

POLYALKOXY-2-AZA-PROPENYL IUM SALTS

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Abstract: The title compounds 3, 8, and 10 have been synthesized by oxygen-alkylation of the alkoxy-substituted N-methylene amides 1, 6, 7, and 9 using triethyloxonium salt 2. The stereochemistry of the new salts is discussed in terms of a competition between the 2-aza-allenium- and the 2-aza-allyl-cation structures (I) and (II).

The major stereochemical question in the structural behaviour of 2-aza-propenyl ions is the determination of their ground state geometry, which may either be the linear 2-aza-allenium structure (I) or the bent, planar 2-aza-allyl cation form (II).

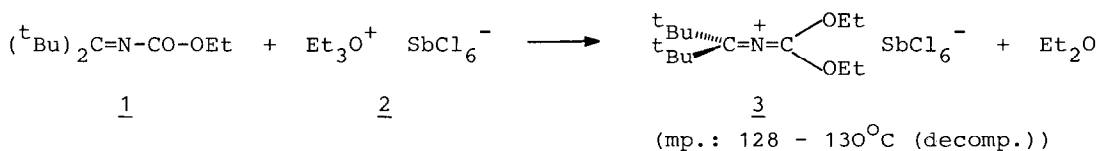


Simple MO arguments predict that the allenic form should predominate for the parent compound $\text{H}_2\text{C}=\text{N}=\text{CH}_2$ and alkyl- and aryl substituted derivatives ^{1,2}. Electron-donating substituents, however, favor the bent allylic structure more, since the LUMO of the 2-aza-allyl cation is significantly lower in energy than that of the 2-aza-allenium ion and is therefore a better electron acceptor ².

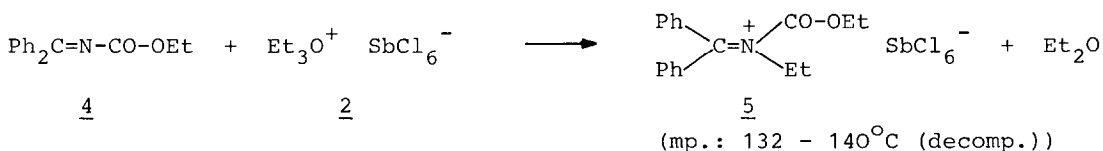
Syntheses and structures of 1-alkoxy-2-aza-allenium ions ³ and 1,3-dialkoxy-2-aza-allenium salts ⁴ have been described in recent studies. In this communication we report the preparation and some structural properties of 1,1-dialkoxy-, 1,1,3-trialkoxy- and 1,1,3,3-tetraalkoxy-2-aza-propenyl ions. The key step for the synthesis of all new salts is the alkylation of the corresponding alkoxy-substituted N-methylene amides using trialkyloxonium salts as alkylating agents in halogenated hydrocarbon solvents.

N-Methylenecarbamates, the starting materials for the 1,1-dialkoxy-2-aza-allenium salts, can be prepared easily and in good yield following a new general procedure ⁵. For instance, ethyl-N-(di-tert.butyl-methylene)-carbamate 1 reacts with triethyloxonium hexachloroantimonate 2 exclusively at the car-

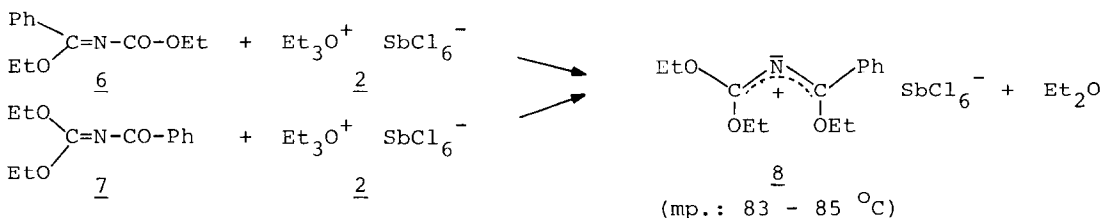
bonyl oxygen atom giving 1,1-diethoxy-3,3-di-tert.butyl-2-aza-allenium hexachloroantimonate 3 in 68 % yield. The ^{13}C -NMR-spectrum supports both the O-attack and the allenic structure of 3: at 30°C (25.15 MHz, CD_3CN) only one CH_2 -signal is found for both ethoxy groups at 73.11 ppm (typical region for an ether CH_2). The low temperature spectrum (-90°C , CH_2Cl_2) does not differ significantly from the room temperature spectrum. We take this observation to strongly support the formulated linear structure 3, or - less likely for steric reasons - a rapidly equilibrating mixture of type (II) cations. In the IR spectrum (Nujol suspension) a very broad, finely structured absorption near 1775 cm^{-1} is observed; shape and structure of this signal are characteristic of an 2-aza-allenium salt ^{3,6}.



Ethyl-N-(diphenylmethylene)-carbamate 4, however, reacts with 2 at the nitrogen atom to form the highly reactive N-ethoxycarbonyl-iminium salt 5 in 47 % yield. Evidence for the N-alkylation is again obtained from the ^{13}C -NMR-spectra: the signal for the N- CH_2 -group is found at 55.03 ppm, whereas the O- CH_2 -group gives rise to a signal at 69.41 ppm. The IR spectrum is dominated by a strong absorption near 1790 cm^{-1} (C=O-stretching vibration).



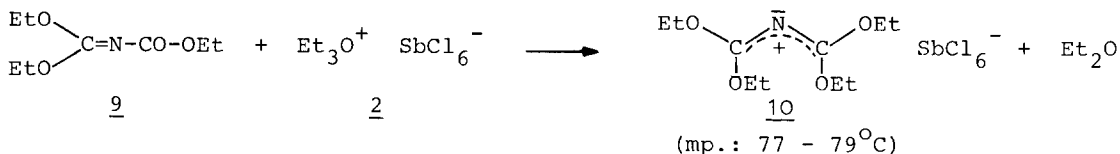
1,1,3-Trialkoxy-2-aza-propenylum salts are accessible from two different classes of starting materials: Thus, both ethyl-N-(ethoxycarbonyl)-benzimidate 6 ⁷ and N-(di-ethoxymethylene)-benzamide 7 ⁸ produce the same new 1,1,3-triethoxy-3-phenyl-substituted salt 8 in 76 and 81 % yield respectively.



The possibility of N-alkylation is quickly ruled out by inspection of the ^{13}C -NMR shifts of the ethoxy- CH_2 -groups (see above). The preference of the allylic

structure 8 over the allenic form is indicated by the three CH₂-signals (71.41, 71.83 and 74.08 ppm) at -95°C (CD₂Cl₂), in good agreement with a planar, bent geometry around the nitrogen atom. A type (I) structure would show only two types of CH₂-groups. We therefore propose a structure like 8 for the ground state, although without specifying the position of the phenyl group (exo or endo). At -65°C (CDCl₃) the ¹³C-NMR spectrum shows substantially broadened CH₂-signals (coalescence), at higher temperature (25°C) only two CH₂-absorptions indicate a rapid equilibration which we interpret as a inter-conversion of the different allylic forms via a low lying transition state having the allenic C_s-geometry. The IR spectrum (CH₂Cl₂, 25°C), showing a strong, broad, finely structured absorption near 1575 - 1595 cm⁻¹ as the predominant signal, is in good agreement with the proposed allyl type structure of 8 in solution. In crystalline samples of 8, however, as we know from earlier X-ray work ^{3,4} and from quantum mechanical calculations ⁹, twisted forms should also be expected, since the unusual molecular flexibility of these salts allows easy distortions, e.g. by intermolecular crystal forces and cation-anion interactions.

Following the same general procedure we were also able to synthesize the first tetraalkoxy-substituted 2-aza-propenylium salt: Starting from ethyl-N-(diethoxy-methylene)-carbamate 9 ¹⁰, alkylation using 2 gives the hitherto unknown 1,1,3,3-tetraethoxy-2-aza-allyl hexachloroantimonate 10 in 71 % yield.



As for 8 we interpret the ¹³C-NMR spectrum (-95°C; CD₂Cl₂) of 10 in favor for a more likely allylic than allenic ground state structure. Two different CH₂-signals at 70.08 and 72.38 ppm exclude D_{2d}-symmetry (allene type (I)) at low temperatures. We find coalescence near -60°C, leading to a room temperature spectrum with only one signal at 71.71 ppm for all four CH₂ groups. Again we interpret these data by an automerization process, whose transition state - as suggested by ab initio calculations (see below) - now has the linear allene type structure (I). From the temperature dependence we estimate an activation barrier of ca. 10.4 kcal/mol (ca. 44 kJ/mol) for this process, indicating the strong preference of this substituted 2-aza-propenylium ion for bent allylic structures. The IR spectrum (CH₂Cl₂) supports this interpretation: we find a strong, relatively sharp signal near 1550 cm⁻¹, a frequency which is much too low for a 2-aza-allenium type structure like (I). The hitherto unknown salt

10 is isoelectronic to 1,1,3,3-tetraalkoxyallene, a molecule which found much interest in synthetic organic chemistry as a very electron rich cumulene derivative ¹¹.

Quantum mechanical ab initio calculations (3-21G//3-21G) are in excellent agreement with the experimental findings: for 1,1-dihydroxy-2-aza-propenylium, a model ion for 3, we calculate a very similar total energy for the best conformers of type (I) and (II) (4.1 kcal/mol in favor for the allylic form (II)). For 1,1,3-trihydroxy-2-aza-propenylium (model for 8) and for 1,1,3,3-tetrahydroxy-2-aza-propenylium we find a preference of 11.30 and 19.63 kcal/mol, respectively, for the allylic isomers ⁹.

We are presently studying the stereochemical properties of the new salts by spectroscopic and theoretical methods and their synthetic applicability in organic chemistry.

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