

131, 130, but singlets at  $m/e = 138$  and 109, a result which clearly locates the amino function in the indole part of the molecule. Finally, Wolff-Kishner reduction of III furnished VII, the mass spectrum of which is practically identical with that of the recently isolated aspidofractinine<sup>11</sup> (major peaks at  $m/e = 280$  (M), 252 (M - 28), 124, and 109).

Attempts to effect the cyclization of I to III with retention of the carbomethoxy grouping at C-3 have thus far proved unsuccessful, a major handicap being the lack of sufficient material to identify clearly the components of the product mixtures obtained in various experiments.

The unexpectedly facile formation of III from minovincine may be understood if one considers the indolenine II and its enol form as the intermediate in the decarboxylation-cyclization process. Molecular models show that the methyl group of the side chain is situated within bond-forming distance above C-2, and an aldol-type condensation should thus proceed fairly readily once the enol is formed. The fact that most of the refractine-type alkaloids isolated so far bear a substituent (usually carbomethoxy) at C-3 would seem to implicate minovincine and related  $\alpha$ -methyleneindole alkaloids as actual biogenetic precursors of this skeleton.

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### An Arylazo Derivative of Molybdenum<sup>1</sup>

Sir:

Reactions between aryldiazonium salts and many anions are useful both for the preparation of substituted aromatic compounds and for the preparation of arylazo compounds often useful as dyes.<sup>2</sup> In attempts to prepare interesting aryl or arylazo complexes of various transition metals we have been investigating reactions between various aryldiazonium salts and various metal carbonyl anions. By this synthetic technique we have prepared the first compound with an arylazo group,  $RN=N$ , directly bonded to a transition metal.

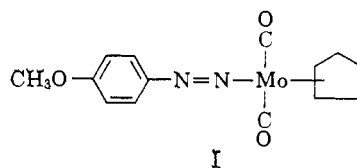
Solid *p*-anisylidiazonium tetrafluoroborate was added gradually to excess  $NaMo(CO)_2C_6H_5$ <sup>3</sup> in tetrahydrofuran at room temperature. After several hours solvent was removed and product extracted from the residue with dichloromethane. After evaporation of the dichloromethane, further purification was accomplished by chromatography on alumina in diethyl ether solution and by low temperature crystallization from pentane to give red-orange crystals, m.p. 78–79°, of  $p-CH_3OC_6H_4N_2Mo(CO)_2C_5H_5$  in ~20% yield. *Anal.* Calcd.: C, 47.7; H, 3.4; N, 8.0; Mo, 27.2; O, 13.6; mol. wt., 352. Found: C, 47.8; H, 3.7; N, 8.0; Mo, 26.9; O, 13.9; mol. wt., 338 (Mechrolab vapor pressure osmometer in benzene solution). In some ex-

periments where excess *p*-anisylidiazonium tetrafluoroborate was present, no  $p-CH_3OC_6H_4N_2Mo(CO)_2C_5H_5$  was obtained. Instead most of the molybdenum was converted to a red-purple solid insoluble in pentane and benzene but soluble in tetrahydrofuran. The nature of this material is still unknown, but its infrared spectrum clearly demonstrates the absence of carbonyl groups and the presence of the  $BF_4^-$  anion.

This new molybdenum complex  $p-CH_3OC_6H_4N_2Mo(CO)_2C_5H_5$  is a red-orange crystalline solid readily soluble in all organic solvents but insoluble in water. On exposure to air its solutions decompose over several hours. Its acetone solution ( $4.15 \times 10^{-4} M$ ) possesses a low conductivity similar to that of pure acetone.

The infrared spectrum (KBr pellet) of  $p-CH_3OC_6H_4N_2Mo(CO)_2C_5H_5$  exhibits two sharp strong metal carbonyl bands at 1960 and 1900  $cm^{-1}$ . Comparison of the infrared spectrum of *p*-anisylidiazonium tetrafluoroborate with that of  $p-CH_3OC_6H_4N_2Mo(CO)_2C_5H_5$  indicates that the  $\nu_{NN}$ , the nitrogen-nitrogen multiple bond stretching frequency, of 2225  $cm^{-1}$  in the diazonium salt has decreased to 1600  $cm^{-1}$  in the molybdenum complex.<sup>4</sup> This large lowering of  $\nu_{NN}$  in  $p-CH_3OC_6H_4N_2Mo(CO)_2C_5H_5$  to a value very similar to the  $\nu_{NO}$  of the nitrosyl group in metal nitrosyls (e.g.,  $\nu_{NO}$  of  $C_5H_5W(CO)_2NO$  at 1630  $cm^{-1}$ ) suggests a large decrease in the nitrogen-nitrogen bond order from the triple bond in the aryldiazonium salt.

The proton n.m.r. spectrum besides demonstrating  $p-CH_3OC_6H_4N_2Mo(CO)_2C_5H_5$  to be diamagnetic exhibits two coupled ( $J = 9$  c.p.s.) doublets at  $\tau$  2.80 and 3.20 attributed to the four protons on the *para*-substituted benzene ring, a single sharp resonance at  $\tau$  4.37 attributed to the five equivalent  $\pi$ -cyclopentadienyl protons, and another single sharp resonance at  $\tau$  6.25 attributed to the three protons of the methoxy group. All of these data are in agreement with the expected structure I for  $p-CH_3OC_6H_4N_2Mo(CO)_2C_5H_5$ .



The diamagnetism of the compound suggests an inert gas configuration for the molybdenum atom. If this is indeed the case and if the  $\pi$ -cyclopentadienyl and carbonyl groups donate the usual numbers of electrons to the metal atom, then the neutral *p*-anisylazo ligand must be acting as a three-electron donor.<sup>5</sup> The compound  $p-CH_3OC_6H_4N_2Mo(CO)_2C_5H_5$  would therefore be isoelectronic with the known compounds  $C_5H_5Mo(CO)_2NO$ ,<sup>3,6</sup>  $C_5H_5Mo(CO)_2C_8H_5$ ,<sup>7</sup>  $C_5H_5Mo(CO)_2-CH_2SCH_3$ ,<sup>8</sup>  $C_5H_5Mo(CO)_2C_7H_9$ ,<sup>9</sup> etc. Indeed, replace-

(1) We are indebted to the Air Force Office of Scientific Research for partial support of this work under Grant AF-AFOSR-580-64.

(2) For detailed discussions on the chemistry of diazonium salts see K. H. Saunders, "The Aromatic Diazo Compounds and Their Technical Applications," Longmans, Green and Co., New York, N. Y., 1949, and H. Zollinger, "Azo and Diazo Chemistry," Interscience Publishers, Inc., New York, N. Y., 1961.

(3) T. S. Piper and G. Wilkinson, *J. Inorg. Nucl. Chem.*, **3**, 104 (1955).

(4) Absorption due to the aromatic rings partially obscures  $\nu_{NN}$  of  $p-CH_3OC_6H_4N_2Mo(CO)_2C_5H_5$  in its infrared spectrum making a comparison with the spectrum of *p*-anisylidiazonium tetrafluoroborate essential for unambiguous identification of  $\nu_{NN}$ .

(5) Alternatively, in I the cationic *p*-anisylazo ligand can be considered as a two-electron donor similar to  $NO^+$  combining with an anionic metal carbonyl fragment.

(6) E. O. Fischer, O. Beckert, W. Hafner, and H. O. Stahl, *Z. Naturforsch.*, **10b**, 598 (1955).

(7) M. Cousins and M. L. H. Green, *J. Chem. Soc.*, 889 (1963).

(8) R. B. King and M. B. Bisnette, *J. Am. Chem. Soc.*, **86**, 1267 (1964).

(9) R. B. King and M. B. Bisnette, *Inorg. Chem.*, **3**, 785 (1964).

ment of the oxygen atom in the nitrosyl ligand, well established to be a three-electron donor, with a *p*-anisylimino group produces the *p*-anisylazo ligand present in the new complex just as replacement of the oxygen atom in the carbonyl ligand with a *p*-anisylimino group produces the *p*-anisyl isocyanide ligand, which has been shown to form complexes with many transition metals<sup>10</sup> similar to metal carbonyls in many respects. Thus the relationship between  $C_5H_5Mo(CO)_2NO^{3,6}$  and *p*- $CH_3OC_6H_4N_2Mo(CO)_2C_5H_5$  appears to be especially close.

Further studies on arylazo derivatives of transition metals are in progress and will be reported in detail in the future.

(10) For a review of isocyanide complexes of metals see L. Malatesta, *Progr. Inorg. Chem.*, **1**, 283 (1959).

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### 1,4-Phenyl Migration in a Base-Catalyzed Elimination-Rearrangement Reaction

Sir:

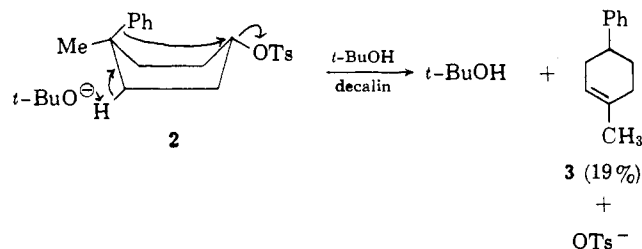
Treatment of 4,4-diphenylcyclohexyl *p*-toluenesulfonate (1) with sodium *t*-butoxide in refluxing *t*-butyl alcohol solution for 4 hr. gave 4,4-diphenylcyclohexanone (7%), 4,4-diphenylcyclohexanol (9%), 1,4-diphenylcyclohexene (14%), and 4,4-diphenylcyclohexene (64%). These products were separated by elution chromatography and identified by comparing their melting points, infrared spectra, and g.l.c. retention times with those of authentic samples.<sup>1</sup> A comparable experiment in which dimethyl sulfoxide was used as the solvent increased the yield of 1,4-diphenylcyclohexene to 21%. When a refluxing *t*-butyl alcohol-decalin solvent mixture was used, the yield of 1,4-diphenylcyclohexene was 16% (determined by g.l.c. analysis).

There is ample mechanistic analogy for the formation of all these products, except 1,4-diphenylcyclohexene. Since the rearrangement reaction fails in the absence of base, a carbonium ion mechanism is unlikely. This view is supported by the failure of 1,4-phenyl migration to occur during solvolysis (acetolysis or formolysis) of tosylate 1, or during deamination of the corresponding amine. Rearrangement *via* a radical or methylene intermediate appears unlikely, and we have some evidence against the latter inasmuch as preliminary experiments on the base-catalyzed decomposition of the *p*-tolylsulfonylhydrazone of 4,4-diphenylcyclohexanone have failed to reveal the presence of rearrangement products.

Examination of molecular models shows that the boat form of 1, or of *cis*-4-methyl-4-phenylcyclohexyl *p*-toluenesulfonate (2),<sup>2</sup> has one of the C-3 hydrogen atoms, the C-3 and C-4 carbon atoms, and the C-C<sub>6</sub>H<sub>5</sub> bond in the correct coplanar orientation for a concerted  $\beta$ -eliminative process. Furthermore, the phenyl group is in a favorable location to initiate bonding at the face of the carbon atom opposite to that holding the *p*-toluenesulfonate grouping. Conceivably, then, 1,4-

diphenylcyclohexene could arise from 1 by a one-step concerted reaction—a merged elimination (E2) and intramolecular displacement (S<sub>N</sub>i) process.

This mechanism predicts that during the reaction the double bond is generated between the C-3 and C-4 carbon atoms, rather than between the C-1 and C-2 carbon atoms. The reaction of 1 gives no evidence on this point, but when applied to 2 this mechanism predicts that the rearrangement product will be 1-methyl-4-phenylcyclohexene (3), rather than 4-methyl-1-phenylcyclohexene.



Treatment of 2 with sodium *t*-butoxide in a refluxing solution of *t*-butyl alcohol and decalin gave 3 (19%), 4-methyl-4-phenylcyclohexene (26%), 4-methyl-4-phenylcyclohexanone (~5%), and a mixture of *cis*- and *trans*-4-methyl-4-phenylcyclohexanol (36%). These products were separated by elution chromatography on silica gel. The isomeric 1-methyl-4-phenyl- and 4-methyl-4-phenylcyclohexenes were identified by comparing them with authentic samples using infrared, ultraviolet, and n.m.r. spectra and g.l.c. retention times.<sup>1</sup> For example, 3 has a series of maxima at 242, 247.5, 253, 257.5, 261, and 267.5  $\mu$ m with  $\epsilon \sim 325$ , whereas 4-methyl-4-phenylcyclohexene has a broad maximum at 241  $\mu$ m ( $\epsilon$  700). There was no indication for the presence of 4-methyl-1-phenylcyclohexene ( $\lambda_{max}$  247  $\mu$ m ( $\epsilon$  21,000)), either in the ultraviolet or the n.m.r. spectrum or the g.l.c. analysis of 3.

A search for merged E2-S<sub>N</sub>i reactions in other cyclic systems and in open-chain analogs is underway.<sup>3</sup>

**Acknowledgment.**—We are grateful to the National Science Foundation for their support of this investigation (NSF-G24095).

(3) Rearrangement products have been observed to be formed under similar conditions from neopentyl *p*-toluenesulfonate (elimination with methyl migration).

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### Synthesis of

### 1(2,3,6-Trideoxy- $\beta$ -D-erythro-hexopyranosyl)cytosine. The Deoxy Sugar Nucleoside Moiety of Amicetin

Sir:

In this work the deoxy sugar nucleoside derived from amicetin<sup>1,2</sup> was synthesized starting from a readily available nucleoside of known  $\beta$ -configuration. More importantly, procedures were developed for the conversion of amicetose,<sup>2</sup> the naturally occurring deoxy sugar which has been synthesized conveniently in this

(1) Microanalyses consistent with the structures assigned were obtained for all new compounds.

(2) The *cis* designation refers to the first group mentioned, *i.e.*, *cis* CH<sub>3</sub> and OTs.

(1) (a) C. L. Stevens, K. Nagarajan, and T. H. Haskell, *J. Org. Chem.*, **27**, 2991 (1962); C. L. Stevens, P. Blumbergs, and F. A. Daniher, *J. Am. Chem. Soc.*, **85**, 1552 (1963).

(2) C. L. Stevens, P. Blumbergs, and D. L. Wood, *ibid.*, **86**, 3592 (1964).