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TRITIATED ETHYLENE AS PRECURSOR OF A FREE VINYL CATION.

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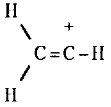
Abstract: A method for the partial hydrogenation of alkynes has been optimized for the synthesis of carrier-free politritiated ethylene. This molecule provides access to the chemistry of the free $C_2H_3^+$ ion in both gaseous and condensed phase.

Substituted vinyl cations are now established as reaction intermediates, some of them endowed with fair stability, but observation of the parent unsubstituted vinyl cation (I) in reactions in solution has never been reported.[1] This communication reports a convenient procedure to generate known amounts of free unsubstituted vinyl cations under conditions allowing investigation of their reactivity features.



I

This was made possible by the use of an unconventional route to carbenium ions which relies on the nuclear decay of tritium in a politritiated precursor[2], in this case labeled ethylene possessing at least two tritium atoms in the same molecule. The decay of one of them generates the cationic site, while the second one acts as a label marking the future fate of the cation.

$$RT \xrightarrow[\text{decay}]{\beta^-} \left[R^3He\right]^+ \xrightarrow{-^3He} R^+ \qquad (1)$$

The synthesis of such a precursor must comply with the following requirements:

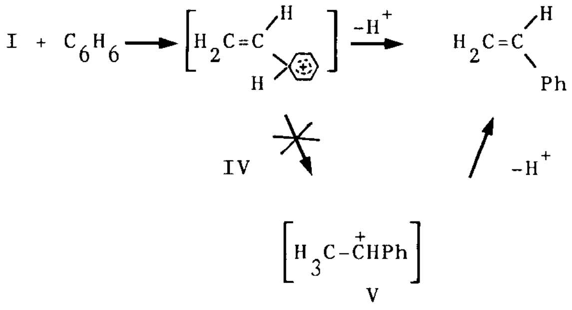
1§. Multiple tritium substitution (at least double).

2§. High chemical and radiochemical purity.

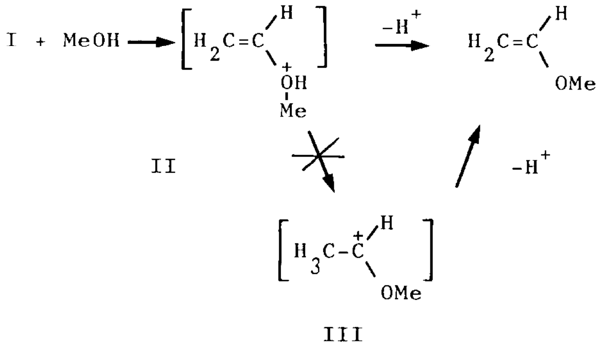
At the same time one must minimize the self radiolysis of the product, due to its high specific activity and to the radiosensitivity of ethylene $\left(G(-C_2H_4) = 15\right)$[3]. Requirement 1§ forced us to choose a one-step synthesis for the simultaneous introduction of more than one tritium atom into the precursor molecule. Reagents such as T_2O or T_2 (and not HTO/H_2O or HT/H_2) must be used. They have a specific activity of ca. 6×10^4 Ci mol^{-1}, which then corresponds to the activity of the carrier-free bitritiated product. Because of requirement 2§ standard routes to polideuterated ethylene[4] or more recent methods for the partial catalytic hydrogenation of acetylenes[5] via solution reactions were discarded. Therefore the preparation of tritiated ethylene was performed in the absence of solvents by the addition of T_2 (1.7×10^{-5} mol, 1 Ci) to acetylene (1.4×10^{-5} mol) catalyzed by 10 mg of Lindlar catalyst.[6] The catalyst had been previously poisoned by quinoline vapour, in order to increase its selectivity towards the triple bond and minimize further reduction of ethylene as it is formed. The products from blank deuteration experiments have been examined by G.L.C./M.S. (multiple ion detection of masses 27, 28, 29, 30, 33) and ^{1}H-NMR Spectroscopy. Ethylene-d and cis-ethylene-d_2 were formed in the 44:56 ratio, revealing the occurrence of some H/D scrambling, which should however be reduced when isotope tritium is used. Radio-g.l.c. of the tritiated reaction product showed the following radiochemical composition: hydrogen 32%, ethylene 53%, acetylene < 0.4%, ethane 1.5.%, C_4 and C_6 hydrocarbons 13%. The mixture was subjected to low temperature distillation and diluted with inactive ethylene. NH_3 and O_2 were added as inhibitors of the radiation induced polimerization of the unsaturated molecules initiated respectively by cationic and radical species. Samples of this gaseous mixture corresponding to 8 mCi (2.2×10^{-5} mol) of ethylene were dissolved in 4 cc liquid MeOH and benzene, and the systems were stored for two months in the dark at room temperature. Radio-g.l.c. detected styrene as the major product (81%) together with minor yields of ethylbenzene (7.6%) in the benzene systems. Only 12% of methylvinyl ether was instead recovered from the methanol samples.[7]

Formation of these tritiated products is not accompanied by any detectable amounts (radio-g.l.c. and flame-ionization-detection g.l.c.) of the corresponding unlabelled forms ($< 10^{-5}$ mol %). This excludes any other conceivable (thermal, photochemical, radiolytic, etc.) source of the radioactive products, besides that involving the decay process (1).

Isolation of methylvinyl ether and styrene in the corresponding systems demonstrates the actual formation of tritiated vinyl cation I via eq. (1) and its subsequent reaction with a solvent molecule (eq. 2a,b).



(2a)



(2b)

α-Methoxyethyl cation III and benzyl cation V, prototropic forms of intermediates II and IV, do not appear to be involved in the reaction sequences (2a,b). If formed, in fact, these ions would add to another solvent molecule to give respectively 1,1-dimethoxyethane and 1,1-diphenylethane, which are not found.

That eq. 2a is the predominant process in the benzene system is demonstrated by the high yield of the labeled aromatic products (ca. 89%). On the contrary, the rather limited product yield observed in the methanol samples suggests the pathway 2b is likely to be accompanied by competitive processes, such as proton or hydride transfer between $C_2H_3^+$ and the solvent, leading to neutral labeled species (eg. ethylene) not distinguishable from those initially present in the decay mixtures.

The present results provide the first evidence on the transient existence of vinyl cation in solution and on its behaviour in the liquid phase. In fact, reaction of a $C_2H_3^+$ cation with benzene has been examined thus far in the gas phase alone, under the low-pressure conditions typically found in a mass spectrometer[8] and the results were subjected to the well known limitations (structural and otherwise) of a purely mass spectrometric approach.

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References and notes.

1. P.J. Stang, R. Rappoport, M. Hanack, and L.R. Subramanian, "Vinyl Cations" Academic Press, New York, 1979.
2. F. Cacace, Adv. Phys. Org. Chem., 8, 79 (1970); M. Speranza, Gazz. Chim. Ital., 113, 37 (1983).
3. J.W.T. Spinks and R.J. Woods, "An Introduction to Radiation Chemistry", Wiley, New York, 1964, p. 224.
4. A. Murray and D.L. Williams, "Organic Synthesis with Isotopes" part II, Interscience, New York, 1958.
5. B.L. Sondengam, G. Charles, and T.M. Akam, Tetrahedron Lett., 21, 1069 (1980); D. Savoia, E. Travaglini, C. Trombini, and A. Umani-Ronchi, J. Org. Chem., 46, 5340 (1981); ibid. 5344; J.J. Brunet, P. Gallois, and P. Caubere, J. Org. Chem., 45, 1937 (1980).
6. E.N. Marvell and T. Li, Synthesis, 457 (1973).
7. Yields are calculated from the initial activity and the isotopic composition of the precursor, the decay rate of tritium, and the absolute counting efficiency of the detector employed.
8. J.D. Morrison, K. Stanney, and J.M. Tedder, J. Chem. Soc. Perkin II, 838 (1981).

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