amine[19] produced the silyl ether of cholesterol. Deprotection of the 3β-hydroxyl group yielded cholesterol which was spectroscopically identical with an authentic sample (^{13}C NMR, 360-MHz ^1H NMR, and IR).

The alkylideneoxirane **5** provided the complementary proof for our methodology. Addition of lithium methylcyanocuprate to **5** resulted in the formation of equal amounts of 1,4 and 1,2 adducts, **7**[20] and **8**,[21] respectively. The unanticipated 1,2 adduct (**8**) can only be rationalized this time by the differences in the steric bulk of the alkylidene substituents (i.e., methyl vs. isohexyl). Comparison of the 360-MHz ^1H NMR spectra of the enantiomeric adducts **6** and **7** revealed a clear distinction in the absorptions for the respective C-21 methyl groups (0.97 for **6** and 1.11 for **7**). Intermediate **7** was then converted to the known isocholesterol[22] by the same sequence of steps used for the preparation of cholesterol.

As a final check on the purity of the C-20 epimers produced in this study, we subjected the dimethyl ethyl silyl (DMES) ethers of compounds **6**, **7**, **9**, **10**, cholesterol, and isocholesterol to GC analysis.[23] While the retention times for the DMES ethers of **6** and **7** were very close, the ethers of compounds **9**, **10**, cholesterol, and isocholesterol separated well enough that it was possible to detect less than 1% epimeric contaminants. The GC analyses[24] confirmed that our synthetic products, **6**, **7**, **9**, **10**, cholesterol, and isocholesterol were >99.5% pure epimers at C-20.

In conclusion, the 1,4-trans addition of alkyl cyanocuprates to alkylideneoxiranes of sterols provides the only stereospecific methodology for the concomitant introduction of the C-21 asymmetric center and the 15β-hydroxyl group. This synthetic strategy should be applicable to a wide variety of functionalized sterol side chains and functionalized D rings of steroids.

Acknowledgment. We are pleased to acknowledge support of this research from the National Cancer Institute (NIH) under Grant CA 22237. The National Science Foundation is acknowledged for providing funds to purchase a Bruker 360-MHz NMR spectrometer. We also thank the G. D. Searle Co. for a generous gift of dehydroepiandrosterone.

Supplementary Material Available: Experimental details and characterization data for compounds **2**–**10** are available upon request (11 pages). Ordering information is given on any current masthead.

(19) Ireland, R. E.; Muchmore, D. C.; Hengartner, U. *J. Am. Chem. Soc.* **1972**, *94*, 5098.

(20) **7**: $[\alpha]^{27}_D$ −87.6° (*c* 0.21, $CHCl_3$); ^1H NMR (360 MHz) δ 1.06 (s, 3 H, H-18) 1.11 (s, 3 H, H-19), H-21 overlapped with 1.11, 3.43–3.52 (m, 1 H, H-3), 4.44–4.48 (br, 1 H, H-15), 5.30–5.38 (br, 1 H, H-6), 5.53 (d, 1 H, *J* = 2.20 Hz).

(21) **8**: $[\alpha]^{27}_D$ −66.9° (*c* 0.22, $CHCl_3$); ^1H NMR (360 MHz) δ 1.03 (s, 3 H, H-18), 1.05 (d, 3 H, *J* = 7.32 Hz, H-16CH_3), 1.18 (s, 3 H, H-19), 3.42–3.52 (m, 1 H, H-3), 3.80 (d, 1 H, *J* = 4.39 Hz, H-20), 5.00–5.08 (br, 1 H, H-20), 5.28–5.36 (br, 1 H, H-6).

(22) Nes, W. E.; Varkey, T. E.; Krevitz, K. *J. Am. Chem. Soc.* **1977**, *99*, 260. Koreeda, M.; Koizumi, N. *Tetrahedron Lett.* **1978**, 1641. See also **5a**. Isocholesterol: mp 151–153 °C; ^1H NMR (360 MHz) δ 0.66 (s, 3 H, H-18), 0.80 (d, 3 H, *J* = 6.59 Hz, H-21), 0.99 (s, 3 H, H-19); ^{13}C NMR (90 MHz) 140.83, 121.70, 71.86, 56.90, 55.91, 50.32, 42.43, 39.81, 39.53, 37.37, 36.62, 35.82, 35.23, 32.05, 31.80, 28.10, 28.00, 24.27, 24.03, 22.75, 22.66, 21.21, 19.43, 18.72, 12.18.

(23) For GC analysis of 20*R* and 20*S* steroidal acetates, see: Schow, S. R.; McMorris, T. C. *J. Org. Chem.* **1979**, *44*, 3760.

(24) The DMES ethers of **6**, **7**, **9**, **10**, cholesterol, and isocholesterol were prepared at room temperature with neat (dimethylethylsilyl)imidazole (Miyazaki, H.; Ishibashi, M.; Itoh, M.; Nambura, T. *Biomed. Mass Spectrom.* **1977**, *4*, 23). GC analyses were carried out on a Shimadzu TP-MI gas chromatograph (FID) with a 1.8-m (5-mm o.d.) column of 3% SE-30. Column temperature: 320 °C for ethers of **6**, **7**, **9**, **10**; 300 °C for ethers of cholesterol and isocholesterol. Gas flow: nitrogen 40 mL/min; hydrogen 40 mL/min. Retention times relative to THF solvent: DMES ether of **6**, 9.6 min; **7**, 9.4 min; **9**, 8.2 min; **10**, 11.2 min; cholesterol, 10.6 min; isocholesterol, 9.8 min.

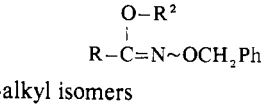
Additions and Corrections

Studies on the Reaction Mechanism of the Photocyclization of *N*-Aryl Enamines. Dependence of Quantum Yields on Back and Side Reactions. [*J. Am. Chem. Soc.* **1980**, *102*, 6098]. THOMAS WOLFF* and REINHARDT WAFFENSCHMIDT, Gesamthochschule Siegen, Physikalische Chemie, D-5900 Siegen 21, West Germany.

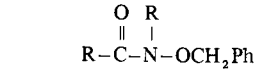
Page 6099, column 1, first paragraph: The NMR data for 1-(*N*-methylanilino)-1-phenyl-1-propene (**3**) should read: ^1H NMR ($CDCl_3$) 1.7 (3 H, doublet), 3.1 (3 H, singlet), 6.1 (1 H, quartet), 6.6–7.4 ppm (10 H, multiplet). The authors are indebted to Professor H. Ahlbrecht, Giessen, for detecting and communicating the error.

Synthesis of β-Lactams from Substituted Hydroxamic Acids [*J. Am. Chem. Soc.* **1980**, *102*, 7026]. M. J. MILLER,* P. G. MATTINGLY, M. A. MORRISON, and J. F. KERWIN, JR., Department of Chemistry, University of Notre Dame, Notre Dame, Indiana 46556.

The products from the intermolecular *N*-alkylation of *O*-benzyl hydroxamates ($RCONHOCH_2Ph$) with alcohols (R^2OH) in the presence to DEAD/PPh_3 (last four entries in Table I) have been subsequently shown to be the *O*-alkyl isomers



and *not* the *N*-alkyl isomers



as reported. The products from the intermolecular alkylation of *O*-acylhydroxamates and the intramolecular alkylations to give β-lactams are correctly assigned.

^{15}N Nuclear Magnetic Resonance Spectroscopy. Products and Rearrangements in the Reaction of *p*-Toluenesulfonyl Azide-3-^{15}N with the Sodium Salt of *p*-Toluenesulfonamide. An *in Situ* ^{15}N NMR Study [*J. Am. Chem. Soc.* **1980**, *102*, 2364]. CARLA CASEWIT and J. D. ROBERTS,* Contribution No. 6112 from the Gates and Crellin Laboratories of Chemistry, California Institute of Technology, Pasadena, California 91125

Page 2365, column 2: Figure 1a should appear as shown below.