

differed from each other by only 1–4 kcal/mol. True transition structures (i.e., the structures with only one negative eigen value for the force-constant matrix) for the interchange of these conformers could not be obtained even at the AM1 level because of the large number of basis sets involved. However, the very small differences in the heats of formation of the several conformers suggests the involvement of low activation enthalpies for the rotation around C⁺–C α or C⁺–C α' bonds, as observed here, experimentally.

Olah, Schleyer, and their co-workers introduced a simple criterion for distinguishing classical carbocations from bridged species, based on ¹³C NMR chemical shift additivity.⁸ The summation of ¹³C NMR chemical shifts of the classical carbocations, as compared with those of their corresponding neutral hydrocarbons, are typically very large, and their difference corresponds to about 350 ppm (or more). The differences in the summation of the chemical shifts for the nonclassical carbocations, on the other hand, is much smaller, usually being less than 200 ppm. Since *trans*-1,2-bis(dicyclopropylmethyl)cyclopropane is not a known compound, we have estimated its additive ¹³C NMR chemical shift value as 169 ppm by subtracting 100 ppm from the value for the diol, the latter value being the usual chemical shift difference of di-tertiary alcohols and their hydrocarbon analogs.⁹ The additive ¹³C chemical shift value for the dication at –50 °C is 1062 ppm. The difference of the summation of the chemical shifts ($\Delta\Sigma\delta$) correspond to 893 ppm, which is nearly double the value for a typical classical monocarbocation, and is similar to those of 1,5-bicyclo[3.3.3]undecyl (830) and 2,5-dimethyl-2,5-hexyl dication (758).⁸ Thus, the dication 7 shows “classical” behavior, with substantial charge delocalization into the adjacent cyclopropane carbons. It is a rather unique bis-cyclopropylcarbinyl carbodication.

(8) Schleyer, P. v. R.; Lenoir, P.; Mison, P.; Liang, G.; Prakash, G. K. S.; Olah, G. A. *J. Am. Chem. Soc.* 1980, 102, 683–691.

(9) Stothers, J. B. *Carbon-13 NMR Spectroscopy*; Academic Press: New York, 1972.

Experimental Section

Diethyl ether was distilled from sodium benzophenone ketyl immediately before use. Lithium metal, cyclopropyl bromide, and 2-adamantanone were obtained from Aldrich Chemical Co. and used as received. SbF₅ and FSO₃H were freshly distilled before use. ¹H and ¹³C NMR spectra were recorded on a Varian Unity-300 or a Bruker-360 instrument equipped with a variable-temperature probe. The ¹H and ¹³C NMR chemical shifts for the carbocations were referenced with respect to the external capillary tetramethylsilane.

***trans*- $\alpha,\alpha,\alpha',\alpha'$ -Tetracyclopropylcyclopropane-1,2-dimethanol (6).** Shiny plates of lithium wire (sodium content 1%; 1.4 g, 0.2 mol) in 20 mL of dry ether were cooled to 0 °C, and cyclopropyl bromide (7.81 g, 64.5 mmol) in 10 mL of ether was added dropwise and stirred. The formation of the cyclopropyl-lithium was exothermic, and the ether refluxed during the addition. After being stirred for an additional 30 min at 0 °C, a solution of *trans*-cyclopropane-1,2-dicarboxylate (2 g, 10.75 mmol) in 10 mL of ether was added and stirred at rt for 1 h and was followed by refluxing for an additional hour. The contents were poured into 100 mL of ice-cold water, and the organic layers were extracted with ether (3 \times 30 mL), washed with saturated NaHCO₃, dried (MgSO₄), and filtered. The solvents were removed on a rotary evaporator. Compound 6 (0.6 g, 21%) was obtained as white crystals after two recrystallizations from pentane at –78 °C: mp 65–68 °C; ¹H NMR (C₆D₆) δ 1.2 (apparent t, *J* = 7.5 Hz, 2 H), 0.96 (br s, 2 H, OH), 0.46–0.8 (overlapping m, 14 H), 0.2–0.3 (m, 8 H); ¹³C NMR (C₆D₆) δ 69.2 (C–OH), 23.1 (C1,C2), 19.8 and 19.1 (C α and C α'), 4.4 (C3), 0.51, 0.36, 0.23 and 0.12 (C β , C γ , C β' , and C γ').

***trans*-Cyclopropane-1,2-diylbis(dicyclopropylmethyl-ium) Dication (7).** A 5-fold excess of Magic Acid (1:1 SbF₅ and FSO₃H) in SO₂ClF was added to a suspension of the alcohol 2 in SO₂ClF, contained in a 5-mm NMR tube, at –78 °C in a dry ice–acetone bath, resulting in an approximately 10% solution of the dication 7. Efficient mixing of the solution was effected using a vortex stirrer.

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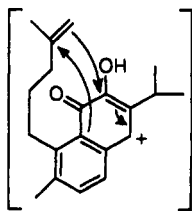
Supplementary Material Available: NMR spectra of 6 and 7 (4 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

Additions and Corrections

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María J. Sexmero Cuadrado, María C. de la Torre, Long-Ze Lin, Geoffrey A. Cordell, Benjamín Rodríguez, and Aurea Perales. Cyclization Reactions of the *o*-Naphthoquinone Diterpene Aethiopinone. A Revision of the Structure of Prionitin.

Page 4725, column 1, Scheme I. The first intermediate should be



Manuel Debono, R. Michael Molloy, John L. Occolowitz, Jonathan W. Paschal, Ann H. Hunt, Karl H. Michel, and James W. Martin. The Structure of A10255B, -G, and -J: New Thiopeptide Antibiotics Produced by *Streptomyces gardneri*.

Page 5202. Reference 5 should read as follows: Matsumoto, M.; Kawamura, Y.; Yasuda, Y.; Tanimoto, T.; Matsumoto, K.; Yoshida, T.; Shoji, J. *J. Antibiot.* 1989, 42, 1465. We would like to thank the authors of this reference for graciously providing us with NMR data which arrived as our publication went to press. Employing 2D long range ¹³C–¹H COSY spectra, as expected, their data fully support their structural assignments for thioxamycin including the presence of a tetra-deala string in the reference cited here.