Table II. Photoelimination of Select p-Anisyl Ketones[a]

$$MeO-\underset{}{\bigcirc}-\overset{\overset{O}{\|}}{C}CH_2CH_2R$$

R	Φ^b	$k_q\tau$, M^{-1}	k_r, 10^6 sec^{-1}	$k_d\pi$, 10^6 sec^{-1}	Rel k_r
A1 CH$_3$	0.04	3550	0.056	1.4	(1)
A2 CH$_2$CH$_3$	0.26	2300	0.56	1.6	10 (1)
A3 CH(CH$_3$)$_2$	0.67	1100	3.0	1.5	51
A4 CH$_2$CH$_2$CO$_2$Me	0.14	2500	0.28	1.7	0.50
A5 CH$_2$CH$_2$CN	0.015	2700	0.03	1.8	0.06

[a] Same conditions as in Table I. [b] Maximum quantum yield of ketone reaction: see P. J. Wagner and H. N. Schott, J. Amer. Chem. Soc., 91, 5383 (1969).

Comparison of ketones P1, P2, and P3 with A1, A2, and A3 indicates that the selectivity of the two carbonyl triplets toward primary, secondary, and tertiary C–H bonds is almost identical—if anything, the anisoyl triplet is slightly *less* selective—despite the fact that the reactivity of the triplet anisoyl group is only 0.5% that of the triplet benzoyl group. Note that the near constant k_d value provides an internal check of the accuracy of the data. These results must be contrasted to the behavior of α-diketones, whose triplets abstract hydrogens intramolecularly at much the same rates displayed by the anisyl ketones but with a significantly greater selectivity among C–H bonds of different strength.[8,9]

Comparison of ketones A2, A4, and A5 with P2, P4, and P5 is even more revealing. All have secondary C–H bonds at the γ position. Electron-withdrawing groups at the δ position deactivate the electrophilic[7,10] n,π^* triplet of the benzoyl group. They have an identical effect on the triplet state reactivity of the anisoyl group.

We feel that it would be extremely unlikely for the π,π^* triplet, which must have a relatively electron-rich oxygen atom (even if a few per cent n,π^* character is present), to be subject to the same inductive effects as the electrophilic n,π^* state. Consequently, most of the hydrogen abstraction probably occurs from a level approximately 3 kcal above the lowest vibrational level of the π,π^* state,[11] an upper level that is mostly n,π^* in character. Whether the $^3n,\pi^*$ state is discrete or entirely mixed with upper vibrational levels of the $^3\pi,\pi^*$ state[5c] is unimportant. The rate at which the lowest triplet returns to the reactive upper level is not known, but would be at least 10^9 sec^{-1} if only vibrational excitation is required The reasonably short-lived triplet of benzophenone apparently has time to equilibrate with the excited singlet 5 kcal higher in energy.[12]

The question of how much n,π^*-like reactivity vibronic mixing can induce in the lowest vibrational level of the π,π^* triplet becomes academic if $X_n k_r{}^n >$

(8) N. J. Turro and T. J. Lee, J. Amer. Chem. Soc., 91, 5651 (1969).
(9) R. G. Zepp and P. J. Wagner, unpublished results.
(10) C. Walling and M. J. Gibian, J. Amer. Chem. Soc., 87, 3361 (1965).
(11) In contrast, phosphorescence excitation spectra of p-methoxy-acetophenone in polar glasses at 77°K have been interpreted to indicate a 5–6 kcal energy separation.[2,5a] We feel that the actual separation at room temperature in a hydrocarbon solvent is lower.
(12) J. Saltiel, H. C. Curtis, L. Metts, J. W. Miley, J. Winterle, and M. Wrighton, J. Amer. Chem. Soc., 92, 410 (1970).

$k_r{}^\pi$. We are investigating other aryl ketones in order to ascertain the generality of our conclusion.[13]

Peter J. Wagner,[14] Alan E. Kemppainen, Herbert N. Schott[15]
Department of Chemistry, Michigan State University
East Lansing, Michigan 48823
Received May 2, 1970

The Structure and Absolute Configuration of the Marine Sterol Gorgosterol

Sir:

Recently we reported[1] chemical evidence which demonstrated the occurrence of a biogenetically unprecedented side chain in the unusual marine sterol, gorgosterol. This evidence led us to conclude that gorgosterol possesses the cholesterol ring skeleton together with the side chain depicted in either partial structure I or II. In order to distinguish between these two structures and to establish the stereochemistry (32 possible stereoisomers), an X-ray diffraction analysis of 3β-bromogorgostene (III, R = Br) was undertaken. We wish to report now that gorgosterol is (22R,23R,24R)-22,23-methylene-23,24-dimethylcholest-5-en-3β-ol,[2] as shown in the three-dimensional structure III (R = OH).

I

II

III
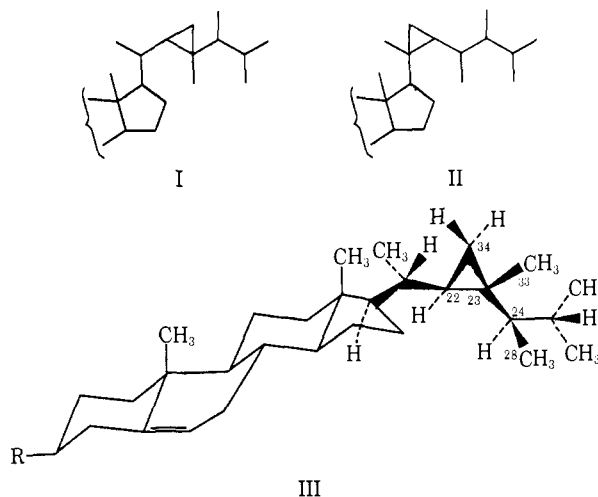
Treatment of an ethereal solution of gorgosterol with aluminum bromide[3] gave 3β-bromogorgostene (III, R = Br; mp 159–160°; [α]D −34.7°; M$^+$ 488–490 = C$_{30}$H$_{49}$Br) which crystallized from acetone to give orthorhombic plates. Diffraction data collected on a single crystal (roughly spherical, 0.1-mm diameter) identified the space group as $P2_12_12_1$ with unit cell dimensions of $a = 10.719 \pm 0.06$, $b = 33.149 \pm 0.05$, $c = 7.786 \pm 0.04$ Å (measured by Syntex P$_\bar{1}$ autodiffractometer); $V = 2766.6$ Å^3. The density (mea-

(1) R. L. Hale, J. Leclercq, B. Tursch, C. Djerassi, R. A. Gross, Jr., A. J. Weinheimer, K. Gupta, and P. J. Scheuer, J. Amer. Chem. Soc., 92, 2179 (1970).
(2) IUPAC-IUB 1967 Revised Tentative Rules for Steroid Nomenclature as reproduced in Steroids, 13, 277 (1969).
(3) J. Broome, B. R. Brown, and G. H. K. Summers, J. Chem. Soc., 2071 (1957).

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 $K\alpha$ 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-bromo-gorgostene 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 (24R) 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, (24R)-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.

(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.
(13) To whom correspondence should be addressed.

Nicholas C. Ling,[11] Ron L. Hale,[12] Carl Djerassi[13]
Department of Chemistry, Stanford University
Stanford, California 94305
Received May 8, 1970

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

A
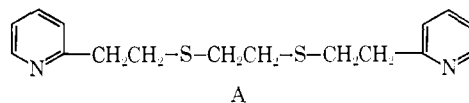
metals in oxidation states that generally are associated with a particular geometry. For instance Pt(II) and Pd(II) complexes containing A were easily isolated as the perchlorate salts and were assumed to be square planar, whereas the Cu(I) and Cu(II) derivatives were assessed to be tetrahedral. Further, the isolation of $[Ru(A)(\alpha,\alpha'-bipyridine)](ClO_4)_2 \cdot 4H_2O$, 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.

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

(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.
(8) G. J. Alexander, A. M. Gold, and E. Schwenk, *J. Amer. Chem. Soc.*, 79, 2967 (1957).
(9) P. T. Russell, R. T. van Aller, and W. R. Nes, *J. Biol. Chem.*, 242, 5802 (1967).

(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).