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# *trans*-Cyclopropane-1,2-diylbis(dicyclopropylmethylium) Dication, a Unique Cyclopropyl Stabilized Carbodication[1a]

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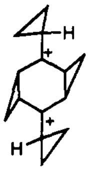
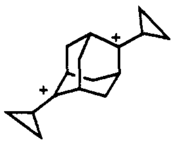
## Introduction

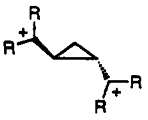
There has been considerable interest in the study of carbodications, both theoretically and experimentally.[2] The carbodications, being doubly positive charged species, exert increased electron demand on the neighboring groups. The charge–charge repulsion leads to the increasing destabilization of the dication when the charged centers are close to each other. Generally, strong electron-releasing groups such as phenyl help to stabilize carbodications.[3] Cycloalkyl carbodications stabilized by cyclopropyl groups, such as 2,6-dicyclopropyl-*anti*-tricyclo[5.1.0.0$^{3,5}$]octane-2,6-diyl dication (**1**)[4] and 2,6-dicyclopropyl-2,6-adamantanediyl dication (**2**)[5] were also prepared. The cationic centers in stable carbodications are generally separated by at least two carbon atoms from each other.



**1**



**2**



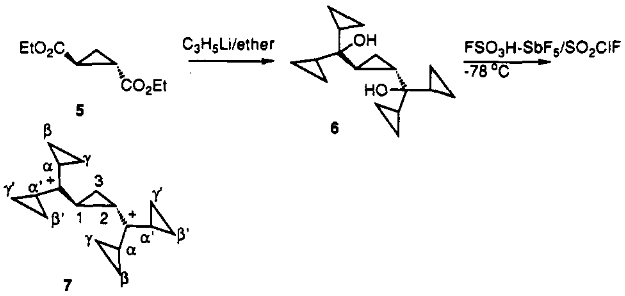
**3**, R = Ph
**4**, R = Me

An acyclic cyclopropanediyldicarbinyl dication stabilized by phenyl groups, i.e., *trans*-cyclopropane-1,2-ylbis(diphenylmethylium) dication (**3**) was reported previously.[3] The dication **3** shows significantly enhanced delocalization of the positive charge into the aromatic rings, compared to the analogous monocation, the diphenylcyclopropylmethyl cation. The cyclopropane ring of the dication **3** also partially stabilizes the carbocationic centers.

Attempts to prepare the corresponding tetramethyl analog, **4**, afforded only the ring-opened product, 2,6-dimethylhepta-3,5-dien-2-yl cation[3], showing that methyl groups are ineffective in stabilizing the dicationic species. The effect of neighboring cyclopropyl groups on the stabilization of the cyclopropane-1,2-diyldicarbinyl dication represents an intriguing challenge. We now report the preparation and $^{13}$C NMR spectral characterization of the *trans*-cyclopropane-1,2-diylbis(dicyclopropylmethylium) dication (**7**), a quite remarkable, stable biscyclopropylcarbinyl carbodication.

## Results and Discussion

*trans*-Diethyl cyclopropane-1,2-dicarboxylate reacted with cyclopropyllithium to give diol **6**. The diol **6** was ionized with $SbF_5/FSO_3H–SO_2ClF$ at −78 °C, resulting in the formation of a light-orange solution of the dication **7**.



The dication **7** showed the following $^{13}$C NMR absorptions at −73 °C. δ($^{13}$C): 39.3 (Cα, Cα′), 37.6, 37.3, 35.9, 34.9, 33.7, 32.5 (C3), and 264.1 (C$^+$). The five absorptions from 37.6 to 33.7 most probably arise from the four distinct cyclopropane methylene carbons and the C1, C2 carbons. Upon warming to −50 °C, the absorptions for the C$^+$, Cα, Cα′, and C3 remained relatively unaltered, appearing at δ($^{13}$C) 264.5 (s), 39.9 (d, $J$ = 175 Hz), and 33.0 (t, $J$ = 178 Hz). The remaining absorptions coalesced to give a broad signal at δ($^{13}$C) 37.3. Cooling the cation again to −73 °C resulted in the regeneration of the original multiline spectrum, showing that the cation exhibits reversible temperature-dependent behavior of its $^{13}$C NMR spectrum. Quenching of the solution with methanol at −78 °C was inconclusive since largely decomposed compounds were observed.

The equivalence of the Cα and Cα′ signals at −73 °C indicates an extremely low barrier to rotation around the C$^+$–C1 or C$^+$–C2 bond. The barrier to rotation around the C$^+$–Cα or C$^+$–Cα′ bond is also very small, on the order of 10–12 kcal/mol (an estimate), as all the absorptions due to the cyclopropane methylenes (Cβ, Cβ′, Cγ, and Cγ′) coalesced at only −50 °C. It is also interesting to note that the carbocation center of tricyclopropylcarbinyl cation[6] shows δ($^{13}$C) at 280.5, much deshielded (16 ppm) from the corresponding absorption for **7**. The carbodication **7**, therefore, is significantly stabilized by delocalization involving the four peripheral cyclopropane rings. The delocalization from the central cyclopropane ring is relatively weak, which is indicated by the extremely low barrier for the rotation around C$^+$–C1 or C$^+$–C2 bonds, as shown by the equivalence of the Cα and Cα′ methine carbons.

Several conformers of the dication involving the rotations of C$^+$–Cα or C$^+$–Cα′ bonds were optimized using tripos force field and at MNDO and AM1 levels.[7] The heats of formation of these conformers (energy minima as shown by the frequency calculations) ranged from 540 to 557 kcal/mol at AM1 level, and many of these conformers

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[1] (a) Stable Carbocations. 290. Part 289: Olah, G. A.; Reddy, V. P.; Casanova, J.; Prakash, G. K. S. *J. Org. Chem.*, in press. (b) California State University, Los Angeles, CA.

[2] For a review, see: Prakash, G. K. S.; Rawdah, T. N.; Olah, G. A. *Angew Chem., Intl. Ed. Engl.* **1983**, *22*, 390–401.

[3] Olah, G. A.; Grant, J. L.; Spear, R.-J.; Bollinger, J. M.; Seroamz, A.; Sipos, G. *J. Am. Chem. Soc.* **1976**, *98*, 2501–2507.

[4] Prakash, G. K. S.; Fung, A. P.; Rawdah, T. N.; Olah, G. A. *J. Am. Chem. Soc.* **1985**, *107*, 2920–2923.

[5] Prakash, G. K. S.; Krishnamurthy, V. V.; Arvanaghi, M.; Olah, G. A. *J. Org. Chem.* **1985**, *50*, 3985–3988.

[6] Olah, G. A.; Westerman, P. W.; Nishimura, J. *J. Am. Chem. Soc.* **1974**, *96*, 3548–3559.

[7] The calculations were carried out using Version 4.00, from Frank J. Seiler Research Laboratory, U.S. Air Force Academy, Colorado Springs, CO 80840, or by using the Spartan program on IBM RS-6000 work station.

0022-3263/93/1958-1639$04.00/0

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 $C^+$–$C\alpha$ or $C^+$–$C\alpha'$ bonds, as observed here, experimentally.

Olah, Schleyer, and their co-workers introduced a simple criterion for distinguishing classical carbocations from bridged species, based on $^{13}C$ NMR chemical shift additivity.[8] The summation of $^{13}C$ 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 $^{13}C$ 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 $^{13}C$ chemical shift value for the dication at −50 °C is 1062 ppm. The difference of the summation of the chemical shifts ($\Delta\sum\delta$) 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.

## 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. $SbF_5$ and $FSO_3H$ were freshly distilled before use. $^1H$ and $^{13}C$ NMR spectra were recorded on a Varian Unity-300 or a Bruker-360 instrument equipped with a variable-temperature probe. The $^1H$ and $^{13}C$ NMR chemical shifts for the carbocations were referenced with respect to the external capillary tetramethylsilane.

***trans*-α,α,α′,α′-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 cyclopropyllithium 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 × 30 mL), washed with saturated $NaHCO_3$, dried ($MgSO_4$), 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 ($C_6D_6$) $\delta$ 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); $^{13}C$ NMR ($C_6D_6$) $\delta$ 69.2 (C-OH), 23.1 (C1,C2), 19.8 and 19.1 ($C\alpha$ and $C\alpha'$), 4.4 (C3), 0.51, 0.36, 0.23 and 0.12 ($C\beta$, $C\gamma$, $C\beta'$, and $C\gamma'$).

***trans*-Cyclopropane-1,2-diylbis(dicyclopropylmethylium) Dication (7).** A 5-fold excess of Magic Acid (1:1 $SbF_5$ and $FSO_3H$) in $SO_2ClF$ was added to a suspension of the alcohol **2** in $SO_2ClF$, 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.

**Acknowledgment.** Support of our work by the National Institutes of Health is gratefully acknowledged.

**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.

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(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.

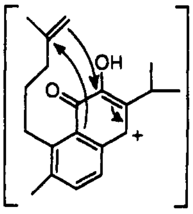
(9) Stothers, J. B. *Carbon-13 NMR Spectroscopy*; Academic Press: New York, 1972.

# *Additions and Corrections*

Vol. 57, 1992

**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 $^{13}C$–$^1H$ 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.