ylene chloride (50 mL), and washed successively with H_2O (50 mL), 1 M HCl (50 mL), saturated $NaHCO_3$ (50 mL), and H_2O (50 mL). Drying over $MgSO_4$ and evaporation of solvents yielded crude *cis*-4-(methoxycarbonyl)-1-(4'-methoxyphenyl)-3-[1'-(trimethylsilyl)benzyl]azetidin-2-one (1.71 g, 86% based on the imine) as a mixture of anti and syn epimers (molar ratio 70:30, respectively). Crystallization from methanol afforded pure *cis-anti*-**10a** isomer (1.03 g, 52%). Mp: 144-145 °C. ^1H NMR ($CDCl_3$): δ 7.30-7.14 (m, 5 H, arom), 6.97 (d, J = 9.3 Hz, 2 H, arom), 6.86 (d, J = 9.3 Hz, 2 H, arom), 4.49 (d, J = 5.4 Hz, 1 H, C*H*COOMe), 4.30 (dd, J = 5.4 Hz, J = 13.5 Hz, 1 H, C*H*CO), 3.79 (s, 3 H, OMe), 3.28 (s, 3 H, OMe), 2.75 (d, J = 13.5 Hz, 1 H, C*H*SiMe$_3$), 0.08 (s, 9 H, SiMe$_3$). ^{13}C NMR ($CDCl_3$): δ 169.5, 164.7, 156.2, 140.9, 131.0, 128.3, 127.2, 125.2, 117.6, 114.1, 55.6, 55.4, 55.3, 52.2, 32.8, -1.9. MS: m/e 397 (M^+). Anal. Calcd for $C_{22}H_{27}NO_4Si$: C, 66.48; H, 6.85; N, 3.52. Found: C, 66.40; H, 6.85; N, 3.35.

Finally, column chromatography (silica gel; eluent, hexane-methylene chloride, 5:1) of mother liquors afforded the *cis-syn*-**11a** isomer (0.45 g, 24%). Syrup. ^1H NMR ($CDCl_3$): δ 7.31-7.10 (m, 5 H, arom), 6.97 (d, J = 9.3 Hz, 2 H, arom), 6.86 (d, J = 9.3 Hz, 2 H, arom), 4.55 (d, J = 6.3 Hz, 1 H, C*H*COOMe), 4.15 (dd, J = 6.3 Hz, J' = 3.6 Hz, 1 H, C*H*CO), 3.79 (s, 3 H, OMe), 3.12 (s, 3 H, OMe), 2.58 (d, J = 3.6 Hz, 1 H, C*H*SiMe$_3$), 0.10 (s, 9 H, SiMe$_3$). ^{13}C NMR ($CDCl_3$): δ 168.9, 165.9, 156.2, 131.3, 129.3, 128.0, 125.3, 118.0, 114.4, 55.4, 55.0, 52.0, 35.2, 29.7, -2.2. MS: m/e 397 (M^+). Anal. Calcd for $C_{22}H_{27}NO_4Si$: C, 66.48; H, 6.85; N, 3.52. Found: C, 66.31; H, 6.92; N, 3.38.

Compounds **10b** and **11b**. The above method was followed starting from 3-*p*-tolyl-3-(trimethylsilyl)propanoic acid to afford *cis-anti*-4-(methoxycarbonyl)-1-(4'-methoxyphenyl)-3-[*p*-tolyl-(trimethylsilyl)methyl]azetidin-2-one (**10b**) (1.08 g, 54%) [Mp: 154-155 °C (MeOH). ^1H NMR ($CDCl_3$): δ 7.21 (d, 2 H, arom), 7.06 (d, 2 H, arom), 6.86 (d, 2 H, arom), 6.83 (d, 2 H, arom), 4.48 (d, 1 H, J = 5.5 Hz, C*H*COOMe), 4.27 (dd, 1 H, J = 5.5 Hz, J' = 13.5 Hz, C*H*CON), 3.70 (s, 3 H, OMe), 3.31 (s, 3 H, COOMe), 2.70 (d, 1 H, J = 13.5 Hz, C*H*SiMe$_3$), 2.32 (s, 3 H, C*H*$_3$Ar), 0.06 (s, 9 H, SiMe$_3$). ^{13}C NMR ($CDCl_3$): δ 169.5, 164.8, 156.2, 137.6, 134.6, 131.1, 129.0, 127.1, 117.6, 114.5, 55.8, 55.2, 52.2, 32.3, 20.9, -2.9. MS: m/e 411 (M^+). Anal. Calcd for $C_{23}H_{29}NO_4Si$: C, 67.12; H, 7.10; N, 3.40. Found: C, 66.98; H, 7.11; N, 3.07.] and *cis-syn*-4-(methoxycarbonyl)-1-(4'-methoxyphenyl)-3-[*p*-tolyl(trimethylsilyl)methyl]azetidin-2-one (**11b**) (0.51g, 25%). Syrup. ^1H NMR ($CDCl_3$): δ 7.28 (d, 2 H, arom), 7.03 (d, 2 H, arom), 6.85 (m, 4 H, arom), 4.48 (d, 1 H, J = 6.3 Hz, C*H*CN), 4.08 (dd, 1 H, J = 6.3 Hz, J' = 3.6 Hz, C*H*CON), 3.75 (s, 3 H, OMe), 2.51 (d, 1 H, J = 3.6 Hz, C*H*SiMe$_3$), 2.23 (s, 3 H, ArC*H*$_3$), 0.06 (s, 9 H, SiMe$_3$). ^{13}C NMR ($CDCl_3$): δ 168.9, 165.9, 156.2, 135.1, 134.7, 131.3, 129.2, 128.7, 118.0, 114.1, 55.5, 55.1, 51.9, 34.6, 29.7, 20.9, -2.2. MS: m/e 411 (M^+). Anal. Calcd for $C_{23}H_{29}NO_4Si$: C, 67.12; H, 7.10; N, 3.40. Found: C, 67.08; H, 7.34; N, 3.30.

Methyl 3-Carboxy-2-((4'-methoxyphenyl)amino)-4-phenyl-4-(trimethylsilyl)butanoate (12). To a solution of *cis-anti*-4-(methoxycarbonyl)-1-(4'-methoxyphenyl)-3-[1'-(trimethylsilyl)benzyl]azetidin-2-one (**10a**) (0.766 g, 2 mmol) in methylene chloride (7 mL) cooled to 0 °C, was added, with stirring, $HBF_4{\cdot}2Et_2O$ (1.68 mL, 10 mmol), and the mixture was stirred at room temperature overnight. It was then diluted with methylene chloride (15 mL) and washed rapidly with cold water (10 mL) and could brine (2 × 10 mL) and dried. Concentration in vacuo gave the crude methyl 3-carboxy-2-((4'-methoxyphenyl)-amino)-4-phenyl-4-(trimethylsilyl)butanoate (**12**) (0.67 g, 83%). Mp: 116-118 °C. ^1H NMR ($CDCl_3$): δ 7.38-7.20 (m, 5 H, arom), 6.75 (d, J = 9 Hz, 2 H, arom), 6.53 (d, J = 9 Hz, arom), 4.08 (d, J = 3.3 Hz, 1 H, C*H*COOMe), 3.76 (s, 3 H, OMe), 3.67 (s, 3 H, OMe), 3.63 (dd, J = 3.3 Hz, J' = 12.6 Hz, C*H*COOH), 2.79 (d, J = 12.6 Hz, 1 H, C*H*SiMe$_3$), 0.06 (s, 9 H, SiMe$_3$). Anal. Calcd for $C_{22}H_{29}NO_6Si$: C, 64.32; H, 7.23; N, 3.26. Found: C 64.41; H, 7.41; N, 3.34.

Cyclization of β-Amino Acids. General Procedure. To a cooled (0 °C) solution of β-amino acid (2.0 mmol) and triethylamine (0.92 mL, 6.5 mmol) in acetonitrile (8 mL), were added phenyl phosphorodichloridate (0.33 mL, 2.2 mmol) and acetonitrile (5 mL). After the resulting solution was stirred for 30-40 h at room temperature, the mixture was diluted with methylene chloride (20 mL) and washed successively with H_2O (10 mL), 1 M HCl (10 mL), saturated $NaHCO_3$ (10 mL), and H_2O (10 mL). Drying over $MgSO_4$ and evaporation of solvents yielded crude β-lactam, which was purified by crystallization or flash chromatography.

Acknowledgment. The present work has been supported by Comisiôn Interministerial de Ciencia y Tecnologia (Plan Nacional, Progect FAR 88:0393).

Supplementary Material Available: Characterizing spectra of **10a**, **10b**, **11a**, and **11b** (16 pages). Ordering information is given on any current masthead page.

The Bridged Methylenedihydroanthracenes: *p*-Cyclophane Tautomers

Stuart Rosenfeld* and Alexandra Shedlow

Department of Chemistry, Smith College, Northampton, Massachusetts 01063

Received October 11, 1990

The tautomers of the simplest alkyl-substituted aromatic compounds toluene, 1-methylnaphthalene, and 9-methylanthracene are all known[1] and are all substantially less stable than their fully aromatic counterparts. The tautomers of 9-methylanthracene are closest in stability but still differ by ca. 40 kJ/mol.[2] Experiment[3] and theory[2] are in agreement that the energy of the methylene tautomer approaches, but never reaches, the energy of the fully aromatic tautomer as the number of annelated rings increases. In anthracenes, substitution at the vinyl and/or peri positions has afforded a number of easily isolable compounds, many of which have been shown to undergo boat-to-boat interconversion on the NMR time scale.[4-7] Also, in some very crowded anthracenes the methylenedihydroanthracene tautomer has been shown to be the more stable tautomer by equilibration in the presence of acid or base.[8] No computational or experimental studies have focused on the bridged counterparts of these compounds, i.e., the exomethylene tautomers of [*n*]-cyclophanes. The [*n*](9,10)anthracenophanes provide an attractive starting point since they have the greatest likelihood of exomethylene-cyclophane tautomeric pairs of similar energy.

Recently we found that deuteration of 3,6-diketo[8]-(9,10)anthracenophane (**1**) in the presence of acid led to incorporation of deuterium at the benzylic positions as well as in the positions α to the carbonyl groups.[9] The likely pathway under these conditions includes the bridged methylenedihydroanthracene (MDA) tautomer **2** as an intermediate. The bridged MDA, in this instance, is the less stable tautomer since there was no evidence (NMR) for its existence in the deuterated sample of **1**. However, since interactions within the bridge of [*n*](9,10)-anthracenophanes, and presumably their MDA tautomers, make significant contributions to the energies of these

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(3) Takagi, M.; Harabe, T.; Nojima, M.; Kusabayashi, S. *J. Chem. Soc., Perkin Trans. 1* **1983**, 1311 and references therein.
(4) (a) Leung, P.-T.; Curtin, D. Y. *J. Am. Chem. Soc.* **1975**, *97*, 6790; (b) **1975**, *97*, 6799.
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(8) Dickerman, S. C.; Haase, J. R. *J. Am. Chem. Soc.* **1967**, *89*, 5458.
(9) Rosenfeld, S. M.; Sanford, E. M. *Tetrahedron Lett.* **1987**, *28*, 4775.

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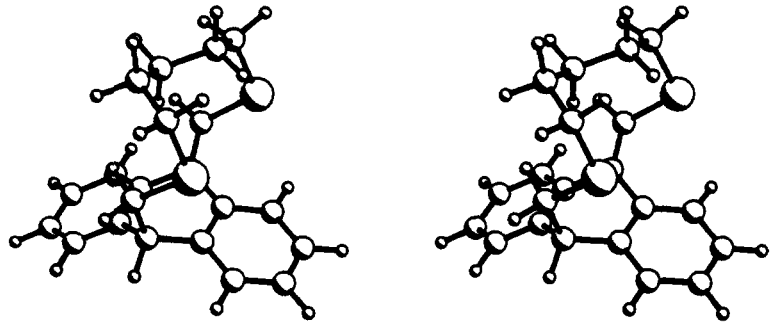


Figure 1. PLUTO stereopair representation of the molecular mechanics geometry for the *S*-syn conformer of **10**.

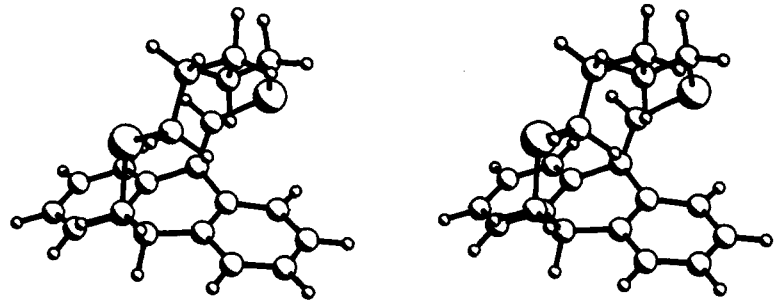
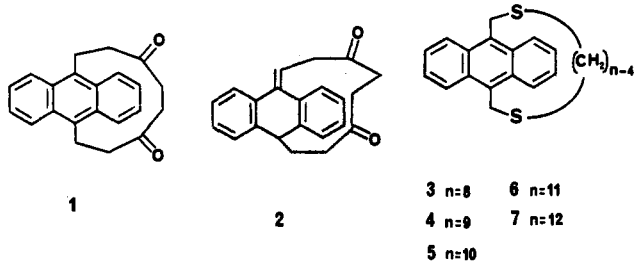


Figure 2. PLUTO stereopair representation of the molecular mechanics geometry for the *S*-anti conformer of **10**.

compounds,[10] it is quite possible that the relative stability of the tautomeric pair would be inverted somewhere within a series of homologous [*n*](9,10)anthracenophanes. If so, this presents the opportunity to make the first spectroscopic observation, and possibly isolation, of a compound that is notable both as a bridged methylenedihydroanthracene and as the tautomer of a paracyclophane. Moreover, elucidation of this chemistry opens new avenues for the synthesis of multicyclic compounds via the MDA tautomer and opportunities to design new adjustable-cavity ligands and complexing agents based on easily available polyhetero [*n*](9,10)anthracenophanes. We therefore initiated an examination of the relative stabilities of the tautomers in the known series of dithia[*n*](9,10)-anthracenophanes **3–5** and **7**.[11]



Molecular mechanics modeling of the tautomers of **3–8**, **9–14**,[12] provides substantial insight into the probable structure and stability of these compounds. Two distinct minima were located for each of the bridged MDAs, and these differ principally in the relative disposition of the sulfurs. PLUTO drawings of these two conformational isomers for MDA **10**, referred to hereafter as S-syn and S-anti, are shown in Figures 1 and 2. Of course, for either *S*-syn or *S*-anti there exists an enantiomeric geometric isomer. The calculated heats of formation and strain energies are included in Table I from which it is apparent that conformational preference depends upon bridge length. Not surprisingly, the *S*-anti conformer consistently exhibits a lower calculated dipole moment. The corresponding anthracene in every case except for **3** has a substantially lower calculated dipole moment[13] than does the lower energy

Table I. Calculated Heats of Formation, Strain Energies, and Dipole Moments for the Methylenedihydroanthracenes 9–14

compd	ΔH_f, kcal/mol	SE, kcal/mol	dipole moment, D
9, *S*-syn	64.6	41.4	1.6
9, *S*-anti	67.2	44.1	0.6
10, *S*-syn	62.1	44.5	3.5
10, *S*-anti	59.5	41.5	2.6
11, *S*-syn	51.1	39.4	3.4
11, *S*-anti	51.4	39.1	2.0
12, *S*-syn	45.0	38.9	3.2
12, *S*-anti	46.4	40.4	1.5
13, *S*-syn	40.7	40.4	2.9
13, *S*-anti	39.1	38.9	1.6
14	35.7	33.1	2.6

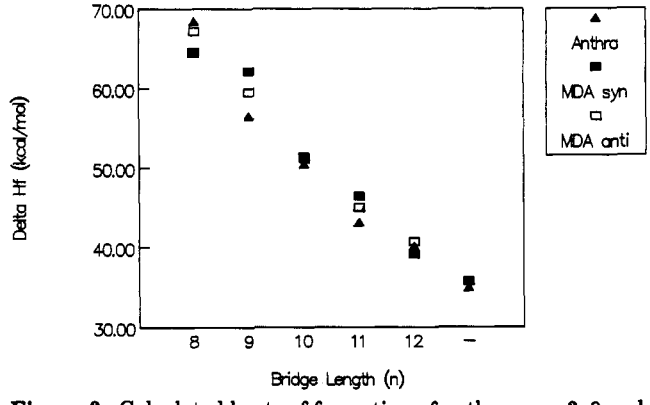
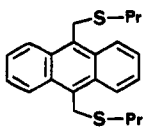


Figure 3. Calculated heats of formation of anthracenes **3–8** and the conformers of methylenedihydroanthracenes **9–14**.

(10) Rosenfeld, S. M.; Shedlow, A. M.; Kirwin, J. M.; Amaral, C. A. *J. Org. Chem.* **1990**, *55*, 1356.
(11) Chung, J.; Rosenfeld, S. M. *J. Org. Chem.* **1983**, *48*, 387.
(12) The IUPAC name for **10**, for example, is 9*H*-9,10-(methanothiopentanothiometheno)anthracene.

(13) Calculated dipole moments for the previously reported[10] lowest energy conformers are **3** (1.4 D), **4** (0.7 D), **5** (0.1 D), **6** (2.9 D), **7** (0.7 D), and **8** (0.3 D).

MDA conformer. The calculated MDA bond angles and torsional angles are generally unexceptional. In *S*-anti **9**, the most strained structure, the largest aliphatic carbon bond angles are ca. 117° and the double bond is twisted 10.3° from planarity. Figure 3 illustrates the relationship between the calculated heats of formation of the MDAs and their anthracene tautomers.[10]



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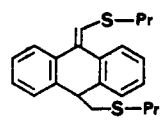

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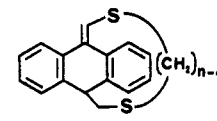

9 n=8 **12** n=11
10 n=9 **13** n=12
11 n=10

When 0.03 M solutions of **3–5**, **7**, and **8** in DMSO-d_6 were treated with ca. 1.5 equiv of sodium methoxide (25 wt %) in methanol, every sample showed ^{1}H NMR evidence of MDA formation on a time scale of minutes. Specifically, the dimunition in size of the starting anthracene peaks was accompanied by growth of new peaks that included, in every case, a singlet at δ 5.77, assignable to the MDA vinyl hydrogen,[14] and aryl multiplets at δ 7.4 and 7.8, as expected for alkyl/vinyl-substituted benzenes. The collapse of the highly characteristic pattern of more widely separated multiplets for 9,10-dialkylanthracenes to this new spectrum is strongly suggestive of conversion to a compound containing isolated benzene rings. Furthermore, the solutions exhibit NMR resonances consistent with expectations for the bridge protons of MDA isomers. For example, in the base-treated sample of **4**, multiplets were present at δ 1.3–1.9 ppm, 2.23, and 2.91 and a 200-MHz COSY spectrum showed the appropriate couplings between the highest field resonances and the two others as well as an additional coupling to a peak at δ 3.2 (benzylic H) that is obscured by solvents in the 1D spectrum. These correspond to the appropriate shift ranges for alicyclic methylene protons adjacent to sulfur and doubly benzylic protons, respectively. The disappearance of the high-field peaks due to methylene protons located over the shielding region of the central part of the anthracene ring in the starting cyclophanes is, again, strong evidence of the anthracene to dihydroanthracene conversion. These spectra are not in agreement with a benzylic carbanion structure since such a species would still exhibit the high-field peaks due to the bridge protons positioned over the anthracene ring and would also show an upfield shift for the carbanion α hydrogen. Additonal broad aryl peaks in some samples suggested formation of small amounts of higher molecular weight material. Very crude MDA/anthracene ratios were determined by integration of appropriate peaks to be **9/3** (20), **10/4** (40), **11/5** (0.3), **13/7** (40), and **14/8** (>50). Lower ratios were observed in samples having less than 1 equiv of base, indicating that this is not a simple base-catalyzed equilibrium.

While we have so far been unable to isolate samples of **9**, **10**, or **11**, our attempts to do so provide additional confirmation of structure. In several tries at quenching the reddish solutions of **9** or **10** in water, we have reisolated the parent anthracene instead. The easy reversibility of this conversion is consistent with both carbanion and MDA structures. A careful quench of a solution of **10** in ice/salt with additional external cooling did afford a crude sample (NMR) of **10**, but a $CDCl_3$ solution of the sample deposited a yellow precipitate on standing in the dark for 2 days, and the NMR spectrum was devoid of peaks due to **10** at that point. The original crude orange solid itself also underwent decomposition within a few days (NMR). Presumably, the instability of these compounds is due to the presence of the relatively short bridge; higher members of this series may be more easily handled.

In summary, we have reported the first spectroscopic observations of bridged methylenedihydroanthracenes, demonstrating that these compounds are accessible via the corresponding [*n*](9,10)anthracenophanes. Though structure and energy calculations suggest similar energies for the members of each tautomeric pair, the higher (calculated) dipole moment of the MDA tautomer was probably important in the consistently high conversions observed in DMSO-d_6 solution.

Experimental Section

Dithia[*n*]anthracenophanes **3–5** and **7** were prepared as previously described.[11] The 25 wt % sodium methoxide in methanol and all solvents for NMR spectroscopy were supplied by Aldrich Chemical Company. NMR measurements were done on a Bruker WP100SY spectrometer except for one COSY spectrum recorded at 200 MHz on a Varian XL200 spectrometer. Chemical shifts are expressed in parts per million downfield from Me_4Si.

General Procedure for ^{1}H NMR Measurements. All NMR spectra except those noted below were recorded on DMSO-d_6 solutions. Dithiacyclophanes were dissolved in the solvent, solutions were filtered, then the appropriate volume of sodium methoxide/methanol solution (25 wt %) was added by syringe, and the solution was mixed. Solutions turned orange-red immediately upon mixing, and the intensity of the color depended upon the amount of added base. NMR spectra were recorded at intervals from a few minutes after mixing to several hours after mixing, but spectra changed very little over a period of ca. 6 h. The dimunition in size of starting compound peaks was dependent upon the amount of base added up to ca. 1 equiv, and all product/starting compound ratios reported in the text refer to solutions containing 1.5 equiv of base.

Our initial attempts to probe this area experimentally met with only very limited success. ^{1}H NMR observations of bridged anthracenes (e.g., in DMSO-d_6 with concentrated DCl/D_2O present) were suggestive of some MDA formation, but rigorous interpretation was confounded by concomitant deuteration of the sample and also decomposition.

Attempted Isolation of MDA Tautomers. A 100-mg sample of **4** was dissolved in 10 mL of DMSO with warming. The solution was cooled to room temperature, 100 μL of sodium methoxide in methanol (25 wt %) was added, and the reaction mixture was mixed thoroughly. After 90 min, the solution was quenched by dropwise addition to ca. 15 mL of ice/salt with additional external cooling. The yellow precipitate was suction filtered and washed with water on the filter. Air drying afforded 43 mg of yellow powder. The ^{1}H NMR spectrum of this material ($CDCl_3$) contained the peaks assigned in the text to aryl and vinyl protons of the MDA tautomer in base-containing DMSO-d_6 solutions of **4**. This NMR sample solution deposited a yellow precipitate upon standing in the dark for 2 days, and all peaks assigned to the MDA tautomer were no longer evident in the spectrum. A sample of the solid product also decomposed completely upon standing for 2 days.

When we mixed samples of the dithiacyclophanes with concentrated H_2SO_4 at temperatures below 0 °C, the green color of the slurry suggested the formation of protonated anthracenes, but rapid quenching with ethanol afforded only higher molecular weight material (as evidence by low solubility and broad NMR peaks), except in the case of model compound **8**, which was simply reisolated upon quenching.

Molecular Mechanics Calculations. We used the MMX87 force field in the computer programs MMX and PCMODEL purchased from Serena Software, P.O. Box 3076, Bloomington, IN 47402-3076. MMX is a derivative of Allinger's MM2 with π VESCF subroutines. The search for low-energy conformations was done by repeated energy minimization from several different starting

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geometries for each compound.

Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this work. We thank Charles Dickenson for running the COSY NMR spectrum at the University of Massachusetts (Amherst) NMR Laboratory.

8-Bromoerythronolide 5,9:6,9-Spiroacetal B: Synthesis, Structure, Conformation, and Nucleophilic Substitution Reactivity

Sergio Auricchio,* Giovanni Fronza, Stefano V. Meille, and Andrea Mele

Dipartimento di Chimica and CNR Centro Sostanze Organiche Naturali, Politecnico di Milano, piazza L. da Vinci 32, 20133 Milano, Italy

Duccio Favara

Pierrel S.p.A., Research laboratories, via Bisceglie 96, 20152 Milano, Italy

Received July 31, 1990

The erythronolides are the aglycons of the erythromycins, important members of the macrolide class of antibiotics. Erythromycin A was first isolated from the fermentation broth of strains of *Saccharopolyspora erythraea* in 1952[1] and from that time on several of synthetic modifications have been investigated. Recently 8-fluoroerythronolides and 8-fluoroerythromicins have been synthesized by using electrophilic fluorinating agents.[2-4] The potential hazard connected with the use of these reagents is a considerable handicap for the industrial development of these derivatives. Alternative pathways, that make use of nucleophilic fluorinating agents, have not been reported in literature to date. Other 8-halogen derivatives, that may be used as substrates for nucleophilic substitution, are not reported in literature.

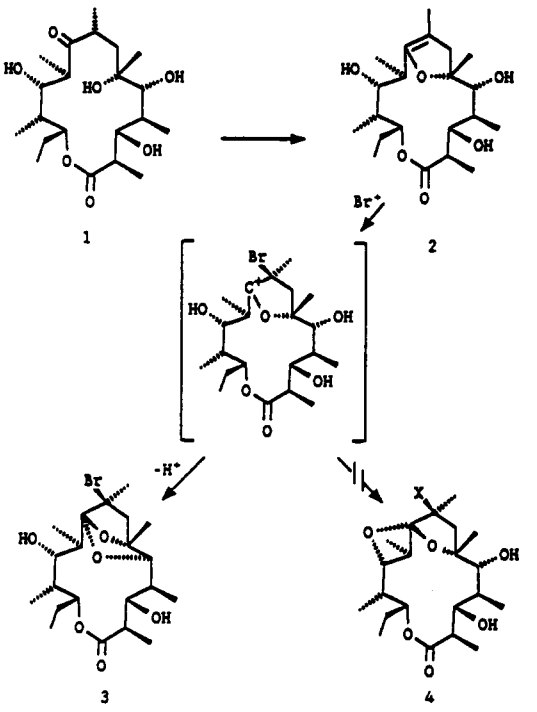
In this paper, we report our efforts for the synthesis of 8-bromoerythronolide B and its reactivity toward nucleophilic substitution. We have chosen as model erythronolide B rather than erythronolide A since the latter affords side products due to the presence of an additional hydroxyl group in position 12.

Results and Discussion

Conversion of erythronolide B (1) to the bromoerythronolide derivative 3 was performed with *N*-bromoacetamide in glacial acetic acid as solvent. The reaction is regio- and stereoselective.

In erythronolide B both positions α to the carbonyl are possibly subject to an easy bromination. Nevertheless the bromination of erythronolide B occurs quantitatively in position 8. This is not surprising, as indeed acid-catalyzed regioselective conversion of erythronolide (1) to its 8,9-anhydro 6,9-hemiacetal derivative 2 is well-known.[5] Derivative 2 is an intermediate of the reaction and is easily converted to bromo derivative 3 with several brominated agents (*N*-bromoacetamide, *N*-bromosuccinimide, sodium hypobromite) in several solvents (acetic acid, ethanol, chloroform) (Scheme I).

Scheme I



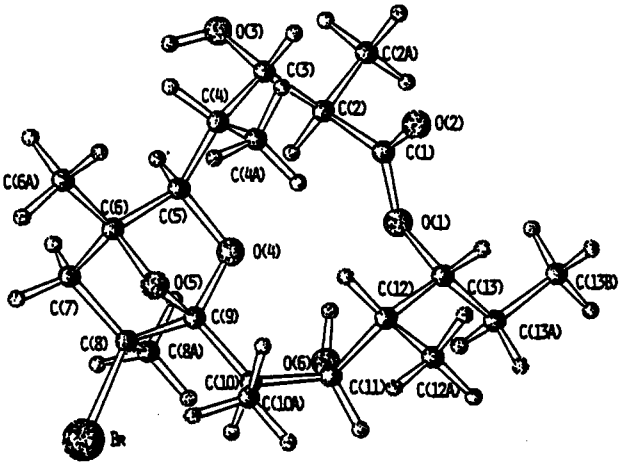


Figure 1. View of the crystal structure of 3.

A quantitative yield was obtained by the reaction of derivative 2 with *N*-bromoacetamide in acetic acid at room temperature. Precipitation of bromo derivative 3 from solvents with different polarity and moisture content yields mixtures in different proportions of two crystalline modifications. This conclusion is supported by the fact that while distinct IR, NMR, and X-ray spectra are obtained from the solids, dissolution of the precipitates gives products with identical IR and NMR spectra. In the present paper only the product crystallized from hexane is discussed; characterization of the second crystalline phase will be presented elsewhere.

Elemental analysis and the IR spectrum (no carbonyl absorption is apparent) of 3 were consistent with the formation of an internal acetal involving the C(9) ketone and the analysis of the X-ray and NMR spectral data proved to be consistent with a 5,9:6,9-spiroacetal.

This class of spiroacetals for the erythronolide ring was previously unknown. The formation of this structure is surprising with respect to what is published in the literature. The reported structures involving spiroacetals at C(9)

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