

The Pentamethoxyallyl Cation

Robert A. Moss,* Wenjeng Guo, Alfred Hagedorn, and Richard Beveridge

Department of Chemistry, Rutgers, The State University of New Jersey, New Brunswick, New Jersey 08903, U.S.A.

The pentamethoxyallyl cation is readily generated from pentamethoxychlorocyclopropane by treatment with AlBr_3 or SnCl_4 in CD_2Cl_2 or with SnCl_4 in SO_2 .

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

We now report the generation and spectroscopic examination of the novel pentamethoxyallyl cation, along with some details of its chemistry. Addition of methoxychlorocarbene⁶ (generated thermally at 25 °C for 24 h from methoxychlorodiazirine)⁷ to tetramethoxyethylene⁸ afforded a 22% isolated yield of pentamethoxychlorocyclopropane (**1**) as a white, crystalline solid, purified by sublimation (30 °C at 0.025 mmHg).†‡

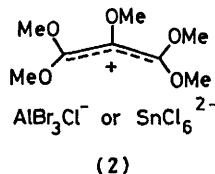
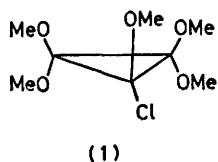
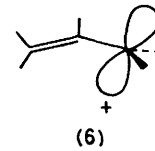
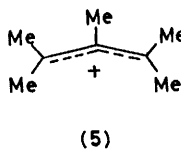
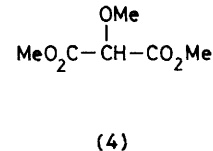
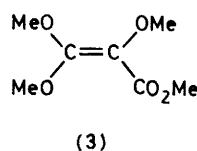
Cyclopropane (**1**) afforded the pentamethoxyallyl cation (**2**) upon treatment with (a) $\text{AlBr}_3\text{-CD}_2\text{Cl}_2$, (b) $\text{SnCl}_4\text{-CD}_2\text{Cl}_2$, or (c) $\text{SnCl}_4\text{-SO}_2$ at -20 to -30 °C. Under conditions (b) and (c), less than a stoichiometric quantity of Lewis acid was used in order to avoid excessive decomposition of the ion. Variable-temperature ¹H 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 δ 4.24-4.27 and δ 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 δ 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 δ 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,²⁻⁴ 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 ΔG^\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⁻, followed by nucleophilic attack of Cl⁻ 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 SO_2) is similar to that of its pentamethyl analogue (**5**) (ΔG^\ddagger ca. 14 kcal/mol in SO_2).³ 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**).³ 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 $\Delta G_2^\ddagger = \text{ca. } \Delta G_5^\ddagger$.



§ δ (CCl_4 , Me_4Si) 3.50, 3.73, 3.80, and 3.87 (each s, 3H, OCH_3); i.r. (neat) ν 1620 (C=C) and 1710 (C=O) cm^{-1} .

¶ Purification by SiO_2 chromatography and distillation (38 °C at 0.25 mmHg) give (**3**) as an oil; δ (CH_2Cl_2 , CCl_4 , Me_4Si) 3.53 (s, 3H, OCH_3), 3.87 (s, 6H, 2 ester OCH_3), and 4.47 (s, 1H, CH); i.r. (neat) ν 1745 (C=O) cm^{-1} .

† M.p., 51-52 °C (decomp.); ¹H n.m.r. (C_6H_6 , Me_4Si) δ 3.42 (2 overlapping s, 12H, 4 \times OCH_3) and 3.53 (s, 3H, OCH_3).

‡ A satisfactory elemental analysis was obtained.

We are grateful to the National Science Foundation for financial support.

Received, 28th June 1982; Com. 743

References

- 1 N. C. Deno in 'Carbonium Ions,' Vol. II, eds. G. A. Olah and P. v. R. Schleyer, Wiley-Interscience, New York, 1970, pp. 783-806.
 - 2 P. v. R. Schleyer, T. M. Su, M. Saunders, and J. C. Rosenfeld, *J. Am. Chem. Soc.*, 1969, **91**, 5174.
 - 3 J. M. Bollinger, J. M. Brinich, and G. A. Olah, *J. Am. Chem. Soc.*, 1970, **92**, 4025; G. A. Olah and J. M. Bollinger, *ibid.*, 1968, **90**, 6082.
 - 4 N. C. Deno, R. C. Haddon, and E. N. Nowak, *J. Am. Chem. Soc.*, 1970, **92**, 6691.
 - 5 R. West and P. T. Kwitkowski, *J. Am. Chem. Soc.*, 1966, **88**, 5280.
 - 6 R. A. Moss and W-C. Shieh, *Tetrahedron Lett.*, 1978, 1935; N. P. Smith and I. D. R. Stevens, *ibid.*, p. 1931.
 - 7 W. H. Graham, *J. Am. Chem. Soc.*, 1965, **87**, 4396.
 - 8 J. W. Scheeren, R. J. F. M. Staps, and R. J. F. Nivard, *Recl. Trav. Chim. Pays-Bas*, 1973, **92**, 11; J. W. Scheeren and W. Stevens, *ibid.*, 1966, **85**, 793.
-