meets all the requirements listed above,[11] we have also investigated the photochemistry of this material. Pertinent spectral and photochemical data for $Co(NH_3)_5N_3^{2+}$ and $Co(NH_3)_4OH_2N_3^{2+}$ are compared in Table I.

After a sample of $Co(NH_3)_5N_3^{2+}$ was irradiated in the cell holder of a Cary 14 spectrophotometer for 1 min, the absorbance of the solution at 254 nm slowly decreased over the course of about 5 min. This transient absorbance exhibited a half-life for the decay of ≥ 40 sec. This is comparable to the half-life of the *trans* → *cis* isomerization of $Co(NH_3)_4OH_2N_3^{2+}$ reported by Haim.[11] The lifetime of this transient (which is presumably due to *trans*-$Co(NH_3)_4OH_2N_3^{2+}$) compared to the time required for photolysis and sampling at high I_a is such that the solution containing $Co(NH_3)_4OH_2N_3^{2+}$ will approach equilibrium only as the ratio of irradiation to dark time becomes very large.

Our observations, summarized above, of the photochemistry of $Co(NH_3)_5N_3^{2+}$, a cobalt(III) complex containing a strongly "reducing" ligand, show quite clearly that the photolabilization of a coordinated ammine has at least as great a quantum yield as photoreduction and that both of these processes are far more important than the formation of $Co(NH_3)_5OH_2^{3+}$. These observations are certainly at odds with a "radical-pair" model[2] for the photochemistry of coordination complexes of cobalt(III). Studies still in progress suggest that similar photolabilization occurs in the 2537-Å irradiation of *cis*-$Co(NH_3)_4(N_3)_2^+$ but not for *trans*-$Co(NH_3)_4(N_3)_2^+$.[10]

Acknowledgment. The authors wish to thank Mr. Laszlo S. Beres for many early studies on this system.

(11) A. Haim, *J. Am. Chem. Soc.*, **86**, 2352 (1964).

John F. Endicott, Morton Z. Hoffman
Department of Chemistry, Boston University
Boston, Massachusetts 02215

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A Nickel(II)-Catalyzed Synthesis of a Triarsine from a Diarsine

Sir:

Some years ago, one of us[1] reported the isolation of a compound which was considered to have the formula $[Ni(diars)_3](ClO_4)_2$ (diars = *o*-phenylenebis(dimethylarsine)), I, and in 1966 we described[2] an improved method of preparation. The compound was of interest in that it was diamagnetic although believed to be[1,2] an octahedral trisbidentate complex.

However, X-ray diffraction studies, which will be reported in detail elsewhere by P. J. Pauling, show that the substance which was isolated is *o*-phenylenebis(dimethylarsine)[bis(*o*-dimethylarsinophenyl)methylarsine]-nickel(II) perchlorate. The compound contains *five* arsenic atoms arranged about the nickel at the corners of an almost regular tetragonal pyramid (Figure 1). We have now shown that the original compound can be prepared directly from the diarsine (I) and the triarsine (II) with nickel(II) perchlorate hexahydrate. Thus, when equal volumes of 0.1 *M* solutions of each of these three compounds in ethanol–ether were mixed, a deep maroon color developed and crystals were deposited within 30 min at room temperature. In this way a quantitative yield was obtained of a substance which had an X-ray powder pattern identical with that of the original material. As further evidence for this formulation it is possible, after breaking down the original complex with sodium cyanide solution, to isolate the triarsine (II) from the reaction mixture.

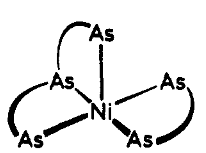
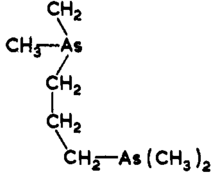


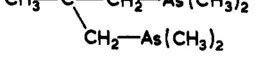
Figure 1. A diagramatic drawing of the coordination polyhedron in $[Ni(diars)(triars)](ClO_4)_2$. Crystals are monoclinic, space group $P2_1/c$; $a = 18.41$, $b = 20.21$, $c = 12.61$ Å, $\beta = 125.80°$, $Z = 4$ formula units per unit cell. At the present stage of least-squares refinement, the residual $R = 0.18$. The basal plane Ni–As distances are 2.26, 2.27, 2.30, and 2.32 Å. The apical Ni–As distance is 2.39 Å. The site below the square plane appears to be unoccupied.

A reexamination of the proton magnetic resonance spectra of the original and the new complex in hexadeuteriodimethyl sulfoxide shows, in addition to the two previously reported peaks, now shifted to τ 8.23 and 8.41, three smaller, broader peaks at τ 6.53, 7.32, and 7.80. These peaks, which are of equal area and together constitute about one-third of the area of the strong peaks, were obscured by the solvent in dimethylformamide.

Thus we have discovered a new reaction whereby, in boiling diethylene glycol, *o*-phenylenebis(dimethylarsine) is converted in some 20% yield to the triarsine, bis(*o*-dimethylarsinophenyl)methylarsine. Phillips[3] reported the preparation of the so-called "tris complex" in some 40% yield by heating an ethanolic solution of $[Ni(diars)_2Cl_2]$ in a sealed tube at 200° but was unable to isolate the complex from the reaction mixture. It is of interest to note[4] that the reaction products from the sealed tubes always smelt more strongly than diarsine. This is probably due to the presence of $As(CH_3)_3$ formed in the disproportionation. This reaction requires the presence of the nickel(II) salt since, if a solution of the diarsine in diethylene glycol is refluxed for the same period of time, subsequent addition of nickel(II) chloride to the cooled solution does not yield the requisite product.

These results still leave unsolved the puzzle of the structures of the diamagnetic nickel(II) complexes of the type $[Ni(triars)_2](ClO_4)_2$, with the terdentate arsines, II, III, and IV. These all have spectra very similar to


III


IV

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(1) R. S. Nyholm, *J. Chem. Soc.*, 2061 (1950).

(2) B. Bosnich, R. Bramley, R. S. Nyholm, and M. L. Tobe, *J. Am. Chem. Soc.*, **88**, 3926 (1966).

(3) D. J. Phillips, Ph.D. Thesis, University of London, 1958.

(4) D. J. Phillips, private communication.

that of the $[Ni(diars)(triars)]^{2+}$ cation, which would suggest that, in all cases, the nickel atom is experiencing a tetragonal pyramidal field from five of the arsenics, and the sixth is either uncoordinated or else very loosely bound. If this is true, the diamagnetism presents no serious theoretical difficulties since many diamagnetic five-coordinate nickel(II) complexes are now known. However, the present system is the first example of a species with *five* arsenic donors.

B. Bosnich, R. S. Nyholm, P. J. Pauling, M. L. Tobe
The William Ramsay and Ralph Forster Laboratories
University College, London, W.C.1. England
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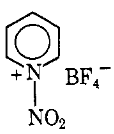
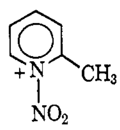
Transfer Nitration *via* N-Nitropyridinium Salts

Sir:

We wish to report that a variety of N-nitropyridinium tetrafluoroborates and related compounds offer a new method for effecting homogeneous nitration of aromatic substrates in organic solvents at room temperature and under essentially neutral conditions. The use of these salts as transfer nitrating agents for aromatics and other substrates offers the further possibility of designing reagents of varied reactivity by suitable choice of the heterocyclic base. The N-nitropyridinium salts are readily prepared by slow addition of the pyridine base to an equimolar suspension of nitronium tetrafluoroborate[1] in acetonitrile according to the procedure reported by Olah[2,3] for preparation of N-nitropyridinium tetrafluoroborate (**1**). Although the latter salt has limited solubility in acetonitrile, alkyl-substituted pyridines give salts which are quite soluble in this solvent and can be used directly without isolation.[4]



1



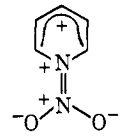
2

Table I. Competitive Nitration of Benzene and Toluene with N-Nitro Salts in Acetonitrile at 25°

N-Nitro salts[a]	$k_{toluene}/k_{benzene}$[b]	Isomer distribution, % *ortho*	*meta*	*para*	*ortho*:*para*	Partial rate factors *ortho*	*meta*	*para*
2	36.5	63.8	3.2	33.0	1.93	69.9	3.5	72.3
4, X = H	39.0	63.9	3.0	33.1	1.93	74.7	3.5	77.4
4, X = CH_3	41.4	63.1	3.1	33.8	1.86	78.5	3.8	84.0
4, X = OCH_3	44.5	64.1	2.6	33.3	1.93	85.5	3.5	88.9
5[c]	13.2	62.1	2.1	35.8	1.73	24.6	0.8	28.4

[a] The gegenion in all cases is BF_4^-. [b] The results are the average of three independent runs and are accurate to ±2%. [c] Reaction was run using nitromethane as solvent because of limited solubility of this salt in acetonitrile.

The behavior of **1** *vs.* the α-picoline salt **2** in the presence of aromatics is striking. Whereas reaction of **1** with toluene produces no nitrated product at 25°, nitration with **2** proceeds readily and quantitatively at room temperature.[5] The most reasonable explanation for these results is that in **1** the resonance structure **3** is an important contributor. Introduction of an alkyl substituent in the 2 position of the pyridine nucleus impedes the nitro group from achieving coplanarity with the pyridine ring and substantially reduces the amount of double-bond character in the N–N bond. The attendant weakening of this N–N bond in **2**, due to steric inhibition of resonance, is then the major factor for allowing transfer nitration to occur.



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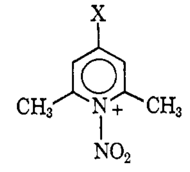

4

The reactivity of various N-nitropyridinium salts can be determined by the method of competitive nitration.[6-8] Thus for **2**, in the presence of equimolar quantities of toluene and benzene[9] at 25°, the observed substrate selectivity ($k_{toluene}/k_{benzene}$) = 36.5. For comparison some recently reported values for nitrating agents at 25° are: $k_T/k_B = 1.62$ for $NO_2^+PF_6^-$ in nitromethane;[10] $k_T/k_B = 28.0$ for HNO_3–H^+ in sulfolane;[11] $k_T/k_B = 26.6$ for acetyl nitrate in acetic anhydride.[12,13]

Under conditions identical with that for **2**, the 2,6-lutidine salt **4** (X = H) is even more selective (k_T/k_B = 39.0). That the latter result is an inductive phenomenon and that the reactivity of N-nitropyridinium ions is a function of both the steric environment around the N–N bond and basicity of the amine are seen in the behavior of trisubstituted N-nitropyridinium ions **4** where electron-releasing 4 substituents result in increasing the selectivity even further. The substitution

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(1) S. J. Kuhn and G. A. Olah, *J. Am. Chem. Soc.*, **83**, 4564 (1961); S. J. Kuhn, *Can. J. Chem.*, 40, 1660 (1962).

(2) G. A. Olah, J. A. Olah, and N. A. Overchuk, *J. Org. Chem.*, **30**, 3373 (1965).

(3) See also J. Jones and J. Jones, *Tetrahedron Letters*, 2117 (1964).

(4) In all cases thus far studied, stable crystalline salts can be isolated. The physical properties of these salts will be reported at a later time.

(5) Nitration of toluene by **1** does occur slowly at 80° (refluxing acetonitrile). However, this reaction is complicated by further reactions of **1** with solvent at this temperature.

(6) C. K. Ingold and M. S. Smith, *J. Chem. Soc.*, 905 (1938), and earlier papers.

(7) For a discussion of the competitive method of nitration, see M. J. S. Dewar, T. Mole, and E. W. T. Warford, *ibid.*, 3576 (1956).

(8) Kinetic studies are also in progress in order to determine the absolute rate constants.

(9) The competitive nitrations were carried out by the addition of a solution of the N-nitro salt in acetonitrile to a well-stirred solution of toluene and benzene in acetonitrile. The mole ratio of the combined aromatic substrate: N-nitro salt was 10:1. All reactions were run under dry nitrogen. The reaction mixtures were analyzed by gas–liquid partition chromatography on a Perkin-Elmer Model F-11 with a 150-ft polypropylene glycol capillary column.

(10) G. A. Olah and N. A. Overchuk, *Can. J. Chem.*, **43**, 3279 (1965).

(11) G. A. Olah, S. J. Kuhn, S. H. Flood, and J. C. Evans, *J. Am. Chem. Soc.*, **84**, 3687 (1962).

(12) A. K. Sparks, *J. Org. Chem.*, **31**, 2299 (1966).

(13) For a recent review of nitration, see J. H. Ridd in "Studies on Chemical Structure and Reactivity," J. H. Ridd, Ed., John Wiley and Sons, Inc., New York, N. Y., 1966, Chapter 7.