and hydrocarbon VI with absorption maxima at λ_{max} (cyclohexane) 235 mμ (ϵ 34,000), 307 (8800), and 320 (7100). The nmr of X indicated the presence of only aromatic protons. The mass spectrum of X at 70 eV and a source temperature of 25° showed a parent peak at *m/e* 336 with correct ^{34}S abundance. A large peak at *m/e* 304 (hydrocarbon VI) was also observed under these conditions. Complete disappearance of the *m/e* 336 peak occurred when the source temperature was raised to 80°. A spectrum identical with that of VI was obtained.

Heating X at 120° either as a solid or in solution instantly and quantitatively converted it to VI and sulfur. Brief exposure of X to ultraviolet light also effected its decomposition to VI.[10] To our knowledge X is the first heterocyclic derivative of this type reported in the acenaphthylene series.[11]

Heating IV at 100° in degassed acetic anhydride with 1 equiv of N-phenylmaleimide present gave rise to hydrocarbon, episulfide, and adduct in approximately equal amounts. Diketone VII along with VI, VIII, and X was obtained from the reaction when partially degassed solvent was used. Appropriate control experiments have shown that X does not yield VII or VIII under a variety of conditions. Indeed when X was added to a melt of N-phenylmaleimide at 150°, adduct VIII was not formed; however, a quantitative yield of VI was obtained. These results indicate that heterocycle I is the precursor of X and that the episulfide undergoes only sulfur extrusion.

Acknowledgments. This work was supported by a Frederick Gardner Cottrell grant from the Research Corporation and by the Petroleum Research Fund (Grant No. 756-G).

[10] A. Padwa, D. Crumrine, and A. Shubber, *J. Am. Chem. Soc.*, **88**, 3064 (1966), and references cited therein.

[11] It has been pointed out by P. D. Bartlett and R. F. Brown, *ibid.*, **62**, 2927 (1940), that the epoxide corresponding to X would not be stable because of the strain already associated with the five-membered ring.

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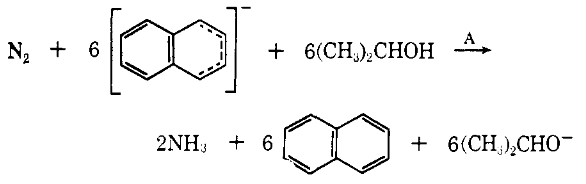
An Organic–Inorganic System for Reaction with Nitrogen of the Air and Operation of a Facile Nitrogen Fixation–Reduction Cycle

Sir:

All present processes[1,2] depending upon coordination compounds for fixing and/or reducing molecular nitrogen (N_2) under mild conditions in solution feature the use of the pure gaseous element and remain noncatalytic. We wish now to disclose certain operational features of a new titanium system (A), including (1) the significant competition of N_2 with molecular oxygen (O_2) in reaction with A and (2) the preparation of ammonia at room temperature and atmospheric pressure in a cyclic process involving N_2, isopropyl alcohol, sodium naphthalide, and A as mediator.

Design of the N_2 fixation agent A is based upon prior investigations[1,3] in this laboratory of lower valent titanium species and various electron sources, including the radical anion of naphthalene,[4] as N_2 fixation and reduction agents. Preparation involves merely the interaction of commercially available titanium tetraisopropoxide with sodium naphthalide in ethereal solvent. For single-stage N_2 fixation–reduction experiments, the active agent was prepared and used in an appropriate closed system under an atmosphere of pure dry N_2 having access to a calibrated vessel. The reducing solution, on being stirred rapidly during titanium isopropoxide addition, absorbed N_2 over a period of 30–60 min, the amount of gas consumed being dependent on factors such as concentration, stirring rate, and solvent. After addition of a proton source as much as 110% of ammonia was liberated.[5]

Operation of a cyclic process depends on a sequence involving (1) judicious addition of the proton source isopropyl alcohol after N_2 absorption is complete, and removal of volatile product ammonia, and (2) addition of either additional sodium naphthalide or metallic sodium to regenerate the radical anion from naphthalene freed in the N_2 reduction stage and attendant regeneration of the titanium species A. By such means, in excess of 340% yield[5] of ammonia was synthesized during the course of five cycles, making the process catalytic in a net, over-all sense. In the operation using naphthalide as a consumable reagent, gross eq 1 is applicable. However, since naphthalide is in fact retrievable by addition of alkali metal to product naphthalene, the net cycle may be expressed properly as eq 2.



(1)

$$N_2 + 6(CH_3)_2CHOH + 6e^- \xrightarrow{A} 2NH_3 + 6(CH_3)_2CHO^- \quad (2)$$

That N_2 might, under propitious circumstances, compete favorably with O_2 in a purely chemical reaction with a suitable agent is implied by the well-known fact that such selection seems to occur during the operation of N_2 fixing legumes, bacteria, and other life forms.[6] This surmise is strengthened by recognition of the known differences in molecular dimension, nature of the unshared electron pairs, and—perhaps most important—electronic multiplicity of N_2 and O_2. Encouraged by such considerations, we attempted the fixation–reduction of N_2 directly from the atmosphere.

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[1] See list of references in E. E. van Tamelen, G. Boche, S. W. Ela, and R. B. Fechter, *J. Am. Chem. Soc.*, **89**, 5707 (1967), and also D. F. Harrison, E. Weissberger, and H. Taube, *Science*, **159**, 320 (1968).

[2] G. Henrici-Olivé and S. Olivé, *Angew. Chem.*, **79**, 898 (1967).

[3] E. E. van Tamelen and M. A. Schwartz, *J. Am. Chem. Soc.*, **87**, 3277 (1965).

[4] The authors in ref 2 have reported in N_2 fixation experiments the use of lithium naphthalide in combination with various metallic halides, including titanium tetrachloride in toluene under 120 atm of N_2.

[5] Yield based on NH_3:Ti molar ratio and determined by titration after entrainment in dilute sulfuric acid.

[6] For a recent review, see W. D. P. Stewart, *Science*, **158**, 1426 (1967).

Although the quantitative aspects of the phenomena are confused by the high instability of the "active" N_2 fixing species, the side reaction of O_2 with naphthalide, and the operation of a two-phase (gas-liquid) reaction, our results nevertheless demonstrate clearly, and for the first time, the nonbiological reaction of a compound with N_2 as a component of air.[7]

In fixation experiments with air, the general method described above was employed, and the active fixation agent (A) was prepared either under argon before exposure to air or under air from the beginning. In the former case yields of fixed ammonia were lower, probably because of the temporal instability of A: ~2% of ammonia was formed with air, as contrasted with ~6% with pure nitrogen, both experiments being carried out under otherwise virtually identical conditions with 4.0 equiv of sodium naphthalide.[8] When both preparation of A and reaction with N_2 were executed under air, ammonia yields of 21% (3 equiv of naphthalide) and 44% (10-12 equiv of naphthalide) were realized. In comparable experiments carried out with pure N_2, 43 and 71% yields, respectively, were observed.[9]

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(7) L. S. Nelson (*Science*, **148**, 1594 (1965)) has reported partitioning of aerial N_2-O_2 in reaction with molten zirconium metal at *ca.* 3000 K.

(8) In this preparation of A, no naphthalide was present, as indicated by esr measurement (authors are grateful to Professor H. M. McConnell, Stanford University, for the determination).

(9) The structural nature of A remains undefined but is under investigation in these laboratories.

(10) Max Kade Foundation, Inc., Fellow, 1967-1968.

(11) National Science Foundation Fellow, 1966-present.

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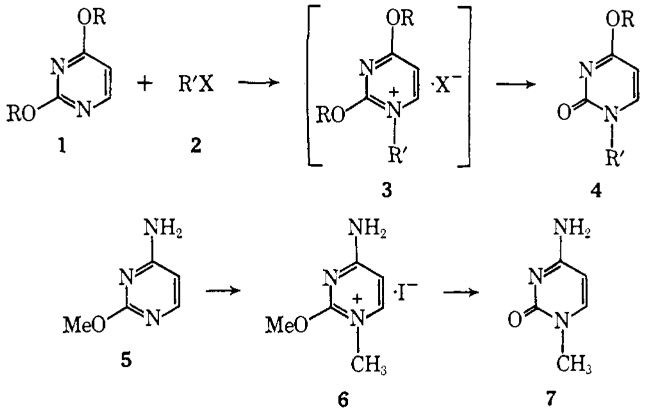
On the Hilbert-Johnson Procedure for Pyrimidine Nucleoside Synthesis

Sir:

We wish to report direct evidence for the presence of an intermediate glycosylpyrimidinium salt in the Hilbert-Johnson procedure for pyrimidine nucleoside synthesis and the extension of this procedure to a general method for the synthesis of 2-oxo-, 2-thio-, and 2-aminopyrimidine nucleosides of potential biochemical interest.

The Hilbert-Johnson precedure[1] has been an excellent method for the synthesis of various 2-oxopyrimidine nucleosides starting from a 2,4-dialkoxypyrimidine (**1**) and a protected glycosyl halide (**2**). Although the 1-substituted pyrimidinium salt **3** as an intermediate had not been detected, its existence had been suggested by the fact[4] that 4-amino-2-methoxypyrimidine (**5**) with methyl iodide gives the 1-methiodide **6** which, in turn, is converted to 1-methylcytosine (**7**).[2,3] The synthesis of 1-glycosylcytosines by the use of **5**, however, has not been successful (see Scheme I).

Scheme I



2,4-Diethoxypyrimidine (**1**, R = Et)[5] was treated with methyl iodide in acetonitrile at room temperature and the course of the reaction was followed by tlc. After 5 hr ether was added to furnish a precipitate (**3**, R = Et; R' = Me; X = I), mp 56.5-58.5°, in *ca.* 35% yield. Prolongation of the reaction time afforded **4** (R = Et; R' = Me) as the major product. The structure of **3** (R = Et; R' = Me; X = I) was confirmed by elemental analysis (*Anal.* Calcd for $C_9H_{15}N_2O_2I$: C, 34.85; H, 4.88; N, 9.03. Found: C, 35.02; H, 4.98; N, 8.73), by uv and nmr spectra, and by its conversion to **4** (R = Et; R' = Me) and then to 1-methyluracil by acid hydrolysis. By a similar method 2,4-diethoxy-5-methylpyrimidine[6,7] was converted to the corresponding 1-methiodide, mp 77.5-78°. *Anal.* Calcd for $C_{10}H_{17}N_2O_2I$: C, 37.05; H, 5.25; N, 8.61. Found: C, 37.17; H, 5.41; N, 8.33.

In the quaternary salt derivatives **3**, the 2-alkoxy group should be susceptible to substitution reactions, thus providing an extension of the Hilbert-Johnson reaction for nucleoside syntheses. In a model study, **3** (R = Et; R' = Me; X = I) was rapidly converted to the known[8,9] 2,4-diaminopyrimidinium 1-methiodide by treatment with methanolic ammonia. When compound **1** (R = Et) was allowed to react with tri-*O*-benzoyl-D-ribofuranosyl chloride in acetonitrile for several days at 0-5° and the reaction mixture then treated with alcoholic ammonia, crude 2,4-diamino-1-(β-D-ribofuranosyl)pyrimidinium chloride (**8**) was obtained, identical with that afforded by an alternate route (see Scheme II).[10]

Attempts to introduce a thiono group on C-2 of **3** (R = Et; R' = Me; X = I) by reaction of **3** with hydrogen sulfide resulted in the formation of **4** (R = Et; R' = Me) which indicated that alkyl oxygen fission

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(1) G. E. Hilbert and T. B. Johnson, *J. Am. Chem. Soc.*, **52**, 4489 (1930). For the recent reviews see ref 2 and 3.

(2) J. J. Fox and I. Wempen, *Advan. Carbohydrate Chem.*, **14**, 283 (1959).

(3) J. Pliml and M. Prystas, *Advan. Heterocyclic Chem.*, **8**, 115 (1967).

(4) G. E. Hilbert, *J. Am. Chem. Soc.*, **56**, 190 (1934).

(5) G. E. Hilbert and T. B. Johnson, *ibid.*, **52**, 2001 (1930).

(6) W. S. Nickels and T. B. Johnson, *ibid.*, **52**, 4511 (1930).

(7) M. Roberts and D. W. Visser, *ibid.*, **74**, 668 (1952).

(8) D. J. Brown, E. Hoerger, and S. F. Mason, *J. Chem. Soc.*, 4035 (1955).

(9) D. J. Brown and N. W. Jacobsen, *ibid.*, 3172 (1962).

(10) The synthesis of 2,4-diamino-1-(β-D-arabinofuranosyl)pyrimidinium picrate and sulfate by anhydronucleoside procedure was recently reported [I. L. Doerr and J. J. Fox, *J. Org. Chem.*, **32**, 1462 (1967)].