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.

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

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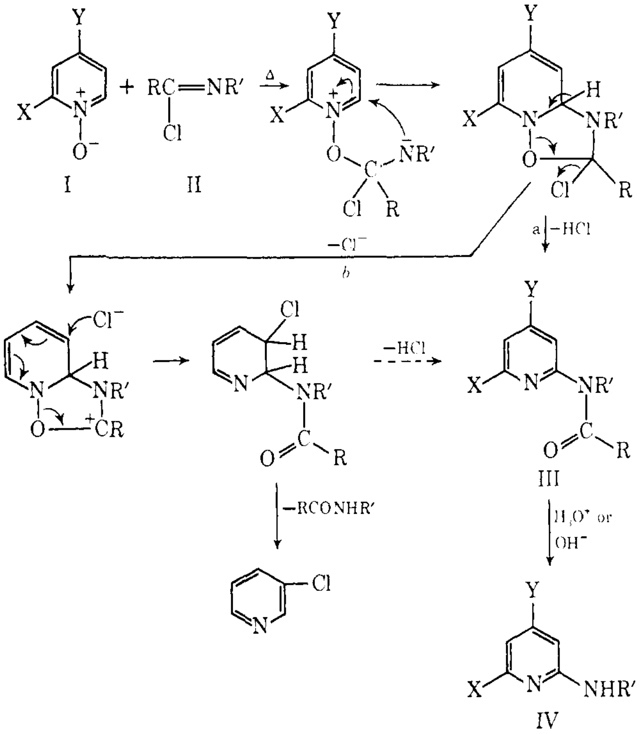
A Direct Alkyl and Aryl Amination of Heteroaromatic Nitrogen Compounds

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_2-C_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.

chloride) was preferable in the reaction between I (X = H, Y = Me) and II (R = R′ = Ph) to give IV (X = H, Y = Me), mp 118–119°. Alternatively, the nitrilium salt $[\mathrm{RC{\equiv}N^{+}R}]\mathrm{Z}^{-}$ may be generated prior to the addition of the N-oxide. Otherwise, the process is the same. In another approach to aryl amination the decomposition of an aromatic diazonium salt in an acetonitrile solution of the pyridine N-oxide gave the nitrilium salt[3] *in situ* which reacted with the N-oxide.[4] The yields were much poorer, however, and many unwanted by-products were formed.

The method has been extended to five-membered-ring heterocycles. For example, 1-benzylbenzimidazole 3-oxide and N-phenylbenzimidoyl chloride in boiling chloroform gave N-(1-benzyl-2-benzimidazolyl)benzanilide (90%), mp 151.5–153.5°, which, on hydrolysis, gave 2-anilino-1-benzylbenzimidazole, mp 188–190°. We are studying the extensions of this process to other heterocyclic ring systems and to open-chain nitrones and the effect of a 3 substituent on the pyridine ring upon the orientation of the attacking group.

While this reaction bears a resemblance to the 1,3-dipolar addition of phenyl isocyanate to N-oxides[5,6] it appears to be more flexible[7] and, in addition, permits the isolation of the intermediate amides, not possible in the isocyanate procedure. The latter are important as potential analgetics or may be reduced, thus providing a convenient synthesis of tertiary amines, of value in the antihistamine field, for example. The heterocyclic amines now readily obtainable by these reactions had previously been accessible only by more tedious procedures and from starting materials (*e.g.*, substituted 2-bromopyridines) not as readily available as the required N-oxides.

In all of the reactions of pyridine N-oxides with N-phenylbenzimidoyl chloride, benzanilide was formed as a by-product and could be isolated before any water was added, though stringent precautions against the intrusion of moisture (preparation of imide chloride and addition to N-oxide carried out in a drybox under nitrogen) were taken. With pyridine N-oxide itself 3-chloropyridine was also isolated as a by-product by gas chromatography of the reaction mixture. Pathway b could account for these products and could also provide an alternate route to III and IV. This is similar to the mechanism proposed[8] for the formation of 3-methyl-5-*o*-tolylpyridine from 3-picoline and *o*-tolyllithium.

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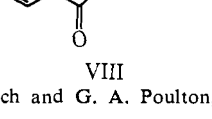
[3] H. Meerwein, P. Laasch, R. Mersch, and J. Spille, *Chem. Ber.*, **89**, 209 (1956).

[4] Preliminary work was carried out on this reaction by Mr. F. F. Gadallah.

[5] R. Huisgen, *Angew. Chem.*, 75, 604 (1963).

[6] S. Takahashi and H. Kanô, *Tetrahedron Lett.*, 1687 (1963); *Chem. Pharm. Bull.* (Tokyo), 12, 1290 (1964).

[7] For example, 3-chlorobenzoisothiazole 1,1-dioxide (ψ-saccharin chloride) reacts with pyridine N-oxide to give N-2-pyridylsaccharin (VIII), mp 210–211°.



VIII

[8] R. A. Abramovitch and G. A. Poulton, *Chem. Commun.*, 274 (1967).

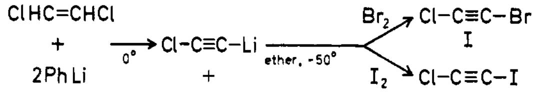
Preparation and Spectra of Pure Hetero and Homo Dihaloacetylenes

Sir:

Dihaloacetylenes, X—C≡C—Y (symmetry $C_{\infty v}$ (X ≠ Y) and $D_{\infty h}$ (X = Y) are obviously key compounds for experimental and theoretical studies of the properties of the carbon–carbon triple bond. However, their extreme chemical reactivity[1] has so far prevented their preparation in spectroscopically pure form and hence limited the investigation of their physical properties.[2,3] In this note we wish to report an alternative synthesis of the known homo dihaloacetylenes C_2Cl_2, C_2Br_2, and C_2I_2, and of the hetero dihaloacetylenes C_2BrCl and C_2ClI, hitherto unknown.[4] This method of preparation yields samples on a gram scale of a purity well in excess of those described so far in the literature, and has furthermore the advantage of allowing the handling of the highly explosive compounds in relative safety. As a consequence homo and hetero dihaloacetylenes are now available for thorough physical investigation.

The synthetic pathway for the new compounds bromochloroacetylene (I) (mp −54°; vapor pressure, 52 Torr (−1°); over-all yield 18.2%) and chloroiodoacetylene (II) (mp −37°; vapor pressure, 6 Torr (−1°); yield 26%) is summarized in Scheme I. Lithium chloroacetylide, prepared[5] in ether solution under nitrogen from *cis*-1,2-dichloroethylene by the action of 2 equiv of phenyllithium at 0°, was allowed to react with molecular bromine or iodine at −50° to produce I and II, respectively. Dichloroacetylene (III) (mp −68 to −65°;[6] yield *ca.* 13%) and dibromoacetylene (IV) (mp −17°;[6] vapor pressure 13 Torr (−1°); yield 41%); were prepared as shown in Scheme II. Dilithium

Scheme I



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[1] Only diiodoacetylene is a relatively stable compound.[2]

[2] For a comprehensive survey on haloacetylenes, *cf.* K. M. Smirnov, A. P. Tomilov, and A. I. Shchekotikhin, *Usp. Khim.*, **36**, 777 (1967); *Russ. Chem. Rev.*, **36**, 326 (1967), and references cited therein.

[3] Electron diffraction investigations; *cf.* H. de Laszlo, *Trans. Faraday Soc.*, 30, 825 (1934); O. Hassel and T. Taarland, *Tidsskr. Kjemi, Bergvesen Met.*, **1**, 172 (1941).

[4] The English edition of ref 2 is erroneously translated regarding this statement.

[5] H. G. Viehe, *Chem. Ber.*, **92**, 1950 (1959).

[6] F. Straus, L. Kollek, and W. Heyn, *ibid.*, **63**, 1868 (1930), give mp −68 to −64° for dichloroacetylene and mp −25 to −23° for dibromoacetylene.