sured by flotation) and microanalysis indicated four molecules of sterol per unit cell (calcd density: 1.175 ± 0.001 g/cm^3; found: 1.171 ± 0.005 g/cm^3. *Anal.* Calcd for $C_{30}H_{49}Br$: C, 73.62; H, 10.02. Found: C, 73.71; H, 10.02).

A total of 2628 diffraction intensities with $\sin 2\theta \leq 90°$ was collected by a Syntex P_1 autodiffractometer, using intensity-weighted average Cu Kα radiation. Averaging according to Friedel's law gave 1363 unique reflections of which 1339 were not systematically extinct (nonzero). The unique bromine atom was located from a sharpened three-dimensional Patterson function, and its positional and anisotropic thermal parameters were subjected to one cycle of full-matrix least-squares refinement using all the data. Trial carbon atoms were selected by searching the Patterson function for bromine–carbon peaks. The results of this search are unambiguous, since the refined bromine position is a general one in $P2_12_12_1$. A total of 136 distinct positions were found to correspond to Patterson values greater than that expected for a bromine–carbon peak. A trial structure composed of 30 of these atoms and the bromine was constructed by the reliable image method,[4] a systematic method of Patterson function analysis, which is free of noncrystallographic assumptions. Six of these trial atoms behaved poorly during least-squares refinement and also appeared to be incorrect on inspection of a model of the trial structure. The positions and isotropic temperature factors of the 24 good atoms and the bromine parameters were refined, and the remaining 6 atoms were located in a difference electron density map based on the refined parameters. After several cycles of full-matrix least-squares refinement with all the data, the discrepancy factor ($R = \Sigma(||F_o| - |F_c||)/\Sigma|F_o|$) was lowered to 13.3%. All bond distances and angles in the final structure (III, R = Br) compared well with the generally accepted values.[5] All the X-ray work, *i.e.*, starting with the raw data from the diffractometer to the completion of the whole project, required less than 4 weeks.

A three-dimensional projection of 3β-bromogorgostene showing its absolute configuration[6] is presented in III (R = Br). The presence of the cyclopropane ring involving carbons 22, 23, and 34 is confirmed by the associated bond lengths (22–23, 1.51; 22–34, 1.50; 23–34, 1.52 Å) and angles (22,23,34 = 59.5; 22,34,23 = 59.5; 23,22,34 = 60.6°).[7] It is noteworthy that the C-24 methyl group has the same absolute configuration (24*R*) as found in ergosterol. In the latter this methyl has been shown[8] to be derived from methionine and it has been clearly demonstrated[9] that a Δ^{24} double bond is necessary for alkylation to proceed. Operation of a similar sequence in the biosynthesis of gorgosterol could give rise to a Δ^{22}-24-methyl precursor (for example, brassicasterol, (24*R*)-24-methylcholest-5,22-dien-3β-ol, which has been shown[10] to co-occur with gorgosterol). Similar alkylation by methionine of the Δ^{22} double bond followed by regeneration of this bond and formation of the cyclopropane ring (by methionine?) may be postulated though no Δ^{22}-23,24-dimethyl precursor has as yet been isolated. Studies are presently under way to answer these and other interesting questions concerning the biogenesis of this intriguing sterol.

Acknowledgment. We wish to thank Drs. P. G. Simpson and J. W. Becker for advice on the application of the reliable image method and for revising the computer programs to handle the general heavy atom case. Thanks are also due to Syntex Analytical Instruments for assistance in collecting the diffraction data on their $P\bar{1}$ autodiffractometer and to the National Institutes of Health (Grants GM-06840 and AM-12758) for financial aid.

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(4) J. W. Becker and P. G. Simpson, paper in preparation.

(5) "Tables of Interatomic Distances and Configuration in Molecules and Ions," The Chemical Society, London, 1958.

(6) Our assignment of absolute configuration is based upon the positive Cotton effect exhibited in the circular dichroism curve of 5α-gorgostan-3-one and the optical rotatory dispersion curve of Δ^4-gorgostenone.

(7) The numbering system shown for III is proposed as a logical extension of steroid nomenclature[2] which assigns positions 28 and 29 to the ethyl group of 24-ethyl sterols and positions 30, 31, and 32 to the C-4α and -β and C-14 methyl groups of the tetracyclic triterpenoids, respectively. The lower numbered position 33 is assigned to the C-23 methyl because of its presumed attachment prior to formation of the cyclopropane ring during its postulated biosynthesis.

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(10) K. C. Gupta and P. J. Scheuer, *Steroids*, 13, 343 (1969).

(11) Postdoctoral Fellow, 1969–1970.

(12) National Institutes of Health Postdoctoral Fellow, 1968–1970.

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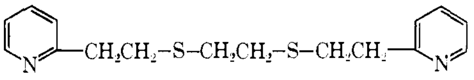
Infrared-Induced Solid-State Isomerization of Diaquo-1,8-bis(2-pyridyl)-3,6-dithiaoctanenickel(II) Perchlorate

Sir:

It has been noted elsewhere that the organic moiety A can function as a "facultative" quadridentate.[1] Goodwin and Lions prepared several derivatives of A with metals in oxidation states that generally are associated with a particular geometry. For instance Pt(II) and Pd(II) complexes containing A were easily isolated as the perchlorate salts and were assumed to be square planar, whereas the Cu(I) and Cu(II) derivatives were assessed to be tetrahedral. Further, the isolation of [Ru(A)(α,α'-bipyridine)]$(ClO_4)_2 \cdot 4H_2O$, in which the bipyridine molecule is believed to occupy two adjacent positions on the octahedron, suggested that A is capable of spanning four positions of an octahedron.



A

In our present work with A and related N–S–S–N quadridentate derivatives[2,3] two important and novel features have become apparent. First, A is capable of forming nickel(II) complexes possessing tetrahedral, square-planar, square-pyramidal, and octahedral geometries; and second, one of these new Ni(II) compounds is very sensitive to low-energy infrared radiation

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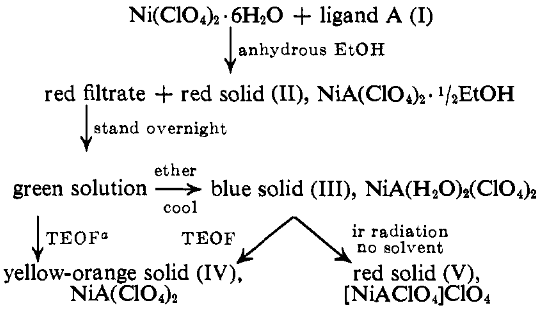
(1) H. A. Goodwin and F. Lions, *J. Amer. Chem. Soc.*, 82, 5013 (1960).

(2) J. H. Worrell and D. H. Busch, *Inorg. Chem.*, 8, 1563 (1969).

(3) J. H. Worrell, T. E. MacDermott, and D. H. Busch, *Chem. Commun.*, 661 (1969).

and, upon exposure, undergoes a solid-state stereochemical isomerization reaction. We wish to report the preparation, properties, and interconversions for several complexes which result from the interaction of nickel(II) perchlorate and 1,8-bis(2-pyridyl)-3,6-dithiaoctane[4] in an alcoholic solution. Scheme I outlines the basic synthetic features.

Scheme I. Preparation of Perchlorate Complexes



^{a} TEOF = triethyl orthoformate.

Ligand I, prepared as described in the literature,[1] was added at room temperature to an ethanolic solution containing a stoichiometric quantity of nickel(II) perchlorate hexahydrate. A red coloration developed immediately with the simultaneous precipitation of a red solid, $NiA(ClO_4)_2\cdot {}^1/_2ETOH$, II, which was collected by filtration and dried *in vacuo* over P_4O_{10}. Upon standing, the red filtrate turned green in color. Addition of ether to the filtrate and cooling overnight yielded a blue paramagnetic crystalline solid which analyzed for $NiA(H_2O)_2(ClO_4)_2$, III. Treatment of III with triethyl orthoformate resulted in the formation of a yellow-orange diamagnetic solid corresponding to the formulation $NiA(ClO_4)_2$, IV. When solid $NiA(H_2O)_2(ClO_4)_2$ is exposed to infrared radiation having a wavelength of ~900–18,000 Å, the complex expels two water molecules,[5] as determined by weight loss measurements and analyses, accompanied by a marked color change from pale blue to dark red. The red product is paramagnetic, having the chemical formulation $[NiAClO_4]ClO_4$ (V). Attempts to affect this conversion thermally were not successful. Samples of III placed in a dark drying oven and heated at 80–85° overnight did not exhibit a weight loss or color change. The same samples, however, did undergo reaction when exposed to infrared radiation.

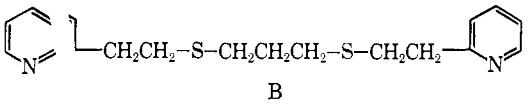
Solid-state structures of II, III, IV, and V have been inferred from analyses,[6] diffuse reflectance electronic absorption spectra, and magnetic and infrared data.[7,8]

In nitromethane, II is a red-colored 2:1 electrolyte [216 cm^2/(ohm mol)] exhibiting absorption bands at 510 (ϵ 1365) and at 380 nm (ϵ 2710), indicative of tetrahedral Ni(II). When compared to V, it is distinctly different in solubility properties, reactivity, and spectra.

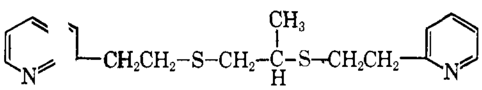
Methanol solutions of III are green (2:1 electrolyte) exhibiting a characteristic pseudooctahedral Ni(II) absorption spectrum with bands at 400, 730, and 1190 nm. Infrared mull spectra of III show strong absorptions at 1645, 3410, and 3500 cm^{-1}, which disappear upon treatment with TEOF or $h\nu$, suggesting the presence of coordinated water.[7] Dehydration of III with triethyl orthoformate produces IV, which possesses characteristics common to square-planar Ni(II) compounds. It is yellow orange in color and diamagnetic, and has the same electronic spectrum in both the solid state and solution with bands at 905 (ϵ 27), 605 (ϵ 31), and 443 nm (ϵ 365) in nitromethane.

The diffuse reflectance spectrum of V is markedly different from that of II or IV. Band positions (1385, 1170, 990, and 490 nm) and intensities are consistent with a square-pyramidal structure[9–11] and Ciampolini's[12] crystal-field model for high-spin five-coordinated Ni(II) complexes. Nitromethane solution spectra of V are identical with those of IV, indicating that the weakly coordinated perchlorate group dissociates upon dissolution. That two different types of perchlorate ion exist in the solid complex is suggested from infrared data. The perchlorate antisymmetric stretch (~1100 cm^{-1}) and antisymmetric bend (~625 cm^{-1}) regions are considerably broader, with fine structure, than for Ni(II) compounds in which the perchlorate ion is ionic or bound *via* a single oxygen atom.[7,8]

In an attempt to determine the steric requirements imposed by the complex $[NiA(ClO_4)]ClO_4$ on the coordinated perchlorate group, two additional ligands were synthesized and are illustrated by B and C. In B



B



C

the number of $–CH_2–$ units between the thioether donors is increased to three and in C a proton on the central ring is replaced by a methyl group. Nickel(II) complexes of structure and stoichiometry similar to III can be prepared from B and C, but do not give the distinct infrared-radiation-induced reaction. Molecular models show that ring size and alkyl substitution on the back-bone chelate ring are critical features germane to perchlorate interaction, supporting the idea that the anion is trapped in a special environment trans to an area which sterically restricts the addition of a second bulky anion or water molecule.

To the authors' knowledge, this is the first example of a single metal–ligand combination which affords solid insolatable products having such varied geometries. In addition, the infrared inducing expulsion of coordinated water followed by the concomitant coordination of perchlorate anion appears unique. Fur-

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(4) We refer to this substance as ligand A in the chemical formulations.

(5) A 1-g sample of complex is completely converted by 45 min of exposure to a standard 250-W laboratory infrared heat lamp at a distance of about 12 in. The temperature need not exceed 40° for the conversion to occur.

(6) C, H, and N analyses were performed by Galbraith Laboratories Inc., Knoxville, Tenn. Analyses were within ±0.2 of that required for the formulations II–V.

(7) S. F. Pavkovic and D. W. Meek, *Inorg. Chem.*, 4, 1091 (1965), and references therein.

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(11) C. R. Hare in "Spectroscopy and Structure of Metal Chelate Compounds," K. Nakamoto and P. J. McCarthy, Ed., Wiley, New York N. Y., 1968, p 120.

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ther experiments to provide additional information relevant to the above are now in progress.

Acknowledgment. Jay H. Worrell wishes to acknowledge financial support for this work from a Research Corporation, Frederic Gardner Cottrell Project Grant, and a release time award from the University of South Florida Research Council.

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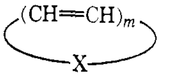
The Synthesis of Fully Unsaturated 11-, 12-, and 13-Membered Sulfur Heterocycles[1]

Sir:

No fully unsaturated monocyclic monoheterocycle (type **1**, X = S, O, NH, etc.) containing a ring larger



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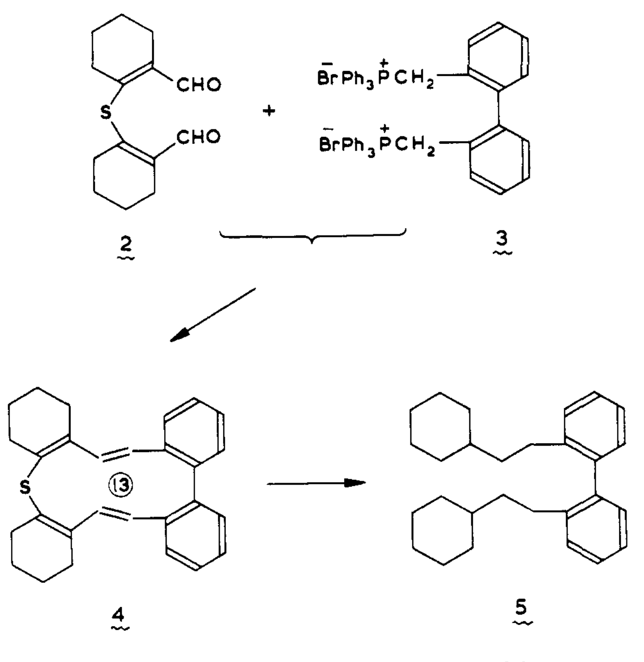
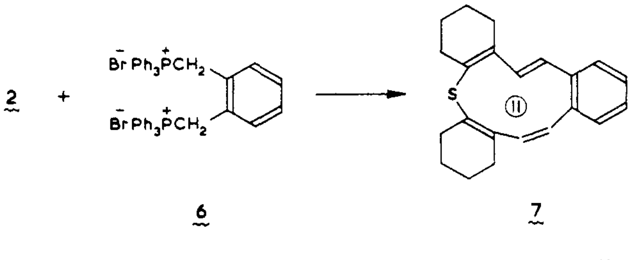
than the nine-membered one ($m = 4$) appears to be known. It was of interest to synthesize macrocyclic members of this series, in order to determine the properties of these higher homologs of thiophene, furan, and pyrrole ($m = 2$). The possibility existed that they would be aromatic when $m = 6, 8, 10$, etc. and nonaromatic when $m = 5, 7, 9$, etc., in the same way as certain [4n + 2]annulenes have been shown to be aromatic and [4n]annulenes nonaromatic.[2] In order to test this possibility, we have prepared the 13-membered sulfur heterocycle **4** (a fused derivative of **1**, X = S, $m = 6$), as well as the 11-membered sulfur heterocycle **7** (a fused derivative of **1**, X = S, $m = 5$). The 12-membered ring sulfur compound **9** has also been synthesized.

Wittig reaction of 2,2′-thiodi-1-cyclohexene-1-carboxaldehyde (**2**)[3,4] and 2,2′-bis(triphenylphosphoniomethyl)biphenyl dibromide (**3**)[5] in dimethylformamide with ethanolic lithium ethoxide at 90°[6] led to a mixture of products, from which *trans,trans*-dibenzo[*f,h*]dicyclohexeno[*b,l*]thiacyclotridecahexaene (**4**)[7] was isolated in 12% yield[8] by chromatography on alumina and then tlc on kieselgel. Substance **4** formed colorless crystals, mp 113–115°;[9] mass spectrum, molecular ion at m/e 396; uv max (C_6H_{12}) ~246 sh (ϵ 19,000), 291



(19,900), and 343 nm (20,800); ir (KBr) 965 s cm^{-1} (*trans*-olefin). The nmr spectrum of **4** (100 MHz, $CDCl_3$) confirmed the assigned structure and stereochemistry, showing signals at τ 2.10–2.50 (m, 2 H), 2.60–3.10 (m, 8 H) (benzenoid and olefinic), 3.74 (broadened d, J = 16.5 Hz, 2 H, olefinic), 7.60–8.15 (broad d, 8 H, allylic methylene), and 8.20–8.65 (broad s, 8 H, nonallylic methylene). Further confirmation for structure **3** was obtained by desulfurization with Raney nickel in ethyl acetate under hydrogen at room temperature (2 hr), which led to 2,2′-di(β-cyclohexylethyl)biphenyl (**5**) as a colorless liquid; mass spectrum, molecular ion at m/e 374; uv max (C_6H_{12}) 264 (ϵ 940) and 271 nm (800);[10] nmr (60 MHz, CCl_4) τ 2.65–3.15 (m, 8 H, benzenoid), 7.50–8.10 (m, 4 H, benzylic methylene), and 8.20–9.65 (m, 26 H, methylene and methine).

Reaction of the aldehyde **2** and *o*-xylylenebis(triphenylphosphonium bromide) (**6**)[6,11] with lithium ethoxide under the previously mentioned conditions,[6] followed by separation as before, gave *cis,trans*-benzo[*f*]dicyclohexeno[*b,j*]thiacycloundecapentaene (**7**) in



2.2% yield. This substance formed colorless needles, mp 130–132°;[9] mass spectrum, molecular ion at m/e 320; uv max (C_6H_{12}) 237 (ϵ 31,000), ~290 sh (7300), 330 (5600), and ~348 sh nm (4300); ir (KBr) 985 s cm^{-1} (*trans*-olefin). The nmr spectrum of **7** (100 MHz, $CDCl_3$) again confirmed the assigned structure and stereochemistry, showing signals at τ 2.30–2.50 (m, 1 H),

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(1) Unsaturated Macrocyclic Compounds. LXXI. For part LXX, see E. P. Woo and F. Sondheimer, *Tetrahedron*, in press.

(2) See F. Sondheimer, I. C. Calder, J. A. Elix, Y. Gaoni, P. J. Garratt, K. Grohmann, G. di Maio, J. Mayer, M. V. Sargent, and R. Wolovsky, *Chem. Soc. Spec. Publ.*, No. 21, 75 (1967).

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(4) For syntheses of other cyclic sulfur compounds by the Wittig reaction of **2**, see P. J. Garratt, A. B. Holmes, F. Sondheimer, and K. P. C. Vollhardt, *J. Amer. Chem. Soc.*, **92**, 4492 (1970).

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(6) See C. E. Griffin and J. A. Peters, *J. Org. Chem.*, **28**, 1715 (1963).

(7) The cis,trans isomer of **4** appeared also to be formed, but was not obtained pure.

(8) Essentially the same yield of **4** was obtained when **3** was first converted to the corresponding bisylide with sodamide in liquid ammonia, followed by reaction with **2** in boiling benzene–ether.

(9) Satisfactory elemental analyses were obtained for all new crystalline compounds.

(10) By comparison, 2,2′-dimethylbiphenyl shows uv max (95% EtOH) 263.5 (ϵ 800) and 271 nm (600) [P. M. Everitt, D. M. Hall, and E. E. Turner, *J. Chem. Soc.*, 2286 (1956)].

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