

into a desolvated active site. Such a proposition is fully consistent with the "electrostatic stabilization" mechanism, with the caveat that carboxylate does no better a job of stabilizing an oxonium ion than does bulk water.

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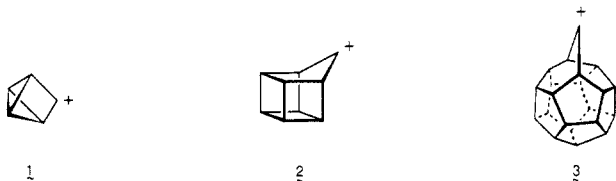
### The Degenerate 21-Homododecahedryl Cation

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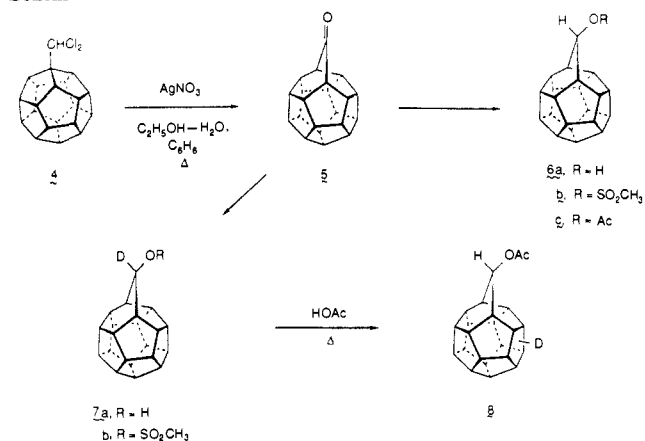
Those rearrangement processes that leave the starting material and product identical except for constitutional realignment of individual atoms and bonds have held the fascination of chemists for years. Such transformations have been observed in neutral molecules<sup>2</sup> and carbocations,<sup>3</sup> the most notable and interesting examples exhibiting *multiple degeneracy*. In the cation area, those  $(\text{CH})_n^+$  ions derived from monohomologated polyhedra have given evidence of spectacular levels of degenerate isomerization. The homotetrahedryl species **1**<sup>4</sup> is, in principle, capable of 5!/2 or 60



possible arrangements if each C-H could somehow be uniquely tagged. The multiplicity of realizable structures understandably increases with molecular size as reflected in the 9-homocubyl cation (**2**).<sup>5</sup> The progression from  $(\text{CH})_5^+$  to  $(\text{CH})_9^+$  carries with it the enormous potential of making 9!/2 or 181 440 degenerate isomers of **2** available.

A still more remarkable entity is the 21-homododecahedryl cation (**3**). In common with its smaller congeners, **3** possesses the latent capacity for exchanging the position of all its carbon-hydrogen units uniquely by means of simple Wagner-Meerwein 1,2-carbon shifts. Should full equivalency materialize in this instance, the number of possible different arrangements is truly vast: 21!/2 or  $2.56 \times 10^{19}$ . We report here, in the context of ongoing research in the dodecahedrane area,<sup>6</sup> a synthetic approach

Scheme I



to **3**, which when generated solvolitically is shown indeed to possess degenerate characteristics.

Earlier, the readiness with which dodecahedrane reacts with dichlorocarbene, generated under phase-transfer conditions, to give **4** was described.<sup>7</sup> Heating of **4** with silver nitrate in a solvent system composed of 25% aqueous ethanol and benzene (4:1) resulted in efficient (93%) ring expansion to give **5** (Scheme I). Clear colorless crystals of **5**, mp > 280 °C, were subjected to X-ray analysis.<sup>8</sup> The  $C_{2v}$  point group symmetry adopted by **5**, a direct consequence of crystallographically imposed *mm* symmetry, generates two mirror planes and causes this ketone to be structurally similar to secododecahedranes,<sup>9,10</sup> although with less distortion of the spherical framework. For example, the two envelope-shaped five-membered rings bonded to the carbonyl group adopt a flap angle of 23.9°, significantly less than those seen in monoseco derivatives (35–37°). The six-membered rings that incorporate the ketonic center adopt an approximate half-chair conformation with the C-CO-C angle being 112.6°, entirely similar to that in 2-adamantanone.<sup>11</sup> On the other hand, the <sup>13</sup>C shift of the carbonyl carbon in **5** (228.2 ppm) appears considerably downfield of that in 2-adamantanone (216.9 ppm), and the weighted split carbonyl absorption for **5** is located at 1690 cm<sup>-1</sup> and not at 1727 cm<sup>-1</sup>.<sup>12</sup> Since MNDO and AM1 calculations on the 2-adamantanyl and homododecahedryl cations provide no indication of any differences that would explain these spectroscopic anomalies,<sup>13</sup> chemical shielding tensor changes and Fermi resonance effects brought on by orbital interaction and vibrational mixing with other sectors of the molecule are thought to be operational in **5**.

Mesyate **6b** was prepared conventionally ( $\text{NaBH}_4$ ,  $\text{CH}_3\text{OH}$ ;  $\text{CH}_3\text{SO}_2\text{Cl}$ , py). Preparative acetolysis of **6b** in hot, unbuffered

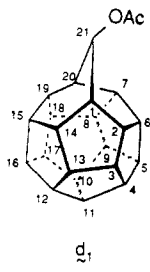
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$$\nu(\text{cm}^{-1}) = 1278 + 68k - 2.2\phi$$

where  $\phi$  is the C-CO-C angle in deg and  $k = 10.244$  to accommodate satisfactorily the fit for acetone. Consult: Halford, J. O. *J. Chem. Phys.* **1956**, *24*, 830.

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**Table I.** Deuterium Labeling Results Based on  $^2\text{H}$  NMR Analysis of **8**


	chemical shift, $\delta$	rel intensity, %	assignment <sup>a</sup>
First Acetolysis			
	5.29	16	C21
	3.60-3.20	9	others
	3.03	9	C1, C20
	2.84	31	C14, C15, C19
$d_1$	2.59	35	C2, C6, C7
Second Acetolysis			
	5.29	11	C21
	3.60-3.20	17	others
	3.03	13	C1, C20
	2.84	30	C14, C15, C19
	2.59	29	C2, C6, C7

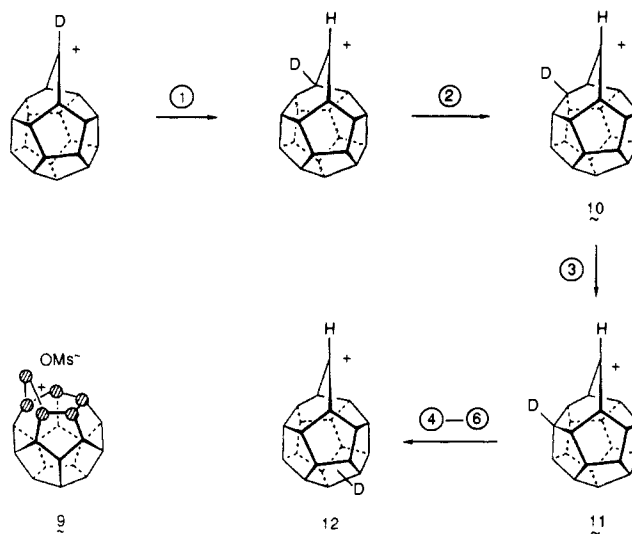
<sup>a</sup>The capability of the acetoxy group for influencing the chemical shift of nearby protons by its magnetic anisotropy effect plays a key role in these assignments. For example, deuterons located at C2, C6, or C7, which find themselves syn to OAc are positioned approximately 0.25 ppm upfield from the 14, 15, 19 triad.

acetic acid for 3 h provided **6c** in 83% isolated yield. Thus, ready ionizability to the 21-homododecahedryl cation with retention of the intact carbon framework was demonstrated. Rate constants for the acetolysis of **6b** and 2-Ad-OMs were determined conductometrically<sup>14</sup> at 110.0 °C. Good first-order kinetics to 2 half-lives was observed in both instances. The respective  $k_1$  values are  $2.18 \times 10^{-4}$  and  $2.81 \times 10^{-4} \text{ s}^{-1}$ , in line with the Foote-Schleyer correlation based on internal dihedral angle considerations.<sup>12,13</sup>

In order to assess the level of C-H peregrination in **3**, monodeuterated mesylate **7b** was prepared and acetolyzed as before. Analysis of recovered acetate **8** by  $^1\text{H}$  and  $^2\text{H}$  NMR showed that a reasonable level of deuterium migration had indeed occurred under these short-lived conditions (Table I). Since complete degeneracy had clearly not been achieved, the  $d_1$ -scrambled acetate was saponified, reconverted to mesylate, and acetolyzed again. More extensive interchange of framework methine units resulted (Table I).

Two mechanistic possibilities for deuterium scrambling require consideration. In the first, localized carbonium mesylate ion pairs are produced, for which backside 1,2-migratory stereospecificity would be enforced. A process having this restriction would, in effect, simply allow but one six-membered ring (viz., C1, C2, C6, C7, C20, and C21) to "rotate" above a [5]peristylane base while precluding migration of deuterium into the larger lower sector of the cation. Exchange would thereby be relegated exclusively to those sites explicitly depicted as shaded circles in **9**. The actual results do not conform to this option.

Rather, the findings are in agreement with predominant adoption of the nonstereospecific process which is limited, however, by covalent capture of acetic acid after relatively few rearrangement steps have transpired. Relevantly, more than three Wagner-Meerwein shifts are necessary before the deuterium label finds it possible to exit the six-membered ring (Scheme II). On the other hand, formation of the *freely solvated* carbocation allows for passage of **10** and **11** to stereoisomeric pairs of acetates (as indeed observed) and for the ultimate production of **8** (from **12**).

**Scheme II**

Consequently, the 21-homododecahedryl cation does exhibit the degeneracy anticipated for it.

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### Optical Memory in $\text{Cu}^+$ -Doped $\beta''$ -Alumina

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The conduction plane of the fast ion conductor, Na  $\beta''$ -alumina, can be doped with a wide variety of metal ions<sup>1</sup> and even small molecules<sup>2</sup> to produce luminescent solids. During the course of studies of the luminescence of single crystals of  $\text{Cu}^+$ -doped  $\beta''$ -alumina, we discovered that the low-temperature luminescence can be deliberately and reversibly changed depending on whether or not the sample was cooled while being irradiated or while in the dark. This dependence on irradiation is a type of optical memory. Regions of the crystals can be *written* by cooling under irradiation, *read* by detecting the new luminescence in the irradiated region, and *erased* by heating. In this communication we describe the conditions required for this memory and the mechanism of the phenomenon.

Single crystals of  $\beta''$ -alumina<sup>3</sup> ( $5 \times 5 \times 0.2$  mm) were prepared by the flux evaporation technique.<sup>4</sup> The  $\text{Cu}^+$ -doped samples were prepared by standard ion exchange techniques. The crystals were immersed in molten salts containing 75 mol %  $\text{CuCl}$  and 25 mol %  $\text{NaCl}$  at 400-600 °C. Typical exchange times were 2 h. A flowing nitrogen atmosphere was used to prevent oxidation of the melt. The resultant crystals were colorless, and no divalent copper could be detected by ESR. X-ray diffraction measurements confirmed retention of the  $\beta''$ -alumina phase. The copper ion

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