tives are generally obtained directly in a chromatographically pure state before recrystallization. The risk of racemization under normal conditions appears to be very small, and the method promises to be particularly useful for the synthesis of large peptides in cases where racemization would otherwise be a serious risk.

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Received June 16, 1969

Relative Stabilities of Alkylbenzene Negative Ions

Sir:

Electron affinities of polynuclear aromatic hydrocarbons have been determined in the gas phase by electron capture techniques[1] and in solution by potentiometric[2] and polarographic[3] determination of the electrochemical potential required for one-electron reduction. Relative electron affinities have also been measured by ultraviolet spectroscopic determination of the concentrations of radical anions in partially reduced mixtures of hydrocarbons.[4] All of the methods of absolute determination, however, require that the one-electron reduction products be relatively easily formed in the gas or liquid phases, while the use of spectroscopy requires that extinction coefficients be accurately known. None of these methods seems to be applicable to the study of the reduction potentials of benzene or alkylbenzenes for which the electron affinities have been estimated to be negative.[5] Such measurements are of interest, however, both on theoretical grounds and for their possible application to the understanding of the chemistry of this important class of hydrocarbons.

We report here an estimate of the relative electron affinities of benzene and some alkylbenzenes based on the free energy change for equilibrium 1 as determined

$$C_6H_6 + R_1R_2C_6H_4\cdot^- \overset{K_1}{\rightleftharpoons} C_6H_6\cdot^- + R_1R_2C_6H_4 \qquad (1)$$

by electron spin resonance of the radical anions in partially reduced binary solutions of the hydrocarbons. Mixtures of carefully measured known concentrations of benzene and alkylbenzenes were reduced *in vacuo* by sodium–potassium alloy in tetrahydrofuran–dimethoxyethane solution.[6a] Esr spectra were recorded at −100°.[6b] Equilibrium constants were calculated from the relative concentrations of the free radicals, as determined by double integration of the esr spectra, in solutions where reduction had proceeded to less than 1%.[7] Separate quantitative determination of the concentrations of both radical species is possible under these conditions because the rate of chemical exchange is slow in these systems[8] and makes it possible for a high concentration of the unreduced species to be present without producing collapse of the multiplet structure or even appreciable broadening of the lines of the esr spectrum.

Values of K_1 are given in Table I. As might be anticipated on chemical grounds, introduction of an alkyl substituent into the benzene ring renders the molecule more resistant to one-electron reduction. A plot of ln K_1 *vs.* σ^* inductive constants[9] for the monosubstituted compounds is linear. The ρ^* value of 5 determined in this way is typical of carbanionic processes.[10] Similar, though smaller, effects of alkyl substitution have been observed in electron addition reactions of the higher polyacenes. For example, the polarographic half-wave potential of naphthalene becomes more negative with increased alkyl group substitution.[11] Similarly, the rate of the metal–ammonia reduction of benzene, which is presumed to proceed *via* the intermediacy of the radical anion, is retarded by alkyl substituents.[12]

Table I. Equilibrium Constants and Free Energy Changes for Benzene Radical Anion Relative to Alkylbenzene Radical Anions[a]

$$R_1R_2C_6H_4\cdot^- + C_6H_6 \overset{K_1}{\rightleftharpoons} C_6H_6\cdot^- + R_1R_2C_6H_4$$

R_1	R_2	K_1[b]	$-\Delta G_{173}°$, eV
CH_3	H	4.4 ± 1.0	0.02_2
CH_2CH_3	H	22 ± 3	0.04_6
$CH(CH_3)_2$	H	40 ± 9	0.05_5
$C(CH_3)_3$	H	110 ± 19	0.07_0
CH_3	*o*-CH_3	890 ± 180[c]	0.10_0
CH_3	*m*-CH_3	51 ± 13[c]	0.05_9
CH_3	*p*-CH_3	9.1 ± 1	0.03_3
CH_2CH_3	*p*-CH_2CH_3	120 ± 20	0.07_1
$CH(CH_3)_2$	*p*-$CH(CH_3)_2$	629 ± 110	0.09_1
$C(CH_3)_3$	*p*-$C(CH_3)_3$	>4300[d]	$>0.12_4$

[a] Solvent THF–DME (1:1, v/v), reducing agent Na–K (1:2), temperature −100 ± 2°, total hydrocarbon concentration 0.15–0.30 *M*. [b] Errors are one standard deviation for the average of eight to ten measurements. [c] Calculated from the equilibrium constants relative to *p*-xylene. [d] 1,4-Di-*t*-butylbenzene does not produce a detectable amount of radical anion under these conditions.

We believe that the equilibrium constants reported in this preliminary communication are a good approximation to the corresponding quantities in the gas phase primarily because the effects of solvation and ion pairing should be approximately constant for ions and molecules, such as those involved here, which are of similar

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(1) (a) W. E. Wentworth, E. Chen, and J. E. Lovelock, *J. Phys. Chem.*, **70**, 445 (1966); (b) R. S. Becker and E. Chen, *J. Chem. Phys.*, **45**, 2403 (1966).

(2) G. J. Hoijtink, E. deBoer, P. H. van der Meij, and W. P. Weijland, *Rec. Trav. Chim.*, **75**, 487 (1956).

(3) J. Chaudhuri, J. Jagur-Grodzinski, and M. Szwarc, *J. Phys. Chem.*, **71**, 3063 (1967).

(4) (a) D. E. Paul, D. Lipkin, and S. I. Weissman, *J. Amer. Chem. Soc.*, **78**, 116 (1956); (b) M. Szwarc, *Progr. Phys. Org. Chem.*, **6**, 323 (1968).

(5) G. Briegleb, *Angew. Chem. Intern. Ed. Engl.*, **3**, 617 (1964).

(6) (a) R. G. Lawler and G. K. Fraenkel, *J. Chem. Phys.*, **49**, 1126 (1968); (b) R. D. Allendoerfer and P. H. Rieger, *J. Amer. Chem. Soc.*, **88**, 3711 (1966).

(7) Under these conditions a small amount of decomposition of the radical ions will not change the concentration of neutral species appreciably and will therefore have negligible effect on K_1 provided that equilibrium between neutral and ionic species and reducing agent is attained at a rate which is rapid compared to that of the side reactions. Failure of these conditions was demonstrated occasionally by the observation of nonreproducible ratios of radical ion concentrations on successive scans of the esr spectrum of a sample. Samples exhibiting this behavior were rejected.

(8) (a) G. L. Malinowski and W. H. Bruning, *J. Amer. Chem. Soc.*, **89**, 5063 (1967); (b) E. deBoer and C. MacLean, *J. Chem. Phys.*, **44**, 1334 (1966).

(9) R. W. Taft, "Steric Effects in Organic Chemistry," M. S. Newman, Ed., John Wiley & Sons, Inc., New York, N. Y., 1956, Chapter 13.

(10) A. Streitwieser, Jr., and H. F. Koch, *J. Amer. Chem. Soc.*, **86**, 404 (1964).

(11) (a) L. H. Klemm and A. J. Kohlik, *J. Org. Chem.*, **28**, 2044 (1963); (b) A. Streitwieser, Jr., and I. Schwager, *J. Phys. Chem.*, **66**, 2316 (1962).

(12) (a) A. P. Krapcho and A. A. Bothner-By, *J. Amer. Chem. Soc.*, **81**, 3658 (1959); (b) A. P. Krapcho and M. E. Nadel, *ibid.*, **86**, 1096 (1964); (c) H. Smith, "Organic Reactions in Liquid Ammonia," Vol. 1, Part 2, John Wiley & Sons, Inc., New York, N. Y., 1963.

size and charge distribution. This is supported by measurements of K_1 for the benzene–p-xylene system over a temperature range of 50° which indicate that $\Delta G°$ and $\Delta H°$ for the equilibrium are essentially the same, suggesting negligible contribution from differences in the entropy effects of solvation. The importance of solvation and ion pairing is, however, being explored more fully despite experimental difficulties attendant on the variation of solvent and cation due to the inherent susceptibility of these radical ions to destructive side reactions.

Perhaps the most surprising aspect of our experimental results is the range of more than three orders of magnitude in the values of K_1 for the monoalkyl- and p-dialkylbenzenes. The perturbing effect of an alkyl substituent on the electron affinity of benzene may be estimated using molecular orbital theory in a manner such as has been employed successfully for predicting the relative ionization potentials of the alkylbenzenes.[13] This simple method leads to the prediction that each of the mono- and p-dialkylbenzenes should have the *same* electron affinity as benzene. This prediction arises simply because the perturbing substituents cannot, to first order, change the energy of the highest filled molecular orbital of the benzene radical anion.[14] Furthermore, this is true for both inductive and hyperconjugative mechanisms of interaction between the alkyl substituent and the aromatic ring.[14]

It should also be pointed out that although the apparent relative strengths of the "electron-donating" effects of alkyl groups inferred from our data are in accord with other chemical substituent effects (*vide supra*), they are *opposite* the order suggested by the esr hyperfine splittings of the radical anions. For example, of the groups studied, the t-butyl group produces the largest decrease in stability of the benzene radical anion but gives rise to the smallest perturbation of the spin density in the aromatic ring.[15] The esr data and our relative stabilities taken together constitute a significant goal for more refined theoretical treatments of the interaction between saturated and unsaturated groups.

Acknowledgments. We wish to thank the National Science Foundation for partial financial support and Professor P. H. Rieger for the generous use of his esr spectrometer.

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(13) (a) A. Streitwieser, Jr., *Progr. Phys. Org. Chem.*, 1, 1 (1963); (b) R. Bralsford, P. V. Harris, and W. C. Price, *Proc. Roy. Soc.* (London), **A258**, 459 (1960).

(14) D. Purins and M. Karplus, *J. Amer. Chem. Soc.*, **90**, 6275 (1968).

(15) J. R. Bolton, A. Carrington, A. Forman, and L. E. Orgel, *Mol. Phys.*, **5**, 43 (1962).

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Received April 7, 1969

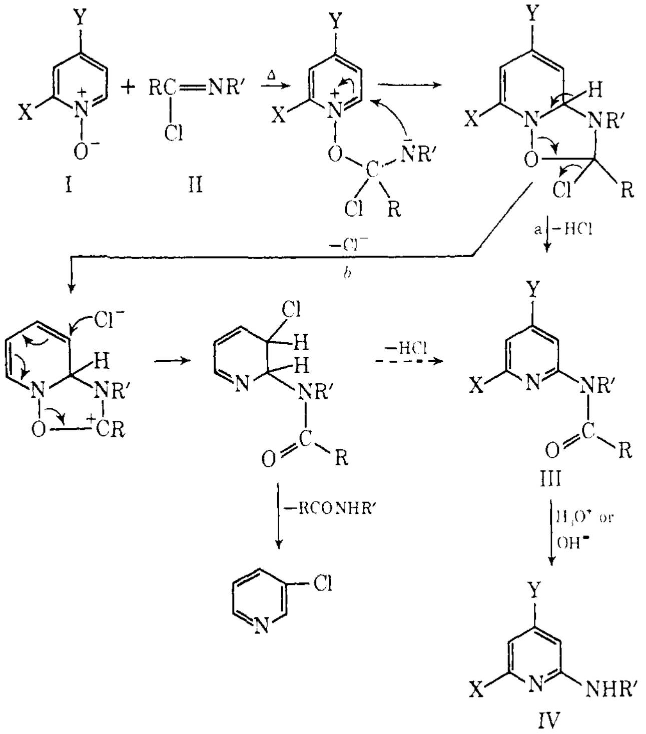
A Direct Alkyl and Aryl Amination of Heteroaromatic Nitrogen Compounds

Sir:

There are relatively few methods available for the direct substitution of hydrogen in six-membered heteroaromatic nitrogen compounds. Some of the best known are the Tschitschibabin reaction which leads to primary amines and the alkylations and arylations using organolithium compounds.[1] We now wish to report a new and apparently general method of alkyl and aryl amination of five- and six-membered heteroaromatic nitrogen compounds which complements the Tschitschibabin reaction very nicely.

A suitable N-oxide is heated with an imidoyl chloride (or with the corresponding nitrilium salt) in a polar nonprotic solvent. For example, pyridine N-oxide (I, X = Y = H) and N-phenylbenzimidoyl chloride (II, R = R′ = Ph) in boiling ethylene chloride give N-benzoyl-2-anilinopyridine (III, R′ = Ph; X = Y = H) (46.5%), mp 165–166°, which, on hydrolysis, gives 2-anilinopyridine (IV, R′ = Ph; X = Y = H), mp 106–108°. Alternatively, the reaction products can be hydrolyzed directly, thus by-passing the isolation of III, to give IV (R′ = Ph; X = Y = H) (70%); see Scheme I.

Scheme I



A variety of N-oxides have been used, and the only one which has failed to react to date is 4-nitropyridine N-oxide. Both R and R′ in II can be modified widely and include both alkyl and aryl groups. For example, I (X = Y = H) and II (R = Ph; R′ = CH_2Ph) give III (X = Y = H; R = Ph; R′ = CH_2Ph)[2] (57%), mp 111–113°. With N-p-nitrophenylbenzimidoyl chloride (II, R = Ph; R′ = p-$NO_2C_6H_4$) boiling chlorobenzene as solvent had to be used to effect intramolecular cyclization to give, after hydrolysis, IV (R′ = p-$NO_2C_6H_4$) (41%), mp 174–175.5°. A lower temperature (ethylene chloride) could be used if $SbCl_5$ was added dropwise at room temperature before the mixture was heated, which gave an 89% yield of IV (X = Y = H; R′ = p-$NO_2C_6H_4$). A lower temperature (methylene

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(1) R. A. Abramovitch and J. G. Saha, *Advan. Heterocycl. Chem.*, **6**, 229 (1966).

(2) All new compounds were characterized by microanalysis, by nmr and mass spectra, and by comparison with samples synthesized by established literature methods.