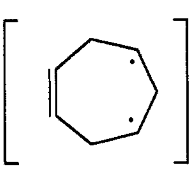
$r(C_1–C_6)$ and $r(C_1–C_2)$ of **1** were 0.015 and 0.008 Å less, respectively, than the corresponding bond lengths in **2**. As indicated above, major changes in bond angles occurred in **1** relative to **2**. For example, $\theta(C_2C_1C_7)$ increased by 21° in **1** to a value of 141.3°. As a consequence, the three exterior angles $\theta(H_1C_1C_x)$ in **1** all show a decrease relative to the corresponding angles of **2**. While the anges at the double bond, e.g., $\theta(C_2C_3C_4)$, were not significantly different for **1** and **2**, the angle at the adjacent carbon C_2 was 12° smaller in **1** as compared to **2**.

Our calculated frequencies showed that the double bond is somewhat more strained in **1** consistent with the longer bond length. The calculated C=C stretch for **2** is 1689 cm^{-1} after scaling by 0.9 in comparison to an experimental value of 1665 cm^{-1}. The trans isomer **1** has a scaled C=C stretch of 1619 cm^{-1} as compared to the experimental value of 1590 cm^{-1}.

Both the geometries and frequencies suggest that **1** is considerably more strained than **2**. The value for ΔE (**1**–**2**)[14] at the SCF level is 32.1 kcal/mol, while the energy difference decreased to 27.1 kcal/mol when a correlation correction (MP2)[14] is included. The experimental activation energy for the conversion of **1** to **2** is 26.4 kcal/mol[1] with **3** postulated as the reaction intermediate.



3

The thermal isomerization of a model compound, *cis*-2,3-dimethylcyclopropane,[15] to the trans isomer has E_a = 61.2 kcal/mol. Subtraction of ΔE(**1**–**2**) from this value gives an estimated E_a for the conversion of **1** to **2** of 34 kcal/mol (assuming no additional stabilization of the transition state **3**). This is in reasonable agreement with the experimental E_a.

The presence of a twist–bent carbon–carbon σ bond in **1** can best be studied in a valence bond framework, i.e., with the use of localized orbitals.[16] We employed our optimum geometry and determined the wave function at the STO-3G level.[17] The wave function was then localized by using the Boys criteria.[18] A GVB-PP[19,20] calculation splitting the $C_1–C_6$ bond pair was also performed in order to examine the localized orbital obtained from energetic considerations.

Consider that the cyclopropane ring defines the *xz* plane with C_7 along the *x* axis. Then a bent σ bond will consists of 2s, $2p_x$, and $2p_z$ orbitals on C_1 and C_6. The $2p_y$ component should be zero if no twisting is present. Any $2p_y$ component (due to the C_2 symmetry) will lead to twisting of the bond. There is clearly a $2p_y$ component to the orbital determined either as a Boys LMO or as a GVB orbital.[21] For the Boys LMO, the valence orbital coefficients on C_1 are 2s = 0.254, $2p_x$ = 0.207, $2p_y$ = 0.045, and $2p_z$ = 0.500. For the GVB pair, the natural orbital occupancy of the bond orbital is 1.974e and that of the antibonding orbital is 0.026e. The coefficients of C_1 in the GVB bond orbital are 2s = 0.116, $2p_x$ = 0.272, $2p_y$ = 0.070, and $2p_z$ = 0.541. In the energetically determined GVB LMO, the $2p_y$:$2p_x$ ratio is 0.26 showing that there is four times the coefficient to bend the orbital as to twist it.[19] For the Boys LMO, the ratio is slightly smaller, 0.22.

With a hybridization of $sp^{4.8}$ at C_1 and C_6, the twist-bent carbon–carbon σ bond has more p character than the other C–C bonding orbitals of the cyclopropane moiety. The $C_1–C_7$ ($C_6–C_7$) bond of **1** has hybridizations of $sp^{2.9}$ at C_1 and $sp^{3.1}$ at C_7. For **2**, the $C_1–C_6$ bond has hybridizations at C_1 and C_6 of $sp^{2.3}$ and hybridizations at C_1 of $sp^{3.5}$ and C_7 of $sp^{3.4}$ for the $C_1–C_7$ bond.

The deviation of the centroid of charge for the twist, bent $C_1–C_6$ bond in **1** (which is in the plane defined by the cyclopropyl carbons due to symmetry) from the $C_1–C_6$ internuclear axis is smaller than the corresponding deviation in **2** (23.0° and 28.4°, respectively). Since each of the hybridized orbitals in the $C_1–C_6$ bond in **1** is "twisted" in opposite directions from the plane of the cyclopropane, they will not have as large a projection in the plane. Thus the centroid of charge will be closer to the C–C internuclear axis for a twist, bent σ bond than for a "normal" bent σ bond as was found in the comparison of the $C_1–C_6$ bonds in **1** and **2**. The LMO for the $C_1–C_6$ bond at C_1 is twisted by 4.8° above the *xz* plane, whereas at C_6, it is twisted by 4.8° below the plane. For the GVB orbital, the amount of twist above and below the plane is larger, 6.6°. These results are all consistent with the presence of twisting in the $C_1–C_6$ σ bond to form an "S" shaped (sinusoidal) electron distribution within the bond.[20] Consistent with the highly strained nature of **1**, we found the $C_1–C_2$ bond in **1** to be quite bent with deviations of the centroid-of-charge from the $C_1–C_2$ internuclear axis of 17.7° at C_1 and 6.8° at C_2. The corresponding deviations in **2** for this bond are 1.7° and 2.4°.

In summary, theoretical calculations have provided substantial evidence for the existence of a rare type of carbon–carbon σ bonding, which we have catagorized as a twist–bent σ bond.

Acknowledgment. P.G.G. acknowledges partial support of this work by a grant from the National Science Foundation. We thank Dr. D. A. Kleier for helpful discussions.

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(14) SCF: $E(\mathbf{1}) = -270.835155$ au, $E(\mathbf{2}) = -270.886281$ au; MP-2: $E(\mathbf{1}) = 271.718056$ au, $E(\mathbf{2}) = -271.761295$ au.

(15) Flowers, M. C.; Frey, H. M. *Proc. Roy. Soc. London, Ser. A* **1961**, *260*, 424.

(16) Lipscomb, W. N. *Acc. Chem. Res.* **1973**, *6*, 257.

(17) Hehre, W. J.; Stewart, R. F; Pople, J. A. *J. Chem. Phys.* **1969**, *51*, 2657.

(18) (a) Boys, S. F. In *Quantum Theory of Atoms, Molecules and the Solid State*; Lowdin, P.-O., Ed.; Academic Press: New York, NY, 1966; p 253. (b) Kleier, D. A.; Halgren, T. A.; Hall, J. H., Jr.; Lipscomb, W. N. *J. Chem. Phys.* **1974**, *61*, 3905.

(19) Goddard, W. A., III; Dunning, T. H., Jr.; Hunt, W. J.; Hay, P. J. *Acc. Chem. Res.* **1973**, *6*, 638.

(20) Geometry optimization at the 3G/GVB level for **1** gives $r(C_1–C_6)$ = 1.531 Å as compared to $r(C_1–C_6)$ = 1.494 Å at 3G/SCF. The 2s coefficient decreases slightly, and the other coefficients show only small changes on optimization.

(21) It is possible that some of the $2p_y$ character in the $C_1–C_6$ bond is required for orthogonality constraints. However, the $2p_y$ coefficient is comparable to or larger than most of the remaining coefficients on the other atoms.

Synthesis of Main Group Heterocycles by Metallacycle Transfer from Zirconium

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Received July 2, 1987

We have been interested in developing new routes to organometallic main group compounds because of their increasing importance in industry as electronic material precursors.[1] Although organozirconium and -titanium reagents have found widespread application in the synthesis of organic compounds,[2] their utility for synthesizing main group compounds has not been fully realized.[3] Here we report the use of the readily available zirconium

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(1) For example, see: (a) Parshall, G. W. *Organometallics* **1987**, *6*, 687–692. (b) Moss, R. H. *Chem. Br.* **1983**, 735–737. (c) Bradley, D. C.; Faktor, M. M.; Scott, M.; White, E. A. D. *J. Crystal Growth* **1986**, *75*, 101–106.

(2) (a) Cardin, D. J.; Lappert, M. F.; Raston, C. L. *Chemistry of Organozirconium and -Hafnium Compounds*; Ellis Horwood Limited: Chichester, 1986; pp 399–439. (b) Negishi, E.; Takahashi, T. *Aldrich. Acta* **1985**, *18*, 31–48. (c) Davies, S. G. *Organotransition Metal Chemistry: Applications to Organic Synthesis*; Pergamon Press: Oxford, 1982. (d) Nugent, W. A.; Thorn, D. L.; Harlow, R. L. *J. Am. Chem. Soc.* **1987**, *109*, 2788–2796.

(3) (a) Fryzuk, M. D.; Bates, G. S.; Stone, C. *Tetrahedron Lett.* **1986**, *27*, 1537–1540. (b) Heisteeg, B. J. J.; Schat, G.; Akkermann, O. S.; Bickelhaupt, F. *Organometallics* **1986**, *5*, 1749–1750. (c) Erker, G.; Muhlenbernd, T.; Benn, R.; Rufinska, A. *Organometallics* **1986**, *5*, 1023–1028. For related chemistry with other transition metals, see: (d) Wakatsuki, Y.; Kuramitsu, T.; Yamazaki, H. *Tetrahedron Lett.* **1974**, 4549–4552. (e) Muller, E. *Liebigs Ann. Chem.* **1971**, *754*, 64–89. (f) Braye, E. H.; Hubel, W. *Chem. Ind.* **1959**, 1250–1251.

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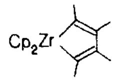
metallacycles **1**–**6** for the preparation of a variety of main group heterocycles. These reagents are quite versatile with respect to the main group electrophiles that can be functionalized and allow convenient syntheses of both new and known types of main group compounds. Since many other zirconium and related early transition-metal metallacycles are known,[4] other ring systems should be obtainable by this route.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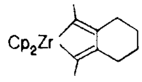
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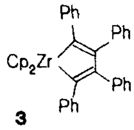
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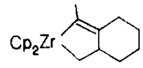
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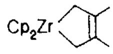
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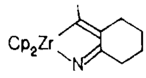
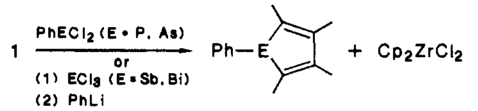

6

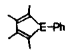
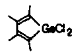
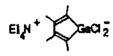
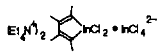
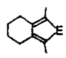
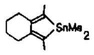
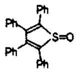
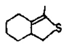
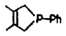
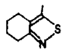
The zirconium metallacycles **1**–**5** can be conveniently prepared by reduction of Cp_2ZrCl_2 ($Cp = \eta\text{-}C_5H_5$) with either Mg turnings or *n*-BuLi in the presence of 2-butyne, 2,8-decadiyne, diphenylacetylene, 1-nonen-7-yne, or 2,3-dimethy-1,3-butadiene, respectively.[2d,5,6] Metallacycle **6** was prepared by addition of 1-cyano-5-heptyne to a solution of Cp_2ZrCl_2 previously reduced in the presence of bis(trimethylsilyl)acetylene. By using these metallacycles, the compounds listed in Table I are readily prepared. Reaction of 0.674 g (2.04 mmol) of the isolated metallacycle **1** in 10 mL of THF with 277 μL (2.04 mmol) of dichlorophenylphosphine in tetrahydrofuran at room temperature results in an immediate reaction. After removal of solvent, the product can be extracted with a total of 10 mL of hexane and isolated by flash chromatography eluting with hexane on alumina(III) to give 0.345 g (78%) of 1-phenyl-2,3,4,5-tetramethylphosphole (**7a**). The arsole **7b** was similarly prepared in high yield (eq 1).[7] The analogous stibole and bismole can be prepared by reaction of **1** with $SbCl_3$ or $BiCl_3$ to generate the 1-chloro-2,3,4,5-tetramethylstibole (**7e**) and bismole **7f**.[8] Addition of 1 equiv of phenyllithium (2.7 M in 70:30 cyclohexane/ether) yields **7c** and **7d** which were purified by high vacuum sublimation. By using similar procedures, the germole **8** was prepared from **1**, the stannole **11** from **2**, and the known phospholene **14**[9] from **5**. Reaction of **1** with $GaCl_3$ in THF followed by addition of a dichloromethane solution of $Et_4N^+Cl^-$ allows isolation of the gallole **9a**. The indium complex **9b** was obtained by reaction of **1** with 2 equiv of $Et_4N^+InCl_4^-$ in THF. This leads to precipitation of **9b** which can be recrystallized from CH_2Cl_2.[10]



(1)

Depending on the synthetic target, the zirconium metallacycle need not be isolated, but "one-pot" syntheses can be carried out. For example, addition of 10 mL of 1.6 M *n*-butyllithium (16 mmol) to a THF (100 mL) slurry of 2.34 g (8.00 mmol) of Cp_2ZrCl_2 at −78 °C in the presence of 1.08 g (8.00 mmol) of 2,8-decadiyne followed by warming to room temperature generates **2**. Dropwise addition of a solution of 1.08 g (8.00 mmol) of S_2Cl_2 in 15 mL of hexane to this solution maintained at 0 °C gives thiophene **10a** in 55% isolated yield following workup. In a similar manner, selenophene **10b**, thiophene oxide **12**, thiacyclopentene **13**, and isothiazole **15** can be prepared from the appropriate metallacycle generated in situ.

Table I. Main Group Heterocycles Prepared from Zr Metallacycles

Zr metallacycle	electrophile	product (isolated yield)	
1	$PhECl_2$ (E = P, As) (1) ECl_3, (2) PhLi (E = Sb, Bi)		**7a** (E = P, 85%) **7b** (E = As, 76%) **7c** (E = Sb, 78%) **7d** (E = Bi, 70%)
	$GeCl_4$		**8** (83%)
	(1) $GaCl_3$, (2) $Et_4N^+Cl^-$		**9a** (80%)
	$2Et_4N^+InCl_4^-$		**9b** (89%)
2	S_2Cl_2; Se_2Cl_2		**10a** (E = S, 55%) **10b** (E = Se, 53%)
	Me_2SnBr_2		**11** (82%)
3	$SOCl_2$		**12** (52%)
4	S_2Cl_2		**13** (48%)
5	$PhPCl_2$		**14** (67%)
6	S_2Cl_2		**15** (65%)[a]

[a] Based on recovered 1-cyano-5-heptyne.

This zirconium-based route to main group heterocycles is in general superior to previous routes which use the difficult to prepare 1,4-dilithiobutadiene reagents.[11,12] For example, this method allows facile preparation of relatively rare arsoles, stiboles, and bismoles, some of which are known to have unusual solid-state properties.[12] Also notable is that unsaturation in the heterocycle rings may be controlled depending on which zirconium metallacycle is used as illustrated by the preparation of **13** and **14**. The ability to include nitrogen in the heterocycle ring as demonstrated by the synthesis of the isothiazole **15** should further expand the scope of these reactions. One limitation we have found is that transfer to $SiCl_4$ is not possible, i.e., reaction of **1** in neat $SiCl_4$ at 60 °C for 12 h results in no observable reaction. Variation of the leaving groups on silicon may alter this current limitation. We have been successful in transferring metallacycles to boron, the results of which will be reported subsequently.[13] We are continuing to explore this metallacycle transfer chemistry as well

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(4) (a) Buchwald, S. L.; Lum, R. T.; Dewan, J. C. *J. Am. Chem. Soc.* **1986**, *108*, 7441–7442. (b) Buchwald, S.; Watson, B. T.; Huffman, J. C. *J. Am. Chem. Soc.* **1986**, *108*, 7411–7413. (c) Reference 2a, Chapter 6–10.

(5) Famili, A.; Farona, M. F.; Thanedar, S. *J. Chem. Soc., Chem. Commun.* **1983**, 435–436.

(6) Negishi, E.; Cederbaum, F. E.; Tamotsu, T. *Tetrahedron Lett.* **1986**, *27*, 2829–2832.

(7) See Supplementary Material.

(8) The compounds **7e** and **7f** are thermally unstable and decompose upon attempted isolation.

(9) Quin, L. D.; Mathewes, D. A. *J. Org. Chem.* **1964**, *29*, 836–839.

(10) The complex **9b** most likely contains a dimeric indium species with chloride bridging the two metals, and its formation presumably reflects the propensity of indium to attain higher coordination numbers. However, other structural formulations cannot be excluded.

(11) For the preparation of phospholes, arsoles, stiboles, and bismoles, siloles, germoles, and stannoles, see: (a) Mathey, F.; Fisher, J.; Nelson, J. H. *Struct. Bonding* **1983**, *55*, 153–201. (b) Mathey, F. *Topics in Phosphorus Chemistry*; Grayson, M., Griffith, E., Eds.; Wiley: New York, 1980; Vol. 10, pp 1–128. (c) Braye, E. H.; Hubel, W.; Caplier, I. *J. Am. Chem. Soc.* **1961**, *83*, 4406–4413. (d) Leavitt, F. C.; Manuel, T. A.; Johnson, F.; Matternas, L. U.; Lehman, D. S. *J. Am. Chem. Soc.* **1960**, *82*, 5099–5102. (e) Dimroth, K. *Comprehensive Heterocyclic Chemistry*; Meth-Cohn, O., Ed.; Pergamon: Oxford, 1984; Vol. 1, pp 518–523. (f) Atkinson, R. E. *Comprehensive Heterocyclic Chemistry*; Meth-Cohn, O., Ed.; Pergamon: Oxford, 1984; Vol. 1, pp 544–550. (g) Armitage, D. A. *Comprehensive Heterocyclic Chemistry*; Meth-Cohn, O., Ed.; Pergamon: Oxford, 1984; Vol. 1, pp 614–617. (h) Markl, G.; Hauptmann, H.; Merz, A. *J. Organomet. Chem.* **1983**, *249*, 335–363. (i) Magnesium diene reagents can also be effective in the preparation of some main group metallacycles, e.g.: Richter, W. J. *Chem. Ber.* **1985**, *118*, 97–106.

(12) (a) Ashe, A. J., III *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 229–230. (b) Ashe, A. J., III; Drone, F. J. *Organometallics* **1985**, *4*, 1478–1480, and references therein.

(13) Fagan, P. J. *J. Am. Chem. Soc.*, in press.

as the use of the main group heterocycles in materials and organic synthesis.

Registry No. 1, 84101-39-3; **2**, 113132-34-6; **3**, 53433-58-2; **4**, 113132-35-7; **5**, 113132-36-8; **6**, 113132-37-9; **7a**, 112549-07-2; **7b**, 113111-17-4; **7c**, 113111-18-5; **7d**, 113111-19-6; **7e**, 113111-26-5; **7f**, 113111-27-6; **8**, 113111-20-9; **9a**, 113132-39-1; **9b**, 113132-41-5; **10a**, 26461-34-7; **10b**, 113111-21-0; **11**, 113111-22-1; **12**, 113111-23-2; **13**, 113111-24-3; **14**, 14409-95-1; **15**, 113111-25-4; $Et_4N^+InCl_4^-$, 20678-78-8; Cp_2ZrCl_2, 1291-32-3; $PhPCl_2$, 644-97-3; $PhAsCl_2$, 696-28-6; $SbCl_3$, 10025-91-9; $BiCl_3$, 7787-60-2; $GeCl_4$, 10038-98-9; $GaCl_3$, 13450-90-3; S_2Cl_2, 10025-67-9; Se_2Cl_2, 10025-68-0; Me_2SnBr_2, 2767-47-7; $SOCl_2$, 7719-09-7; $SiCl_4$, 10026-04-7; 2,8-decadiyne, 4116-93-2.

Supplementary Material Available: ^{1}H NMR, ^{13}C NMR, ^{31}P NMR, and mass spectral data for the compounds **7–15** (4 pages). Ordering information is given on any current masthead page.

An Organochromium-Mediated Synthesis of 11-Deoxydaunomycinone via a Tandem Benzannulation/Friedel–Crafts Double Cyclization[†]

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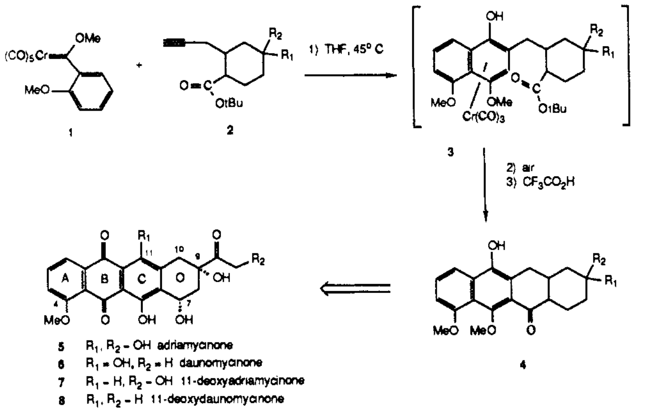
Received October 28, 1987

Members of the anthracycline family of antitumor antibiotics are well established clinically important agents in cancer chemotherapy[2] and have attracted the interest of synthetic organic chemists for the last 12 years.[3] The clinically effective agents are members of the 11-oxy class of anthracyclines, and members of the 11-deoxy class are presently in human trials. The tetracyclic carbon skeleton of the anthracycline family has served as the anvil against which a large array of elegant and practical new synthetic methods in the chemistry of aromatic rings have been forged and is revealed, for example, in the reported syntheses of 11-deoxydaunomycinone.[4] The reactions of chromium carbene complexes with acetylenes produce substituted 4-alkoxyphenols with a high degree of control of regiochemistry under neutral conditions and at near ambient temperatures.[5] Together with the fact that chromium carbene complexes are relatively inexpensive and easy to make and handle, the benzannulation reaction of chromium carbene complexes is one of the most powerful methods for the preparation of substituted 4-alkoxyphenols (and therefore quinones) and should thus be well suited for utilization in anthracyclinone synthesis. Three years ago we reported the first anthracyclinone synthesis[6,7] utilizing the benzannulation reaction of a chromium carbene complex and an acetylene which in terms of efficiency fell short of state of the art. The synthesis of 11-deoxydaunomycinone described herein[8] from the carbene complex **1** is comparable in overall efficiency to the best of the syntheses that have been reported to date[4] and is highlighted by the first synthetic application of a one-pot double-cyclization incorporating a tandem benzannulation/Friedel–Crafts sequence.

Scheme I



5 R_1, R_2 - OH adriamycinone
6 R_1 = OH, R_2 = H daunomycinone
7 R_1 - H, R_2 - OH 11-deoxyadriamycinone
8 R_1, R_2 - H 11-deoxydaunomycinone

The plan in Scheme I was designed to include several members of the class of 11-deoxyanthracyclines, and has as its ultimate feature the construction of the anthracycline tetracyclic carbon skeleton in a single pot from the carbene complex **1** and an acetylene of the general structure **2**. It has been demonstrated that naphthalenes can be prepared from the annulation of the *o*-methoxyphenyl complex **1**[5c,9,10c] and it has also previously been demonstrated that terminal acetylenes are regioselectively incorporated into the annulated products with the acetylene substituent adjacent to the hydroxyl group.[10] With the preparation of the requisite acetylene of the type **2**, the anticipated sequence of events begins with the formation of a solution of the naphthol chromium tricarbonyl complex **3** from the reaction of acetylene **2** with the carbene complex **1**. It has been our experience that naphthol chromium tricarbonyl complexes are very rapidly oxi-

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[†] Dedicated to Professor N. C. Yang on the occasion of his 60th birthday.

(1) Eli Lilly Young Scholar, 1986–1987.

(2) For reviews of anthracyclines, see: (a) El Khadem, H. S., Ed.; Academic Press: New York, 1982. (b) Arcamone, F. *Med. Chem.* (*Academic*) **1981**, 17.

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