

STUDIES IN CARBOTRICATIONS:  
PREPARATION AND CARBON-13 NUCLEAR  
MAGNETIC RESONANCE SPECTROSCOPIC  
STUDY OF 3,7,9-TRIHYDRO TETRACYCLO  
[3.3.1.0<sup>2,8</sup>.0<sup>4,6</sup>] NONANE-3,7,9-  
TRIYLTRICATION: A TRI-  
PROTONATED TETRACYCLO-[3.3.1.0<sup>2,8</sup>.0<sup>4,6</sup>]   
NONANE-3,7,9-TRIONE AND ATTEMPTED  
PREPARATION OF  
RELATED TRICATIONS

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**Abstract**

Synthetic approaches have been described for the preparation of precursors to triasterane trications and related carboxenium ions. The investigation on carbocationic intermediates from treatment of these precursors with FSO<sub>3</sub>H/SbF<sub>5</sub>/SO<sub>2</sub>ClF system has led to the preparation and <sup>13</sup>C-NMR spectroscopic characterization of the isomeric 3,7,9-tri-hydrote-tracyclo [3. 3.1. 0<sup>2,8</sup>. 0<sup>4,6</sup>] nonane-3,7,9-triyltrications.

**Introduction**

Cyclopropylmethyl and related cations continue to receive considerable attention [1-3]. Cyclopropylmethyl cations are generally stable [3-5], and the direct observation of a variety of cyclic and acyclic cyclopropylmethyl cations by NMR spectroscopy provides clear examples that cyclopropyl groups have a strong stabilizing effect on neighboring carbocation centers by delocalizing charges through bent  $\sigma$ -bonds ( $\pi\sigma$  or banana bonds) [5-9].

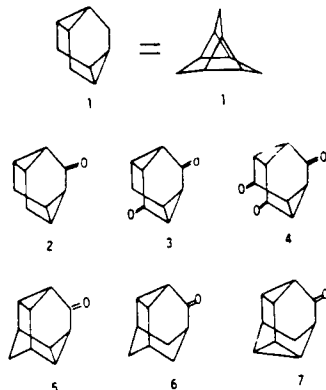
It has been generally conceded that substantial stabilization arises when there is complete overlap of an empty

p orbital with the exocyclic cyclopropane ring orbitals which are rich in p-character; that is when the plane of carbinyl cation bisects the cyclopropyl ring [4]. Molecular orbital calculations indicate that there is a variation in stabilization of 9-26 kcal/mole between **a** and **b**, the bisected and perpendicular conformations, respectively [10-12].



**Keywords:** Carbotrications; NMR of carbotrications

Strained dicyclopentyl ketones comprise an interesting class of compounds for carbocation studies. In this context, ketones 2-7 offer access to a variety of polycyclic carbocations, [13-19].

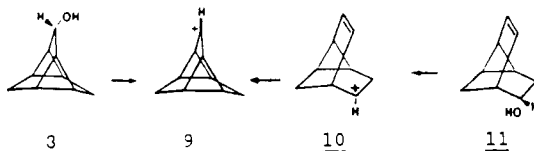


The triasterane skeleton **1** is of particular interest since all six cyclopropyl methylene bridge bonds ideally "bisect" a cyclopropane ring, and therefore the orbitals of any trigonal bridge carbon atoms are favorably disposed for a strong interaction.

Reaction of triasteranol **8** with  $\text{FSO}_3\text{H}$  at  $-30^\circ\text{C}$  produced species which according to  $^1\text{H}$ -NMR spectrum attribute to the triasteryl cation **9** [13]. Similarly, when rearranged alcohol **11** was subjected to  $\text{FSO}_3\text{H}$  at  $-70^\circ\text{C}$  it too provided a  $^1\text{H}$ -NMR spectrum with a wide range of absorptions that were subsequently assigned to both cations **9** and **10**. Quenching this solution formed the starting alcohols **8** and **11** [14].

These and other interesting observations led us to focus our attention on triasteranetrione and its derivatives for possible carbocationic studies.

Triasterane **1** and its derivatives have been prepared by

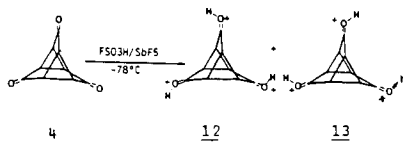


several methods [16-18].

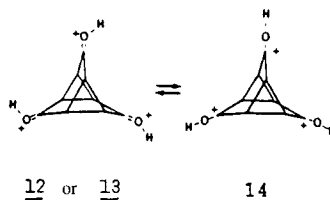
## Results and Discussion

We have investigated carbocations formed under stable ion conditions from various tetracyclic precursors of triasterane skeleton.

Treatment of triasteranetrione **4** in  $\text{FSO}_3\text{H}/\text{SbF}_5/\text{SO}_2\text{ClF}$  at  $-78^\circ\text{C}$  gave a yellow-colored solution whose  $^{13}\text{C}$  NMR spectra were consistent with the isomeric oxycarbenium ions **12** and **13**.



The diagnostic  $^{13}\text{C}$  NMR chemical shifts are shown in Table 4.1. Protonated tetracyclotrione obtained from ketone **4** in  $\text{FSO}_3\text{H}/\text{SO}_2\text{ClF}/\text{SbF}_5$  at  $-78^\circ\text{C}$  can be considered as a model 3,7,9-trihydroxy-tetracyclo [3.3.1.0<sup>2,8</sup>.0<sup>4,6</sup>] -nonane-3,7,9-triyl trication **14**. Comparing its  $^{13}\text{C}$  shifts to the shifts of the precursor, the protonated carbonyl carbons are deshielded by 21.5 ppm, but at the same time there is little deshielding of the cage carbon atoms. The shifts indicate that the contribution from the structure **14** is not extensive.



**Table 1.**  $^{13}\text{C}$ -NMR data for 3,7,9-trihydro - tetracyclo-[3.3.1.0<sup>2a</sup>.0<sup>4a</sup>] nona-3,7,9-trityl trications **12** and **13** and its progenitor triasterane-3,7,9 trione **4**

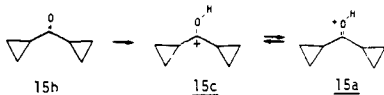
Substrate	$^{13}\text{C}_a$
<b>Trication<sup>b</sup></b>	
Ion <b>12</b>	42.9 (C <sub>1</sub> , C <sub>2</sub> , C <sub>4</sub> , C <sub>5</sub> , C <sub>6</sub> , and C <sub>8</sub> ) 215.76 (C <sub>3</sub> , C <sub>7</sub> , and C <sub>9</sub> )
Ion <b>13</b>	39.6 (C <sub>2</sub> and C <sub>4</sub> ) 44.09 (C <sub>1</sub> , C <sub>5</sub> , C <sub>6</sub> and C <sub>8</sub> ) 211.58 (C <sub>3</sub> ) 220.49 (C <sub>7</sub> and C <sub>9</sub> )
<b>Triketone 4c</b>	
	35.2 (C <sub>1</sub> , C <sub>2</sub> , C <sub>4</sub> , C <sub>5</sub> , C <sub>6</sub> , and C <sub>8</sub> ) 194.36 (C <sub>3</sub> , C <sub>7</sub> , and C <sub>9</sub> )

a: Chemical shifts in ppm from external tetramethyl silane

b: In 1:4  $\text{SbF}_5/\text{HSO}_3\text{F}/\text{SO}_2\text{ClF}$  at  $-85^\circ\text{C}$

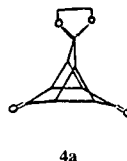
c: In  $\text{C}_5\text{D}_8\text{N}$  at  $22^\circ\text{C}$

When comparing  $^{13}\text{C}$  chemical shifts differences of **13** and **14** to the differences in  $^{13}\text{C}$  chemical shifts of protonated dicyclopropyl ketone **15a** and dicyclopropyl ketone **15b**, it is seen that the former is about 6 ppm less than the latter, indicating the rigidity of the cage system [20].



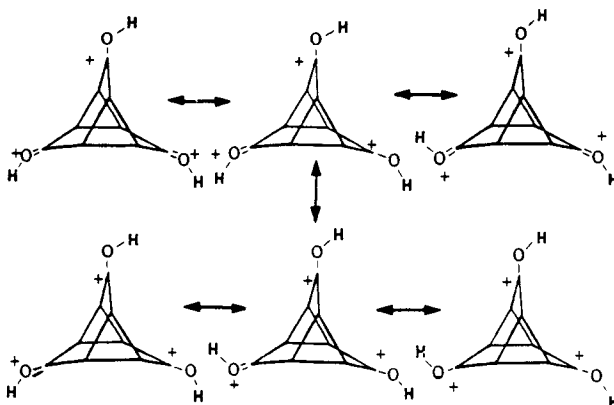
Contribution from the structure **15c** seems to be more significant in protonated dicyclopropyl ketone as the  $\alpha$ -carbon shifts are more deshielded than those of other protonated higher cyclic homologues. Thus, the contribution from structure **14** is more limited as the cage ring carbons show no significant deshielding. This conclusion may be, however, somewhat ambiguous as the rigid cage structure may not allow sufficient predictions to be made from  $^{13}\text{C}$  NMR shifts as to the carbocationic nature of **13**. Scheme 1 exhibits possible isomer forms of the carboxenium ions **13** and **14**.

Our attempts to functionalize **4** by phenyl and methyl Grignard reagents have been unsuccessful due to limited solubilities in common solvents. The precursor of **4**,



monoacetal **4a**, was, as expected, dissolved easily in cyclic ethers, but its functionalization using similar procedures was tedious and no isolable products could be identified.

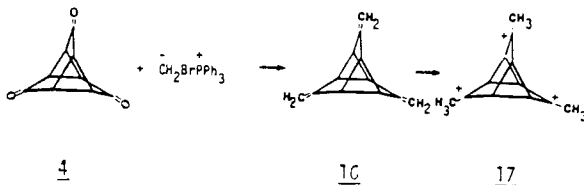
**Scheme 1.** Possible resonance forms of carboxenium ions **12**, **13** and **14**



Many attempts to achieve the reduction or functionalization of **4** were made, however none proved successful; nor was **4** recovered in most cases. It has been suggested that electronic and steric factors may have dominated the extreme sensitivity of **4** to alkylations or reductions.

An alternate approach to the trimethyl trication **17** via protonation of tris-methylene precursor **16** was also tried.

Preparation of 3,7,9-trimethylene-tetracyclo- [3.3.1.0<sup>2,6</sup>.0<sup>4,8</sup>] nonane **16** was achieved quantitatively via the Wittig reaction.



Attempts to observe trication **17** were however inconclusive. The treatment of olefin **16** with excess  $\text{HSO}_3\text{F}/\text{SbF}_5$  in  $\text{SO}_2\text{ClF}$  did not give rise to a clear enough absorption in the  $^{13}\text{C}$  NMR spectrum that could be assigned to trication **17**.

The apparently high sensitivity of the intended trication has precluded us from proceeding further with the elaboration of substituted trications of **1** until other alternative workable procedures are devised.

### Experimental Section

All starting materials were obtained from the Aldrich Chemical Company, generally with 98% purity or higher. THF and ether solvents were dried and freshly used. Tetramethoxy cyclohexadiene was purchased from the Aldrich Chemical Company. Preparation of triasterane trion **4** was achieved using the procedure of Drieding *et al.* [19]. In acetalization a different method was employed by using a catalytic amount of *p*-toluenesulfonic acid at 5°C. The product was isolated by precipitation as white powder. Mono deacetalization of *p*-benzoquinone-bis-ethylene acetal was carried out using acetone 100 ml per 0.14 mole of the diacetal and two drops of 70% perchloric acid in 15 minutes. Dichloroethane extraction formed benzoquinonemono (ethylene) acetal. Other procedures for preparation of 3,7,9-triasterane trion were employed as indicated in the literature [19].

Melting points were determined by capillary tubes using a Mettler FP-1 apparatus. The  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra were obtained on a Varian Associates Model XL-

200 NMR spectrometer equipped with variable temperature broadband and  $1\text{H}/^{19}\text{F}$  fixed frequency probes. IR spectra were performed on a Perkin-Elmer-Transform Infrared Spectrometer Model 1550 equipped with a Perkin-Elmer Laboratory Computer Model 7500. High pressure liquid chromatography was achieved by using a Varian Associates Liquid Chromatography Model 5000.

### Preparation of Carboxenium Ions

The preparation of carboxenium ions was achieved by the addition of triasterane trion **4** to a 1:1 mixture of

$\text{SO}_2\text{ClF}$  and  $\text{HSO}_3\text{F}/\text{SbF}_5$  (4:1) at  $-78^\circ\text{C}$ . The suspension of **4** was vigorously stirred with a homogenizer and a slight warming was needed to complete the ionization, whereupon a homogeneous solution was formed with slight color change.

### Preparation of Carbenium Ions

A saturated solution of antimony pentafluoride-fluorosulfonic acid (1:1) in  $\text{SO}_2\text{ClF}$  was prepared at  $-20^\circ\text{C}$ . Portions (1 ml) of this solution were cooled to  $-78^\circ\text{C}$ . This suspension was slowly added, with a regular pipet, to the suspension of olefin **16** (100 mg) in  $\text{SO}_2\text{ClF}$  at  $-78^\circ\text{C}$ . Vigorous stirring with the homogenizer and slight warming was generally required to complete the ionization, whereupon a homogeneous solution resulted with only slight traces of color.

### Preparation of 3,7,9-Trimethyl-ene- Tetracyclo [3.3.1.0<sup>2,6</sup>.0<sup>4,8</sup>] Nonane **16**

Sodium amide (1.56g, 0.04 mole) was stirred in 80 ml dry tetrahydrofuran for 10 minutes and to this was added 10.1 g (0.025 mole) triphenyl methylphosphonium iodide over a period of 30 minutes. The mixture was refluxed for 3 hours, and the precipitates filtered under argon. The filtered solution was cooled to room temperature and to this was added 0.26 g (1 mole) triasterane-3,7,9-trione **4** all at once. The mixture was stirred continuously for four days, then poured onto 40 g ice and the organic phase extracted four times with 40 ml methylbutane. The combined organic layers were washed twice with 50 ml water,

then with 50 ml saturated ammonium chloride and finally with saturated sodium chloride. They were then dried over magnesium sulfate and the solvent was removed by heating over a 30 cm column distillation apparatus. Sublimation of concentrated materials (0.05 torr, 100°C) gave 0.2 g (80%), 3,7,9-trimethylenetetracyclo [3.3.1.0<sup>2,6</sup>.0<sup>4,8</sup>] -nonane **16**, m.p. 140°C.  $\delta^1\text{H-NMR}$  (200 MHz,  $\text{CDCl}_3$ , TMS) = 2.15 (s; 6H, 1-H), 4.80 (s; 6H, 10-H).  $\delta^{13}\text{C-NMR}$  (50 MHz,  $\text{CDCl}_3$ ) = 29.4 (d, 1j - 167 Hz, 2j = 11 Hz; C-1), 105.4 (t, j = 158 Hz; C-10), 141.2 (s; C-3).

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