

The aldehyde was obviously α,β -unsaturated judging from the nmr and uv spectra of the hydrolysate,¹⁷ and the value of J_{23} (15.0 Hz) indicated *trans*-olefinic protons¹⁸ as in **4**. However, it could not be separated from **11** either by chromatography or distillation. The mixture was therefore acetylated at 0° with acetic anhydride and pyridine to enable fractionation by reverse-phase chromatography¹⁹ whereby compound **5** was obtained as an oil: λ_{\max} 217 m μ ; $[\alpha]_D^{23} + 12.0^\circ$ (*c* 2.32, CHCl₃). Its 100-MHz nmr spectrum in CCl₄ (TMS)²⁰ showed: H-1, τ 0.43 (doublet); H-2, 3.30 (quartet); H-2, 3.81 (quartet of doublets); H-4, 4.30 (triplet of doublets); H-5, 4.82 (multiplet); H-6, 5.75 (quartet); H'-6, 5.81 (quartet). The coupling constants (Hertz) observed²⁰ were: $J_{12} = 7.2$; $J_{23} = 15.5$; $J_{24} = 1.5$; $J_{34} = 5.0$; $J_{45} = 5.0$; $J_{56} = 4.0$; $J_{56'} = 5.3$; $J_{66'} = 11.5$. For the 2,4-dinitrophenylhydrazone of **5**: mp 108–109°; λ_{\max} 370 m μ (ϵ 22,500). *Anal.* Calcd for C₁₈H₂₀N₄H₁₀: C, 47.79; H, 4.42; N, 12.39. Found: C, 47.39; H, 4.06; N, 12.49.

Hydrogenation of an ethanolic solution of **5** at ice-salt temperature using 5% palladized carbon ceased after 1 mol of hydrogen had been consumed. The saturated aldehyde produced (nmr, CCl₄, TMS, τ

(16) Although Bergmann represented his "diacetyl pseudoglucal" (11) as the open chain form (structure II in ref 11c), it is clear from the text that he believed that the compound existed as, and certainly reacted from, the cyclic form. In this he was indeed correct for under his reaction conditions (15-min reflux) the hydrolysate actually comprised 90–95% of the cyclized structure 11. (Note that he also represented the "dihydro pseudoglucal" (12), 2-deoxyglucose, and glucose itself as open chain structures (VII, VI, and V, respectively).)

(17) Nmr features of **4** recognizable in the mixture (CDCl₃, TMS): H-1, τ 0.38 (d); H-2, 3.73 (quartet of doublets); H-3, 3.01 (q); $J_{12} = 7.5$, $J_{23} = 15.0$, $J_{34} = 5.0$ Hz; μ_{\max} (CHCl₃) 3.58 3.70, 5.88; λ_{\max} (H₂O) 217 m μ .

(18) Reference 15, p 87.

(19) B. Wickberg, *Acta Chem. Scand.*, **12**, 615 (1958).

(20) We are grateful to our colleague, Dr. K. Shaw, for this determination using an instrument kindly made available by Professor L. W. Reeves. The coupling constants were read directly from the spectrum.

0.22, -CHO)¹⁸ was characterized as its 2,4-dinitrophenylhydrazone: mp 123–124°; λ_{\max} 356 m μ (ϵ 18,200). *Anal.* Calcd for C₁₈H₂₂N₄O₁₀: C, 47.57; H, 4.84; N, 12.34. Found: C, 47.43; H, 4.68, N, 12.20. Upon deacetylation the aldehyde group vanished suggesting that hemiacetal **12** may have formed. This was confirmed by converting olefin **10** into **12** by an alternative route involving (i) hydrogenation, (ii) mild acid hydrolysis, and (iii) deacetylation. This information also indicated that no epimerization had occurred in the formation of **4** from **11**.

The hydroxy aldehyde **13** is undoubtedly the substance initially formed from **11** and subsequently isomerized to **4**. Thus, when the hydrolysis of **1** was done (a) in the presence of 10 mol % of hydroquinone or (b) in the dark, compound **4** was, respectively, completely absent or present in drastically reduced quantities. The inhibition was not in the conversion of compound **11** to **13** since **6** was still completely converted to **8** in the presence of hydroquinone. Evidently small amounts of **13** in equilibrium with **11** undergo photochemical (or less efficiently, thermal) conversion to the more stable *trans* isomer²¹ **4**, and it is the latter process that is inhibited by hydroquinone.

Further study of equilibria of the type $\mathbf{10} \rightleftharpoons \mathbf{13} \rightleftharpoons \mathbf{4}$ is under way and will be reported in due course.

Acknowledgments. We acknowledge generous financial support from the National Research Council of Canada and Bristol Laboratories.

(21) P. G. Wagner and G. S. Hammond, *Advan. Photochem.*, **5**, 21 (1968).

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Additions and Corrections

Conformational Analysis. LVII. The Calculation of the Conformational Structures of Hydrocarbons by the Westheimer-Hendrickson-Wiberg Method [*J. Amer. Chem. Soc.*, **89**, 4345 (1967)]. By NORMAN L. ALLINGER, MARY ANN MILLER, FREDERIC A. VANCATLEDGE, and JERRY A. HIRSCH, Department of Chemistry, Wayne State University, Detroit, Michigan 48202.

The van der Waals equation in Table II should read

$$E_v = -2.25\epsilon(d^*/r)^6 + 8.28(10)^6(\epsilon)\exp(-r/0.0736d^*)$$

The correct form of the equation was used for all of the calculations reported. We are indebted to Dr. Steven D. Stellman for calling this misprint to our attention.

On the Question of Bridge-Proton Absorptions in the Nuclear Magnetic Resonance Spectra of Norbornene and Related Systems [*J. Amer. Chem. Soc.*, **90**, 3724

(1968)]. By ALAN P. MARCHAND and JOSEPH E. ROSE, Department of Chemistry, The University of Oklahoma, Norman, Oklahoma 73069.

The captions under Figures 5 and 6 have been reversed. As they appear in the paper, Figure 5 shows the nmr spectrum of isodrin (IX); Figure 6 shows the nmr spectrum of aldrin (VIII).

Ligand Penetration Rates into Metal Ion Coordination Spheres. Aluminum(III), Gallium(III), and Indium(III) Sulfates [*J. Amer. Chem. Soc.*, **90**, 6967 (1968)]. By JOHN MICELI and JOHN STUEHR, Department of Chemistry, Case Western Reserve University, Cleveland, Ohio 44106.

The quantity F_4 , defined as $1 + [C_H(1 + d \ln \gamma_{SO_4/d} \ln C_{SO_4})(K'_{14} + C'_H) + K'_{14}C'_{SO_4}]/[K'_a(K'_{14} + C'_{MeOH}) + C'_H(K'_a + C'_{SO_4})]$ was omitted in the follow-

ing places where it should multiply τ^{-1} : the left side of eq 3; twice near the bottom of p 6970; and in the ordinates of Figure 2. Reference 15 in Figure 2 should be 19a. The second line in eq 2 should begin with γ_{MeSO_4} instead of $\gamma_{\text{Me}}\gamma_{\text{SO}_4}$. In footnote 21, the second last equality should end with $\delta C_{\text{HOMeSO}_4}$ instead of δC_{MeSO_4} . The inequality at the bottom of p 6971 should read $\text{In} > \text{Ga} < \text{Al}$. All numerical results remain unchanged.

Stereochemistry at Trivalent Nitrogen. V. Origin of Sulfur-Nitrogen Torsional Barriers in N-Sulfonylsulfonamides [*J. Amer. Chem. Soc.*, **91**, 2180 (1969)]. By MORTON RABAN and FREEMAN B. JONES, JR., Department of Chemistry, Wayne State University, Detroit, Michigan 48202.

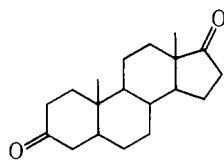
A redetermination of the free energies of activation reported in our communication has indicated that the value reported for one of these compounds is in error.

The free energy of activation for N-isopropyl-2,4-dinitrobenzenesulfonyl-4-nitrobenzenesulfonamide (**2c**) is 18.9 rather than 15.6 kcal/mol as reported. This change substantially alters the Hammett reaction constant for series **2** from 3.0 to 0.9.

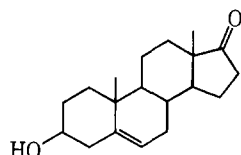
The corrected values are more in accord with expectation and do not substantially alter our interpretation of the phenomena observed.

Nuclear Magnetic Resonance Spectroscopy. Carbon-13 Spectra of Steroids [*J. Amer. Chem. Soc.*, **91**, 7445 (1969)]. By HANS J. REICH, MANFRED JAUTELAT, MARK T. MESSE, FRANK J. WEIGERT, and JOHN D. ROBERTS, Gates and Crellin Laboratories of Chemistry, California Institute of Technology, Pasadena, California 91109.

On page 7452, the formulas for **12** and **13** are both upside down and interchanged. The correct identifications and structures are



androstane-3,17-dione, **12**



5-dehydroisoandrosterone, **13**

Thermolysis of Pentacyclo[4.4.0.0^{2,5}.0^{3,8}.0^{4,7}]dec-9-ene [*J. Amer. Chem. Soc.*, **91**, 7512 (1969)]. By H. H. WESTBERG, E. N. CAIN, and S. MASAMUNE, Department of Chemistry, University of Alberta, Edmonton, Alberta, Canada.

On page 7513, column 2, line 16, "During this process, **2'** was completely equilibrated with **4''**" should read "During this process **2'** was largely, if not completely (calcd for 100% scrambling: 0.67 D at C-1, -8, and -9; experimental error: probably 0.1 D), equilibrated with **4''**".

On the Probable Intermediacy of Tetrahedrane [*J. Amer. Chem. Soc.*, **92**, 406 (1970)]. By PHILIP B. SHEVLIN and ALFRED P. WOLF, Chemistry Department, Brookhaven National Laboratory, Upton, New York 11973.

There is a regrettable arithmetic error in Table II. In the last column, under calculated % of total activity, 12.9, 61.8, 25.3 actually should read 9.2, 65.6, and 25.2. Fortunately this does not change the argument any. The numbers are basically within experimental error and far away from what might be expected from a random distribution.

Magnetic Resonance Studies of Some Low-Spin d⁵ Tris Diimine Complexes [*J. Amer. Chem. Soc.*, **92**, 2343 (1970)]. By RICHARD E. DESIMONE and RUSSELL S. DRAGO, W. A. Noyes Laboratory, University of Illinois, Urbana, Illinois.

Equation 5 should read

$$|-\rangle = -\sin \alpha |0^-\rangle + \cos \alpha [\sqrt{2/3} |2^+\rangle - \sqrt{1/3} |-1^+\rangle] \quad (5)$$

In our derivation and solution of eq 1-8, we inadvertently used a convention *opposite* to that stated in the text and also opposite to that used by ref 17. We define the axial field to be *negative* if the singlet lies lowest. A negative v as found now implies an A ground state in agreement with Figgis. No calculated quantities are affected.

Figure 2 is now a diagram with a *positive* trigonal field by our definition.

In Table II, $\Delta\nu_{6,6'}$ for $\text{Fe}(4,4'\text{-dmb})_3(\text{PF}_6)_3 = +3139$.

The right-hand side of eq 11 should be preceded by a minus sign.

Book Reviews

Spectroscopy. Edited by D. R. BROWNING, Department of Chemistry, Bristol Polytechnic, Bristol, England. McGraw-Hill Publishing Co., Maidenhead, Berkshire, England. 1970. vii + 183 pp. 14 × 22 cm. \$8.50.

Electronic, infrared, Raman, mass, nmr, esr, and atomic emission, absorption, and fluorescence spectroscopy, all in 183 pages! This is rather like a tour of "Fourteen Foreign Countries in Ten Days"; it can be done in the sense that the visitor can say afterwards that he has been there, and has learned some names to throw

around. But apart from this, unless the guide has gone to special pains to explain some item to him, all that the tourist is likely to be left with is a confused jumble of impressions and of people talking in strange languages on every side throughout the trip.

In a tour, at least the guide is likely to remain the same person throughout, whereas in this book, the ten chapters are independently contributed by six different authors. This leads to differences in the quality of writing and minor confusions and contradictions. For example, one author says (p 25) that vacuum spectrometers have to be used below 2000 Å because of atmospheric absorption,