield determinations were carried out in accordance with procedure b, ref 20. *p*-CNB, *p*-AMB, 2-NA, and 2-AN were irradiated at 344, 366, 334, and 334 nm, respectively. Aberchrome-540 was used as actinometer.<sup>23</sup> Its absorbance at 494 nm increased appropriately at the irradiation wavelengths. This increase was followed for several periods of 0.5–1.0 min each. The light flux, *I*, is given by eq 12, where  $\Delta OD/\Delta t$  is the rate of increase in

$$I = \frac{(\Delta OD/\Delta t)V}{\phi \epsilon d} \text{ (mol photon } t^{-1}\text{)} \quad (12)$$

absorbance of Aberchrome-540; *V* is volume of the solution in liters;  $\phi$  is the quantum yield, and its value is 0.2; *d* is absorption cell pathlength in centimeters; and  $\epsilon$  is the molar extinction coefficient,  $\epsilon = 8225$  for Aberchrome-540. Light intensity measurements were made before and after sample irradiation, and the average intensity was used.

The decrease in the amount of carbonyl compound,  $\Delta C/\Delta t$  was calculated from eq 13, where  $\Delta OD/\Delta t$  is the rate of decrease of

$$\frac{\Delta C}{\Delta t} = \frac{(\Delta OD/\Delta t)V}{\epsilon d} \text{ (mol } t^{-1}\text{)} \quad (13)$$

absorbance of the sample solution, *V* and *d* are as above, and  $\epsilon$  is the molar extinction coefficient of the carbonyl compound. The quantum yield of photoreduction,  $\phi_{red}$ , is  $(\Delta C/\Delta t)/I$ . The procedure gave results consistent with those found with ferrioxalate actinometer in photoreduction of fluorenone by TEA.<sup>13</sup> The quantum yields reported below are the averages of several determinations with experimental error of  $\pm 10\%$ .

In reduction by tertiary amines the dependence of  $\phi_{red}$  on amine concentration is formulated in eq 14,<sup>18</sup> where *a* includes the

$$1/\phi = 1/af + k_d/afk_{ir} \text{ (amine)} \quad (14)$$

fractional triplet yield and the contribution of the second reduction, eq 3, and *f* is the fraction of reaction of triplet which leads to hydrogen abstraction. The ratio of slope to intercept of the plot of  $1/\phi$  vs  $1/(\text{amine})$  is  $k_d/k_{ir}$ , where  $k_d$  is the rate constant for self- and solvent-induced deactivation of triplet, and  $k_{ir}$  is the rate constant for consumption of the triplet by amine. The reciprocal of the intercept is the limiting quantum yield,  $\phi_{lim}$ . Values of  $k_{ir}$  for reactions of 2-NA and 2-AN with TEA in acetonitrile and in benzene were estimated previously from retardation of these reactions by the quencher, piperylene, and these in turn led to values of  $k_d$  in these solvents<sup>18</sup> which are applied in this study.

The effect of aniline, as quencher Q, on photoreduction of *p*-AMB by TEA is formulated in eq 15,<sup>18</sup> where  $k_{ir} = 4 \times 10^7 \text{ M}^{-1}$

$$\phi_o/\phi = 1 + \frac{k_q(Q)}{k_{ir}(\text{TEA}) + k_d} \quad (15)$$

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**Table I. Photoreduction of 0.0006 M 2-Naphthaldehyde, 2-NA, and 0.0006 M 2-Acetonaphthone, 2-AN, by 2-Butylamine: Effects of 0.004 M 1-Pentanethiol, RSH, and 0.004 M Aniline**

carbonyl compd	amine, M	RSH	C <sub>6</sub> H <sub>5</sub> NH <sub>2</sub>	solvent	$\phi_{red}$
2-NA	0.025	+	–	CH <sub>3</sub> CN	0.00
	0.025	+	+		0.31
	0.10	–	–		0.00
	0.10	+	+		0.54
	0.50	+	–		0.11
2-NA	0.50	+	+	C <sub>6</sub> H <sub>6</sub>	0.34
	0.10	+	–		0.00
	0.10	+	+		0.44
2-AN	0.50	+	+	CH <sub>3</sub> CN	0.61
	0.10	–	–		0.00
	0.10	+	–		0.03
2-AN	0.50	+	+	C <sub>6</sub> H <sub>6</sub>	0.46
	1.0	+	+		0.34
	0.10	+	+		0.29
2-AN	0.50	+	+	C <sub>6</sub> H <sub>6</sub>	0.48
	1.0	+	+		0.37

**Table II. Photoreduction of 0.0006 M 2-Naphthaldehyde and 0.0006 M Acetonaphthone by Diisopropylamine: Catalysis by 0.004 M 1-Pentanethiol (RSH)**

carbonyl compd	amine, M	RSH	solvent	$\phi_{red}$
2-NA	0.026, 0.10, 1.0	–	CH <sub>3</sub> CN	<0.02
	0.026, 0.10, 1.0	+		0.61
2-NA	0.10	–	C <sub>6</sub> H <sub>6</sub>	0.00
	0.10, 0.50, 1.0	+		0.13
2-AN	0.10	–	CH <sub>3</sub> CN	0.00
	0.10	+		0.20
	0.50	+		0.51
2-AN	0.10	–	C <sub>6</sub> H <sub>6</sub>	0.00
	0.1, 0.5	+		0.11

$s^{-1}$  and  $k_d = 4 \times 10^5 \text{ s}^{-1}$ ,<sup>2a</sup>  $\phi_o$  and  $\phi$  are the quantum yields of photoreduction in the absence and presence of aniline, respectively.

### Results

Irradiation of 2-NA with a primary amine, 2-butylamine, in acetonitrile, alone or with 0.004 M thiol, led to little reduction at 0.5 M amine, and none at lower concentration, Table I. Thiol plus aniline (0.004 M) catalyzed reduction to  $\phi_{red}$  0.31, 0.54, and 0.34 at 0.025, 0.10, and 0.50 M amine, respectively. In benzene, added thiol again led to no reduction, while in combination with aniline,  $\phi_{red}$  values of 0.44 and 0.61 were found at 0.10 and 0.50 M 2-butylamine, respectively. The amine, and amine plus thiol, also led to little or no photoreduction of 2-AN, while thiol plus aniline catalyzed reduction to  $\phi_{red}$  0.3–0.5, again with some evidence of lower  $\phi_{red}$  at highest concentration of amine. Thiol plus aniline, without aliphatic amine, lead to very little reduction,  $\phi < 0.1$ .

Irradiation of 2-NA with a secondary amine, diisopropylamine, led to very little if any reduction in acetonitrile, and none in benzene, Table II. 1-Pentanethiol, 0.004 M, catalyzed reduction in acetonitrile to  $\phi_{red} = 0.61$  at the three concentrations of amine examined; catalysis in benzene was less effective, leading to  $\phi_{red} = 0.13$ . No reduction of 2-AN by diisopropylamine was observed in either solvent; the thiol-catalyzed reduction in acetonitrile was slightly less than that of 2-NA,  $\phi_{red} = 0.51$ , and similarly low in benzene, 0.11. Addition of 0.004 M aniline had little effect.

Results of photoreduction of 2-NA and 2-AN by DEOA, TEOA, and TEA, are summarized in Table III. Values of  $k_{ir}$  with TEA are those reported previously.<sup>18</sup> Reduction of 2-NA by DEOA in acetonitrile is efficient,  $\phi_{lim} = 1.5$ –1.6, while  $k_{ir}$  appears relatively low,  $9 \times 10^5 \text{ M}^{-1} \text{ s}^{-1}$ . Reduction

Table III. Photoreduction of 2-Naphthaldehyde and 2-Acetonaphthone by Tertiary Amines in Acetonitrile and Benzene

carbonyl compd	M	amine		solvent	$\phi_{red}^a$	1/ $\phi$ vs 1/(amine)		$k_{ir}^b$ M <sup>-1</sup> s <sup>-1</sup>
		compound	M			slope	intercept	
2-NA	0.0006	HOCH <sub>2</sub> CH <sub>2</sub> N(C <sub>2</sub> H <sub>5</sub> ) <sub>2</sub>	0.004–0.10	CH <sub>3</sub> CN	0.62–1.4	0.0038	0.68	9 × 10 <sup>5</sup>
2-NA	0.003	HOCH <sub>2</sub> CH <sub>2</sub> N(C <sub>2</sub> H <sub>5</sub> ) <sub>2</sub>	0.10, 0.50	CH <sub>2</sub> CN	1.6, 1.6	–	–	–
2-NA	0.003	(C <sub>2</sub> H <sub>5</sub> ) <sub>2</sub> N	0.10, 1.0	CH <sub>3</sub> CN	1.5, 1.5	–	–	8 × 10 <sup>6</sup>
2-NA	0.0006	HOCH <sub>2</sub> CH <sub>2</sub> N(C <sub>2</sub> H <sub>5</sub> ) <sub>2</sub>	0.005–0.50	C <sub>6</sub> H <sub>6</sub>	0.41–0.72	0.0054	1.4	2 × 10 <sup>6</sup>
2-NA	0.0006	(HOCH <sub>2</sub> CH <sub>2</sub> ) <sub>3</sub> N	0.001–0.05	C <sub>6</sub> H <sub>6</sub>	0.20–.44	0.0028	2.3	5 × 10 <sup>6</sup>
2-NA	0.003	HOCH <sub>2</sub> CH <sub>2</sub> N(C <sub>2</sub> H <sub>5</sub> ) <sub>2</sub>	0.10, 0.50	C <sub>6</sub> H <sub>6</sub>	0.83, 0.77	–	–	–
2-NA	0.003	(C <sub>2</sub> H <sub>5</sub> ) <sub>3</sub> N	0.10, 0.50	C <sub>6</sub> H <sub>6</sub>	0.43, 0.47	–	–	5 × 10 <sup>5</sup>
2-AN	0.0006	HOCH <sub>2</sub> CH <sub>2</sub> N(C <sub>2</sub> H <sub>5</sub> ) <sub>2</sub>	0.001–0.50	CH <sub>3</sub> CN	0.09–0.64	0.0097	1.6	1 × 10 <sup>6</sup>
2-AN	0.0006	(HOCH <sub>2</sub> CH <sub>2</sub> ) <sub>3</sub> N	0.001–0.50	CH <sub>3</sub> CN	0.14–0.60	0.0053	1.8	2 × 10 <sup>6</sup>
2-AN	0.0006	(C <sub>2</sub> H <sub>5</sub> ) <sub>3</sub> N	0.10, 0.50	CH <sub>3</sub> CN	0.48, 0.52	–	–	6 × 10 <sup>5</sup>
2-AN	0.0006	HOCH <sub>2</sub> CH <sub>2</sub> N(C <sub>2</sub> H <sub>5</sub> ) <sub>2</sub>	0.005–0.50	C <sub>6</sub> H <sub>6</sub>	0.12–0.51	0.031	2.4	6 × 10 <sup>5</sup>
2-AN	0.0006	(HOCH <sub>2</sub> CH <sub>2</sub> ) <sub>3</sub> N	0.005–0.25	C <sub>6</sub> H <sub>6</sub>	0.11–0.32	0.031	3.8	8 × 10 <sup>5</sup>
2-AN	0.0006	(C <sub>2</sub> H <sub>5</sub> ) <sub>3</sub> N	0.10, 0.50	C <sub>6</sub> H <sub>6</sub>	0.06, 0.08	–	–	1 × 10 <sup>5</sup>

<sup>a</sup>The larger numbers approximate the extrapolated quantum yields,  $\phi_{lim}$ . <sup>b</sup>Based on  $k_d$  values: 2-NA, in CH<sub>3</sub>CN, 5 × 10<sup>3</sup> s<sup>-1</sup>; in C<sub>6</sub>H<sub>6</sub>, 6 × 10<sup>3</sup> s<sup>-1</sup>; 2-AN, in CH<sub>3</sub>CN, 6 × 10<sup>3</sup> s<sup>-1</sup>; in C<sub>6</sub>H<sub>6</sub>, 7 × 10<sup>3</sup> s<sup>-1</sup>.

Table IV. Photoreduction of 0.001 M *p*-Aminobenzophenone by Amines in Benzene: Effects of 0.004 M 1-Pentanethiol and 0.004 M Aniline

amine compound	M	C <sub>5</sub> H <sub>11</sub> SH	C <sub>6</sub> H <sub>5</sub> NH <sub>2</sub>	$\phi_{red}$
CH <sub>3</sub> CH <sub>2</sub> CH-(CH <sub>3</sub> )NH <sub>2</sub>	0.10, 1.0	–	–	0.0
	0.10, 1.0	+	–	0.11
	0.10, 0.50, 1.0	+	+	0.32, 0.35, 0.37
((CH <sub>3</sub> ) <sub>2</sub> CH) <sub>2</sub> NH	0.10	–	–	0.0
	0.025, 0.05, 0.10	+	± <sup>b</sup>	0.51, 0.54, 0.40
	1.0	+	–	0.35
(C <sub>2</sub> H <sub>5</sub> ) <sub>3</sub> N	0.10, 1.0	–	–	0.27, 0.32
	0.10	+	–	0.23
	0.10	+	+	0.21
	0.10	++ <sup>a</sup>	–	0.16
	1.0	–	0.004	0.22
	1.0	–	0.008 <sup>c</sup>	0.19
	1.0	–	0.012	0.15
	1.0	–	0.040	0.09
	1.0	–	0.080	0.06

<sup>a</sup>0.04 M. <sup>b</sup>Addition of aniline had no effect. <sup>c</sup>Molar.

by TEA has similar high  $\phi_{lim}$ , and  $k_{ir}$  is 8 × 10<sup>6</sup> M<sup>-1</sup> s<sup>-1</sup>. In benzene,  $\phi_{lim}$  for reduction of 2-NA by DEOA is lower, 0.7–0.8,  $k_{ir}$  is 1 × 10<sup>6</sup> M<sup>-1</sup> s<sup>-1</sup>. Reduction by TEOA and TEA appears less efficient,  $\phi_{lim}$  0.45, and  $k_{ir}$  values are 5 × 10<sup>6</sup> and 5 × 10<sup>5</sup> M<sup>-1</sup> s<sup>-1</sup>, respectively.

Reduction of 2-AN in acetonitrile shows similar  $\phi_{lim}$  values for the three tertiary amines, 0.5–0.6, with that for TEA at the lower end. Values of  $k_{ir}$  with the (hydroxyalkyl)amines are similar to that for 2-NA with DEOA; that with TEA is an order of magnitude lower than for the aldehyde. In benzene, values of  $k_{ir}$  are lower by factors of 3–6 than in acetonitrile, and in the same order, highest for TEOA and lowest for TEA. Values of  $\phi_{lim}$  for the hydroxyalkyl compounds are somewhat lower than in acetonitrile, and very low for TEA, 0.07.

*p*-AMB was not photoreduced by the primary and secondary amines in benzene, Table IV. A low concentration of thiol, 0.004 M, catalyzed reduction by the secondary amine effectively, to  $\phi = 0.5$ , with no additional effect on addition of aniline. Catalysis by thiol of reduction by the primary amine was less efficient,  $\phi = 0.1$ , but addition of aniline increased this to  $\phi = 0.35$ . *p*-AMB was photoreduced by TEA,  $\phi = 0.3$ , and addition of thiol or aniline led to decreased quantum yield. The effect of aniline, in quenching photoreduction of *p*-AMB by TEA, leads to  $k_q = 2 \times 10^9$  M<sup>-1</sup> s<sup>-1</sup>, about 50 times that for reaction with TEA.

*p*-CNB, with  $n,\pi^*$  triplet, is photoreduced by the three classes of amines, Table V,  $\phi_{red} = 0.33$  with 2-butylamine and diisopropylamine, increased by thiol to 0.84 and 0.50, respectively, with no additional effect on addition of an-

Table V. Photoreduction of 0.005 M *p*-Cyanobenzophenone by Amines in Benzene: Effects of 0.004 M 1-Pentanethiol and 0.004 M Aniline

amine compound	M	C <sub>5</sub> H <sub>11</sub> SH	C <sub>6</sub> H <sub>5</sub> NH <sub>2</sub>	$\phi_{red}$
CH <sub>3</sub> CH <sub>2</sub> CH(NH <sub>2</sub> )CH <sub>3</sub>	0.05, 0.10	–	–	0.34
	0.05, 0.10, 0.50	+	–	0.84
	0.05, 0.10, 0.50	+	+	0.80
((CH <sub>3</sub> ) <sub>2</sub> CH) <sub>2</sub> NH	0.05, 0.10	–	–	0.33
	0.05, 0.10	+	–	0.50
	0.05, 0.10	+	+	0.54
(C <sub>2</sub> H <sub>5</sub> ) <sub>3</sub> N	0.10, 0.50, 1.0	–	–	1.4 <sup>a</sup>
	0.50	+	–	1.4
	0.50	–	+	1.1
(C <sub>2</sub> H <sub>5</sub> ) <sub>2</sub> NCH <sub>2</sub> CH <sub>2</sub> OH	0.01, 0.05	–	–	1.4

<sup>a</sup>Quantum yield was unchanged at 0.01 M and 0.10 M *p*-CNB.

iline. It is reduced most efficiently by the tertiary amines, TEA and DEOA,  $\phi_{red} = 1.4$ , and addition of thiol and aniline to TEA led to no effect and a decrease, respectively.

## Discussion

Reactions of 2-NA, 2-AN, and *p*-AMB with the primary amine, Tables I and IV are similar to each other and to those of fluorenone:<sup>20</sup> no reduction by primary amine alone, very little if any catalysis by thiol, substantial catalysis by the aniline–thiol pair, to  $\phi = 0.5$ –0.6 for 2-NA, 2-AN, and fluorenone, and 0.35 for *p*-AMB. However, these carbonyl compounds vary widely, (i) in triplet energy,<sup>24</sup> high for *p*-AMB, 67 kcal/mol, similar to that for *p*-CNB and benzophenone, lowest for fluorenone, 53.3 kcal/mol, and intermediate for the naphthyl compounds, 59 kcal/mol; (ii) in reduction potential,<sup>5,22</sup> favorable for fluorenone, 2-NA, and *p*-CNB, 28, 31, and 28 kcal/mol, respectively, and less favorable for *p*-AMB, 2-AN, and benzophenone, 37, 40, and 35 kcal/mol, respectively; and (iii) in the sum of these properties (<sup>3</sup> $E_{o,o} + E_{A/A}$ ), relatively favorable for *p*-AMB and 2-NA, 30 and 29 kcal/mol, unfavorable for 2-AN, 20 kcal/mol, intermediate for fluorenone, 25 kcal/mol, and in all these less favorable than for the reactive ketones with  $n,\pi^*$  triplets, *p*-CNB and benzophenone, 38 and 34 kcal/mol, respectively.

The low reactivity accompanying less favorable (<sup>3</sup> $E_{o,o} + E_{A/A}$ ) may indicate that a favorable combination of these factors is necessary for substantial hydrogen abstraction from  $\alpha$ -C or N of primary amines, compounds of high N–H bond dissociation energy, BDE, 100 kcal/mol,<sup>25</sup> and high ionization potential, IP, 8.7 eV.<sup>26</sup> Neither the high triplet

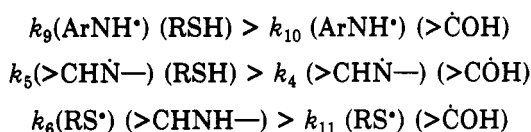
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energy of *p*-AMB nor the low reduction potentials of 2-NA and fluorenone suffice for high reactivity. Alternatively, the  $\pi, \pi^*$  character,<sup>27</sup> with high electron density retained on the carbonyl oxygen, may be the dominant common property leading to this low reactivity, as compared with those of  $n, \pi^*$  triplets.<sup>4</sup> The absence of catalysis by thiol alone indicates that these triplets also do not abstract H from S of aliphatic thiol, of BDE 89 kcal/mol, IP 9.1 eV. They do abstract H from N of aniline, with its low BDE, 82 kcal/mol, and a low IP, 7.7 eV, similar to that of secondary and tertiary aliphatic amines, 7.7 and 7.5 eV, respectively, initiating catalysis by the aniline-thiol-amine hydrogen transfer sequence eqs 8, 9, 6. The catalysis is similar for 2-NA and 2-AN in acetonitrile and benzene, indicating that solvent polarity may not be necessary for these three hydrogen abstractions.

Failure of reduction of the  $\pi, \pi^*$  triplets by the secondary amine, and catalysis by thiol to  $\phi = 0.5-0.6$ , Tables II and IV, results from successful abstraction of H from N of the amine of lower IP, 7.7 eV, and lower N-H BDE, 92 kcal/mol, followed, however, by disproportionation, eq 3, in the absence of thiol, and the catalytic sequence, eqs 5 and 6, in its presence. Weaker catalysis for 2-NA and 2-AN in benzene rather than in acetonitrile indicates that the initial abstraction by these triplets from aliphatic N is facilitated by solvent polarity in contrast to abstraction from N of aniline. The more favorable reduction potential of fluorenone and high triplet energy of *p*-AMB may lead to their high reactivity in benzene. The failure of aniline to enhance catalysis indicated that initial reaction is completely with the aliphatic amine, present at substantially higher concentration.

Catalysis to  $\phi_{\text{red}} = 0.5-0.6$  in these systems is notable in view of the several competing disproportionations, and depends on reactant concentrations and rate constants favoring the following inequalities.<sup>12,20</sup>



Abstractions of hydrogen by the anilinyll and alkylaminyll radicals from S of thiol, eqs 9 and 5, and by thiyl radical from  $\alpha$ -C of the aliphatic primary and secondary amines, eq 6, must be more rapid than their disproportionations with ketyl, eq 4 and its analogues, eqs 10 and 11, which regenerate the starting carbonyl compounds. Finally, ketyl dimerization to pinacol must compete favorably with these disproportionations. The common observed result,  $\phi_{\text{red}} \sim 0.5$ , appears to be the resultant of these competing processes. In photoreduction by tertiary amines, aminyl radicals are not formed, this mechanism for catalysis is not possible, and retardation by thiol and aniline may occur.

Hydrogen transfer from thiol to anilinyll radical, eq 9, is essentially thermoneutral, that from thiol to secondary aminyl radical, eq 5, is exothermic by  $\sim 3$  kcal/mol, and much more so to primary aminyl. The BDE of tertiary  $\alpha$ -C-H of primary and secondary amines may be estimated as 90 and 84 kcal/mol, respectively,  $\sim 3$  kcal less than those of primary C-H in methylamine and dimethylamine respectively,<sup>25</sup> their transfers to aliphatic thiyl radical would be essentially thermoneutral and exothermic by 5 kcal/

mol, respectively. These hydrogen transfers from and to S, involving d orbitals, proceed rapidly, apparently with little if any activation energy.<sup>28</sup> Aromatic thiols do not catalyze, but retard photoreduction by amines, as they do that of  $n, \pi^*$  triplets by alcohols.<sup>19</sup> Abstraction of H from the weaker aryl-SH bond, BDE 83 kcal/mol, occurs readily, but the stabilized arylthiyl radical may not abstract H from  $\alpha$ -C rapidly, and it largely disproportionates with ketyl. Aliphatic thiol retards photoreduction by 2-propanol, in which initial abstraction occurs only from  $\alpha$ -C; there is no opportunity for catalysis, and reactions of thiol and thiyl with aliphatic and aromatic ketyl radicals, respectively, regenerate starting materials.

Reduction of the  $\pi, \pi^*$  triplets by tertiary amines appears largely influenced by the reduction potentials of the carbonyl compounds. 2-NA, with favorable reduction potential but low triplet energy, is reduced efficiently by TEA and DEOA in acetonitrile,  $\phi_{\text{lim}} = 1.5-1.6$ , Table III, similar to that of benzophenone.<sup>10</sup> Lower efficiency in benzene,  $\phi_{\text{lim}} 0.5-0.8$ , indicates that the initial abstraction and subsequent reduction of ground-state 2-NA by aminoalkyl radical are favored by charge-transfer interaction, eqs 1 and 3; 2-AN, with less favorable reduction potential than 2-NA and the same triplet energy, is reduced substantially less efficiently, in both acetonitrile and benzene. The polar microenvironment of the hydroxyethyl compounds compensates for the lower solvent polarity. In the absence of both effects, reduction by TEA is very inefficient,  $\phi_{\text{lim}} = 0.08$ . Similar effects are found in values of  $k_{\text{ir}}$ , in Table III, polar solvent, polar microenvironment, and favorable reduction potential generally leading to higher values. Fluorenone, with more favorable reduction potential than 2-NA, shows higher  $\phi_{\text{red}}$ , 0.9,<sup>13</sup> in reduction by TEA in cyclohexane, despite lower triplet energy; the polar microenvironment of the hydroxyethylamines leads to nearly the maximum possible value of 2, while the hydrogen abstraction is largely from the unsubstituted ethyl groups of DEOA. Fluorenone also has higher  $k_{\text{ir}}$  than the naphthyl compounds in reaction with TEA,  $\sim 10^7 \text{ M}^{-1} \text{ s}^{-1}$ .<sup>13,20</sup> *p*-AMB, with reduction potential intermediate between those of 2-NA and 2-AN, and much higher triplet energy, has intermediate  $\phi_{\text{red}}$  in reduction by TEA in benzene, 0.3, higher than 0.08 for 2-AN, lower than 0.45 for 2-NA. With less favorable reduction potential than fluorenone, *p*-AMB showed lower  $\phi_{\text{red}}$ <sup>2a</sup> in reduction by TEA in cyclohexane, 0.6 as compared with 0.9, and similar high  $k_{\text{ir}}$ . Its higher  $\phi_{\text{red}}$  in cyclohexane than in benzene may be related to the possibly deactivating charge-transfer character of the ketone and its triplet,<sup>29</sup> arising from *p*-aminocarbonyl donor-acceptor resonance, greater in the more polar solvent.

Values of  $k_{\text{d}}$  and  $k_{\text{ir}}$  indicate complete trapping of triplets in these  $\pi, \pi^*$  systems at high tertiary amine concentrations; low reduction quantum yields of naphthyl compounds in benzene as compared with acetonitrile may reflect quenching in the initial charge-transfer complexes. Substantial formation of product of cross-coupling of carbonyl- and amine-derived radicals was found in reduction of *p*-AMB, indicating inefficient reduction of ground-state ketones, but such quantum yield reducing products were not found in reduction of the naphthyl<sup>18</sup> compounds and fluorenone.<sup>1,20</sup> The value of  $k_{\text{q}}$  in reaction of *p*-AMB with aniline,  $2 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ , is much higher than for the naphthyl compounds<sup>18</sup> and may be attributed to its high triplet energy.

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*p*-CNB, with a high energy  $n, \pi^*$  triplet, like that of benzophenone, and a more favorable reduction potential, due to its electronegative substituent, shows a similar reduction pattern, Table V. Photoreduction is most efficient with the tertiary amine, and similar to benzophenone, while primary and secondary amines lead to lower  $\phi_{\text{red}}$ , lower than with the unsubstituted ketone. This may indicate greater initial abstraction of H from N. These reductions are catalyzed by thiol, but less efficiently than

those of benzophenone, possibly indicating more rapid disproportionation reactions of the more acidic ketyl radical. Aniline does not enhance catalysis, indicating predominant trapping of this reactive triplet by the higher concentration of aliphatic amine.

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## The $^{18}\text{O}$ Isotope Shift in $^{13}\text{C}$ Nuclear Magnetic Resonance Spectroscopy. 14. Kinetics of Oxygen Exchange at the Anomeric Carbon of D-Ribose and D-2-Deoxyribose<sup>1</sup>

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The kinetics of the oxygen-exchange reaction at the anomeric carbon atoms of D-ribose and D-2-deoxyribose (2-deoxy-D-erythro-pentose) were compared using the  $^{18}\text{O}$  isotope induced shift in  $^{13}\text{C}$  NMR spectroscopy. Measurements were made at a number of temperature and pH values. The oxygen-exchange reaction for these sugars is strongly pH-dependent, displaying regions of acid, water, and base catalysis. At 25 °C the oxygen-exchange rate of D-ribose was found to be approximately 20-fold greater than the rate for D-glucose between pH 2 and 9. In turn, the oxygen-exchange rate for D-2-deoxyribose was greater than the rate for D-ribose by approximately 5-fold above pH 4 and by greater than 10-fold below pH 4. The results are analyzed in terms of steric and inductive effects on the hydration kinetics of the open-chain forms and by comparison with the hydration reaction of simple aldehydes. The study also includes quantitative data, based upon  $^{13}\text{C}$  NMR line intensities, for the various anomeric forms that exist in solutions of these sugars at the different temperature and pH values used in the kinetic measurements reported here. In each case, the oxygen-exchange reactions of the anomers are slow relative to the rate of anomerization, so that the anomers appear to exchange oxygen at the same rate.

### Introduction

The mutarotation of monosaccharides in aqueous solution involves the reversible, intramolecular attack of a sugar hydroxyl group upon the carbonyl carbon of the open-chain species to form the various anomers.<sup>2</sup> The carbonyl carbon of the open-chain form can also be hydrated upon attack by water. In fact, at room temperature the ratio of hydrate to aldehyde in solutions of common aldoses<sup>3</sup> is approximately 10:1. While the hydration reactions of simple aldehydes and ketones have received extensive study,<sup>4</sup> the corresponding reactions of the open-chain forms of sugars have received little attention.<sup>5</sup> A major hindrance to direct studies of monosaccharide hydration is the extremely small percentages of the reactive carbonyl species that are present in solution.<sup>6</sup> However, the hydration reaction can be studied indirectly by observing the oxygen-exchange process that accompanies it.<sup>7</sup> Furthermore, since the oxygen-exchange rate is proportional to the (low) mole fraction of open-chain species present in solution,<sup>8</sup> the kinetics of the rapid hydration process can be studied at slower, more convenient rates.

Oxygen exchange at carbon is readily assayed using the  $^{18}\text{O}$  isotope shift in  $^{13}\text{C}$  NMR spectroscopy.<sup>9,10</sup> We have applied this technique to study the oxygen-exchange kinetics of D-erythrose, glucose, mannose, and fructose.<sup>1,11</sup> These data are valuable not only because they more fully characterize the solution chemistry of carbohydrates, but also because they are critical in the interpretation of mechanistic investigations involving bond breakage or

bond formation at the anomeric carbon atom.<sup>12</sup> Consequently, it appeared useful to extend our oxygen-exchange studies to the biologically important monosaccharides D-ribose and D-2-deoxyribose (2-deoxy-D-erythro-pentose). Comparison of these sugars also allows one to assess the influence of the hydroxyl group adjacent to the carbonyl function with respect to its effect on the hydration of an aldose.

### Experimental Section

**Materials.** D-[1- $^{13}\text{C}$ ]Ribose was obtained from Omicron Biochemicals and D-2-deoxyribose (natural abundance) was purchased from Aldrich and Sigma. [ $^{18}\text{O}$ ]Water (98 atom %  $^{18}\text{O}$ ) was purchased from Merck, and deuterium oxide (99.8 atom %

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