

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 metals¹⁰ 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:

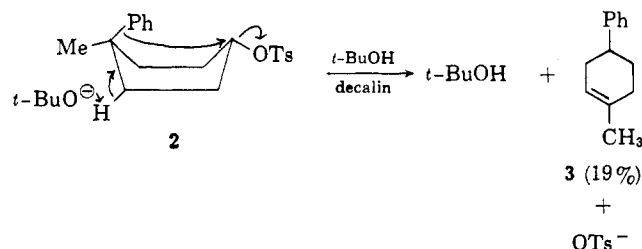
Treatment of 4,4-diphenylcyclohexyl *p*-toluenesulfonate (1) with sodium *t*-butoxide in refluxing *t*-butyl alcohol solution for 4 hr. gave 4,4-diphenylcyclohexanone (7%), 4,4-diphenylcyclohexanol (9%), 1,4-diphenylcyclohexene (14%), and 4,4-diphenylcyclohexene (64%). These products were separated by elution chromatography and identified by comparing their melting points, infrared spectra, and g.l.c. retention times with those of authentic samples.¹ 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),² has one of the C-3 hydrogen atoms, the C-3 and C-4 carbon atoms, and the C-C₆H₅ bond in the correct coplanar orientation for a concerted β -elimination 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_Ni) 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.¹ For example, 3 has a series of maxima at 242, 247.5, 253, 257.5, 261, and 267.5 $m\mu$ with $\epsilon \sim 325$, whereas 4-methyl-4-phenylcyclohexene has a broad maximum at 241 $m\mu$ (ϵ 700). There was no indication for the presence of 4-methyl-1-phenylcyclohexene (λ_{max} 247 $m\mu$ (ϵ 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_Ni reactions in other cyclic systems and in open-chain analogs is underway.³

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- β -D-erythro-hexopyranosyl)cytosine. The Deoxy Sugar Nucleoside Moiety of Amicetin

Sir:

In this work the deoxy sugar nucleoside derived from amicetin^{1,2} was synthesized starting from a readily available nucleoside of known β -configuration. More importantly, procedures were developed for the conversion of amicetose,² 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* CH₃ 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).