of a small, negative activation volume for a cycloaddition is not enough to rule out a concerted reaction; it is also necessary to verify that unusual loss of polarity of the two molecules participating is not responsible.

Acknowledgment. This work has been generously supported by the National Science Foundation. We thank Professor K. N. Houk for comments.

References and Notes

(1) Paper XXXVI in the series "Kinetics of Reactions in Solutions under Pressure".

(2) (a) C. Walling and J. Peisach, *J. Am. Chem. Soc.*, **80**, 5819 (1958); (b) R. A. Grieger and C. A. Eckert, *ibid.*, **92**, 2918, 7149 (1970); (c) W. G. Dauben and A. P. Kozikowski, *ibid.*, **96**, 3664 (1974); (d) K. Seguchi, A. Sera, and K. Maruyama, *Tetrahedron Lett.*, 1585 (1973); (e) C. Brun and G. Jenner, *Tetrahedron*, **28**, 3113 (1972).

(3) C. A. Stewart, *J. Am. Chem. Soc.*, **94**, 635 (1972).

(4) (a) W. J. le Noble and R. Mukhtar, *J. Am. Chem. Soc.*, **96**, 6191 (1974); (b) for further discussion of the basis of this criterion, see W. J. le Noble, H. Guggisberg, T. Asano, L. Cho, and C. A. Grob, in preparation.

(5) (a) R. C. Cookson, B. V. Drake, J. Hudec, and A. Morrison, *Chem. Commun.*, 15 (1966); (b) S. Ito, Y. Fujise, T. Okuda, and Y. Inoue, *Bull. Chem. Soc. Jpn.*, **39**, 1351 (1966).

(6) K. N. Houk and R. B. Woodward, *J. Am. Chem. Soc.*, **92**, 4143, 4145 (1970).

(7) K. N. Houk, L. J. Luskus, and N. S. Bhacca, *J. Am. Chem. Soc.*, **92**, 6392 (1970).

(8) H. Tanida and H. R. Pfaendler, *Helv. Chim. Acta*, **55**, 3062 (1972).

(9) As noted by one of the referees, an exceptionally voluminous product would also account for the observed pressure effect; however, unusual tenuousness among molecules is unprecedented, and the facts as described here rule it out.

(10) W. J. le Noble and T. Asano, *J. Am. Chem. Soc.*, **97**, 1778 (1975).

(11) O. R. Quayle, *Chem. Rev.*, **53**, 439 (1953).

(12) W. von E. Doering and F. L. Detert, *J. Am. Chem. Soc.*, **73**, 876 (1951).

(13) H. J. Dauben and H. J. Ringold, *J. Am. Chem. Soc.*, **73**, 876 (1951).

(14) D. Kubo, T. Nozoe, and Y. Kurita, *Nature (London)*, **167**, 688 (1951).

W. J. le Noble,* B. A. Ojosipe

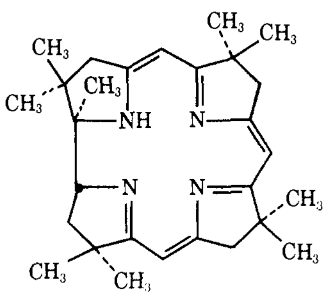
Department of Chemistry, State University of New York
Stony Brook, New York 11794

Received May 12, 1975

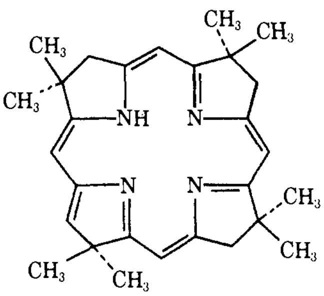
The Total Synthesis of Nickel(II) Octamethylcorphin

Sir:

At the very heart of any project whose ultimate goal is the synthesis of vitamin B-12 must lie a concept for the construction of the macrocyclic ligand. In consonance with this fact we have initiated a fundamentally different approach to the synthesis of corrins and related ligands.[1] The method utilizes isoxazole nuclei as latent synthons for the crucial



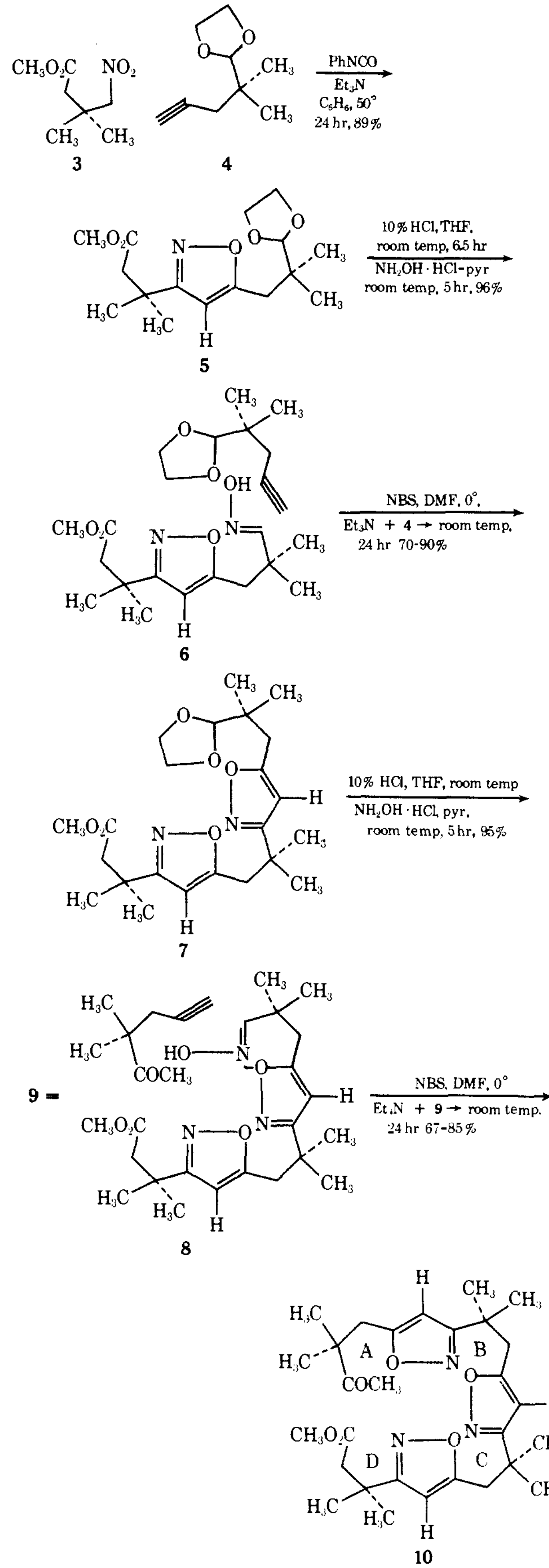
1



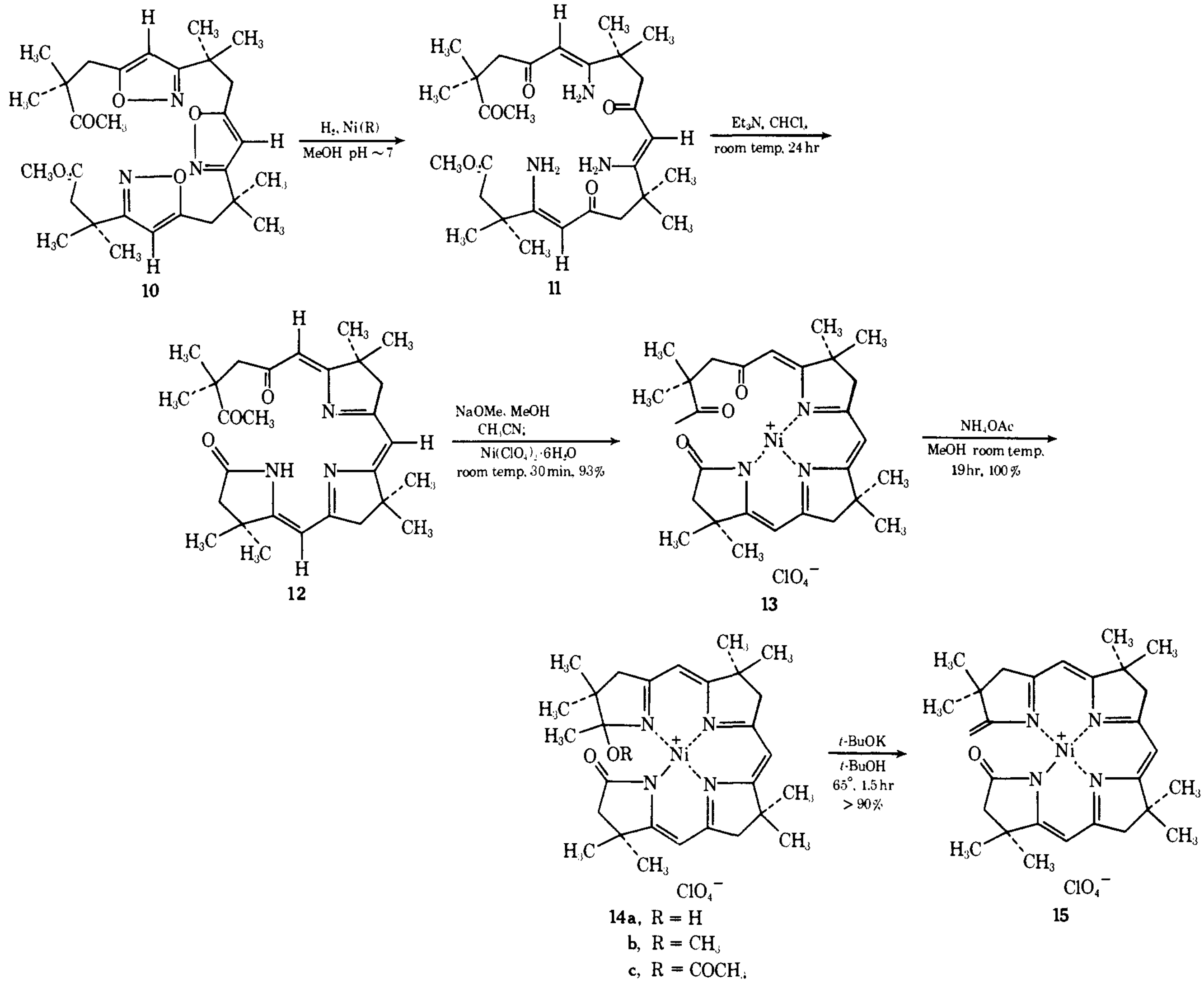
2

ring-bridging vinylogous amidine chromophores found in octamethylcorrin (**1**) or octamethylcorphin (**2**).[2,3] In principle, all of the structural features of these two substances can be incorporated into an appropriately substituted trisisoxazole (**10**) which, in turn, can be assembled from carefully selected nitrile oxides and terminal acetylenes. Thus, cycloaddition of the nitrile oxide generated[1,5] from nitroester **3** and acetylenic acetal[6] **4** gave monoisoxazole **5** (Scheme I).[7] Mild acid hydrolysis of the acetal function and treatment of the resultant aldehyde with $NH_2OH \cdot HCl$-pyr pro-

Scheme I



Scheme I



vided oxime **6**. Conversion of this intermediate to bisisoxazole **7** was readily achieved by treatment with NBS in DMF followed by addition of acetylenic acetal **4** and triethylamine.[5] Repetition of this sequence employing acetylenic ketone **9** provided the desired trisisoxazole **10** (mp 56.5–57.5°). Under optimum conditions the overall yield for the entire sequence (starting with **3** and **4**) was a very respectable 40%.

The crucial reduction of **10** was found to proceed smoothly and virtually quantitatively by employing a Raney nickel catalyst[8] adjusted to a pH of about 7 with acetic acid. The product of this reduction (**11**) was a labile white crystalline solid which upon exposure to a trace of triethylamine produced a yellow-orange gummy solid whose ^{1}H NMR and mass spectra were consistent with the conjugated ligand structure **12** (Scheme II). However, due to its lability it was immediately treated with 1 equiv of $NaOCH_3$ followed by 1.1 equiv of $Ni(ClO_4)_2$ in CH_3CN. This reaction sequence provided the beautifully crystalline orange nickel complex **13** (mp 205–208° dec) in essentially quantitative yield. The last nitrogen was incorporated by simply stirring a methanolic solution of **13** with excess ammonium acetate. This produced a solid whose ^{1}H NMR indicated it was a mixture of products **14a–c**. Without purification this mixture was treated with *t*-BuOK–*t*-BuOH to provide the known[9] nickel precorphin complex **15**.[10] The overall yield of the sequence starting with trisisoxazole **10** was 30–50%. The conversion of nickel precorphin complex **15** into a variety of metal complexes of octamethylcorphin (**2**) has recently been recorded.[9]

Acknowledgments. This research was generously supported by The Robert A. Welch Foundation, the National Science Foundation, and Merck Sharp and Dohme Research Laboratories.

References and Notes

(1) R. V. Stevens, C. G. Christensen, W. L. Edmonson, M. Kaplan, E. B. Reid, and M. P. Wentland, *J. Am. Chem. Soc.*, **93**, 6629 (1971); R. V. Stevens, L. E. DuPree, Jr., W. L. Edmonson, L. L. Magid, and M. P. Wentland, *ibid.*, **93**, 6637 (1971).

(2) The incorporation of quaternary centers at the alternate peripheral carbons of these ligands is intended to mimic the environment found in the vitamin itself *and* to minimize potentially troublesome oxidative and/or tautomeric transformations.

(3) The term "corphin" was first introduced by Professor Eschenmoser[4] to describe a macrocyclic ligand intermediate in structure between the naturally occurring corrinoid and porphinoid types.

(4) A. P. Johnson, P. Wehrli, R. Fletcher, and A. Eschenmoser, *Angew. Chem., Int. Ed. Engl.*, **7**, 623 (1968).

(5) Cf. inter alia, C. Grundmann, *Synthesis*, 344 (1970), and N. K. Kochetkov and S. D. Sokolov, *Adv. Heterocycl. Chem.*, **2**, 365 (1963).

(6) We had found in our previous studies[1] that failure to protect an aldehyde function provided a mixture of products resulting from competitive cycloaddition to the carbonyl group.

(7) The ir, ^{1}H NMR, and mass spectra for each intermediate in this series were in complete agreement with the assigned structures. Further confirmation rests on the success of the synthesis.

(8) We are indebted to Dr. Pius Wehrli of Hoffman-La Roche, Inc., Nutley, N.J., for providing us with generous supplies of this catalyst.

(9) P. M. Müller, S. Farooq, B. Hardegger, W. S. Salmond, and A. Eschen-

moser, *Angew. Chem., Int. Ed. Engl.*, **12**, 914 (1973).
(10) The physical and chemical properties of **14** were identical with those reported by Eschenmoser.[9] We are most grateful to Professor Eschenmoser for providing us with additional detailed spectral data.

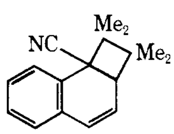
Robert V. Stevens,* C. G. Christensen
Robert M. Cory, Eugene Thorsett
Department of Chemistry, Rice University
Houston, Texas 77001
Received May 27, 1975

Exciplex and Electron-Transfer Chemistry.[1] Reactions of Naphthonitrile S_1 States with Tetramethylethylene

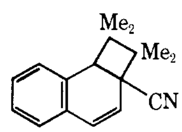
Sir:

There is much current interest in the photophysics[2-11] and photochemistry[1,10-18] of excimers and exciplexes, with particular regard to their role in cycloadditions and other photochemical processes. We have been active in this field for some time,[1,18] and have used nitriles in studying the photochemical effects of charge transfer. Aryl nitriles have recently attracted considerable attention because they can form fluorescent exciplexes with olefins.[7,11]

We now report recent work with 1- and 2-naphthonitrile (1-NN and 2-NN) and tetramethylethylene (TME), which indicates that (a) exciplexes of the nitriles and TME are intermediates in the cycloadditions which occur in benzene, (b) different factors seem to determine the formation of the exciplexes, and their collapse to products, and (c) in polar solvents, electron transfer dominates the chemistry. The results are as follows. Irradiation[19] of 1-NN and 2-NN with TME in benzene gives 1-cyano-7,7,8,8-tetramethyl-2,3-benzobicyclo[4.2.0]octa-2,4-diene (**1**), and the previously described[20] 6-cyano isomer (**2**), respectively.



1



2

The cycloadducts were isolated by chromatography. **1** had mp 60–61.5° and in the NMR spectrum (100 MHz, CCl_4 or $CDCl_3$) showed resonances at δ 1.40, 1.32, 1.00 and 0.81, singlets (area of each, 3), assigned to the methyl groups; a doublet of doublets at δ 3.20, J = 4.5 and 2.0 Hz (area 1), is assigned to the bridgehead methine proton; two doublets of doublets at δ 5.71, J = 10.0 and 4.5 Hz, and at δ 6.31, J = 10.0 and 2.0 Hz, are assigned to the vinylic protons, and multiplets at δ 7.1 (area 3) and at 6.9 (area 1) are assigned to the aromatic ring protons. **2** was obtained as an oil, and had NMR[20] and other spectra, in full agreement with the assigned structure.

Dilution plots for both of these addition reactions in benzene solvent are shown in Figure 1. The linear form of these plots is described by eq 1.

$$\Phi_a^{-1} = \Phi_{lim}^{-1}\,(1 + K_{sv}^{-1}[\text{TME}]^{-1}) \qquad (1)$$

Φ_a is the quantum yield of addition, Φ_{lim} is its value at infinite TME concentration, and K_{sv} is the slope of the Stern–Volmer plot for quenching of the naphthonitrile fluorescence by TME. Scheme I, which involves an exciplex intermediate,[11a] will be used to interpret the photochemistry in benzene. In this scheme,[11a]

$$K_{sv} = \frac{k_q(k_p + k_d' + k_f')\tau}{k_{-q} + k_p + k_d' + k_f'},$$

where $\tau = (k_f + k_d)^{-1}$, and $\Phi_{lim} = k_p/k_p + k_d' + k_f'$

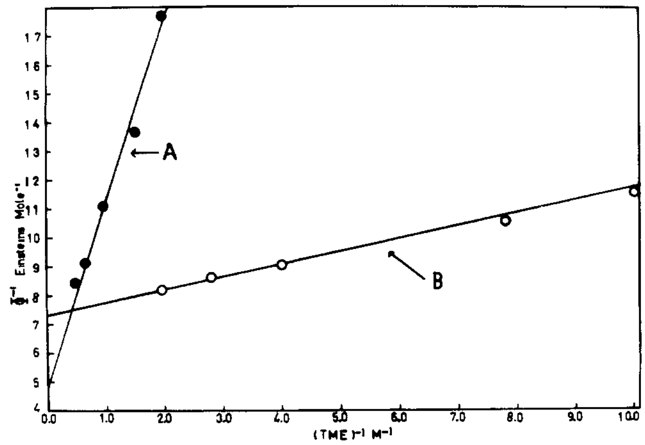


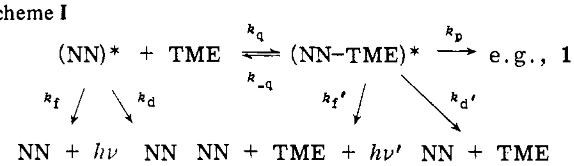
Figure 1. Dilution plots for cycloadduct formation in deoxygenated benzene: (A) 2-NN and TME giving **2**, (B) 1-NN and TME giving **1**. Values of slopes and intercepts are given in Table I.

Table I. Stern-Volmer Data and Limiting Quantum Yields for Naphthonitrile–TME Reactions[a] in Benzene

	1-Naphthonitrile	2-Naphthonitrile
K_{sv} (from fluorescence quenching), M^{-1}	41.7[b]	0.72
K_{sv} (from formation of adduct), M^{-1}	18.4, 22.8	0.68
Φ_{lim}	0.14	0.21

[a] All determinations were in deaerated benzene at 20°. [b] Value for hexane, taken from results of Taylor, ref 7, is 23.1.

Scheme I



Values for Φ_{lim} and K_{sv} for 1-NN and 2-NN are given in Table I. K_{sv}'s derived from fluorescence quenching, and from the plots in Figure 1, are in reasonable agreement. The additions clearly involve the naphthonitrile S_1 states.[21]

The simplest explanation for the different K_{sv}'s but similar Φ_{lim}'s for the two naphthonitriles is that formation of the exciplex determines K_{sv}, while its collapse to product determines Φ_{lim}.[1,22] A scheme involving separate, parallel processes for S_1 quenching and addition, respectively,[22,23] can also explain the results, but would require that the two processes vary in the same way with substitution of the naphthonitrile.

Calculation[24] of the enthalpies of exciplex formation using the reduction potentials and S_1 excitation energies of the naphthonitriles, and the oxidation potential of TME,[25] gives $\Delta H = -7.4$ and -1.8 kcal/mol for 1-NN and 2-NN, respectively, with TME. The more negative ΔH for 1-NN and TME is consistent with the larger K_{sv} in that case.[26a] The difference in K_{sv} between 1-NN and 2-NN is not due to the difference in lifetimes of S_1.[27] Similar suggestions have been made[7,11a] concerning the relationship between ionization potentials of olefins and their behavior as quenchers of 1-NN fluorescence.

The similarity in Φ_{lim} for the two reactions (Table I) shows that different factors control Φ_{lim} ($=k_p/k_p + k_f' + k_d'$) and K_{sv}. Thus, the exciplex which is the more stable (from 1-NN) collapses to product *less efficiently*. This could be consistent with a heteroexcimer bond which is longer in the more stable case (1-NN-TME) and shorter in the 2-NN-TME exciplex.[26b] Thus, radiationless processes