provided by H. S. Hair, and preparative assistance was provided by J. Nunberg.

**M. J. Goldstein,* R. C. Krauss, S.-H. Dai**
*Department of Chemistry, Cornell University*
*Ithaca, New York 14850*
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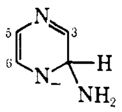
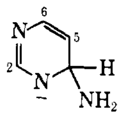
## Anionic $\sigma$ Complexes between Amide Ions and the Diazines in Liquid Ammonia

*Sir:*

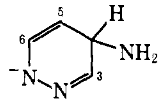
We wish to report the first direct evidence for the existence of anionic $\sigma$ complexes of the type long postulated[1] to occur in the Chichibabin amination reaction of heterocyclic compounds.[2] The nmr spectra of the amide ion–diazine complexes I–III in liquid ammonia were obtained.[3,4]



I



II



III

Complexes were formed by the addition of a diazine to $NaNH_2$ or $KNH_2$ in ammonia. Nmr spectra of the deeply colored solutions obtained at $-40$ to 0° about 30 min after mixing showed no free diazine when excess amide ion was employed. Adduct formation is characterized by the usual upfield shifts[5] (2.2–4.5 ppm). In the presence of a deficiency of amide ion, the spectra of both free and complexed diazine are seen and no noticeable signal averaging is found. Also, spin coupling of the amine protons with a ring proton of the adduct results. With excess amide ion, however, hydrogen exchange occurs and this spin coupling is not found. This change in coupling serves as a useful way to identify the signal of the tetrahedral center of the adduct. Adducts are stable in solution for days at $-70°$, but solutions at room temperature give new signals in what appear to be irreversible reactions.[6,7]

The adduct of pyrazine and amide ion showed the following chemical shifts and coupling constants: $\tau$ 3.40 (H-6), 4.18 (H-5), 4.39 (H-3), 5.78 (H-2), $J_{2,3} = 3.0$ Hz, $J_{3,6} \sim 0.5$ Hz, $J_{5,6} = 3.0$ Hz, and $J_{NH_2,H} = 7.7$ Hz. No signals were found for the amino group of this or any other complex, probably because they are included in that for the main solvent peak. This spectrum is consistent with the structure 2-amino-1,2-dihydropyrazinide ion (I) and provides direct evidence for it. Free pyrazine in ammonia shows a signal at $\tau$ 1.2; note the large changes in chemical shift on complex formation.

Three adducts are possible in the case of pyrimidine. Addition of amide ion to C-2 or C-5 is expected to give anions in which H-4 and H-6 are equivalent, owing to symmetry. However, addition to C-4 should give rise to an anion with four nonequivalent protons. The observed spectrum shows four nonequivalent protons at $\tau$ 2.93 (H-2), 3.73 (H-6), 5.37 (H-4), 5.68 (H-5), $J_{2,4} = J_{2,6} = 0.5$ Hz, $J_{2,5} = 1.5$ Hz, $J_{4,5} = 3.5$ Hz, $J_{5,6} = 6.5$ Hz, and $J_{NH_2,H} = 7.0$ Hz. Hence the major adduct is 4-amino-1(or 3),4-dihydropyrimidinide ion (II). Signals of a minor component were not characterized, owing to low intensity and overlap.

Two different adducts are possible for pyridazine, resulting from addition of amide ion to C-3 or C-4. The assignment of a 4-amino-1,4-dihydropyridazinide ion structure (III) follows from the spectra of the pyridazine and pyridazine-*3,6-$d_2$*[8] adducts. The proteo adduct is characterized as follows: $\tau$ 3.30 (H-6), 3.45 (H-3), 5.73 (H-5), 6.27 (H-4), $J_{3,4} = 3.5$ Hz, $J_{3,5} = 3.0$ Hz, $J_{3,6} = 0.5$ Hz, $J_{4,5} = 4.5$ Hz, $J_{5,6} = 7.0$ Hz, and $J_{NH_2,H} = 7.0$ Hz. (These coupling constants have a larger uncertainty than those for the other adducts, because there is signal overlap.) The dideuterio adduct did not show the low-field multiplets, and the upfield spectrum consisted of a pair of doublets for H-4 and H-5. Because there is decoupling, another pair of doublets at $\tau$ 4.20 ($J = 8.0$ Hz) and 5.49 now could clearly be seen above the noise level. These may represent H-4 and H-5 of a small amount of the other adduct.

In the absence of adduct formation, pyridazine-*3,6-$d_2$* is expected to undergo significant H–D exchange in ammonia.[9] But little, if any, dedeuteration took place after 19 hr at $-78°$ or after 0.5 hr at 0°, owing to adduct formation. The spectrum of the deuterated pyridazine could be regenerated by the addition of ammonium ions to a reaction mixture. It is interesting to consider earlier reports[10] in the light of our results.

An upper limit to the dissociation constants, $K = [C_4H_4N_2][NH_2^-]/[\text{complex}]$, for the diazine complexes may be estimated. When both complex and free diazine are present in similar amounts in solution, coupling between a ring proton and the amino group of the adduct is found and the solvent peak is a triplet. This means amide ion-catalyzed hydrogen exchange is slow.[11] Hence, an upper limit to the amide ion concentration may be estimated from the coupling constant ($J = 44$ Hz) and the rate constant ($1.5 \times 10^7$ $M^{-1}$ sec$^{-1}$ at 25°)[12] for hydrogen exchange of ammonia. When NH coupling is present, $[NH_2^-] \leqslant 44\pi/(\sqrt{2} \times 10^7)$ and

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(1) K. Ziegler and H. Zeiser, *Chem. Ber.*, **63**, 1847 (1930).

(2) M. T. Leffler, *Org. React.*, **1**, 91 (1942); R. N. Shreve and L. Berg, *J. Amer. Chem. Soc.*, **69**, 2116 (1947); M. L. Crossley and J. P. English, U. S. Patent 2394963 (1946); *Chem. Abstr.*, **40**, $3143^7$ (1946).

(3) The nmr spectra of the complexes between the diazines and amide ions will appear following these pages in the microfilm edition of this volume of the journal. Single copies may be obtained from the Reprint Department, ACS Publications, 1155 Sixteenth St., N.W., Washington, D. C. 20036, by referring to author, title of article, volume, and page number. Remit check or money order for $3.00 for photocopy or $2.00 for microfiche.

(4) Trimethylamine, $\tau$ 7.87, is the shift standard. Spectra were obtained with a Varian A-60A spectrometer equipped with a V-6040 variable-temperature controller.

(5) M. J. Strauss, *Chem. Rev.*, 70, 667 (1970).

(6) Solids which were assumed to be adducts between an alkali amide and isoquinoline or several quinolines have been isolated.[7] They are too unstable to be characterized. In view of these reports, we have not attempted to isolate the diazine complexes.

(7) F. W. Bergstrom, *Justus Liebigs Ann. Chem.*, **515**, 34 (1934); *J. Org. Chem.*, **2**, 411 (1937); **3**, 424 (1938).

(8) Prepared by hydrogen–deuterium exchange using the method reported by J. A. Zoltewicz and C. L. Smith, *J. Amer. Chem. Soc.*, **89**, 3358 (1967).

(9) J. A. Zoltewicz, G. Grahe, and C. L. Smith, *ibid.*, **91**, 5501 (1969); I. F. Tupitsyn and N. K. Seminova, *Tr. Gos. Inst. Prikl. Khim.*, **49**, 120 (1962); *Chem. Abstr.*, **60**, 6721*c* (1964).

(10) H. J. den Hertog and H. C. van der Plas in "Chemistry of Acetylenes," H. G. Viehe, Ed., Marcel Dekker, New York, N. Y., 1969, Chapter 17.

(11) R. A. Ogg, Jr., *Discuss. Faraday Soc.*, 17, 215 (1954); J. D. Roberts, "Nuclear Magnetic Resonance Applications to Organic Chemistry," McGraw-Hill, New York, N. Y., 1959, Chapter 4.

(12) T. J. Swift, S. B. Marks, and W. G. Sayre, *J. Chem. Phys.*, **44**, 2797 (1966).

$K \leqslant 10^{-5}$ *M*. Hence the affinity of the diazines for amide ions is very high.

No nmr evidence was found for the formation of an adduct between pyridine and amide ion in ammonia, although the solution gradually discolored at room temperature.

Other complexes will be reported shortly.

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(13) Cedarville College, Cedarville, Ohio.

**John A. Zoltewicz,* Larry S. Helmick**[13]
*Department of Chemistry, University of Florida*
*Gainesville, Florida 32601*

*Received October 28, 1971*

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## A Principle for Establishing a Carbon Chain on an Aromatic Ring in Place of Nitrogen, Oxygen, Fluorine, Sulfur, Chlorine, Bromine, or Iodine Functionality[1]

*Sir:*

Methods for attaching a carbon chain to an aromatic ring are few and subject to severe limitations. Thus, Friedel–Crafts reactions, SNAr arylation of carbon nucleophiles,[2] and arylation of carbanions *via* arynes[3] afford mixtures of isomers or require the presence of special activating groups. Organometallic methods suffer from other disadvantages.

Table I. Reactions with Potassium Acetonate in Ammonia at −78°, Provoked by Potassium Metal

| Substrate | [Substrate], *M* | [CH$_3$-COCH$_2^-$K$^+$], *M* | [K],[a] *M* | Method[b] | Yields, %[c]: C$_6$H$_5$CH$_2$-COCH$_3$ | Yields, %[c]: C$_6$H$_5$CH$_2$-CH(OH)CH$_3$ | Yields, %[c]: Other |
|---|---|---|---|---|---|---|---|
| C$_6$H$_5$F | 0.064 | 0.27 | 0.10 | B | 3 | 46 | (C$_6$H$_5$)$_2$CHCOCH$_3$, 2 |
| C$_6$H$_5$Cl | 0.30 | 0.80 | 0.46 | B | 68[d] | | |
| C$_6$H$_5$Br | 0.38 | 0.94 | 0.35 | B | 52[d] | | |
| C$_6$H$_5$Br | 0.12 | 0.33 | 0.044 | A | 67 | 10 | (C$_6$H$_5$)$_2$CHCOCH$_3$, 14<br>C$_6$H$_5$Br, 3 |
| C$_6$H$_5$I | 0.18 | 0.60 | 0.18 | B | 71[d] | | |
| C$_6$H$_5$I | 0.18 | 0.68[e] | 0.17[e] | B | 52[d] | | |
| (C$_6$H$_5$)$_2$O | 0.024 | 0.25 | 0.018 | A | | 4.5 | (C$_6$H$_5$)$_2$O, 93 |
| C$_6$H$_5$OP(O)(OEt)$_2$ | 0.040 | 0.27 | 0.068 | B | 4 | 42 | |
| (C$_6$H$_5$)$_2$S | 0.030 | 0.14 | 0.045 | A | 18 | 71 | C$_6$H$_5$SH, 84 |
| C$_6$H$_5$NMe$_3^+$I$^-$ | 0.024 | 0.20 | 0.022 | A | 46 | 18 | (C$_6$H$_5$)$_2$CHCOCH$_3$, 7 |
| C$_6$H$_5$NMe$_3^+$I$^-$ | 0.12 | 0.68[e] | 0.18[e] | B | 56[d] | | |
| *p*-CH$_3$C$_6$H$_4$Br | 0.053 | 0.28 | 0.060 | A | 57[f] | 17[g] | C$_6$H$_5$CH$_3$, 26 |
| *p*-CH$_3$C$_6$H$_4$NMe$_3^+$I$^-$ | 0.045 | 0.43 | 0.064 | A | 30[f] | 42[g] | C$_6$H$_5$CH$_3$, 6 |
| *p*-CH$_3$OC$_6$H$_4$Br | 0.061 | 0.21 | 0.043 | A | 36[h] | 10[i] | C$_6$H$_5$OCH$_3$, 44 |
| *p*-CH$_3$OC$_6$H$_4$NMe$_3^+$I$^-$ | 0.016 | 0.56 | 0.024 | A | 20[h] | 39[i] | C$_6$H$_5$OCH$_3$, 40 |

[a] Concentration of K (or Na) if no reaction had occurred. [b] Method A, substrate added to CH$_3$COCH$_2^-$K$^+$ and K in NH$_3$; method B, K added to substrate and CH$_3$COCH$_2^-$K$^+$ in NH$_3$ until blue color persisted. [c] Yields are based on substrate introduced; unless otherwise specified, they are by glpc, with nmr and ir confirmation of product identities. [d] Yield of isolated product, after oxidation of product mixture;[7] no 1-phenyl-2-propanol isolable by this procedure. [e] Na instead of K. [f] *p*-Tolylacetone. [g] 1-(*p*-Tolyl)-2-propanol. [h] *p*-Anisylacetone. [i] 1-(*p*-Anisyl)-2-propanol.

The recently recognized affinity of aryl radicals for certain nucleophiles[4,5] and the fact that aryl radicals can be generated through the action of solvated electrons upon aromatic compounds carrying nucleofugic[6a] substituents[4,6b] suggest a new and general principle of synthesis. A carbon moiety, provided as a suitable carbanion, is caused to attach to an aromatic ring by exposing it and an aromatic system carrying a suitably nucleofugic substituent to stimulation by solvated electrons; the electrons provoke formation of an aryl radical which coordinates with the nucleophile, and finally an excess electron is relinquished. The mechanism is in part as sketched in Scheme I.

**Scheme I**

$$e^- + ArX \longrightarrow [ArX]\cdot^- \qquad (1)$$

$$[ArX]\cdot^- \longrightarrow Ar\cdot + X^- \qquad (2)$$

$$Ar\cdot + R:^- \longrightarrow [ArR]\cdot^- \qquad (3)$$

$$[ArR]\cdot^- + ArX \longrightarrow ArR + [ArX]\cdot^- \qquad (4)$$

We now report that the acetone enolate ion is a suitable carbanion, that liquid ammonia is a suitable solvent, and that sodium or potassium metal is a suitable source of electrons for synthesis according to this principle. Moreover, we find that several substituents in which the first atom is variously nitrogen, oxygen, fluorine, sulfur, chlorine, bromine, or iodine are sufficiently nucleofugic to allow substantial yields of arylation products to be obtained. Details on a number of reactions are set forth in Table I.

The products obtained are in part arylacetones, ArCH$_2$COCH$_3$, in part 1-aryl-2-propanols, ArCH$_2$CH(OH)CH$_3$, and in part 1,1-diarylacetones which represent double arylation. The sum of arylacetone and 1-aryl-2-propanol yields is as high as 89% as analyzed by glpc or as high as 71% as isolated and weighed. Little effort has been made to optimize yields. For isolation purposes, the mixture of arylacetone and 1-aryl-2-propanol formed was sometimes treated with an oxidizing reagent[7] so that both could be isolated as the ketone.

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(1) Supported in part by the National Science Foundation.

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(6) (a) J. Mathieu, A. Allais, and J. Valls, *Angew. Chem.*, **72**, 71 (1960); (b) E. J. Hart and M. Anbar, "The Hydrated Electron," Wiley, New York, N. Y., 1970, pp 126 and 149.

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