

## The Pentamethoxyallyl Cation

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The pentamethoxyallyl cation is readily generated from pentamethoxychlorocyclopropane by treatment with  $\text{AlBr}_3$  or  $\text{SnCl}_4$  in  $\text{CD}_2\text{Cl}_2$  or with  $\text{SnCl}_4$  in  $\text{SO}_2$ .

Allyl or enylic cations have long been of interest as simple examples of electronically delocalized, spectroscopically observable carbonium ions.<sup>1</sup> A particular focus of attention has been the magnitude of the rotational barrier about the C-C bonds of the allylic triad.<sup>2-4</sup> In the course of this work, various methyl-substituted allyl cations, including the pentamethyl derivative,<sup>3</sup> have been prepared and studied. The pentachloroallyl cation has also been reported, but rotational barriers were not assessed.<sup>5</sup>

We now report the generation and spectroscopic examination of the novel pentamethoxyallyl cation, along with some details of its chemistry. Addition of methoxychlorocarbene<sup>6</sup> (generated thermally at 25 °C for 24 h from methoxychlorodiazirine)<sup>7</sup> to tetramethoxyethylene<sup>8</sup> afforded a 22% isolated yield of pentamethoxychlorocyclopropane (**1**) as a white, crystalline solid, purified by sublimation (30 °C at 0.025 mmHg).†‡

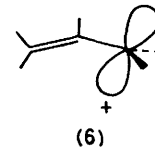
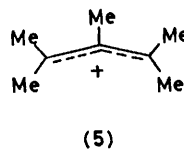
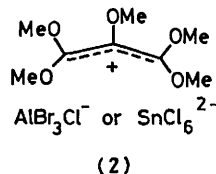
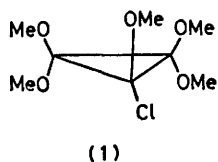
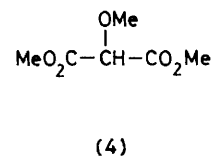
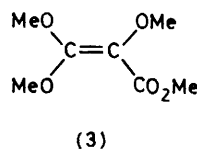
Cyclopropane (**1**) afforded the pentamethoxyallyl cation (**2**) upon treatment with (a)  $\text{AlBr}_3\text{-CD}_2\text{Cl}_2$ , (b)  $\text{SnCl}_4\text{-CD}_2\text{Cl}_2$ , or (c)  $\text{SnCl}_4\text{-SO}_2$  at -20 to -30 °C. Under conditions (b) and (c), less than a stoichiometric quantity of Lewis acid was used in order to avoid excessive decomposition of the ion. Variable-temperature <sup>1</sup>H n.m.r. spectroscopy (80 MHz) revealed very similar chemical shift behaviour for cation (**2**) under each set of conditions. At ambient temperatures [(a) and (b)], and at -33 °C [(c)], the spectra of (**2**) featured two sharp absorptions in the ranges  $\delta$  4.24-4.27 and  $\delta$  3.54-3.60 (integral ratio, 4:1), assignable to four terminal methoxy-groups and the 2-methoxy-group, respectively. As the temperature was lowered, the terminal methoxy-signal broadened, ultimately splitting into two equal-intensity singlets; *e.g.*, at -80 °C, systems (a) and (b) displayed three absorptions at  $\delta$  4.30 or 4.34, 3.99 or 4.03, and 3.45 or 3.51 (integral ratio, 2:2:1). A spectrum of (**2**) under condition (c), obtained at -73 °C was similar, with terminal methoxy-absorptions at  $\delta$  4.37 and 4.18. All temperature-dependent spectral changes were reversible, and coalescence temperatures of the terminal methoxy-signals were -48 °C (a) or (b) and -62 °C (c).

The near invariance of the n.m.r. behaviour of (**2**) under differing conditions of solvent and counterion, taken together with previous studies of methyl-substituted allylic cations,<sup>2-4</sup> suggest that the observed temperature-dependent n.m.r. properties of (**2**) are best attributed to 'equilibration' of its 'inner' and 'outer' terminal methoxy-groups, caused by rapid rotations about the C-1-C-2 or C-2-C-3 bonds of this

allylic cation above -48 °C. Calculations of  $\Delta G^\ddagger$  for this process from the coalescence temperatures and the low temperature (slow exchange) chemical shift data give values of 10.8-11.2  $\pm$  1.0 kcal/mol (45.2-46.9 kJ/mol) under conditions (a)-(c).

Heating neat cyclopropane (**1**) (52 °C for 1 h), followed by Kugelrohr distillation (50 °C at 0.5 mmHg), afforded 90% of methyl trimethoxyacrylate (**3**)†§ as a colourless oil. This product can be accounted for by ring-opening of (**1**) to (**2**)-Cl<sup>-</sup>, followed by nucleophilic attack of Cl<sup>-</sup> on the methyl carbon of a terminal methoxy-group of (**2**). Quenching n.m.r. solutions of cation (**2**) with methanol (containing an insufficiency of NaOMe) gave 60% of dimethyl methoxymalonate (**4**),†¶ which could also be obtained (85%) directly from (**1**) upon exposure of the latter to  $\text{AgClO}_4\text{-MeOH}$ . We suggest that methanolysis of cation (**2**) affords (**3**), which subsequently affords (**4**) by an acid-catalysed enol ether-to-carbonyl transformation. Indeed, (**3**) does give (**4**) when treated with  $\text{AgClO}_4\text{-MeOH}$ .

The rotational barrier attending the n.m.r. equilibration of the terminal methoxy-groups of cation (**2**) (*ca.* 11 kcal/mol in  $\text{SO}_2$ ) is similar to that of its pentamethyl analogue (**5**) ( $\Delta G^\ddagger$  *ca.* 14 kcal/mol in  $\text{SO}_2$ ).<sup>3</sup> Complete rationalization of the magnitudes of these barriers requires knowledge of the effects of MeO or Me substituents on the energies of both the ground state [(**2**) or (**5**)] and 'twisted' [*i.e.*, rotational transition state, (**6**)] allylic cations. An analysis has been offered for (**5**).<sup>3</sup> Although we prefer to withhold a detailed discussion of (**2**) for the full paper, it is at least qualitatively apparent that, relative to (**5**), the additional stabilization realized upon methoxy-substitution at the isolated carbonium ion centre of (**6**) must be matched by a nearly comparable additional methoxy-stabilization of the ground state allylic cation (**2**), so that  $\Delta G_2^\ddagger = \text{ca. } \Delta G_5^\ddagger$ .



§  $\delta$  ( $\text{CCl}_4$ ,  $\text{Me}_4\text{Si}$ ) 3.50, 3.73, 3.80, and 3.87 (each s, 3H,  $\text{OCH}_3$ ); i.r. (neat)  $\nu$  1620 (C=C) and 1710 (C=O)  $\text{cm}^{-1}$ .

¶ Purification by  $\text{SiO}_2$  chromatography and distillation (38 °C at 0.25 mmHg) give (**3**) as an oil;  $\delta$  ( $\text{CH}_2\text{Cl}_2$ ,  $\text{CCl}_4$ ,  $\text{Me}_4\text{Si}$ ) 3.53 (s, 3H,  $\text{OCH}_3$ ), 3.87 (s, 6H, 2 ester  $\text{OCH}_3$ ), and 4.47 (s, 1H, CH); i.r. (neat)  $\nu$  1745 (C=O)  $\text{cm}^{-1}$ .

† M.p., 51-52 °C (decomp.); <sup>1</sup>H n.m.r. ( $\text{C}_6\text{H}_6$ ,  $\text{Me}_4\text{Si}$ )  $\delta$  3.42 (2 overlapping s, 12H, 4  $\times$   $\text{OCH}_3$ ) and 3.53 (s, 3H,  $\text{OCH}_3$ ).

‡ A satisfactory elemental analysis was obtained.

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