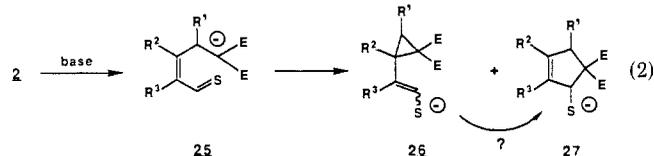


The major limitation in scope is encountered where substitution α to the sulfur of the dihydrothiopyran is present. Bicyclic cycloadduct **9** (entry 6) undergoes only reductive cleavage, while the minor regioisomers of **6** and **11** (entries 3 and 8) fail to give any recognizable product under any of the rearrangement conditions.

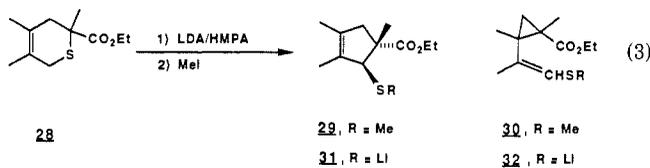
The mechanism of the ring contraction, which is equivalent to a [1,2] Wittig rearrangement, can only be conjectured at this point. Presumably the first step involves deprotonation α to the sulfur of **2** followed by β elimination of the more stable malonate carbanion to give **25** (eq 2). The reactive carbon-sulfur double bond



could then be trapped internally by 1,4- or 1,2-addition leading to **26** or **27**, respectively. The fact that cyclopentenes are virtually the sole products implies that **26** would be rapidly converted back to **25** or directly to **27**.

To expand the scope of this methodology, the monoester **28** was prepared from ethyl 2-bromopropionate and 2,3-dimethyl-1,3-butadiene (67%, eq 3). Rearrangement with LDA/HMPA

proceeded smoothly to give cyclopentene **29** (87%, 8:1 mixture of diastereomers⁵) as long as the reaction was warmed to 0 °C prior to quenching. Addition of iodomethane at -45 °C, however, resulted in a 1:2 mixture of **29**/cyclopropane **30** (total yield = 64%) being isolated along with 10% of unchanged **28**. The similar mass balances suggest the intriguing possibility that **32** is an intermediate in the formation of **31**.



Work to further expand the scope of this annulation and to more clearly understand the mechanism of the ring contraction is in progress.

Acknowledgment. We gratefully acknowledge the assistance provided by Dave Kloosterman and Steve Mizsak of Physical and Analytical Chemistry in running NOE and ¹³C NMR experiments.

Supplementary Material Available: Detailed experimental procedures for the preparation of **12**, **22**, **28**, and **29** along with full spectral data and NOE data for **29** (5 pages). Ordering information is given on any current masthead page.

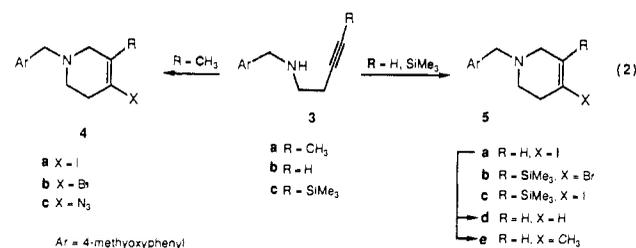
Additions and Corrections

Structure and Conformation of Two Coprogen-Type Siderophores: Neocoprogen I and Neocoprogen II [*J. Am. Chem. Soc.* **1987**, *109*, 4948-4954]. M. B. HOSSAIN, M. A. F. JALAL, B. A. BENSON, C. L. BARNES, and D. VAN DER HELM*

Corrected versions of Table SI (atomic coordinates) and Table SII (bond distances) have been deposited as supplementary materials (6 pages). Ordering information is given on any current masthead page.

Nucleophile-Promoted Electrophilic Cyclization Reactions of Alkynes [*J. Am. Chem. Soc.* **1988**, *110*, 612]. LARRY E. OVERMAN* and MATTHEW J. SHARP

Page 613: The structures reported in this communication for compounds **4a**, **4b**, and **4c** are incorrect. Chemical correlation of **4a** and **4b** with 3-methylpyridine and **4c** with 4-piperidone establishes that eq 2 should be modified as shown. Thus, nucleophile-promoted cyclizations of **all** the homopropargyl amines (**3a-3c**) investigated occur in the *endocyclic* sense to afford 4-substituted-1,2,5,6-tetrahydropyridine products. This correction does not change the basic conclusions of this communication.



Revised supplementary material has also been deposited (7 pages). Ordering information is given on any current masthead page.