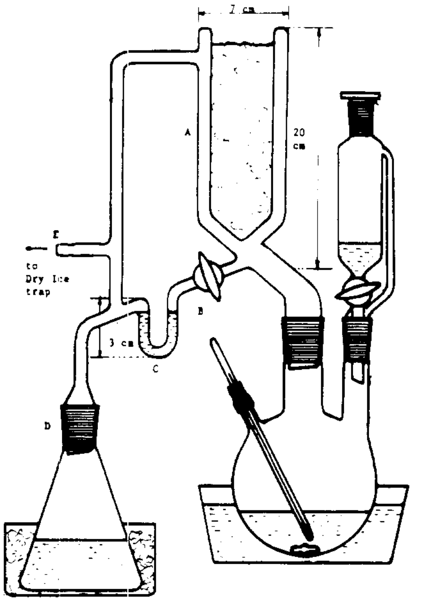

Figure 1.

moved during the whole operation, the only mobile parts being the Teflon-coated stirring bar and two Teflon stopcocks. The apparatus is disassembled only when all the diazomethane solution has distilled off.

Just to be on the safe side, all other precautions necessary for the work with diazomethane[1,2] such as working in a hood with the hood door of shatter-proof glass, etc.[1,2] were strictly observed.

Registry No. Diazomethane, 334-88-3.

Synthesis of the C_{2v}- and S_4-Symmetric Tetraesters of Tricyclo[3.3.0.0^{3,7}]octane

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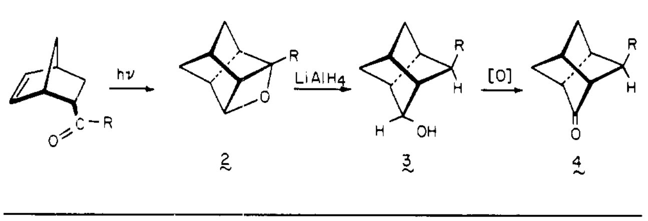
The tricyclo[3.3.0.0^{3,7}]octane ring system (1) brings to

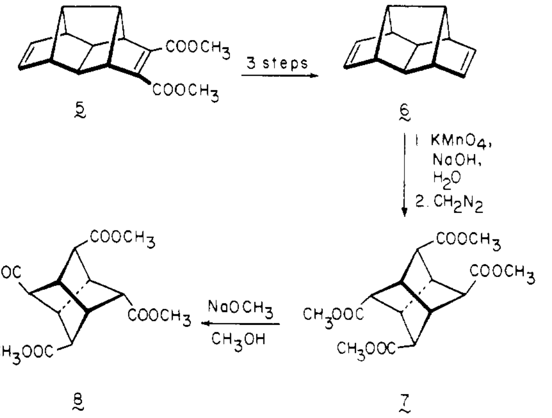
1

the polyquinane field[1] the same degree of fascination which tetrahedrane, cubane, and adamantane offer to the alicyclic chemistry of polycondensed three-, four-, and six-membered rings, respectively. Despite the highly symmetrical arrangement of the fused cyclopentane rings within 1, its properties have not been widely exploited. Sauers and co-workers have developed an apparently general approach to tricyclo[3.3.0.0^{3,7}]octan-2-ols (3) which consists of the Paterno–Büchi photocyclization of *endo*-5-acylnorbornenes followed by reductive cleavage of the resultant oxetanes 2.[2] Oxidation of 3 affords the ketones 4 to which Windhorst has assigned the trivial name "natones" to emphasize the relationship of their four-pointed-star appearance to the NATO symbol.[3] Although other syntheses of this ring system are known,[4] none have provided access to derivatives having more than one functional group at the secondary sites. It has already been made clear that care must be exercised in handling certain monosubstituted tricyclo[3.3.0.0^{3,7}]octanes since they are particularly prone to rearrangement.[2c,4d,5]



In this note, we detail a convenient synthesis of two highly symmetric tetracarboxylate esters of 1 and make mention of certain observations which relate to the sensitivity of these molecules.

Our strategy centered around the diene 6 which we have earlier shown to be available by three-step chemical manipulation[6] of 5, a domino Diels–Alder adduct of 9,10-dihydrofulvalene and dimethyl acetylenedicarboxylate.[7] This diene possesses, in somewhat masked form, the complete tricyclo[3.3.0.0^{3,7}]octane framework (note the cross-hatched arrangement of upper and lower bonds in the central region of the molecule) and a pendant carbon atom at each of the five-membered rings. Ozonolysis of 6 under a variety of conditions followed by oxidative workup (H_2O_2, MCPBA, etc.) led invariably to a mixture of difficulty separable materials, esterification of which provided no detectable amounts of the desired tetraester 7. The ^1H NMR spectra of the residues indicated clearly that no 6 remained and suggested that skeletally rearranged materials had been produced (no evidence of symmetry). Previously, we had demonstrated that the perhydromethenocyclopenta[*a*]pentalene framework which 6 possesses is particularly susceptible to cationic Wagner–Meerwein shift.[8] Conceivably, therefore, electrophilic attack by ozone at the double bonds in 6 is accompanied by framework isomerization. Whatever the difficulty, the problem persisted when 6 was treated with potassium permanganate in dry acetone at room or reflux temperature for varying amounts of time.[9]



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(1) Paquette, L. A. *Fortschr. Chem. Forsch.* **1979**, *79*, 43.

(2) (a) Sauers, R. R.; Schinski, W.; Mason, M. M. *Tetrahedron Lett.* **1969**, 79. (b) Sauers, R. R.; Sickles, B. R. *Ibid.* **1970**, 1067. (c) Sauers, R. R.; Kelly, K. W.; Sickles, B. R. *J. Org. Chem.* **1972**, *37*, 537.

(3) Windhorst, J. C. A., Ph.D. Dissertation, University of Leiden, 1975.

(4) (a) Webster, O. W.; Sommer, L. H. *J. Org. Chem.* **1964**, *29*, 3103. (b) Freeman, P. K.; Rao, V. N. M.; Bigam, G. E. *Chem. Commun.* **1965**, 511. (c) Vogt, B. R.; Suter, S. R.; Hoover, J. R. E. *Tetrahedron Lett.* **1968**, 1609. (d) Freeman, P. K.; Kinnel, R. B.; Ziebarth, T. D. *Ibid.* **1970**, 1059.

(5) Nickon, A.; Weglein, R. C. *J. Am. Chem. Soc.* **1975**, *97*, 1271.

(6) (a) Paquette, L. A.; Wyvratt, M. J. *J. Am. Chem. Soc.* **1974**, *96*, 4671. (b) McNeil, D.; Vogt, B. R.; Sudol, J. J.; Theodoropoulos, S.; Hedaya, E. *Ibid.* **1974**, *96*, 4673.

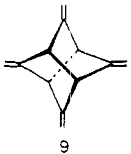
(7) (a) Snow, R. A.; Degenhardt, C. R.; Paquette, L. A. *Tetrahedron Lett.* **1976**, 4447. (b) Paquette, L. A.; Wyvratt, M. J.; Berk, H. C.; Moerck, R. E. *J. Am. Chem. Soc.* **1978**, *100*, 5845.

(8) Battiste, M. A.; Timberlake, J. F.; Paquette, L. A.; Degenhardt, C. R.; Martin, J. T; Hedaya, E.; Su, T. M.; Theodoropoulos, S. *J. Chem. Soc., Chem. Commun.* **1977**, 941.

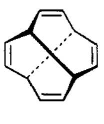
Success was achieved upon reaction of a suspension of **6** in water containing sodium hydroxide with 3 equiv of potassium permanganate at 0 °C for 1 h and at room temperature for 15 h. After filtration, acidification with hydrochloric acid, and freeze drying, the crude carboxylic acid was esterified with diazomethane in ether. After separation of the inorganic salts, **7** was obtained in 51% yield. Structural identification is based on the simplified ^{1}H NMR spectrum which consists of singlets at δ 3.85 (2 H) and 3.57 (12 H), a multiplet of area 4 at δ 3.24, and a two-proton doublet (J = 2 Hz) at δ 2.75. The five-line ^{13}C NMR spectrum was particularly confirmatory of the molecule's C_{2v} symmetry.

No epimerization occurred when **7** was treated with sodium hydroxide in anhydrous methanol (reflux, 6 h) or with catalytic amounts of sodium methoxide in the same solvent (25 °C, 12 h). Whereas equimolar amounts of sodium methoxide in hot methanol (reflux, 3 h) led to decomposition and/or polymerization, catalytic quantities of the same base (reflux, 6 h) resulted in complete conversion to **8**. After silica gel chromatography, the colorless crystalline solid was found to exhibit a ^{1}H NMR spectrum consisting of three peaks at δ 3.59 (s, 12 H), 2.97 (m, 4 H), and 2.46 (m, 4 H). In agreement with the S_4 symmetry of this tetraester, its ^{13}C NMR spectrum is characterized by only four signals.

Many attempts to achieve the reduction of **8** were made with Red-Al, lithium aluminum hydride, or diisobutylaluminum hydride. None proved successful in delivering the tetraol; nor was **8** recovered in most cases. The apparently high sensitivity of the intended product has precluded us from proceeding with the elaboration of tetraenes **9** and **10**[10] until alternative workable procedures are devised.



9



10

Experimental Section

2,4,6,8-*syn,syn*-Tricyclo[3.3.0.0^{3,7}]octanetetracarboxylic Acid. To a suspension of **6** (0.029 g, 0.186 mmol) in 10 mL of water containing 41 mg of sodium hydroxide was added potassium permanganate (0.164 g, 1.038 mmol) at 0 °C with stirring. After 1 h, the reaction mixture was allowed to warm to room temperature where it was stirred for 15 h. The mixture was filtered and the manganese dioxide cake was washed with 20 mL of hot water. The combined filtrate and washing was acidified to pH 1–2 with concentrated hydrochloric acid. After the removal of water by freeze-dry techniques, the white solid which remained was used for further reaction without purification.

2,4,6,8-*syn,syn*-Tetrakis(carbomethoxy)tricyclo[3.3.0.0^{3,7}]octane (7). The crude tetracarboxylic acid from above was treated with excess diazomethane in ether. Since the resulting tetramethyl ester is soluble in ether, the inorganic salts were removed by filtration. After concentration of the filtrate, there remained 0.032 g (51%) of **7** which was recrystallized from methanol: mp 206.0–207.0 °C; ^{1}H NMR (CDCl$_3$) δ 3.85 (s, 2 H), 3.57 (s. 12 H), 3.24 (m, 4 H), 2.75 (d, J = 2 Hz, 2 H); ^{13}C NMR (CDCl$_3$) 171.84, 59.01, 51.80, 43.57, 42.92 ppm.

Anal. Calcd for $C_{16}H_{20}O_8$: C, 56.47; H, 5.92. Found: C, 56.88; H, 6.35.

2,4,6,8-*anti,anti*-Tetrakis(carbomethoxy)tricyclo[3.3.0.0^{3,7}]octane (8). A solution of sodium methoxide was prepared by dissolving 0.1 g of sodium metal in 25 mL of dry methanol under an argon atmosphere. To a solution of **7** in 15 mL of methanol was added a few drops of the sodium methoxide solution and the mixture was heated to the reflux temperature for 6 h. After the reaction mixture was cooled and concentrated, a quantitative yield of **8** was obtained as a colorless solid: mp 203.5–204.5 °C (after sublimation); ^{1}H NMR (CDCl$_3$) δ 3.59 (s, 12 H), 2.97 (m, 4 H), 2.46 (m, 4 H); ^{13}C NMR (CDCl$_3$) 172.49, 55.30, 52.04, 42.63 ppm.

Anal. Calcd for $C_{16}H_{20}O_8$: C, 56.47; H, 5.92. Found: C, 56.28; H, 6.07.

Acknowledgment. This investigation was financed by a research grant from the National Institutes of Health (Grant AI-11490).

Registry No. 6, 53283-11-7; **7**, 75599-73-4; **8**, 75658-51-4; 2,4,6,8-*syn,syn*-tricyclo[3.3.0.0^{3,1}]octanetetracarboxylic acid, 75599-74-5.

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(9) (a) Cope, A. C.; Moon, S.; Park, C. H. *J. Am. Chem. Soc.* **1962**, *84*, 4843. (b) Akhtar, I. A.; Fray, G. I.; Yarrow, J. M. *J. Chem. Soc. C* **1968**, 812. (c) Alder, K.; Hartmann, R.; Roth, W. *Justus Liebigs Ann. Chem.* **1958**, *613*, 6. (d) Cristol, S. J.; Seifert, W. K.; Soloway, S. B. *J. Am. Chem. Soc.* **1960**, *82*, 2351. (e) Hanna, E. R.; Finley, K. T.; Saunders, W. H., Jr.; Boekelheide, V. *Ibid.* **1960**, *82*, 6342. (f) Youngblood, G. T.; Wilder, P., Jr. *J. Org. Chem.* **1956**, *21*, 1436. (g) Playtis, A. J.; Fissekis, J. D. *Ibid.* **1975**, *40*, 2488. (h) Birch, S. F.; Oldham, W. J.; Johnson, E. A. *J. Chem. Soc.* **1947**, 818. (i) Sam, D. J.; Simmons, H. E. *J. Am. Chem. Soc.* **1972**, *94*, 4024.

(10) For other attempts to prepare **10**, see: (a) Vedejs, E.; Wilber, W. R.; Tureg, R. *J. Org. Chem.* **1977**, *42*, 401; (b) Miyashi, T.; Kawamoto, H.; Nakajo, T.; Mukai, T. *Tetrahedron Lett.* **1979**, 155; (c) Aumann, R. *Angew. Chem., Int. Ed. Engl.* **1976**, *15*, 376.

1-Semibullvalenylcarbinyl Cation

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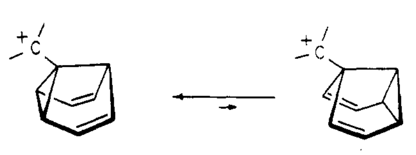
Because the CH$_2^+$ substituent is simultaneously a powerful σ withdrawer and a very strong π acceptor, cyclopropane rings are capable of exhibiting an intense stabilizing interaction with an adjacent carbocation center if conformationally bisected.[1,2] In their theoretical consideration of the 1(5)-semibullvalenylcarbinyl cation (1),



a

b

1

Hoffmann and Stohrer showed through calculation that bond order and overlap population changes expectedly favor overwhelming adoption of that valence tautomeric form in which the charge-deficient carbon is bonded to position 1 as in **1a**.[3] Due to the high reactivity of semibullvalene derivatives in general, we considered it unlikely that **1** would persist in solution for any length of time.[4] Nonreversible electronic shifts were anticipated. The nature of these cationic isomerizations were considered of

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(1) Radom, L.; Pople, J. A.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1972**, *94*, 5935.

(2) Hehre, W. J. "Modern Theoretical Chemistry"; Schaefer, H. F., III, Ed.; Plenum Press: New York, 1977; Vol. 4, pp 277–331.

(3) Hoffmann, R.; Stohrer, W.-D. *J. Am. Chem. Soc.* **1971**, *93*, 6941.

(4) (a) Cristol, S. J.; Schloemer, G. C.; James, D. R.; Paquette, L. A. *J. Org. Chem.* **1972**, *37*, 3852. (b) Paquette, L. A.; Birnberg, G. H. *Ibid.* **1975**, *40*, 1709.