The present results complete the gross structures of neomycins B (I) and C (II). The stereochemistry of the glycosidic linkages is discussed in the accompanying communication.

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disaccharide closely resembling neobiosamine C. Strong acid hydrolysis of the disaccharide affords neosamine C, characterized as the crystalline N,N′-diacetyl derivative. The principal diaminohexose of paromomycin (PI), paromose, forms a crystalline N,N′-diacetyldihydro derivative,[22] which we find to be identical with that obtained from neosamine B. It has been reported that the *p*-nitrophenylhydrazones of the N,N′-diacetyl derivatives of paromose[22] and of neosamine B[23] (diaminohexose I from zygomycin[23]) differ markedly in rotation ($[\alpha]_D$ +6°, $[\alpha]_D$ +162°), but by separate authors neither describing the method of preparation, or crystallization. Since the phenylhydrazones of hexoses are well known to exist in several modifications, and to exhibit complex and often very slow mutarotations,[24] this anomaly appears to be merely unfortunate. However, we are presently reinvestigating these derivatives. These observations point strongly to the great similarity, if not identity, of the zygomycin A complex,[23] and the two-component paromomycin.

(22) T. H. Haskell, J. C. French and Q. R. Bartz, *J. Am. Chem. Soc.*, **81**, 3481 (1959).

(23) (a) S. Horii, T. Yamaguchi, H. Hitomi, and A. Miyake, *Chem. Pharm. Bull. Japan*, **9**, 541 (1961); (b) S. Horii, *J. Antibiotics* (*Japan*), ser. A, XIV, 249 (1961).

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(25) National Science Foundation Predoctoral Fellow.

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THE E.P.R. OF GROUND STATE TRIPLET NITRENES[1]

Sir:

Recently electron paramagnetic resonance (e.p.r.) has been observed for transitions between neighboring sublevels of randomly oriented triplet species in rigid glasses.[2] This technique also has been employed to detect diphenylmethylene, a ground state triplet.[3] Since monovalent nitrogen is isoelectronic with divalent carbon, we have investigated the e.p.r. of several nitrenes.

Thermolysis[4] and photolysis[5] of organic azides generally leads to the formation of primary or secondary amines and azo compounds. These products have been interpreted as arising from a nitrene intermediate which reacts as a radical.[4,5] Kinetic evidence obtained from a study of the thermal decomposition of aromatic and aliphatic azides[6] supports this assumed radical nature of the nitrene, as does a study of the orientation and relative rate factors of the products resulting from the decomposition of benzenesulfonyl azide in substituted benzenes.[7]

The experimental procedure was essentially that used previously.[2,3] A dilute solution of the azide in Fluorolube[3] at 77°K. was irradiated with a mercury arc and the resonance absorption recorded with a Varian 100 kc. field modulation e.p.r. spectrometer.[8] Eight azides were investigated: phenyl (I),[4c] *o*-trifluoromethylphenyl (II),[4d] benzenesulfonyl (III),[9] *p*-toluenesulfonyl (IV),[10] cyclohexyl (V),[6] styryl (VI),[4c] ethyl azidoformate (VII)[11] and phenylazidoformate (VIII).[12] No resonance was observed with V to VIII. These negative results can be rationalized by noting that in each case any nitrenes formed can undergo further reaction by processes less likely to occur with compounds I to IV.

With I, II, III, and IV e.p.r. was detected and the intensity of the signal from I was stable at 77°K. for at least eighteen hours after irradiation was discontinued. On warming the signals disappeared. These findings are indicative of a ground state triplet. For I and II there was one line each near 1620 gauss and one at high-field, 6701 and 6713 gauss, respectively. The low field line corresponds to the $\Delta m = 2$ (half-field) transition,[13] the high field lines to $\Delta m = 1$ transitions. No other resonances were observed below 10,000 gauss. Most probably there are additional absorptions at higher fields but the limitations of our magnet precluded their investigation. The over-all width of the resonance is determined by hyperfine interactions[2] and is found to be greater for II (180 gauss) than for I (130 gauss); this is due to the interaction of the unpaired spin with the nearby fluorine atoms in II. With III and IV, a broad (over 300 and 350 gauss) line was seen at 7795 and 7740 gauss, respectively. No half-field transition was found.

Assignment of the zero-field parameters, D and E,[14] which give the interaction of the unpaired spins, requires the measurement of additional resonances. However, if we assume that there are no unobserved weak lines below 10,000 gauss, some crude estimates can be made. A possible assignment for I or II would be $D = 1.67$ and $E = 0.27$ cm.$^{-1}$; another is $D = 1.33$ and $E = 0.30$ cm.$^{-1}$.[15,16] These values are considerably

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(1) We agree with Lwowski and Mattingly[5b] that "nitrene" is a more suitable term for monovalent nitrogen compounds than "azene" or "imine."

(2) W. A. Yager, E. Wasserman and R. M. R. Cramer, *J. Chem. Phys.*, to be published.

(3) R. W. Murray, A. M. Trozzolo, E. Wasserman and W. A. Yager, *J. Am. Chem. Soc.*, **84**, 3213 (1962).

(4a) G. Smolinsky, *ibid.*, **82**, 4717 (1960); (b) **83**, 2489 (1961); (c) **83**, 4483 (1961); (d) *J. Org. Chem.*, **26**, 4108 (1961).

(5a) D. H. R. Barton, L. R. Morgan, Jr., *J. Chem. Soc.*, 622 (1962); (b) W. Lwowski and T. W. Mattingly, *Tetrahedron Letters*, 277 (1962).

(6) P. Walker and W. A. Waters, *J. Chem. Soc.*, 1632 (1962).

(7) J. F. Heacock and M. T. Edmison, *J. Am. Chem. Soc.*, **83**, 3460 (1960).

(8) We wish to thank R. M. R. Cramer for measuring the spectra.

(9) O. C. Dermer and M. T. Edmison, *J. Am. Chem. Soc.*, **77**, 70 (1955).

(10) W. von E. Doering and C. H. DePuy, *ibid.*, **75**, 5955 (1953).

(11) M. O. Forster and H. E. Fierz, *J. Chem. Soc.*, **93**, 81 (1908).

(12) Prepared from phenylchloroformate and sodium azide in a manner similar to the preparation of ethyl azidoformate.[11]

(13) J. H. van der Waals and M. S. de Groot, *Mol. Phys.*, **2**, 333 (1959), *ibid.*, **3**, 190 (1960).

(14a) K. W. H. Stevens, *Proc. Roy. Soc.* (London), **A214**, 237 (1952); (b) C. A. Hutchison, Jr., and B. W. Mangum, *J. Chem. Phys.*, **34**, 908 (1961).

(15) These values will give only one $\Delta m = 1$ transition below 10,000 gauss and that at 6700 gauss.[14]

higher than any found for phosphorescent hydrocarbons.[2,13,14b] In the nitrenes there are two unpaired electrons at least partially on the same atom. Such localization causes considerable interaction. This arrangement is forbidden in the excited states of aromatic hydrocarbons where there is only one available atomic orbital in each atom. In addition, these values are higher than any likely to be required for diphenylmethylene.[3] In the latter the presence of the second phenyl group aids delocalization, and the smaller nuclear charge of the carbon atom permits a larger interelectronic separation. Both effects should reduce the spin-spin dipole energy and lead to smaller values of *D*.

(16) Computations by J. Higuchi have given values of *D* of 1.0 and 1.8 cm.$^{-1}$ for CH_2 and NH, respectively (J. Higuchi, private communication).

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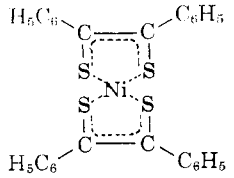
REACTION OF DIPHENYLACETYLENE WITH NICKEL SULFIDES

Sir:

The hypothesis that W. Steinkopf's well-known synthesis of thiophene from acetylene and pyrite[1] might yield organometallic complexes if conducted under milder conditions has led us to investigate the reaction of metallic sulfides with acetylenes. Technical-grade nickel sulfide, prepared by the addition of ammonium sulfide to neutral or slightly acidic solutions of a nickel salt, usually contains a non-stoichiometric excess of sulfur.[2] This nickel sulfide was found to react with diphenylacetylene in toluene in a closed tube at 160° to produce large amounts of tetraphenylthiophene. If, however, the reaction was conducted at 120°, the toluene solution became dark green within 24 hours and upon cooling deposited a nearly black, crystalline complex (I) of composition $NiC_{28}H_{20}S_4$ (Calcd. C, 61.89; H, 3.70; S, 23.61; Ni, 10.80; mol. wt. 543. Found C, 61.9; H, 3.7; S, 23.5; Ni, 10.5; mol. wt. 578). Under these conditions only small amounts of tetraphenylthiophene are formed suggesting that I is an intermediate in the tetraphenylthiophene formation. I is completely stable to air and decomposes at 290° into nickelous sulfide, sulfur and (exclusively) 2-phenylthianaphthene. Reduction with HI-phosphorus in acetic acid at 140° yields mainly desoxybenzoin and small amounts of bibenzyl. Reaction with diphenylacetylene at 140° in toluene afforded up to 76% of the theoretical amount of tetraphenylthiophene. Diethylacetylenecarboxylate reacted even at 80° producing diethyl 4,5-diphenylthiophene-2,3-dicarboxylate (m.p. 98°). I is moderately soluble in most nonpolar solvents, forming deeply green solutions. Enhanced solubility in bases such as pyridine and piperidine and a color change to brown-red suggest the formation of complexes of I with solvent molecules. Indeed, labile bis-adducts of both bases were isolated in crystalline form. The proton magnetic resonance spectrum of I in CS_2 solution consists of but one signal of the phenyl protons. From these observations a structure is deduced in which a nickel atom is surrounded by two molecules of dithiobenzil in a square planar arrangement.



Magnetic measurements[3] indicate a weak paramagnetism of I at room temperature ($\mu_{\text{found}} = \sim 0.8$ B.M.). The bis-piperidine adduct or the solutions of I in pyridine are more strongly paramagnetic with moments of 1.9 ± 0.1 and 2.5 ± 0.2 B.M., respectively. The magnetic properties of I thus are consistent with those frequently observed for square planar Ni(II) complexes. However, the particular nature of the ligands in I forces us to assume that two electrons must be placed into a low-lying unoccupied molecular orbital of the complex as I would otherwise have to be formulated as a Ni(0) complex. I is also isolated in yields up to 14% per run if $Ni(CO)_4$ or finely divided metallic nickel is refluxed with a solution of diphenylacetylene and sulfur in toluene. This mode of preparation of I implies that the intermediate formation of a highly reactive, possibly free-radical-type, nickel sulfide (NiS_4 ?) may be responsible for this unusual reaction. A similarly reactive nickel sulfide may also be present as an "impurity" at the surface of the sulfur-rich nickelous sulfide used in the initial experiments. We are currently investigating the full scope of this reaction.

(1) W. Steinkopf and G. Kirchhoff, *Ann.*, **403**, 1 (1914); W. Steinkopf, *ibid.*, **403**, 11 (1914).

(2) E. Dönges, *Z. Naturforschung*, **1**, 221 (1946).

(3) The magnetic measurements were performed by H. Mödl, Technische Hochschule at Munich.

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THE RELATIVE STRENGTHS OF ALKYL HALIDES AS PROTON ACCEPTOR GROUPS IN HYDROGEN BONDING[1]

Sir:

In 1959 data were published on the shifts in frequency of the O–H stretching absorption bands of phenol and methanol upon hydrogen bond formation to alkyl halides.[2] The frequency shifts, $\Delta\nu$, increased as the halogen atom was changed in the order F < Cl < Br < I (Table I, column 2).[3] By application of the Badger–Bauer rule[5] relating

(1) Acknowledgment of partial support of this research is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society (R.W.) and to the National Science Foundation (P.S.).

(2) P. von R. Schleyer and R. West, *J. Am. Chem. Soc.*, **81**, 3164 (1959). Also see M.-L. Josien, *et al.*, *Bull. soc. chim. France*, 423 (1957); 188 (1958); G. J. Korinek and W. G. Schneider, *Can. J. Chem.*, **35**, 1157 (1957).

(3) The same order of basicity holds for charge-transfer interactions of alkyl halides with halogens.[4]

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(5) R. M. Badger and S. H. Bauer, *J. Chem. Phys.*, **5**, 839 (1937); R. M. Badger, *ibid.*, **8**, 288 (1940); ref. 7, pp. 82–84.