bonding.[9] Potassium acetate, which provides a strong hydrogen-bonding anion, also shows some promoting effect in this reaction. The absence of **3** in product solutions suggests its formation is rate limiting. However, the use of KBr in place of KF gives both p-$BrC_6H_4CF_3$ and **2**.

The conversion of **2** to **4** likely occurs by a mechanism involving ammonolysis of the CF_3 substituent to give p-$H_2NC_6H_4CF_2NH_2$. Subsequent elimination of HF would generate **4**.[10]

Experimental Section

Materials. All reagents were commercially available and used without further purification. Anhydrous KF was handled under N_2 to prevent deliquescence. Precautions were taken to prevent oxidation of cuprous chloride.

Ammonolysis of p-Chlorobenzotrifluoride. Two procedures were used for the ammonolysis reactions. For the first procedure, an 80-mL Hastelloy shaker tube was charged with reactants, catalysts, and promoters. The tube was chilled to −80 °C, evacuated, and, if desired, additional gas added prior to heating for a specified time. After reaction, the tube contents were removed and analyzed by GC or GC/mass spectrometry. The second, and most frequently used, procedure is similar to that described by Cramer.[11] The reaction components were charged by weight to matched glass tubes (internal volume of 4.8–6.0 mL). Ammonia was condensed into the chilled, evacuated tubes, using standard vacuum line techniques, and the tubes were sealed. A 400-mL autoclave was charged with the tubes (usually five) with ethanol (as the heat transfer fluid) and N_2 (for external pressure) and heated with agitation for the specified time.

After reaction, the glass tubes were chilled, opened, and stoppered with a rubber septum containing a hollow needle through which the ammonia distilled as the tubes warmed to room temperature. The tube contents were then quantitatively transferred to 25-mL volumetric flasks with carrier solution (79.7% cyclopentane, 20% chloroform, and 0.3% morpholine) for analysis by high-pressure liquid chromatography, high-pressure LC. Alternatively, the reactions were run with 1% n-undecane as internal standard for GC analysis. Experimental results are summarized in Table II.[12]

Hydrolysis of p-Aminobenzotrifluoride (2). A mixture of 4.0 mL of **2**, 0.3 g each of copper powder and Cu_2Cl_2, 1.5 g of CaO, and 28 mL of 28% aqueous ammonia was heated for 2 h at 240 °C. Analysis by GC of the resulting solution showed that **2** had been completely consumed. No fluorine-containing components were detected by ^{19}F NMR. GC/mass spectrometry and ^1H NMR confirmed that aniline was the only aromatic product. Under these same reaction conditions, p-aminobenzoic acid, which is postulated as the initial hydrolysis product in the conversion of **2** to aniline (eq 1), was also converted quantitatively to aniline. The hydrolysis of **2** does not occur in ethanolic ammonia in the presence of Cu_2Cl_2, Cu^0, and CaO.

Conversion of p-Aminobenzotrifluoride (2) to p-Cyanoaniline (4). A solution of 0.318 g of **2** in 1.27 g of C_2H_5OH with 855 mg of NH_3 was heated for 5 h at 200 °C in a sealed glass tube. Only 1.5% of **2** is converted to **4**. Addition of 19.1 mg of Cu_2Cl_2 raises this conversion to 5.9%. With 20.4 mg of Cu_2Cl_2 and 191 mg of KF, the conversion is 15%. The rate at which **2** is converted to **4** is competitive with the rate of ammonolysis. A sealed glass tube was charged as follows: 0.532 mmol of **2**; 17.8 mg of Cu_2Cl_2; 1.158 mmol of **1**; 255 mg of KF; 1.17 g of CH_3OH; 793 mg of NH_3; 27.9 mg of NH_4Cl (equivalent to the amount generated during formation of **2**). The tube was heated for 5 h at 200 °C. Analysis of the resulting solution by high-pressure LC showed 0.768 mmol of **1**, 0.310 mmol of **2**, and 0.630 mmol of **4**. Assuming **1** → **2** → **4**, this product distribution corresponds to 34% conversion of **1** to **2** and 66% conversion of **2** to **4**. Formation of **4** is somewhat slower in C_2H_5OH but still competitive.

Registry No. **1**, 98-56-6; **2**, 455-14-1; **3**, 402-44-8; **4**, 873-74-5; $C_6H_5CF_3$, 98-08-8; $C_6H_5NH_2$, 62-53-3; KF, 7789-23-3.

(9) J. H. Clark and J. Emsley, *J. Chem. Soc., Dalton Trans.*, 2129 (1975).

(10) Y. Kobayashi and I. Kumadaki, *Acc. Chem. Res.*, **11**, 197 (1978).

(11) R. Cramer and D. R. Coulson, *J. Org. Chem.*, **40**, 2267 (1975).

(12) High-pressure LC analyses were run using a 25 cm × 4.6 mm column of PSM-149-3 or PSM-149-2 (porous silicone microspheres-50, 6 μm particle size, 50 Å pore size, 300 m^2/g surface area) at ambient temperature. A carrier solution flow rate from 2.86 to 1.11 mL/min at 1000 to 725 psig was maintained. Components as they eluted were detected by ultraviolet absorption at 254 nm. GC analyses were run using an 8 ft × $^1/_8$ in. column of Tenax GC 60/80 and a temperature programmed from 175 to 300 °C at 16 °C/min; % conversion = (total mol of product/mol of reactant) × 10^2; % yield of X = (mol of X/total mol of product) × 10^2; % conversion to X = (mol of X/mol of reactant) × 10^2.

N-Bromosuccinimide-Dimethylformamide: A Mild, Selective Nuclear Monobromination Reagent for Reactive Aromatic Compounds

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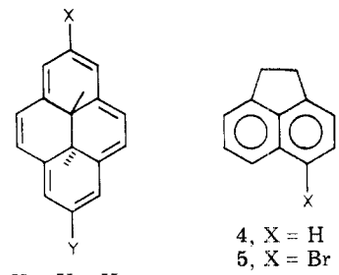
Although electrophilic substitution of aromatic hydrocarbons by bromine is a well-known organic reaction,[1] no reliable[2] and mild method exists for the selective monobromination of reactive aromatic hydrocarbons. This point was reinforced for us when we required a sample of 2-bromo-*trans*-10b,10c-dimethyl-10b,10c-dihydropyrene (**2**).



1, X = Y = H
2, X = Br; Y = H
3, X = Y = Br

4, X = H
5, X = Br

Boekelheide[3] had reported that treatment of the parent, **1**, with bromine produced a mixture of polysubstituted[4] bromo compounds, whereas *N*-bromosuccinimide (NBS) in CCl_4, under free-radical conditions, gave ~19% of the 2,7-dibromide **3**. The electrophilic substitution of an aromatic ring by NBS in nonpolar solvents such as CCl_4 is in fact well documented,[5] although the results are highly variable in terms of both products and yields. The use of NBS in polar solvents, however, is less well-known.[5] Ross et al.[6] have studied the reaction of toluene, fluorene, and acenaphthene (**4**) in propylene carbonate, where predominantly nuclear bromination takes place. In the case of

(1) For reviews see: R. C. Fuson, "Reactions of Organic Compounds", Wiley, New York, 1962, pp 58–65, 98–102; R. O. C. Norman and R. Taylor, "Electrophilic Substitution in Benzenoid Compounds", Elsevier, New York, 1965, pp 130–2; H. P. Braendin and E. T. McBee, "Friedel-Crafts and Related Reactions", Vol. III, G. A. Olah, Ed., Wiley, New York, 1964, Chapter 46.

(2) Perusal of "Organic Syntheses" shows examples where monobromination can be achieved often in excellent yields, but each example has its own specific set of conditions.

(3) J. B. Phillips, R. J. Molyneux, E. Sturm, and V. Boekelheide, *J. Am. Chem. Soc.*, **89**, 1704 (1967).

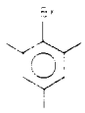
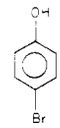
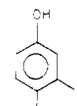
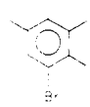
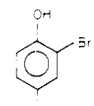
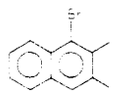
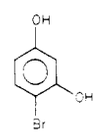
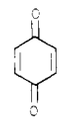
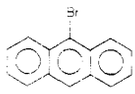
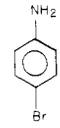
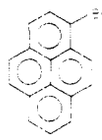
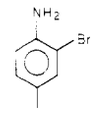
(4) We have found that even at −78 °C a complex mixture of bromides results.

(5) C. Djerassi, *Chem. Rev.*, **48**, 271 (1948); L. Horner and E. H. Winkelmann, "Newer Methods of Preparative Organic Chemistry", Vol. III, W. Foerst, Ed., Academic Press, New York, 1964, p 151.

(6) S. D. Ross, M. Finkelstein, and R. C. Petersen, *J. Am. Chem. Soc.*, **80**, 4327 (1958).

0022-3263/79/1944-4733$01.00/0

Table I. Bromination with NBS-DMF at Room Temperature[a]

product[c]	yield,[b] %	properties[c]	product[c]	yield,[b] %	properties[c]
	87	see ref 8, Vol. 4, 64B		70	see ref 8, Vol. 4, 116C; mp 64 °C (lit.[14] mp 64-65 °C)
	83	^{1}H NMR δ 7.25 (d, 1 H, J = 8 Hz), 6.27 (d, 1 H, J = 8 Hz), 2.34 (s, 3 H), 2.18 (s, 6 H)		89	^{1}H NMR δ 8.5 (br s, 1 H, OH), 7.25 (d, 1 H, J = 8 Hz, H-5), 6.68 (dd, 1 H, J_o = 8 Hz, J_m = 3 Hz, H-6), 6.47 (d, 1 H, J_m = 3 Hz, H-2), 2.27 (s, 3 H); mp 58-60 °C (lit.[15] mp 57 °C)
	87	^{1}H NMR δ 6.86 (s, 1 H), 2.36 (s, 3 H), 2.31 (s, 3 H), 2.15 (s, 6 H)			
	94	^{1}H NMR δ 7.22 (s, 1 H), 2.34 (s, 3 H), 2.20 (s, 6 H), 2.11 (s, 3 H)		86	see ref 8, Vol. 4, 124C
	88	^{1}H NMR δ 8.3-7.2 (m, 5 H), 2.38 (s, 3 H), 2.24 (s, 3 H); mp 62 °C (lit.[12] mp 62-64 °C)		62	see ref 8, Vol. 4, 139D; mp 98 °C (lit.[16] mp 100-102 °C)
5	98	see ref 7 and ref 8, Vol. 4, 80C; mp 54-55 °C (lit.[6] mp 51-52 °C)	 [d]	*f*	see ref 8, Vol. 2, 141D; mp 112-114 °C (lit.[17] mp 113-115 °C)
	88	see ref 8, Vol. 4, 82B; mp 99 °C (lit.[13] mp 101-102 °C)		93	see ref 8, Vol. 5, 55A; mp 62 °C (lit.[17] mp 62-64 °C)
	89	^{1}H NMR δ 7.4-8.4 (m, all H); mp 94 °C (lit.[9] mp 94.5 °C)			
				92	see ref 8, Vol. 5, 70B
2	70	^{1}H NMR δ 8.70 (s, 2 H, H-1,3), 8.65-8.50 (m, 6 H), 8.07 (t, 1 H, J = 9 Hz, H-7), ~4.07 and ~4.08 (s, 3 H each); mp 111-112 °C			

[a] See Experimental Section for conditions. [b] Determined by ^{1}H NMR and GC. Product identification was by ^{1}H NMR and mass spectra and where appropriate melting point. [c] Substrates have Br of product replaced by H. [d] Substrate is hydroquinone. [e] ^{1}H NMR spectra taken in $CDCl_3$. [f] Quantitative.

4, they also note that NBS–DMF gives exclusively 5-bromoacenaphthene (**5**). We have verified this previously,[7] and found that NBS–DMF was the most convenient and reliable method to prepare **5** on both millimolar and molar scales. We thus treated a DMF solution of **1** with a solution of NBS in DMF at room temperature and obtained **2**, relatively pure by ^{1}H NMR. Direct crystallization then yielded 65–70% of pure **2**, mp 111–112 °C.

The general applicability of this reagent for a number of other reactive aromatics was then investigated, and the results are presented in Table I. In all cases the same reaction conditions were used, which makes the reagent particularly useful.[2] As can be seen, clean monobromination occurs in excellent yields. The products were checked for purity by GC and ^{1}H NMR. Some products had definitive ^{1}H NMR spectra, while others were compared with spectra in the Aldrich catalogues.[8] All were checked by mass spectroscopy, to ensure the absence of dibromides.

The results with the phenols and amines are noteworthy in that normally it is quite difficult to obtain, in these cases, good yields of monobrominated product easily.[1] Hydroquinone, however, is oxidized to *p*-benzoquinone. This has been observed previously by using NBS in water.[5] Catechol yields highly colored solutions, which may contain *o*-benzoquinone, but we have not been able to isolate *o*-benzoquinone. The reaction is not useful for diamines where colored products also result. In the case of aromatic hydrocarbons, the nucleus must be sufficiently activated before significant reaction occurs. Thus the reagent is not effective for benzene, toluene, the xylenes, indan, tetralin, and phenanthrene. However, it is extremely useful for the higher aromatics such as pyrene, which are more difficult[9] to monobrominate with bromine itself. The above results indicate that the reagent (particularly for phenol and aniline) is more selective than Br_2 and thallium(III) acetate, a reagent recently introduced by McKillop et al.[10] We have also found that for preparation of **2** from **1**, NBS–DMF gives better yields and cleaner product than $CuBr_2$, which has also recently been used to brominate aromatics.[11]

(7) R. H. Mitchell, T. Fyles, and L. M. Ralph, *Can. J. Chem.*, **55**, 1480 (1977).
(8) "The Aldrich Library of NMR Spectra", Aldrich Chemical Co., Milwaukee, Wis., 1974.
(9) G. Lock, *Chem. Ber.*, **70**, 926 (1937).
(10) A. McKillop, D. Bromley, and E. C. Taylor, *J. Org. Chem.*, **37**, 88 (1972).
(11) D. Mosnaim and D. C. Nonhebel, *Tetrahedron*, **25**, 1591 (1969).
(12) R. T. Arnold and R. W. Liggett, *J. Am. Chem. Soc.*, **64**, 2875 (1942).
(13) L. F. Fieser and S. T. Putnam, *J. Am. Chem. Soc.*, **69**, 1038 (1947).

Experimental Section

Melting points were determined on a Kofler hot stage and are uncorrected. ^{1}H NMR spectra were determined on a Perkin-Elmer R12A (60-MHz) spectrometer and are reported in parts per million downfield from tetramethylsilane as internal standard. Mass spectra were determined on a Hitachi Perkin-Elmer RMU-7 mass spectrometer at 70 eV. Microanalyses were performed by this department.

Standard Procedure Used for All Examples. A solution of NBS (1 mmol) in dry DMF (5 mL) was added to a solution of substrate (1 mmol) in dry DMF (5 mL) and stirred at room temperature for 24 h. The mixture was poured into water (50 mL) and extracted with pentane or dichloromethane (50 mL). The extract was washed well with water, dried ($MgSO_4$), and evaporated under reduced pressure to yield crude monobromide. For larger scale reactions, concentrations may be increased to 0.1 mol in 50 mL of solvent.

2-Bromo-*trans*-10b,10c-dimethyl-10b,10c-dihydropyrene (2). From 1 as described above, direct recrystallization from aqueous methanol yielded green crystals of **2**: mp 111–112 °C; ^{1}H NMR, see Table I; mass spectrum, *m/e* (rel intensity) 312, 310 (10, M^+), 297, 295 (5, M – CH_3), 282, 280 (10, M – $2CH_3$), 231 (24, M – Br), 216 (65), 215 (86), 201 (100). Anal. Calcd for $C_{18}H_{15}Br$: C, 69.47; H, 4.86. Found: C, 69.30; H, 4.92.

Acknowledgment. We thank the National Sciences and Engineering Research Council of Canada and the University of Victoria for financial support.

Registry No. 1, 956-84-3; **2**, 71807-14-2; **4**, 83-32-9; **5**, 2051-98-1; 1,3,5-trimethylbenzene, 108-67-8; 1,2,3-trimethylbenzene, 526-73-8; 1,2,3,5-tetramethylbenzene, 527-53-7; 1,2,3,4-tetramethylbenzene, 488-23-3; 2,3-dimethylnaphthalene, 581-40-8; anthracene, 120-12-7; pyrene, 129-00-0; phenol, 108-95-2; 3-methylphenol, 108-39-4; 4-methylphenol, 106-44-5; 1,3-benzenediol, 108-46-3; hydroquinone, 123-31-9; benzenamine, 62-53-3; 4-methylbenzenamine, 106-49-0; 2-bromo-1,3,5-trimethylbenzene, 576-83-0; 1-bromo-2,3,4-trimethylbenzene, 40101-33-5; 1-bromo-2,3,4,6-tetramethylbenzene, 3349-15-3; 1-bromo-2,3,4,5-tetramethylbenzene, 40101-36-8; 1-bromo-2,3-dimethylnaphthalene, 5334-79-2; 9-bromoanthracene, 1564-64-3; 1-bromopyrene, 1714-29-0; 4-bromophenol, 106-41-2; 4-bromo-3-methylphenol, 14472-14-1; 2-bromo-4-methylphenol, 6627-55-0; 4-bromo-1,3-benzenediol, 6626-15-9; quinone, 106-51-4; 4-bromobenzenamine, 106-40-1; 2-bromo-4-methylbenzenamine, 583-68-6; NBS, 128-08-5.

(14) J. W. Williams and J. M. Fogelberg, *J. Am. Chem. Soc.*, **52**, 1356 (1930).
(15) R. C. Huston and J. A. Hutchinson, *J. Am. Chem. Soc.*, **54**, 1504 (1932).
(16) R. B. Sandin, A. Gillies, and S. C. Lynn, *J. Am. Chem. Soc.*, **61**, 2919 (1939).
(17) Aldrich sample.

Evidence for a Violation of the Reactivity–Selectivity Principle from a Study of Substituent Effect Transmission in α-Activated Arylmethyl Carbanions

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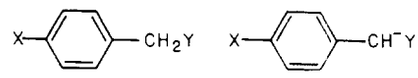
The response of side chain magnetic monitors[1] to aryl substituents is a sensitive probe of factors[2] and mechanisms[3] governing the transmission of effects. To take advantage of this we investigated in the pair of conjugated substrates **1** and **2** the influence of Y on the sensitivity of



1 **2**

the benzylic proton(s) to effects exerted by para substituents X.[4] Evidence is provided that the sensitivity of the benzylic proton in carbanions **2** depends upon the stereochemistry of the anion and responds to the effectiveness of the Y group in removing the negative charge from the carbanide carbon. High sensitivities are thus found for those Y groups such as Y = CN and SO_2R for which we anticipated[5] poor capacities in stabilizing adjacent carbanions by delocalizative mechanisms.

^{1}H chemical shifts of the methylene protons of a family of compounds (e.g., **1**, Y = SO_2Ph) are plotted vs. shifts of another family (e.g. Y = COMe): an analogous treatment

Table I. Relative Sensitivities of Methylene Protons in α-Substituted Arylmethanes (Equation 1)[a]

entry no.	Y	$\lambda_{CH_2} \pm s^b$	r^c	n^d
1	H	0.68 ± 0.07	0.969	9
2	SPh	0.55 ± 0.03	0.991	9
3	Ph	0.68 ± 0.04	0.990	8
4	CN	0.89 ± 0.08	0.978	8
5	$CONMe_2$	0.83 ± 0.06	0.989	7
6	CO_2Me	0.90 ± 0.04	0.995	7
7	COMe	1.03 ± 0.02	0.998	7
8	COPh	1.03 ± 0.02	0.999	7
9	SOPh[e]	0.73 ± 0.04	0.992	8
9	SOPh[f]	0.95 ± 0.04	0.996	8
10	SOMe[e]	0.62 ± 0.05	0.975	9
10	SOMe[f]	0.80 ± 0.04	0.990	9
11	SO_2Me	1.17 ± 0.11	0.969	9
12	NOH[g]	0.72 ± 0.04	0.991	9
13	NOH[h]	1.01 ± 0.04	0.995	7

[a] Chemical shifts for Me_2SO solutions (0.2 M in substrate). [b] Standard deviation of the slope. [c] Correlation coefficient. [d] Number of points. [e] High-field proton. [f] Low-field proton. [g] Synoximes. [h] Antioximes.

Table II. Relative Sensitivities of Methine Protons in α-Substituted Arylmethyl Carbanions (Equation 2)[a]

entry no.	Y	$\lambda_{CH^-} \pm s^b$	r^b	n^b
3	Ph	0.72 ± 0.05	0.992	5
4	CN[c]	0.95 ± 0.07	0.994	4
5	$CONMe_2$	0.49 ± 0.01	0.998	6
6	CO_2Me	0.53 ± 0.02	0.995	8
7	COMe	0.45 ± 0.01	0.998	7
8	COPh	0.36 ± 0.02	0.993	7
9	SOPh	0.78 ± 0.05	0.994	5
11	SO_2Me	1.06 ± 0.07	0.987	8

[a] Carbanions in Me_2SO solution (0.2 M) are prepared in situ from sodium dimsyl, 0.3 M in Me_2SO. [b] See Table I for explanation. [c] Only a limited number of points are available, since Me_2SO obscures resonances of methine proton in many $ArCH^-CN$.

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