

as a mixture of diastereoisomers in 25% yield (80% based on **9** recovered in the acid fraction).

Attempts to convert the 3-methyl-3-(alkylthio)oxindole **10** to **11** with lithium aluminum hydride^{14,19} proved unsuccessful. Indeed, the procedure was sluggish or completely ineffective in several model studies. Borane reduction of 3-substituted oxindoles has been reported to afford indolines.²⁰ However, with the additional 3-alkylthio substituent, we observed essentially quantitative conversion to the 3-substituted indoles on several model oxindoles with $\text{BH}_3\cdot\text{SMe}_2$. Treatment of **10** with an excess of $\text{BH}_3\cdot\text{SMe}_2$ at room temperature for 24 h likewise afforded **11** in 95% yield. Normally, the entire procedure **9** \rightarrow **11** was accomplished without isolation of intermediates in a 2-pot, 24-h process.

Our initial efforts in the synthesis of **13** involved the methyl ether as the phenol protecting group (e.g., **5**, $\text{R} = \text{CH}_3$). After numerous failures with acidic-type reagents²¹ to deprotect **11** to **12**, we found that mercaptide anions²² accomplished this transformation in 40–60% yields. However, the yields decreased on

(19) Wieland, T.; Grimm, D. *Chem. Ber.* **1965**, *98*, 1727.

(20) McEvoy, F. J.; Allen, G. R., Jr. *J. Org. Chem.* **1973**, *38*, 3350–3352. Borane dimethyl sulfide is preferred for the reduction of 3,3-dimethyloxindole to 3,3-dimethylindoline (Hester, J. B., unpublished results, The Upjohn Company).

(21) For example: McOmie, J. F. W.; Watts, M. L.; West, D. E. *Tetrahedron* **1968**, *24*, 2289–2292. Vickery, E. H.; Pahler, L. F.; Eisenbraun, E. J. *J. Org. Chem.* **1979**, *44*, 4444–4446. Hanessian, S.; Guindon, Y. *Tetrahedron Lett.* **1980**, 2305–2308. Williard, P. G.; Fryhle, C. B. *Ibid.* **1980**, 3731–3734. This procedure afforded some of the desired **12**.

(22) Kelly, T. R.; Dali, H. M.; Tsang, W.-G. *Tetrahedron Lett.* **1977**, 3859–3860 and ref 2–4 described therein.

(23) Prepared in 95% yield from 4-chloro-3-nitroanisole: 48% HBr/AcOH , 120 °C, 24 h; PhCH_2Br , K_2CO_3 , acetone, DMF; mp 46.5–48.7 °C.

scaleup. Therefore, the synthesis was repeated with benzyl ether (**5**, $\text{R} = \text{CH}_2\text{Ph}$),²³ which was readily removed to give **12**⁹ [90%; NMR (acetone- d_6) δ 7.8 (br s, 1 H), 7.03 (s, 1 H), 6.83 (s, 1 H), 4.25–3.25 (m, 5 H), 2.86 (s, 3 H), 2.36 (s, 3 H)]. The methylsulfonyl group on anilines can be cleaved with sodium (2-methoxyethoxy)aluminum hydride.²⁴ This procedure was successful with **6** and should allow for the introduction of other groups on the indoline nitrogen at this, or later, juncture.

The concept of forming bond **a** as an entry to the cyclopropylspirocyclohexadiene moiety was validated by first converting the alcohol to the bromide²⁵ followed by exposure to a tertiary amine to give **13**. This can be accomplished in one pot in 70% yield. The structure of **13** was based on ^1H NMR, IR, UV, MS,²⁶ and single-crystal X-ray analysis.²⁹

(24) Gold, E. H.; Babad, E. *J. Org. Chem.* **1972**, *37*, 2208–2210.

(25) The bromide derivative of **12** was isolated by rapid preparative TLC and structure determined by ^1H NMR and MS (positive Beilstein). On prolonged contact with silica gel it is converted to **13**.

(26) ^1H NMR (CDCl_3 , 200 MHz) δ 9.5 (br s, 1 H), 6.83 (dd, H_a), 6.34 (s, H_b), 4.10 (d, H_c), 3.93 (dd, H_d), 3.04 (s, 3 H), 2.93 (m, H_e), 2.00 (d, 3 H), 1.97 (dd, H_f), 1.37 (dd, H_g); $J_{ce} = 0.0$, $J_{cd} = 9.7$, $J_{de} = 4.7$, $J_{ef} = 7.7$, $J_{eg} = 4.4$, $J_{fg} = 4.4$, $J_{NH,a} = 2.0$, $J_{a,CH_3} \leq 1.0$ Hz is consistent with ^1H NMR of CC-1065² and 3-azabicyclo[3.1.0]hexane.²⁷ IR (CHCl_3)²⁸ 3450, 3400–3100 (NH, OH), 1620 (CO), 1360, 1160 cm^{-1} (SO_2). UV (MeOH)² λ 224 (ϵ 3×10^4), 272 (4.8×10^4) 338 (3×10^4). MS, m/e calcd for $\text{C}_{13}\text{N}_{14}\text{N}_2\text{O}_3\text{S}$: 278.0725. Found: 278.0725.

(27) Wendisch, D.; Naegele, W. *Org. Magn. Reson.* **1970**, *2*, 619–624.

(28) Marx, J. N.; Argyle, J. C.; Norman, L. R. *J. Am. Chem. Soc.* **1974**, *96*, 2121. See also: Gramlich, W.; Plieninger, H. *Helv. Chim. Acta* **1979**, *112*, 1573–1582.

(29) $R = 0.079$ on 2322 reflections: Chidester, C. G., unpublished results, Upjohn Co., 1981. Full details will be disclosed later.

Additions and Corrections

Photochemistry of Cis-Fused Bicyclo[4.n.0]-2,4-dienes. Ground State Conformational Control [*J. Am. Chem. Soc.* **1980**, *102*, 4456]. WILLIAM G. DAUBEN* and MICHAEL S. KELLOGG, Department of Chemistry, University of California, Berkeley, California 94720.

On page 4459, the last paragraph in the left column should read as follows: The minor primary product, *anti,cis*-tricyclo-[5.4.0.0^{8,11}]undec-9-ene (**27**), the product predicted by orbital symmetry consideration (disrotatory), was formed in 3% yield upon extended irradiation. The structure was determined by spectral analysis and by its stereospecific conversion to the cis diene **3** at 220 °C. Assignment of the anti stereochemistry was based on the very small NMR coupling of the bridgehead allylic protons.

Crystal and Molecular Structure of Cofacial Dicopper Hexyldiporphyrin-7 [*J. Am. Chem. Soc.* **1980**, *102*, 7115]. MARCOS H. HATADA, A. TULINSKY,* and C. K. CHANG, Department of Chemistry, Michigan State University, East Lansing, Michigan 48824

Page 7116: the intra- and intermolecular slip angles are interchanged—*intra* should be 46.4°, *inter* should be 43.5°.

Pauling “3-Electron Bonds”, “Increased-Valence”, and 6-Electron 4-Center Bonding [*J. Am. Chem. Soc.* **1980**, *102*, 5195]. RICHARD D. HARCOURT, Department of Physical Chemistry, University of Melbourne, Parkville, Victoria 3052, Australia.

Page 5196 above eq 3 and page 5197 two lines above references: replace “obtained” with “obtain”.

Page 5197: add “,12” after “ref 7” in the text.

Page 5198: (i) two lines below eq 16, replace “9” with “4”; (ii) in ref 18, replace “2, 1.5 and 1” with “1, 1.5 and 2”; (iii)

column 2, omit “of eq 10” after “the CI wave function”.

Page 5200: (i) in the caption for Figure 6, interchange c and d; (ii) in ref 41, replace “P. Passmore” with “J. Passmore”.

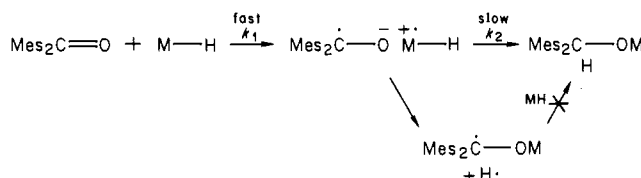
Page 5201: in ref 52, replace “2f” with “2g”.

Evidence for an Electron-Transfer Mechanism in the Reduction of Ketones by Main Group Metal Hydrides [*J. Am. Chem. Soc.* **1980**, *102*, 7779]. EUGENE C. ASHBY,* ANIL B. GOEL, and ROBERT N. DEPRIEST, School of Chemistry, Georgia Institute of Technology, Atlanta, Georgia 30332

Page 7780: in ref 7 M_2SO_4 should be H_2SO_4 .

Page 7780: Scheme I should read as follows.

Scheme I



Accurate and Sensitive Determination, by a New Cobalt-59 Nuclear Magnetic Resonance Method, of Electron Acceptance and Hydrogen Bond Donation by Protic Solvents [*J. Am. Chem. Soc.* **1980**, *102*, 7818–7820]. PIERRE LASZLO* and ARMEL STOCKIS, Institut de Chimie Organique et de Biochimie, Université de Liège, Sart-Tilman, B-4000 Liège, Belgium.

References 14 and 15 have been inadvertently interchanged. They should read: (14) Samo, M.; Yamatera, H.; Hatano, Y. *Chem. Phys. Lett.* **1979**, *60*, 257–260; and (15) Cotton, F. A.; Wilkinson, G. “Advanced Inorganic Chemistry”, 3rd ed.; Wiley: New York, 1972.