amorphous white solid. Two crystallizations from H_2O afforded 16 mg of chromatographically homogeneous material: UV λ_{max} (pH 1) 259 (ϵ 14 200), 282 nm (sh) (ϵ 8190); UV λ_{max} (pH 6.9) 253 (ϵ 14 100), 274 nm (sh) (ϵ 9400); UV λ_{max} (pH 13) 257 (ϵ 12 500), 270 nm (sh) (ϵ 11 200); MS *m/e* 373 (M^+), 241 ($B + 1^+$), 91 ($C_7H_7^+$); NMR δ 4.50 (m, 3, H-2′ + $C_6H_5CH_2$, changes shape on addition of D_2O), 5.72 (d, 1, H-1′), 6.92 (t, 1, $C_6H_5CH_2NH$, J = 6 Hz, disappears on addition of D_2O), 7.36 (br s, 5, $C_6H_5CH_2$), 7.96 (s, 1, H-8), 10.66 (br s, 1, 1-H, disappears on addition of D_2O). Anal. Calcd for $C_{17}H_{19}N_5O_5 \cdot {}^1/_2H_2O$: C, 53.40; H, 5.27; N, 18.32. Found: C, 53.40; H, 5.22; N, 18.14.

Hydrolysis of this material in 1 N HCl at 65–70 °C for 12 h afforded a single UV-absorbing component which was chromatographically and spectroscopically indistinguishable from N^2-benzylguanine.[34]

Benzylation of Adenosine. Reactions of adenosine (0.12 or 0.25 g, 0.4 or 0.8 mmol for the hemihydrate, respectively) and [^{3}H]benzyl bromide (**2a**) or [^{3}H]benzyl tosylate (**2c**) were carried out in 25 mL of reaction solvent (Table II) containing 0.12 g (1.4 mmol) of $NaHCO_3$. The solutions were saturated with gaseous CO_2 to arrive at a final pH in the range 6.8–7.4. Following temperature equilibration (15 min) **2a** or **2c** (0.084 mmol in 0.25 mL of dry DMF) was added and the resulting solutions were stirred continuously during the reaction incubation. When reactions were complete (~5 half-times for **2a** and **2b** or 24 h for **2c**) an aliquot (0.1 mL) of reaction solution was withdrawn and mixed with an equal volume of marker solution (5 mM in both **3** and **4**). The sample was loaded on a 0.72 × 18 cm Aminex A-6 column (ammonium ion form). The column was initially eluted with 0.1 M ammonium formate (pH 4.5) in MeOH/H_2O (3:7) at 40 °C (flow rate 0.3 mL/min; operating pressure 90 psi). Column effluent was continuously monitored at 254 nm. Fractions (1.0 mL) were collected and mixed with 10 mL of PCS (Amersham/Searle) for scintillation counting. [^{3}H]Benzyl alcohol eluted in fractions 15,16; unmodified adenosine (**1**) in fractions 20–23; N^6-benzyladenosine (**3**) eluted in fractions 26–40. When 48 mL of initial buffer had passed through the column, elution was carried out at 60 °C using 1.0 M ammonium formate (pH 4.5) in MeOH/H_2O (3:7). 1-Benzyladenosine (**4**) eluted in fractions 75–77.

For reactions involving [G-^{3}H]adenosine, a 10-μL aliquot of an aqueous stock solution of labeled nucleoside (1.1×10^{-4} M) was added to 1 mL of buffered reaction solution (Table II). A 10-μL aliquot of 0.35 M benzyl chloride (**2b**) in DMF or EtOH was added and the solutions were incubated at 25 °C. Product analyses by column chromatography were carried out as above.

Benzylation of Guanosine. Reactions involving [5′-^{3}H]-guanosine were prepared by adding a 10-μL aliquot of a 5×10^{-5} M solution of labeled guanosine to 1 mL of buffered reaction solution (Table III). A 10-μL aliquot of an appropriately concentrated solution of unlabeled **2a**, **2b**, or **2c** in either EtOH or DMF was added to arrive at the final concentrations of benzylating agents cited (Table III).

Guanosine and [^{3}H]benzyl bromide reactions in aqueous ethanol were carried out in 25 mL of buffered solutions like those for adenosine (see above).

When reactions were complete, aliquots were removed and were mixed with marker solutions containing 1-benzylguanosine, **6**, **7**, and **8**. These solutions were loaded on a 0.72 × 30 cm Aminex A-5 column (ammonium ion form). The column was initially eluted with 1 M ammonium formate in DMF/H_2O (1:9) (pH 4.2) at 40 °C (flow rate 0.5 mL/min; operating pressure 250 psi). Column effluent was monitored at 254 nm and fractions (1.0 mL) were collected for scintillation counting. Unmodified guanosine eluted in fractions 15–17; 1-benzylguanosine eluted in fractions 33–38; N^2-benzylguanosine eluted in fractions 45–53; O^6-benzylguanosine eluted in fractions 58–67. When 75 mL of solvent had passed through the column, the eluting buffer was changed to 1 M ammonium formate in DMF/H_2O (3:7), pH 7, 50 °C. 7-Benzylguanosine eluted in fractions 100–105.

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Registry No. **1**, 58-61-7; **2a**, 100-39-0; **2b**, 100-44-7; **2c**, 1024-41-5; **3**, 4294-16-0; **4** (X = Br), 20757-58-8; **4** (X = Cl), 71171-55-6; **4** (X = OTs), 71171-57-8; **5**, 118-00-3; **6**, 4552-61-8; **7**, 71171-58-9; **8** (X = Br), 71171-59-0; **8** (X = Cl), 71171-60-3; **8** (X = OTs), 71171-62-5.

Base-Catalyzed Dehydrogenation of 2,2′,4,4′,6,6′-Hexanitrobibenzyl by Quinones†

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The dehydrogenation of 2,2′,4,4′,6,6′-hexanitrobibenzyl by quinones takes place only in basic medium, particularly in hexamethylphosphoramide alone, or in dimethylformamide in the presence of a suitable base. A study of the reaction mechanism indicates that hydrogen is transferred heterolytically and that the abstraction of H^- occurs only after removal, or partial removal, of H^+. The yield of 2,2′,4,4′,6,6′-hexanitrostilbene was highest with 2,3-dichloro-5,6-dicyanobenzoquinone and generally decreased with declining quinone redox potential.

In a study of the dehydrogenation of tetralin, acenaphthene, and bibenzyl by quinones in aromatic solvents, Braude, Brook, and Linstead[1] found 2,3-dichloro-5,6-dicyanobenzoquinone (DDQ) to be the most effective hydrogen-transfer reagent. Dehydrogenated product was obtained from bibenzyl in rather low yield (22%), however, in contrast to tetralin (70%) and acenaphthene (51%). It has been reported[2] that 4,4′-dimethoxystilbene is formed in 85% yield from the bibenzyl and DDQ in dioxane. The dehydrogenation of hydroaromatic compounds appears to proceed, at least in some cases, via hydride ion abstraction and is catalyzed by proton donors. Less is known about the dehydrogenation of bibenzyl compounds, which may

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(1) E. A. Braude, H. G. Brook, and R. P. Linstead, *J. Chem. Soc.*, 3569 (1954).

(2) H. O. House, "Modern Synthetic Reactions", 2nd ed., W. A. Benjamin, Menlo Park, CA, 1972, p 42.

Table I. Effect of Solvent on the Dehydrogenation of HNBB by Quinones[a]

quinone	solvent	temp, °C[b]	HNS yield, %
DDQ	1,4-dioxane	70	0
	HMPA	70	89
chloranil	xylene	135	0
	tetrahydrofuran	65	0
	HMPA	70	80
p-benzoquinone	*o*-dichlorobenzene	150	0
	DMF	70	0
	HMPA	70	78
	1-methyl-2-pyrrolidinone	70	23
	Me_2SO	70	18
	Me_2SO	95	33

[a] Molar ratio quinone/HNBB = 2; reaction time 3 h. [b] Approximate.

proceed similarly or involve hydrogen atom transfer.[3-5]

We have found that the conditions for dehydrogenating bibenzyl or 4,4′-dimethoxybibenzyl cannot be used for the dehydrogenation of 2,2′,4,4′,6,6′-hexanitrobibenzyl (HNBB) but must be essentially changed for the reaction to take place. We have investigated the dehydrogenation of HNBB with a series of quinones and in view of the relatively acidic character of the aliphatic protons in this compound have attempted to shed some light on the reaction mechanism.

Results and Discussion

The effect of various solvents on the dehydrogenation of HNBB by DDQ, chloranil, and benzoquinone was determined, and the results are summarized in Table I. All three quinones produced 2,2′,4,4′,6,6′-hexanitrostilbene (HNS) in high yield when hexamethylphosphoramide (HMPA) was used as the solvent. The product was not detected in the case of dioxane, xylene, *o*-dichlorobenzene, tetrahydrofuran, or *N,N*-dimethylformamide (DMF). Low yields of HNS were obtained with dimethyl sulfoxide (Me_2SO) and 1-methyl-2-pyrrolidinone as solvents. Thus, HMPA solutions were used for determining the ability of the entire series of quinones to convert HNBB to HNS.

The quinones were generally employed in molar excess of HNBB. With molar equivalents of benzoquinone and HNBB as required by theory (below), the yield of HNS (73%) approached that obtained on doubling the molar ratio (78%). Not surprisingly, further reduction of the quinone/HNBB molar ratio to 0.5 resulted in a significantly lower yield (49%). As might be expected on the basis of the extremely high oxidation–reduction potential, electron affinity, and one-electron reduction potential of the quinone, the highest yield of HNS was obtained with DDQ. Yields in general decreased with declining quinone potential (Table II) (and with declining electron affinity[7] and one-electron potential[8]), in accordance with a similar relationship that exists between redox potentials of quinones and their reactivities in hydrogen-transfer reactions with hydroaromatic compounds.[3] A notable exception to this trend was tetrafluoro-*p*-benzoquinone. In this case, the reaction largely took another course and produced unidentified solids representing the major portion of the original HNBB.

Table II. Variation of HNS Yields with Oxidation-Reduction Potentials of Quinones[a]

quinone	E°, V[b]	HNS yield, %
DDQ	~1.0[c]	89
tetrafluoro-*p*-benzoquinone		17
o-chloranil	0.870	83
chloranil	0.703[d]	80
p-benzoquinone	0.711	78
2,5-diphenylbenzoquinone		70
methyl-*p*-benzoquinone	0.656	72[e]
1,4-naphthoquinone	0.493	71[f]
tetramethyl-*p*-benzoquinone	0.466	46[g]
tetrahydroxy-*p*-benzoquinone		0
9,10-anthraquinone	0.154	0

[a] Molar ratio quinone/HNBB = 2, solvent HMPA, temperature 70 °C, reaction time 3 h. [b] Oxidation-reduction potential in ethanol at 25 °C.[6] [c] See ref 5. [d] Braude, Jackman, and Linstead have pointed out that the E° of chloranil is abnormally low in ethanol (cf. references cited by them[3] and by Walker and Hiebert[4]). [e] 73% on irradiating with ultraviolet light. [f] 71% with 2,4-dichlorobenzoyl peroxide present. [g] None with picric acid present.

Table III. Effect of Pyridine on the Dehydrogenation of HNBB by *p*-Benzoquinone[a]

py/HNBB[b]	rctn time, h	HNS yield, %	py/HNBB[b]	rctn time, h	HNS yield, %
0	3	0	1.2	3	65
4.7	3	55	1.2	1.5	74
2.3	3	63	0.5	1.5	70
2.3	5	51			

[a] Molar ratio benzoquinone/HNBB = 2, solvent DMF, temperature 70 °C. [b] Molar ratio.

Table IV. Effect of Base on the Dehydrogenation of HNBB by *p*-Benzoquinone[a]

base	pK_a[b] (T, °C)	HNS yield, %
p-nitroaniline	1.0 (25)	0
aniline	4.63 (25)	53
quinoline	4.90 (20)	73[c]
N,N-dimethylaniline	5.15 (25)	21
pyridine	5.25 (25)	65[d]
2-picoline	5.97 (20)	68
4-picoline	6.02 (20)	70
morpholine	8.33 (25)	0
cyclohexylamine	10.66 (24)	0
triethylamine	11.01 (18)	0

[a] Molar ratio benzoquinone/HNBB = 2, molar ratio base/HNBB = 1.2, solvent DMF, temperature 70 °C, reaction time 3 h. [b] In aqueous solution at temperatures indicated.[10] [c] 75% with reaction time of 1.5 h. [d] 74% with reaction time of 1.5 h.

The remarkable facility with which the reactions occurred in HMPA (Tables I and II) appeared to be related to the ability of the solvent to accept a proton, and product formation in Me_2SO and in 1-methyl-2-pyrrolidone (Table I) tended to support this concept.[9] That the dehydrogenation is indeed promoted by base was confirmed by the finding that HNS is produced upon addition of pyridine to HNBB and benzoquinone in DMF, a solvent that apparently is not a sufficiently strong proton acceptor itself

(3) E. A. Braude, L. M. Jackman, and R. P. Linstead, *J. Chem. Soc.*, 3548, 3564 (1954).
(4) D. Walker and J. D. Hiebert, *Chem. Rev.*, **67**, 153 (1967), and references cited therein; ref 2, pp 37–44, and references therein.
(5) D. H. Reid, M. Fraser, B. B. Molloy, H. A. S. Payne, and R. G. Sutherland, *Tetrahedron Lett.*, 530 (1961).
(6) J. B. Conant and L. F. Fieser, *J. Am. Chem. Soc.*, **45**, 2194 (1923); **46**, 1858 (1924).
(7) G. Briegleb, *Angew. Chem., Int. Ed. Engl.*, **3**, 617 (1964).
(8) M. E. Peover, *J. Chem. Soc.*, 4540 (1962).
(9) The superior hydrogen-bond acceptor (HBA) basicities of HMPA, Me_2SO, and 1-methyl-2-pyrrolidinone (with HMPA showing the highest basicity) are well documented; cf. M. J. Kamlet and R. W. Taft, *J. Am. Chem. Soc.*, **98**, 377 (1976).

to effect the reaction. The highest yield (74%) was obtained when the pyridine–HNBB molar ratio was adjusted downward to 1.2 and the reaction time was reduced to 1.5 h (Table III). The yield was almost as high when the ratio was reduced to 0.5, and it became clear that a base-catalytic effect was operative.

Under comparable conditions, quinoline and 2- and 4-picoline, with pK_a's in the range 4.9–6.0, were at least as effective as pyridine, whose pK_a falls within this range (Table IV). Aniline, a weaker base than quinoline, gave a lower yield of HNS. The yield fell precipitously in the case of *N,N*-dimethylaniline, whose pK_a lies between those of quinoline and pyridine, possibly for steric reasons as mentioned below. No HNS was obtained with stronger bases such as morpholine, cyclohexylamine, and triethylamine. Morpholine caused oxides of nitrogen to evolve, while the latter two amines both yielded a product which has lower nitrogen content than HNS and has not yet been identified. *p*-Nitroaniline gave a negative result, even when used in solvent quantity, and this will be discussed later.

In the conversion of HNBB to HNS by quinones, if the reaction proceeded via homolytic hydrogen transfer, then diphenylpicrylhydrazyl might be expected to be a powerful reagent for accomplishing the dehydrogenation.[11] This was not found to be the case, however. No HNS was produced by the picrylhydrazyl either in *m*-xylene or in HMPA, tending to exclude the possibility that the reaction with quinones involves hydrogen atom transfer. The reactions of methyl-*p*-benzoquinone and 1,4-naphthoquinone, moreover, were unaffected by ultraviolet irradiation and 2,4-dichlorobenzoyl peroxide,[12] respectively (Table II), indicating that it is unlikely a radical chain process is involved. Thus, as postulated in the case of hydroaromatic compounds and bibenzyl,[1,3] the hydrogen more likely is removed heterolytically, but with an important difference. Hydride ion cannot be removed from HNBB without the assistance of a base. The following sequence, analogous to that proposed for the dehydrogenation of hydroaromatic compounds,[3] is, therefore, not applicable.

$$\underset{\text{HNBB}}{\text{PiCH}_2\text{CH}_2\text{Pi}} + \text{Q} \rightleftharpoons \text{PiCH}_2\overset{+}{\text{C}}\text{HPi} + \text{QH}^- \rightarrow \underset{\text{HNS}}{\text{PiCH=CHPi}} + \text{QH}_2$$

Pi = picryl = 2,4,6-trinitrophenyl; Q = quinone

The finding that HNBB and quinones do not react in the absence of base is understandable in terms of the inability of the quinone to abstract hydride ion due to the presence of the picryl groups which labilize the protons in the acidic sense. Not surprisingly, picric acid, a proton donor known to catalyze aromatic dehydrogenation,[3] failed to promote the reaction of HNBB with tetramethyl-*p*-benzoquinone in HMPA (Table II). Instead, the acid inhibited the reaction, and no HNS was obtained at all. Thus, the species QH^+, formed via complexing of the quinone and the proton donor and suggested to be a more powerful hydride ion abstractor than the quinone,[3] was totally ineffective if indeed it was present in this instance.

The initial step in the dehydrogenation of HNBB is seen to involve the removal (or partial removal) of H^+ by appropriate base (B), generating the carbanion (or incipient carbanionic center) (eq 1).[13] This is followed by abstraction of H^- by the quinone to produce HNS and the semiquinone anion (eq 2), with the driving force for removal of H^- provided by the formation of HNS.[14] It can be seen from eq 3 and 4 how the reaction might proceed with only a catalytic amount of base present. QH^- could either regenerate the base (eq 3) or assume the function of the base (eq 4) on the way to forming the hydroquinone. The solvents, HMPA, Me_2SO, and 1-methyl-2-pyrrolidinone, are viewed as proton acceptors strong enough to induce the formation of the incipient carbanion, thus facilitating the removal of H^- by quinone.

$$\underset{\text{HNBB}}{\text{PiCH}_2\text{CH}_2\text{Pi}} + \text{B} \rightleftharpoons \text{PiCH}_2\overset{\delta^-}{\text{C}}\text{H}\text{--}\text{H}\text{--}\overset{\delta^+}{\text{B}} \rightleftharpoons \underset{\text{Pi}}{} \quad (1)$$

$$\text{PiCH}_2\text{CHPi} + \text{BH}^+$$

$$\left.\begin{array}{l}\text{PiCH}_2\overset{\delta^-}{\text{C}}\text{H}\text{--}\text{H}\text{--}\overset{\delta^+}{\text{B}} \\ \quad\text{Pi} \\ \quad\Downarrow \\ \text{PiCH}_2\text{CHPi} + \text{BH}^+\end{array}\right\} + \text{Q} \rightarrow \underset{\text{HNS}}{\text{PiCH=CHPi}} + \text{QH}^- + \text{BH}^+ \quad (2)$$

$$\text{QH}^- + \text{BH}^+ \rightarrow \text{QH}_2 + \text{B} \quad (3)$$

$$\text{PiCH}_2\text{CH}_2\text{Pi} + \text{QH}^- \rightleftharpoons \text{PiCH}_2\overset{\delta^-}{\text{C}}\text{H}\text{--}\overset{\delta^+}{\text{H}}\text{--}\text{QH}^- \rightleftharpoons \underset{\text{Pi}}{} \quad (4)$$

$$\text{PiCH}_2\text{CHPi} + \text{QH}_2$$

The inhibition of HNS formation by picric acid, a relatively strong acid compared to HNBB, is very likely due to the disruptive influence of the acid on the equilibrium in the first step (eq 1). The sharply lower yield of HNS obtained with *N,N*-dimethylaniline relative to aniline, quinoline, and pyridine (Table IV) may be due to hindrance of the approach of the bulky substituted aniline to HNBB in the same step. The failure of *p*-nitroaniline to promote the quinone reaction when used in solvent quantity (above), despite a higher pK_a (Table IV) than the solvents (HMPA, Me_2SO, 1-methyl-2-pyrrolidinone) which yielded HNS, is attributable to an inability to accept a proton from HNBB (eq 1), contrary to the case of the three solvents.[9] Moderately strong bases with benzoquinone in DMF tended to produce HNS in lower yields (Table IV) than benzoquinone in HMPA without added base (Table II), and this is attributable to a greater tendency to form byproducts via competing side reactions in the presence of such bases. For instance, substituted trinitrobenzenes, like 2,4,6-trinitrobenzene itself, show a propensity for

(10) "Handbook of Chemistry and Physics", 52nd ed., Chemical Rubber Publishing Co., Cleveland, OH, 1971–1972, p D-117.

(11) E. A. Braude, A. G. Brook, and R. P. Linstead, *J. Chem. Soc.*, 3574 (1954), have reported that hydrogen atom transfer between bibenzyl and diphenylpicrylhydrazyl occurs to a slight extent (<2%).

(12) 2,4-Dichlorobenzoyl peroxide undergoes rapid homolysis at 70 °C: D. F. Doehnert and O. L. Mageli, *Proc. Annu. Conf. Reinf. Plast./Compos. Inst. Soc. Plast. Ind.*, 13, 108 (1958); *Chem. Abstr.*, 53, 18534i (1959).

(13) Preliminary spectroscopic evidence indicates that the carbanion of HNBB forms in basic ethanolic solutions and shows absorption maxima at 460 and 500 nm (C. Capellos, private communication).

(14) The alternative to hydride ion abstraction (eq 2) is electron transfer to the quinone, followed by hydrogen atom transfer to the quinone radical anion as follows:

$$\text{PiCH}_2\text{CHPi} + \text{Q} \rightarrow [\text{PiCH}_2\dot{\text{C}}\text{HPi} + \text{Q}^{-}\cdot] \rightarrow \text{PiCH=CHPi} + \text{QH}^-$$

This pathway is considered less likely in view of the negative result obtained with diphenylpicrylhydrazyl and HNBB in HMPA solution (above) and in view of the resistance of 2,4,6-trinitrobenzyl anion to transfer of an electron to oxygen (cf. footnote 15, ref 15).

(15) K. G. Shipp and L. A. Kaplan, *J. Org. Chem.*, 31, 857 (1966).

Table V. Effect of Air on the Dehydrogenation of HNBB by Quinones[a]

quinone	medium	atmosphere[b]	HNS yield, %
none	HMPA	air	10
DDQ	HMPA	air	89
		nitrogen[c]	87
p-benzoquinone[d]	HMPA	air	49
		air[c]	50
		nitrogen	50
methyl-*p*-benzoquinone	HMPA	air	72
		nitrogen	71
1,4-naphthoquinone	HMPA	air	71
		nitrogen	70
none	DMF/pyridine[e]	air	6
p-benzoquinone	DMF/pyridine[e]	air	65
		nitrogen	64
	DMF/quinoline[e]	air	73
		nitrogen[c]	73

[a] Molar ratio quinone/HNBB = 2 unless otherwise specified, temperature 70 °C, reaction time 3 h. [b] Stirring in air or nitrogen, modified as indicated. [c] Bubbled through reaction mixture. [d] Molar ratio quinone/HNBB = 0.5. [e] Molar ratio base/HNBB = 1.2.

forming anionic σ (Meisenheimer) complexes in basic solution.[16]

It should be noted that, with no quinone present, solutions of HNBB in HMPA, or in DMF containing pyridine, are capable of producing small amounts of HNS (6–10%) by air oxidation under the conditions employed in the present study, i.e., stirring in air for 3 h at 70 °C.[17] Yields obtained from reactions with quinones, however, were virtually the same whether air was excluded or not. Yields under nitrogen were not significantly different from those in air, even when the nitrogen or air was bubbled through the reaction mixtures (Table V). It is thus concluded that there was no significant contribution from air oxidation on performing the reactions with quinones in air. In attempted reactions with tetrahydroxy-*p*-benzoquinone and 9,10-anthraquinone, no HNS was obtained either by the action of the quinones or by air oxidation (Table II), indicating that quinones may possibly inhibit the air oxidation of HNBB.[18] Further evidence is necessary, however, before a firm conclusion may be drawn in this regard.

Experimental Section

Caution! HNS and HNBB, like TNT, are explosives and may detonate on grinding or impact.

Materials. HNBB was prepared from TNT and sodium hypochlorite by the method of Shipp and Kaplan[15] and recrystallized by dissolving 26 g in 780 mL of glacial acetic acid under gentle reflux, filtering the solution, and allowing it to stand overnight. The crystalline product, yellow-tan platelets, mp 225–228 °C (lit.[15] mp 218–220 °C, faintly yellow needles from acetone–water), was collected on a filter, washed with 2-propanol, and dried; yield 20 g. The various quinones, 2,3-dichloro-5,6-dicyanobenzoquinone (DDQ) and *o*-chloranil from Aldrich, chloranil, *p*-benzoquinone, methyl-*p*-benzoquinone, 1,4-naphthoquinone, tetrahydroxy-*p*-benzoquinone, and 9,10-anthraquinone from Eastman, tetrafluoro-*p*-benzoquinone from PCR, Inc., 2,5-diphenylbenzoquinone from K&K Labs, and tetramethyl-*p*-benzoquinone from Pfaltz and Bauer, were used as received. HMPA from Aldrich and the other solvents and amines were the best grades commercially available. 2,2-Diphenylpicrylhydrazyl from Aldrich, 2,4-dichlorobenzoyl peroxide (50% in silicone oil) from Lucidol Division, Pennwalt, and picric acid from Baker were used as received.

Table VI. Reactions under Modified Conditions

quinone	modification	HNS yield, %
1,4-naphthoquinone	2,4-dichlorobenzoyl peroxide (0.05 g, 0.13 mmol) present; N_2 atmosphere	71
methyl-*p*-benzoquinone	ultraviolet irradiation[a]	73
tetramethyl-*p*-benzoquinone	picric acid (0.70 g, 3.1 mmol) present	0
none	diphenylpicrylhydrazyl (2.09 g, 5.3 mmol) present; N_2 atmosphere	0[b]
p-benzoquinone	HMPA replaced as solvent by *p*-nitroaniline (21.4 g) dissolved in DMF (18 mL)[c]	0

[a] Reaction was run at ~60–70 °C in a quartz reaction vessel in an RPR-100 Rayonet photochemical reactor (16 lamps, ~35 W each). [b] Result was the same with *m*-xylene instead of HMPA. HNBB was predissolved in 175 mL of *m*-xylene at 60 °C. Workup consisted of evaporation of solvent followed by the usual acetone wash. [c] Quantities of water and acetone used during workup were doubled.

General Methods. Spectra were obtained from KBr disks on a Perkin-Elmer 457A grating infrared spectrophotometer. High-pressure LC analysis for hydroquinone was obtained on a Perkin-Elmer Series 3 liquid chromatograph (HC-ODS-C_{18} column, 15:85 acetonitrile–water, 1100 psi, 1 mL/min) with a LC-65T detector (254 nm, 60 °C). Melting points were taken in a Mel-Temp apparatus and are uncorrected. The elemental analysis was carried out by Schwarzkopf Microanalytical Laboratory, Woodside, NY.

Reactions of HNBB with Quinones in HMPA (General Procedure). The reaction of HNBB (1.22 g, 2.7 mmol) with DDQ (1.20 g, 5.3 mmol) in HMPA (15 mL) exemplifies the general procedure used for the reactions summarized in Table II. The mixture was heated 3 h in a constant-temperature bath at 70 ± 0.5 °C with gentle stirring by means of a bar magnet and then diluted with water (150 mL), and the separated solids were removed by filtration and air-dried. The solids were stirred 15 min in 150 mL of acetone, and the insoluble, pale yellow, powdery solid, mp 316–317 °C dec (lit.[15] mp 316 °C dec, pale yellow needles from nitrobenzene or DMF[19]), was collected on a filter; yield 1.07 g (89%). The infrared spectrum was identical with that of an authentic sample of HNS[20] prepared by the method of Shipp and Kaplan.[15] The presence of hydroquinone in the aqueous filtrate was confirmed by high-pressure LC.[21]

The product from other quinones (Table II) varied in color after the acetone wash from pale yellow to gray: mp ~315 °C; IR spectra identical with that of authentic HNS. The yields summarized in Table I were obtained when various solvents were substituted for HMPA at temperatures indicated. Tables V and VI summarize the results of reactions attempted under modified conditions.

Reactions of HNBB with *p*-Benzoquinone and Bases in DMF (General Procedure). The reaction of HNBB (1.22 g, 2.7 mmol) with *p*-benzoquinone (0.57 g, 5.3 mmol) and pyridine (0.25 g, 3.2 mmol) in DMF (15 mL) exemplifies the general procedure used for the reactions summarized in Table IV. After the mixture was heated for 3 h in a constant-temperature bath

(16) M. J. Strauss, *Chem. Rev.*, **70**, 667 (1970), and references therein.
(17) HNBB in DMF solution yielded no HNS under the same conditions, as was the case with benzoquinone present (Table I). Nevertheless, HNS can be produced by bubbling air through a solution of HNBB in DMF for 16–40 h at 30 °C. (This is reported in detail in a paper submitted for publication by E. E. Gilbert.) Thus, the air oxidation of HNBB may not require carbanion formation, unlike the case of the quinone reactions.
(18) Cf. G. Scott, "Atmospheric Oxidation and Antioxidants", Elsevier, Amsterdam, 1965, pp 164–166, and references therein, concerning the ability of quinones to combine with alkyl radicals.
(19) Small samples of HNS are also crystallizable from acetone and toluene.
(20) K. G. Shipp, *J. Org. Chem.*, **29**, 2620 (1964).
(21) The authors thank Dr. W. Fisco for this determination.

at 70 ± 0.5 °C with gentle stirring by means of a bar magnet, workup similar to the above procedure gave tan to brown, powdery product: mp 315–316 °C dec; yield 0.78 g (65%). The IR spectrum was identical with that of authentic HNS.[20] The presence of hydroquinone in the aqueous filtrate was detected by high-pressure LC.[21]

The products from other bases (Table IV) varied in color after the acetone wash from gray to light tan to brown: mp ~315 °C; IR spectra identical with that of authentic HNS. The yields summarized in Table III were obtained when the quantity of pyridine and the reaction time were varied as indicated. The yields obtained in reactions with air excluded are cited in Table V.

A bright orange, acetone-washed solid, mp 404–406 °C dec (acetone), was obtained from both cyclohexylamine and triethylamine. Anal. Calcd for $C_{14}H_6N_6O_{12}$ (HNS): C, 37.33; H, 1.34; N, 18.67. Found: C, 43.64; H, 1.54; N, 16.93.

Registry No. HNBB, 5180-53-0; HNS, 20062-22-0; DDQ, 84-58-2; tetrafluoro-*p*-benzoquinone, 527-21-9; *o*-chloranil, 2435-53-2; chloranil, 118-75-2; *p*-benzoquinone, 106-51-4; 2,5-diphenylbenzoquinone, 844-51-9; methyl-*p*-benzoquinone, 553-97-9; 1,4-naphthoquinone, 130-15-4; tetramethyl-*p*-benzoquinone, 527-17-3; tetrahydroxy-*p*-benzoquinone, 319-89-1; 9,10-anthraquinone, 84-65-1; *p*-nitroaniline, 100-01-6; aniline, 62-53-3; quinoline, 91-22-5; *N,N*-dimethylaniline, 121-69-7; pyridine, 110-86-1; 2-picoline, 109-06-8; 4-picoline, 108-89-4; morpholine, 110-91-8; cyclohexylamine, 108-91-8; triethylamine, 121-44-8.

Correlation of Activation Energies with Taft's Alkyl Inductive Substituent Constants and Its Implications to the Respective Steric Parameters. Dual Kinetic Parameter Relationships

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Fourteen sets of activation energies and four sets of steric parameters have been correlated with Taft's alkyl inductive substituent constants $\sigma_I(R)$. The correlated activation energies are from bimolecular processes either in solution or in the gas phase, polar or nonpolar, and from unimolecular decomposition reactions in the gas phase. Substitution of the E_a vs. $-\sigma_I(R)$ correlations into the Arrhenius equation leads to eq 6, where a and b are the coefficients of the linear regression equation of E_a vs. $-\sigma_I(R)$ and A is the Arrhenius preexponential factor. The function E_s' (eq 3) could be viewed as a "steric function" but does not seem to be related to any conventional steric parameter. However, the ratio $(\ln A - b/RT)/\ln k_{calcd}$, or its inverse, in certain cases is linearly related to $E_s^c(R)$ constants. Possibly the linearity between the ratio $(\ln A - b/RT)/\ln k_{calcd}$, or its inverse, and $E_s^c(R)$ indicates that the function $(\ln A - b/RT)/\ln k_{calcd}$ can separate the steric effect of the substituent, provided that the steric effect has an entropic component that dominates over the respective enthalpic component. In such a case the physical meaning of the function is "the fraction of energy attributed to the steric effect of the substituent". Combining eq 6 with the appropriate equations of the transition-state theory, one obtains eq 7. Equation 7 indicates that kinetic data that can be analyzed by eq 6 may involve the isokinetic effect. It has been noted that the various substituent constants, i.e., $E_s(R)$, v_{OR}, and $\sigma_I(R)$, used in alternative representations of a given set of kinetic data are interrelated. This led to the conclusion that "a correlation amounts to the division of energy expressed either by E_a or by $\log (k/k_0)(\log k)$ into two (and possibly more) parts in a more or less arbitrary albeit self-consistent way". This, perhaps, is the main source of the existing controversy on the validity of $\sigma^*(R)$ and $\sigma_I(R)$ scales.

Activation energies for reactions such as nucleophilic displacements (eq 1a), alkaline hydrolysis of alkyl acetates (eq 1b), gas-phase unimolecular decomposition reactions (eq 1c), or hydrogen atom abstraction by free radicals (eq 1d) all show a marked dependence on the structure of the

$$RX + Y^- \rightarrow RY + X^- \quad (1a)$$

$$ROAc + OH^- \rightarrow ROH + AcO^- \quad (1b)$$

$$RCl \rightarrow R'_{ene} + HCl \quad (1c)$$

$$CD_3\cdot + RH \rightarrow CHD_3 + R\cdot \quad (1d)$$

substituent R. Thus, considering specifically the reaction series for R = CH_3, Et, *n*-Pr, *i*-Pr, *n*-Bu, *i*-Bu, *s*-Bu, and *t*-Bu, the respective ranges in E_a's for the reactions 1a–d are 5.3[1] (X = Br, Y = Cl), 4.7,[2] 11.5,[3] and 6.2.[4] It is of interest to investigate the basis for such marked dependence of E_a on R. This problem has been stated previously but concerned mainly reactions of type 1b[5] and to a lesser extent reactions such as 1a.[6a,b]

Taft[5] has represented data of alkaline hydrolysis of esters with structural variation at the acyl or alkoxy moieties as two-parameter relationships. According to this analysis, differences in energies of activation in a given series of similar reactions are assumed to arise from differences in the polar and steric effects of the varied substituent. Charton has introduced[7–11] an alternative representation of the same data and of data from reactions such as 1a, which attributes differences in free energy of activation to primarily steric effects of the varied sub-

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