$6\pi + 2\sigma \rightarrow 8\pi$ electrocyclic reactions probably amounts to at least 18–20 kcal/mol, a figure substantially larger than the previously suggested minimum value of 11–12 kcal/mol.[5,25]

Acknowledgment. We are pleased to acknowledge the support of this work by the National Science Foundation. Samples of cyclooctatetraene were kindly provided by Badische Anilin-und Soda-Fabrik AG.

(25) It is possible that the transformation to the "nonallowed" system (ref 5) actually occurs *via* allowed hydrogen shifts from *all-cis*-2,4,6,8-decatetraene. We acknowledge a stimulating discussion with Professor W. R. Roth concerning this point.

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Reaction between Azide Ion and $[Ru(bipy)_2(NO)Cl]^{2+}$

Sir:

The preparation of a series of cis complexes $[Ru(AA)_2(NO)X]^{3+}$ {AA = 2,2′-bipyridine and 1,10-phenanthroline; X = Cl^-, Br^-, NO_2^-, and pyridine} was reported recently.[1,2] In the complexes, coordinated nitrosyl behaves chemically as NO^+ since reaction with hydroxide ion gives the corresponding nitro complexes.

$$[Ru(AA)_2(NO)X]^{3+} + 2OH^- \longrightarrow [Ru(AA)_2(NO_2)X]^+ + H_2O \quad (1)$$

We find that the reactivity of the nitrosyl as NO^+ extends to a variety of nitrogen bases, including azide ion. In aqueous solution, a stoichiometric amount of N_3^- (3×10^{-3} *M*) reacts with $[Ru(bipy)_2(NO)Cl]^{2+}$ (3×10^{-3} *M*) according to

$$H_2O + Ru(bipy)_2(NO)Cl^{2+} + N_3^- \longrightarrow Ru(bipy)_2(OH_2)Cl^+ + N_2 + N_2O \quad (2)$$

The aquo complex has been identified spectrophotometrically, and nitrogen and nitrous oxide have been identified by mass spectrometry. The reaction of N_3^- with HNO_2 apparently involves the formation of a nitrosyl azide intermediate, N_4O,[3] but no evidence for the existence of $[Ru(bipy)_2(N_4O)Cl]^+$, $[Ru(bipy)_2(N_2O)Cl]^+$, or $[Ru(bipy)_2(N_2)Cl]^+$ has yet been obtained.

The rate law for the reaction in solutions containing either excess acid or excess azide ion is

$$\frac{-d[Ru(bipy)_2(NO)Cl^{2+}]}{dt} = k[Ru(bipy)_2(NO)Cl^{2+}][N_3^-]$$

At 25.0° in 0.5 *M* lithium chloride, k is $32 \pm 4\ M^{-1}\ sec^{-1}$. $Ru(bipy)_2Cl_2$ is *not* observed as a product of the reaction in 0.5 *M* LiCl.

Reaction 2 is analogous in the opposite sense to the nitrosation of azidopentaamminecobalt(III) studied by Haim and Taube[4] (reaction 3), since the nitrosating group is coordinated, and N_3^- free. When carried out in nonaqueous solvents using $NO^+ClO_4^-$ as the nitrosating agent, reaction 3 has led to labile solvent complexes $Co(NH_3)_5S^{3+}$ {S = triethyl phosphate, sulfolane, etc.} which have proven useful as synthetic intermediates.[4–7]

$$H_2O + Co(NH_3)_5N_3^{2+} + NO^+ \text{ (or } H_2NO_2^+) \longrightarrow Co(NH_3)_5OH_2^{3+} + N_2 + N_2O \quad (3)$$

Reaction 2 can also be carried out in nonaqueous solvents, and it appears to be as synthetically useful for the ruthenium complexes as reaction 3 is for the cobalt complexes. A stoichiometric amount of sodium azide suspended in acetonitrile rapidly converts $[Ru(bipy)_2(NO)Cl]^{2+}$ into the acetonitrile complex with gas evolution

$$CH_3CN + Ru(bipy)_2(NO)Cl^{2+} + N_3^- \longrightarrow Ru(bipy)_2(NCCH_3)Cl^+ + N_2 + N_2O \quad (4)$$

The complex has also been prepared by refluxing $Ru(bipy)_2Cl_2$ in acetonitrile.[8] The same reaction in acetone apparently gives the acetone complex, $[Ru(bipy)_2(OC(CH_3)_2)Cl]^+$ [λ_{max} 511 ($\epsilon \sim 7250$) and 359 nm ($\epsilon \sim 7850$)]. The coordinated acetone molecule is labile and addition of excess chloride ion, pyridine, or water gives $Ru(bipy)_2Cl_2$, $[Ru(bipy)_2(py)Cl]^+$, and $[Ru(bipy)_2(OH_2)Cl]^+$, respectively, within a few minutes at room temperature.

Reactions analogous to (2) and (4) also occur for $[Ru(bipy)_2(NO)NO_2]^{2+}$, and several complexes of the type $[Ru(bipy)_2(NO_2)X]$ have been isolated. Initial experiments indicate that the entire series of complexes $[Ru(AA)_2(NO)X]^{3+}$ behave chemically as a controlled source of nitrosonium ion.

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(3) See, for example, G. Stedman, *J. Chem. Soc.*, 1702 (1960).

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(5) R. B. Jordan, A. M. Sargeson, and H. Taube, *ibid.*, **5**, 1091 (1966).

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(9) National Science Foundation Undergraduate Research Participant, Summer, 1970.

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A Novel Synthesis of 3-Substituted Pyridines from Pyridine

Sir:

While a wide variety of 3-substituted pyridines and their derivatives find many important applications, *e.g.*, in biological studies,[1] insecticide,[2] and anticorrosion formulations,[3] as intermediates in organic and pharmaceutical synthesis, and in mechanistic investigations,[4] the preparation of these compounds has been a problem. The direct alkylation, aralkylation, or arylation at the 3 or 5 position of the pyridine ring has been particularly difficult.[4,5] Thus, the alkylation

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(2) L. Goodhue, U. S. Patent 3,325,355 (1967); *cf. Chem. Abstr.*, **67**, 63301 (1967).

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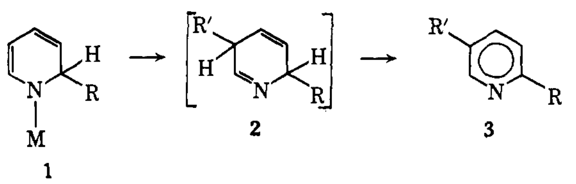
of pyridine by nucleophilic reagents, *e.g.*, organolithium compounds or Grignard reagents, produces 2- or 4-substituted pyridines, rather than the 3-substituted derivatives.[6] Free-radical substitution reactions produce mixtures of substituted pyridines,[4–6] and the 3-substituted pyridine, if present at all,[7] is a minor component of the mixture.[4–6] Finally, alkylation *via* electrophilic substitution, *e.g.*, Friedel–Crafts reaction, which is so facile in benzene has to date not been successfully carried out with pyridine.[4,5] Current procedures for the synthesis of 3-substituted pyridines involve cumbersome cyclizations, gas-phase reactions,[8] modification of substituents of available 3-substituted pyridines,[9] and coupling reactions.[10]

Recently, we showed that the highly reactive and versatile intermediate, 1-lithio-2-phenyl-1,2-dihydropyridine (**1**, R′ = H, R = C_6H_5),[11] isolated from the reaction of phenyllithium with pyridine, reacted with alkyl halides to give 2-phenyl-5-alkylpyridines (**3**, R′ = alkyl, R = C_6H_5).[12] Other 2,5-disubstituted pyridines can similarly be prepared.[13,14] This procedure, however, produces 2,5-disubstituted pyridines rather than 3-monosubstituted pyridines. We now wish to report a new and simple preparation of 3-substituted pyridines from pyridine itself.



A mixture of lithium aluminum hydride and excess pyridine was stirred at room temperature for 24 hr—the procedure is similar to that reported by Lansbury and Peterson[15] for the preparation of lithium tetrakis(*N*-dihydropyridyl)aluminate (LDPA). To this mixture was carefully added an alkyl halide, benzyl chloride, or bromine. After 1 hr, the reaction mixture was worked up and analyzed by gas chromatography. Under these conditions good yields of 3-methyl-, 3-ethyl-, and 3-benzylpyridine were obtained, but the yield of 3-bromopyridine was low (Table I).

The above reaction shows promise as an especially convenient route to the 3-substituted pyridines, and isolation of products is not a problem, *e.g.*, fractional distillation can be readily accomplished for compounds which have boiling points different from pyridine. If necessary, the product can be further purified by eluting it from an alumina column.

Table I. Reaction of LDPA with Some Electrophilic Reagents at Room Temperature[a,b]

Reagent	Product	Yield, %
CH_3I	3-Picoline[b]	86
C_2H_5I	3-Ethylpyridine[b]	89
$PhCH_2Cl$	3-Benzylpyridine	63
Br_2	3-Bromopyridine[b]	41

[a] Yield is based on LDPA; ethylation and benzylation experiments indicate optimum yields at the mole ratio RX/LDPA = 1.0. [b] Analytical samples of the products were obtained by preparative gas chromatography, and their identity was confirmed by comparison with authentic samples.

A typical procedure is as follows. To a suspension of LDPA prepared from 150 ml of pyridine and 5.8 g (0.153 mol) of lithium aluminum hydride and aged for 24 hr at room temperature was slowly added 38.7 ml (0.34 mol) of benzyl chloride with stirring and cooling. After 1 hr the reaction mixture was hydrolyzed with 50 ml of water, made basic with NaOH, and repeatedly extracted with ether (seven 200-ml portions). These extracts were combined and repeatedly extracted with 50% v/v HCl (five 100-ml portions). These acid extracts were combined, neutralized (Na_2CO_3), made basic with NaOH, and repeatedly extracted with ether (five 250-ml portions). These ether extracts were combined, and the ether and excess pyridine were removed by distillation. Vacuum distillation of the syrupy residue gave 12.9 g of crude 3-benzylpyridine: bp 284° (760 mm) [lit.[16] 286° (740 mm)]. An analytical sample was obtained by preparative gas chromatography and subjected to spectrometric analysis: nmr (CCl_4) δ 8.38 (m, 2, C-2 and C-6), complex multiplet centered about 7.08 (m, 7, C-4, C-5, and phenyl), and 3.93 (s, 2, CH_2Ph). The ir spectrum exhibited absorption bands characteristic for a benzyl pyridine. Mass calcd for $C_{12}H_{11}N$: 169.08909. Found: 169.0887. The picrate, mp 118.5–119° (lit.[16] 119°), was also consistent with the assigned structure. A pure sample was also obtained by eluting the crude 3-benzylpyridine from alumina with benzene–ether (95:5 v/v).

The reaction probably involves the alkylation of the 1,2-dihydropyridyl moiety (**1**, R = H) of the LDPA[17a] to give a 2,5-dihydropyridine (**2**, R = H; R′ = alkyl) which is easily oxidized to the 3-substituted pyridine (**3**, R = H; R′ = alkyl).[17b] A similar mechanism has been invoked to explain related additions and aromatizations.[18–20]

The scope and applicability of the reaction with other heterocyclic substrates (substituted pyridines, quinoline, and isoquinoline) and with other electrophilic reagents are now being investigated.

Acknowledgment. We are grateful to Texas A&M Research Council for a research grant and to the Gradu-

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(14) R. Grashey and R. Huisgen, *Chem. Ber.*, **92**, 2641 (1969).

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(17) (a) Only the 1,2-dihydropyridyl moiety is shown here; for the detailed structure of LDPA see Lansbury and Peterson.[15] (b) We thank one of the referees for the suggestion that the 1,4-dihydropyridyl moiety may be involved; this and other aspects of the mechanism will be studied.

(18) R. E. Lyle, P. S. Anderson, C. K. Spicer, S S. Pelosi, and D. A. Nelson, *Angew. Chem.*, **75**, 386 (1963).

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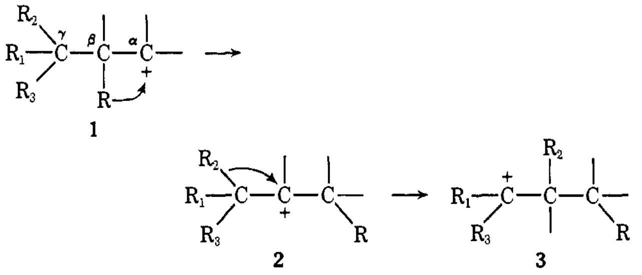
Magnification of the Memory Effect by Methyl Substitution. The Ring Expansions of the 1-Methylnorborn-2-enyl-7-*anti*- and -7-*syn*-carbinyl and the 1-Methyl-*endo*- and -*exo*-2-norbornylcarbinyl Systems[1]

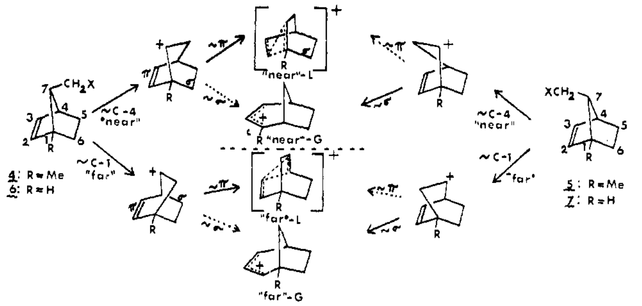
Sir:

Consecutive multiple carbonium ion rearrangements (*e.g.*, **1** → **2** → **3**) frequently select between two potential migrating groups (R_1 and R_2), even though in principle there is an opportunity for complete symmetrization, quasisymmetrization, or crossover at the once-rearranged intermediate stage **2**. Competition between stereochemical symmetrization or crossover and the second rearrangement **2** → **3** determines the magnitude of this type of "memory effect."[2] One might expect that alkyl for hydrogen substitution of the nonmigrating group (R_3) γ to the original cationic charge, in providing a means for generation of a more stable doubly rearranged ion (**3**, R_3 = alkyl), would favor rearrangement more than symmetrization in **2** and thereby magnify the memory effect. In this and the accompanying paper,[3] we report experiments that demonstrate this phenomenon. The results provide the first roughly quantitative estimate of the amount by which a substituent so placed enhances the specific rate of rearrangement of a carbonium ion.



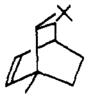
Because the starting materials are unsymmetrically substituted, the double rearrangements of 1-methylnorborn-2-enyl-7-*anti*- and -7-*syn*-carbinyl derivatives **4** and **5** (Scheme I) permit not only an external comparison with the previously studied unsubstituted parent systems[4] **6** and **7** but also an internal one, since the selectivities on the "far" side (methyl group remote from the site of charge) serve as calibration points for those on the "near" side.

Scheme I



Scheme I predicts the occurrence of four distinct sets of products in proportions that will be determined by the competitions ~C-4 *vs.* ~C-1 and $\sim\pi$ *vs.* $\sim\sigma$ shown. Memory-destroying crossover steps are shown with dashed arrows. The products expected or conceivable by analogy with the unsubstituted series[2,5,6] are those derived from the four cations[7] "near"-L, "near"-G, "far"-L, and "far"-G. Unambiguous independent syntheses and characterizations of these 23 potential ring-expanded products as well as those of several side products support the structural assignments.[8]

The validity of the analogy with the unsubstituted system is demonstrated in each case when independent generation of the product-forming cationic intermediate by acetolysis of the corresponding once-rearranged substrate, namely the appropriate 1- (or 4-) methylbicyclo[2.2.2]oct-5-en-2-yl *p*-toluenesulfonate (**8**-OTs → "near"-L, **9**-OTs → "near"-G, **10**-OTs → "far"-L, and **11**-OTs → "far"-G), gives the predicted products. Crossover between the cation systems, although detectable at 120°, is negligibly small at 35°.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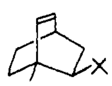
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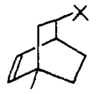
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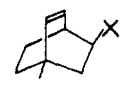
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The results of ring expansions of the syn and anti systems by way of intermediates generated in the nitrosative deamination of the amines at room temperature are reported in Table I, which also includes

Table I. Memory Effects in Deaminations

Type of product ratio	Product ratio from amine system[a]			
	Parent		1-Methyl	
	Syn (**7**-NH_2)	Anti (**6**-NH_2)	Syn (**5**-NH_2)	Anti (**4**-NH_2)
Total "near"/total "far"	1.00[g]	1.00[g]	2.0[f]	0.84[d]
Memory effect (ME)[b]				
"Near" [h]	3.3[c]	33[c]	20[g]	65[g]
"Far" [h]			6.5[d]	33[d]
Mult ME (MME)				
"Near" [h]	110[e]		1300[e]	
"Far" [h]			215[f]	

[a] Refers to ring-expanded products only. [b] ME = G/L product ratio from syn, L/G product ratio from anti. [c] Reference 4b. [d] Estimated uncertainty ±15%. [e] Estimated uncertainty ±30%. [f] Estimated uncertainty ±20%. [g] By symmetry. [h] Applies only to 1-methyl series.

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