the 565-nm band are both, within experimental uncertainty, the same as those for the 514-nm band of $Pt_2{}^*$ in the absence of Tl^+.[17,18] These similarities, along with the single exponential luminescence decay observed in both cases, suggest the radiative and nonradiative decay rates for the two species are nearly the same.[10,19]

The 565-nm luminescence is assigned to the exciplex Pt_2Tl^{+*}, and a value of $2.0 \pm 0.3 \times 10^4$ at 25 °C for the equilibrium constant for $Pt_2{}^* + Tl^+ \Leftrightarrow Pt_2Tl^{2+*}$ has been determined,[20] giving $\Delta G° = -25$ kJ mol^{-1}. This value can be used in an energy cycle analysis[2,21] to derive a free energy difference of 10 ± 5 kJ mol^{-1} for the process $Pt_2Tl^+ \Leftrightarrow Pt_2 + Tl^+$. This free energy difference does not refer to the equilibrium ground state of Pt_2Tl^+ but rather to an excited vibrational state having the same internuclear configuration as Pt_2Tl^{+*}. This state is produced directly as a result of the deactivation of Pt_2Tl^{+*} via exciplex luminescence.[22]

In 2:1 1,2-ethanediol/water solutions, as the temperature is lowered from 250 to 190 K to give a frozen solution, the 565-nm luminescence disappears as the 514-nm phosphorescence reappears, suggesting the likelihood of a diffusional process for exciplex formation. This interpretation is supported by the lack of an effect of Tl^+ on the 405-nm fluorescence of $Pt_2{}^*$ ($\tau \approx 1$–3 ps[11]) in water. HNO_3 (0.1 M), KNO_3 (0.1 M), and O_2 (air-saturated solutions) all reduce the 565- to 514-nm luminescence intensity ratio, the first two presumably by ion pairing effects and O_2 by competitive quenching of $Pt_2{}^*$.

The tendency for Tl^+ and $Pt_2{}^*$ to form an exciplex can be viewed in terms of a simple molecular orbital picture.[23] In the present case the half-filled σ^* ($5d_{z^2}$) and σ ($6p_z$) orbitals of $Pt_2{}^*$[11] are expected to interact at an axial site with the filled 6s and empty $6p_z$ orbitals of Tl^+, respectively,[24] to yield a net two-electron stabilization. Such a covalent interaction (formal bond order of one between $Pt_2{}^*$ and Tl^+) differs from the charge-transfer behavior normally attributed to singlet organic exciplex formation.[1-3] Exciplex luminescence in the present case is then expected to result in a reduction in the formal bond order between Pt_2 and Tl^+ from one to zero,[23] implying a relatively weak ground-state interaction between Pt_2 and Tl^+.[25] This suggests a reason why the 368-nm absorption band of Pt_2Tl^+ is relatively unaffected under these conditions.

The present results lend support to suggestions that triplet exciplex formation may often involve relatively little charge transfer.[6,8,26] Pt_2Tl^{+*} is the first reported example of an exciplex involving a metal–metal-bonded complex and adds to the growing evidence[6-10] that triplet exciplex formation involving metal complexes may be surprisingly common.

Acknowledgement is made to the donors of The Petroleum Research Fund, administered by the Americal Chemical Society, for the support of this research. Funds from a DuPont College Science Grant were used to purchase the laser.

---

(17) Determined relative to 0.52 for $Pt_2{}^*$ (Heuer, W. B.; Totten, M. D.; Rodman, G. S.; Hebert, E. J.; Tracey, H. J.; Nagle, J. K. *J. Am. Chem. Soc.* **1984**, *106*, 1163-1164).

(18) Che, C.-M.; Butler, L. G.; Gray, H. B. *J. Am. Chem. Soc.* **1981**, *103*, 7796-7797.

(19) Hui, M.-H.; Ware, W. R. *J. Am. Chem. Soc.* **1976**, *98*, 4718-4727.

(20) The ratio $[Pt_2Tl^{+*}]/[Pt_2{}^*]$ in deoxygenated solutions with 368-nm excitation was determined by using relative luminescence intensities as a function of $[Tl^+]$ (approximated as the formal concentration of Tl^+) over a range of ratios of 2–20 $[Tl^+]/[Pt_2]$ ($[Pt_2] = 10^{-5}$ M). Constant values of K over this range were obtained and support our assignment of a 1:1 $Pt_2{}^*/Tl^+$ stoichiometry at these concentrations.

(21) Ware, W. R. *NATO Adv. Sci. Inst. Ser., Ser. A* **1983**, *69*, 341-362. Stevens, B. *Adv. Photochem.* **1971**, *8*, 161-226. Beens, H.; Weller, A. In *Organic Molecular Photophysics*; Birks, J. B., Ed.; Wiley: New York, 1975; Vol. 2, Chapter 4. No evidence for diabatic contributions to the process has been obtained (see ref 2, pp 72-73).

(22) The uncertainty in the free energy value is largely due to the estimate of E_{0-0} for $Pt_2{}^*$ (245 ± 4 kJ mol^{-1}: Fordyce, W. A.; Brummer, J. G.; Crosby, G. A. *J. Am. Chem. Soc.* **1981**, *103*, 7061-7064. Rice, S. F.; Gray, H. B. *J. Am. Chem. Soc.* **1983**, *105*, 4571-4575, ref 17). The decrease in the entropy of the singlet ground state relative to the triplet excited state (R ln 3) has been included in the calculation.

(23) Reference 2, pp 138-139.

(24) See: Nagle, J. K.; Balch, A. L. *J. Am. Chem. Soc.* **1988**, *110*, 319-321, for a consideration of Pt-Tl bonding in $Tl_2Pt(CN)_4{}^{2-}$.

(25) Although $Tl_2Pt(CN)_4$ exists in the solid state with Pt-Tl bonds of 314.0 (1) pm,[24] ^{195}Pt NMR results indicate there are no Pt-Tl interactions in $(CH_3)_2SO$ solutions containing Tl^+ and $Pt(CN)_4{}^{2-}$ and no Pt-Pb interactions in aqueous solutions containing Pb^{2+} and $Pt(CN)_4{}^{2-}$ (Balch, A. L.; Wood, F. E.; Nagle, J. K., unpublished results). Furthermore, recent electronic structure calculations on $Tl_2Pt(CN)_4$ indicate a relatively weak covalent interaction exists between Pt and the Tl^+ ions in this compound (Ziegler, T.; Nagle, J. K.; Snijders, J. G.; Baerends, E. J.; Ravenek, W., unpublished results).

(26) Reference 2, p 140.

A Stereoselective Synthesis of Functionalized Cyclopentenes via Base-Induced Ring Contraction of Thiocarbonyl Diels-Alder Adducts

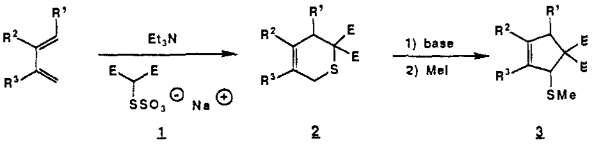
Scott D. Larsen

Metabolic Diseases Research
The Upjohn Company
Kalamazoo, Michigan 49001

Received May 9, 1988

Despite recent advances in the synthesis of cyclopentanoids, interest in this area remains high.[1] One approach which has received relatively little attention is the conversion of 1,3-dienes to cyclopentenes.[2] Considering the enormous number of methods now available for preparing conjugated dienes, this route has considerable potential.

We have developed a two-step procedure for the preparation of usefully functionalized cyclopentenes from conjugated dienes which is both efficient and stereoselective. The overall transformation is presented in eq 1. Bunte salt **1**, prepared from diethyl chloromalonate and sodium thiosulfate, is reacted with triethylamine in the presence of 1,3-dienes. The diethyl thioxomalonate thus generated undergoes smooth cycloaddition in a regioselective fashion.[3,4] When the cycloadducts **2** are exposed to either $LiN(iPr)_2$ or $KN(SiMe_3)_2$ at low temperature followed by quenching with iodomethane, a novel ring contraction occurs, leading to cyclopentenes **3**.



(1)

1 2 3

E = CO_2Et

---

(1) Ramaiah, M. *Synthesis* **1984**, 529. Paquette, L. A. *Top. Curr. Chem.* **1984**, *119*, 1. Trost, B. M. *Chem. Soc. Rev.* **1982**, *11*, 141. Trost, B. M.; Chan, D. M. T. *J. Am. Chem. Soc.* **1983**, *105*, 2315 and references cited therein.

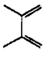
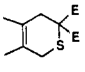
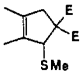
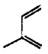
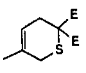
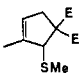
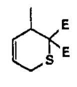
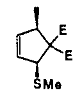
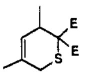
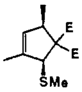
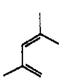
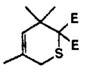
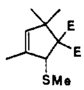
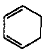
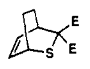
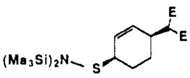
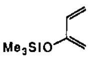
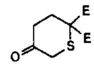
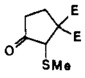
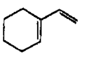
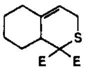
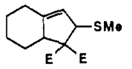
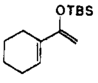
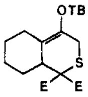
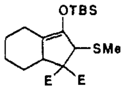
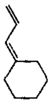
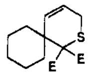
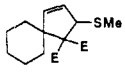
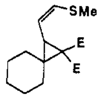
(2) Corey, E. J.; Walinsky, S. W. *J. Am. Chem. Soc.* **1972**, *94*, 8932. Negishi, E.-I.; Brown, H. C. *Synthesis* **1974**, 77. Hudlicky, T.; Koszyk, F. J.; Kutchan, T. M.; Sheth, J. P. *J. Org. Chem.* **1980**, *45*, 5020. Danheiser, R. L.; Martinez-Davila, D.; Auchus, R. J.; Kadonaga, J. T. *J. Am. Chem. Soc.* **1981**, *103*, 2443. Danheiser, R. L.; Bronson, J. J.; Okano, K. *J. Am. Chem. Soc.* **1985**, *107*, 4579.

(3) This is an extension of a method reported by Kirby for generating thioaldehydes: Kirby, G. W.; Lochead, A. W.; Sheldrake, G. N. *J. Chem. Soc., Chem. Commun.* **1984**, 922. The generation of diethyl thioxomalonate and its *S*-oxide by other methods has been reported: Beelitz, K.; Hohne, G.; Praefcke, K. *Z. Naturforsch., B: Anorg. Chem., Org. Chem.* **1978**, *33B*, 417. Saalfrank, R. W.; Rost, W. *Ang. Chem., Int. Ed. Engl.* **1985**, *24*, 855.

(4) For references to other recent methods of generating thiocarbonyl compounds see: Weinreb, S. M.; Staib, R. R. *Tetrahedron* **1982**, *38*, 3087. Vedejs, E.; Krafft, G. A. *Tetrahedron* **1982**, *38*, 2857. Krafft, G. A.; Meinke, P. T. *Tetrahedron Lett.* **1985**, *26*, 1947. Bladon, C. M.; Ferguson, I.; Kirby, G. W.; Lochead, A. W.; McDougall, D. C. *J. Chem. Soc., Perkin Trans. 1* **1985**, 1541. Schaumann, E. *Bull. Soc. Chim. Belg.* **1986**, *95*, 995. Vedejs, E.; Eberlein, T. H.; Mazur, D. J.; McClure, C. K.; Perry, D. A.; Ruggeri, R.; Schwartz, E.; Stults, J. S.; Varie, D. L.; Wilde, R. G.; Wittenberger, S. *J. Org. Chem.* **1986**, *51*, 1556.

0002-7863/88/1510-5932$01.50/0

Table I. Annulation of 1,3-Dienes[k,5]

	Diels–Alder reaction				ring contraction			
entry	diene	cycloadduct[a]		yield[b]	conditns[c]	product[d]		yield[b]
1		 **4**		80	A	 **14**		76
2		 **5**	(3:1)	82	B	 **15**		90
3		 **6**	(5:1)	88	C	 **16**	(13:1)	88[e]
4		 **7**	(12:1)	94	B	 **17**	(16:1)	74[e]
5		 **8**		93	B	 **18**		90
6		 **9**		88	B[j]	 **19**		72
7		 **10**		79[f]	A	 **20**		70
8[g]		 **11**	(3:2)	94	A	 **21**	(>18:1)	76[h]
9[g]		 **12**		82	A	 **22**	(>20:1)	92[h]
10		 **13**		72	C	  **23** (8:1) **24**[i]		95

[a] Where mixtures were obtained, only the major regioisomer is shown. The ratio of regioisomers formed is in parentheses. [b] Isolated total yields following flash chromatography. All new compounds were fully characterized spectrally and had elemental composition established by combustion analysis or high resolution MS. [c] Condition A: LDA (1.3 equiv), HMPA (1.3 equiv) in THF (0.2 M), −78 °C, 30 min; B: $KN(SiMe_3)_2$ (1.5–2.0 equiv) in THF (0.2 M), −64 °C, 4–6 h; C: $KN(SiMe_3)_2$ (2 equiv) in Et_2O (0.2 M), −78 °C, 4 h. [d] Only major diastereomer shown. Ratio of mixture is in parentheses. [e] Stereochemistry was assigned by conversion[7] [1. MCPBA, 2. $(MeO)_3P$, 80 °C] to the corresponding allylic alcohols and comparison of the vicinal methine proton coupling constants. The major diastereomer had a larger J value (6.3 Hz versus 3.5 Hz).[8] [f] Isolated yield following hydrolysis (THF/aqueous HCl/0 °C) of the crude reaction mixture. [g] Reference 9. [h] Stereochemistry not determined. [i] Isolated as a 9:1 mixture of Z:E olefins. [j] Reaction warmed to 25 °C for 10 min before water quench. [k] E = CO_2Et.

The scope of this annulation is evident from the results presented in Table I.[5] The hetero-Diels–Alder reactions proceed in good to excellent yields under mild conditions (25–70 °C) and are easily run on multigram scale. The observed pattern of regioselectivity is consistent with literature precedent.[4] For the subsequent rearrangement, three different sets of conditions had to be developed since no single protocol proved successful in every case. The high level of stereoselectivity is evident in entries 3, 4, 8, and 9 and is particularly high with bicyclic substrates. Also noteworthy are entries 5 and 10 where contiguous quaternary centers are established without difficulty and entry 7 where a cyclopentanone is successfully obtained from cyclohexanone **10**. Where rearrangement does occur, only cyclopentenoid products are obtained in each case.[6] The sole exception is found in entry 10 where a small amount of cyclopropane is isolated.

---

(5) A detailed experimental procedure is provided in the Supplementary Material.

(6) Biellmann has reported closely analogous rearrangements which led only to vinyl cyclopropanes: Biellmann, J. F.; Ducep, J. B. *Tetrahedron Lett.* **1970**, 2899. Biellmann, J. F.; Ducep, J. B.; Vicens, J. J. *Tetrahedron* **1976**, *32*, 1801. For further related work, see: Reglier, M.; Julia, S. A. *Tetrahedron Lett.* **1983**, *24*, 2387. Reglier, M.; Julia, S. A. *Tetrahedron Lett.* **1985**, *26*, 2319.

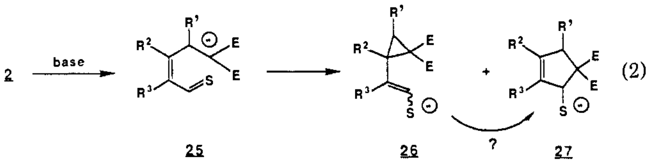
(7) Evans, D. A.; Andrews, G. C. *Acc. Chem. Res.* **1974**, *7*, 147.

(8) There is ample literature precedent for the cis vicinal coupling constant being larger than the trans in cyclopentenes: Partridge, J. J.; Chadha, N. K.; Uskokovic, M. R. *J. Am. Chem. Soc.* **1973**, *95*, 532. Trost, B. M.; Verhoeven, T. R. *J. Am. Chem. Soc.* **1980**, *102*, 4730. Trost, B. M.; Molander, G. A. *J. Am. Chem. Soc.* **1981**, *103*, 5969. Danheiser, R. L.; Martinez-Davila, D.; Auchus, R. J.; Kadonaga, J. T. *J. Am. Chem. Soc.* **1981**, *103*, 2443. Marino, J. P.; Fernandez de la Pradilla, R.; Laborde, E. *J. Org. Chem.* **1987**, *52*, 4898.

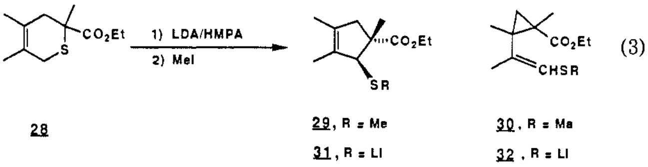
(9) Diene preparation: Ireland, R. E.; Thompson, W. J. *J. Org. Chem.* **1979**, *44*, 3583.

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 diastereomers[5]) 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 ^{13}C 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.

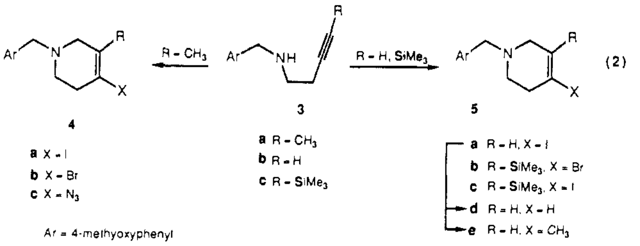
Additions and Corrections

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 cycliations 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.