with the nmr spectra of *cis*- and *trans*-2-methyl-2-penten-1-ol.[23] Vinyl proton absorption occurred at 5.25 and 5.40, respectively; sirenin exhibited a signal at 5.38.

These data establish I uniquely as the structure of sirenin.

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[23] Prepared by Robert A. Jewell by lithium aluminum hydride reduction of *cis*- and *trans*-2-methyl-2-pentenoic acids (H. J. Lucas and A. N. Prater, *J. Am. Chem. Soc.*, **59**, 1682 (1937)).

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Some Novel Reactions of a "Tetravalent Sulfur" Species

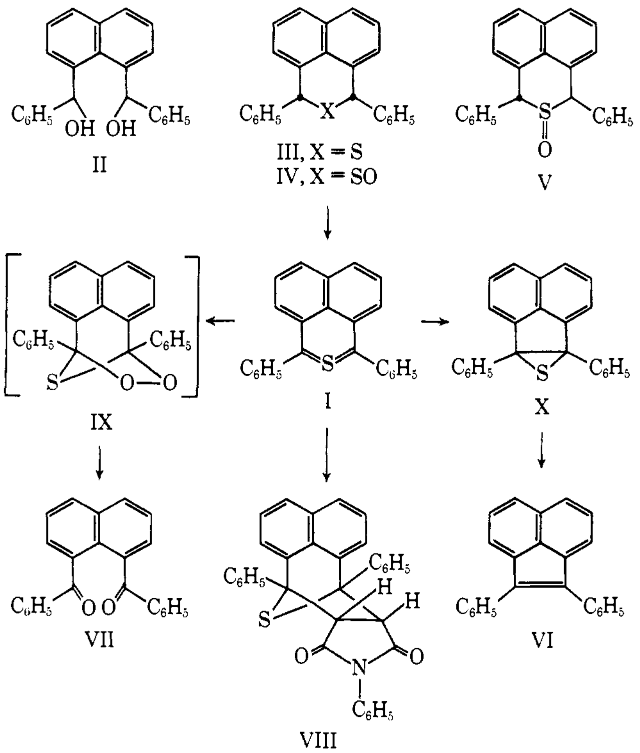
Sir:

Recently, a new class of highly reactive heterocycles containing a tetravalent sulfur atom has been described.[1] Chemical studies on these compounds have been confined thus far to their behavior in the Diels–Alder reaction. We wish to report some novel reactions arising from 1,3-diphenyl-2-thiaphenalene (I), a transient tetravalent sulfur species obtained by dehydration of its corresponding sulfoxide.

Reaction of α,α'-dihydroxy-1,8-dibenzylnaphthalene (II)[2] with phosphorus pentasulfide in pyridine[3] gave in 95% yield a single highly crystalline sulfide, III, mp 168°.[4] Oxidation of III with *m*-chloroperbenzoic acid in ether afforded the corresponding sulfoxide IV, mp 247° dec, in 90% yield. Treatment of this sulfoxide with sodium methoxide in methanol gave in quantitative yield a new sulfoxide, V, mp 250°.

Sharp singlets for the two protons α to the sulfur atom in V appeared at δ 5.18 and 5.45, indicating *trans* geometry for this sulfoxide.[5] The corresponding protons of sulfide III and sulfoxide IV appeared as singlets at δ 5.67 and 5.55, respectively. This resonance is compatible with the *cis* stereochemistry assigned to these compounds.

Upon heating the *cis* sulfoxide IV with acetic anhydride in the presence of excess N-phenylmaleimide at 120° three products were obtained. These materials were identified as 1,2-diphenylacenaphthylene (VI),[6] 1,8-dibenzoylnaphthalene (VII),[7] and the Diels–Alder adduct VIII[8] formed in yields of 15, 7, and 11%, respectively. The following series of experiments indicate heterocycle I to be involved in the formation of all of these products.



When the previous reaction was carried out in rigorously degassed acetic anhydride the only products formed were adduct VIII, 70% yield, and hydrocarbon VI, 15% yield. The same reaction run in the presence of oxygen gave the diketone VII as the major product, along with VI and VIII. Hydrocarbon VI, adduct VIII, and N-phenylmaleimide were found to be stable under these conditions.

These results suggest that I undergoes an addition reaction with oxygen giving rise to an intermediate peroxide adduct IX. Collapse of IX with loss of sulfur would yield diketone VII. Heterocyclic systems similar to I have not been observed to react with oxygen.[1]

Upon treatment with acetic anhydride at 120° in the absence of oxygen and added dienophile sulfoxide IV afforded VI in quantitative yield. Decomposition of IV at 100° gave a second component in addition to the orange hydrocarbon VI. Careful thick layer chromatography of the reaction mixture resulted in the isolation of colorless crystals, mp 110–120° dec, in 40% yield. This material has been identified as the episulfide X.

Compound X showed an ultraviolet spectrum intermediate between that of 1,2-diphenylacenaphthene[9]

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[1] (a) R. H. Schlessinger and I. S. Ponticello, *J. Am. Chem. Soc.*, **89**, 3641 (1967); (b) R. H. Schlessinger and I. S. Ponticello, *Tetrahedron Letters*, 4057 (1967); (c) M. P. Cava and N. M. Pollack, *J. Am. Chem. Soc.*, **89**, 3639 (1967); (d) M. P. Cava, N. M. Pollack, and D. A. Repella, *ibid.*, **89**, 3640 (1967).

[2] R. L. Letsinger and P. T. Lansbury, *ibid.*, **81**, 935 (1959).

[3] We are deeply indebted to Dr. P. M. Weintraub for the discovery of this reaction.

[4] All melting points are uncorrected. Satisfactory analyses were obtained for all new compounds reported.

[5] Nmr spectra were determined in $CDCl_3$.

[6] G. Wittig, M. Leo, and W. Wiemer, *Ber.*, **64**, 2405 (1931).

[7] W. Schlenk and J. Holtz, *ibid.*, **50**, 268 (1917).

[8] The structure of VIII was confirmed by the following observations. The mass spectrum of VIII showed a retro-Diels–Alder-type fragmentation pattern with peaks at m/e 336 (heterocycle I) and 173 (N-phenylmaleimide) as well as the parent ion at 509. That the peak at m/e 336 represents I is substantiated by the occurrence of a strong peak at 304 (hydrocarbon VI; sulfur extrusion from I). The peaks at 509 and 336 showed correct ^{34}S isotopic abundance. The nmr spectrum of VIII showed resonance for the two protons α to the imide carbonyls at δ 4.88, a position similar to the corresponding proton of the adduct of 9-phenylanthracene and N-phenylmaleimide. Molecular models indicate deshielding of these protons by the adjacent phenyl substituent for both compounds.

[9] H. J. Richter and W. C. Feist, *J. Org. Chem.*, **25**, 356 (1960).

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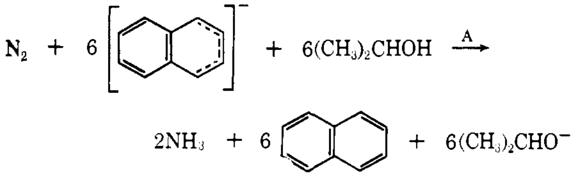
An Organic–Inorganic System for Reaction with Nitrogen of the Air and Operation of a Facile Nitrogen Fixation–Reduction Cycle

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).