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TRAPPING OF VINYL CATIONS BY CARBON MONOXIDE[1]

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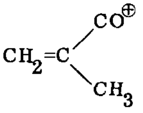
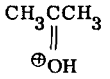
The behaviour of vinyl cations in solvolysis and other reactions is becoming a popular subject of investigation[2]. Evidence of the occurrence of such species as short-lived intermediates is steadily increasing, but the cations have not yet been prepared in super-acid solutions with life-times long enough to permit direct observation by spectroscopic means. Previously[1,3], we intercepted with carbon monoxide two other unstable cations, viz. the methyl and ethyl cations, which - until now - have also escaped direct observation. The same technique has now been applied to some vinyl cations, and the results are reported in this paper.

The vinyl cations investigated were generated by protonation of the corresponding alkynes in $FHSO_3/SbF_5$ solution at room temperature by bubbling the alkyne/carbon monoxide mixtures through the super-acid solution in an NMR tube. The products were analysed and the relative yields determined by NMR spectroscopy. Quenching of the formed oxocarbonium ions in water and normal work-up afforded the corresponding acids. Some of the results are presented in the Table.

TABLE

REACTION PRODUCTS OF ALKYNES AND CARBON MONOXIDE IN $FHSO_3/SbF_5$

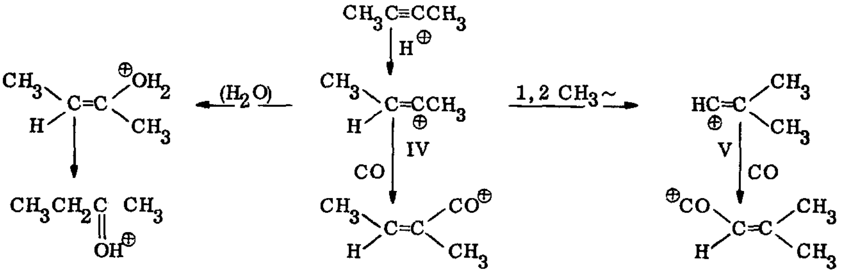
Alkyne	Alkyne/CO molar ratio	$FHSO_3/SbF_5$ molar ratio	Identified* products (ratio)
$CH_3C{\equiv}CH$	1 : 20	1 : 10	 $CH_2{=}C(CO^{\oplus})CH_3$
"	1 : 20	1 : 1	 $CH_3C(={}^{\oplus}OH)CH_3$
$CH_3C{\equiv}CCH_3$	1 : 25	1 : 10	I
"	1 : 25	1 : 1	I+II+III (1 : 7 : 4)
"	1 : 8	1 : 1	I+II+III (1 : 2 : 2)
"	1 : 4	1 : 1	II+III (1 : 2)
"	1 : 1	1 : 1	III

* Unidentified products were sometimes formed in yields of up to 20-30%.

The results show that the product distribution depends on the alkyne/carbon monoxide and the FHSO$_3$/SbF$_5$ molar ratio. When the carbon monoxide and SbF$_5$ concentrations are high, there is predominant formation of oxocarbonium ions. Decreasing the amount of SbF$_5$ in the super-acid solvent system favours the formation of trivial products, such as (protonated) acetone and butanone, which can be accounted for by the acid-catalysed addition of water - present as impurity in the solvent system - to the alkynes. We have not been able to intercept the vinyl cation from acetylene by means of carbon monoxide: either (protonated) acetaldehyde or unidentifiable products were formed.

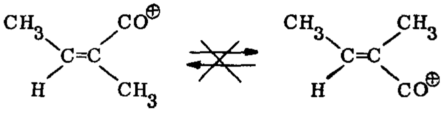
The two main points of interest, besides the factual formation of the oxocarbonium ions, are the stereochemistry of oxocarbonium I[4] and the rearrangement of the 1,2-dimethylvinyl cation IV[5] to the 2,2-dimethylvinyl cation V.

Scheme



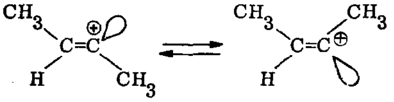
III I II

The formation of the (Z)-2-methyl-2-butenoyl ion I is not, or, at least less than 3-5% accompanied by the formation of the stereoisomeric (E)-2-methyl-2-butenoyl ion VI[4], nor does it proceed via isomerization of ion VI. This was demonstrated by separate experiments, which have shown that the isomerization[6] of I to VI, and vice versa,

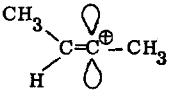


I VI

does not occur at temperatures up to 150° for at least 30 minutes. One might wonder whether the formation of only one of the two possible stereoisomeric oxocarbonium ions could give an indication of the geometrical structure of the precursory vinyl cation IV. If this ion were non-linear at the positive centre (sp^2-hybridized C), then the preferred structure would, for steric reasons, be VII and, consequently, the addition of carbon monoxide would lead direct to the observed product I. This reasoning



VII VIII

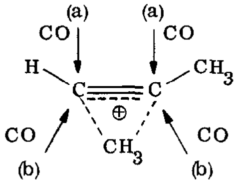


IX

is weakened, however, if one allows for an easy interconversion of structures VII and VIII - occurring via inversion, not via rotation[11] - which would result in the formation of both ions I and VI. If the structure of the vinyl cation were linear (sp-hybridized C in IX), then only a stereospecific attack of carbon monoxide on the most hindered side of the ion would explain the formation of I. An additional complicating factor in this discussion is the fact that the bonding interactions between solvent molecules and vinyl cations will be stronger than between solvent molecules and tertiary or secondary alkyl cations, so that a consideration of steric effects in the free structures VII-IX alone is likely to be an oversimplification. Therefore, we think that any definite preference for either the linear or the non-linear structure of the 1,2-dimethylvinyl cation IV cannot be expressed on the basis of the data reported[12].

The formation of oxocarbonium ion II[4] may be formulated as to proceed via a 1,2-CH$_3$ shift across the double bond in ion IV, followed by addition of carbon monoxide to ion V. In some solvolytic reactions aryl or alkyl shifts across C=C bonds in vinyl cations have been observed[2], the product ions always being more stable than the reacting ions. In the case reported here, however, the rearrangement of IV to V leads to an increase in energy, and as the carbonylation is controlled kinetically and not thermodynamically - in contrast to the carbonylation of tertiary and secondary butyl and pentyl ions studied earlier[14] - the formation of II is not readily understood. It may be that the SbF$_5$ present in the super-acid system not only keeps the solvent weakly nucleophilic, but also plays a more specific part in complexing[15] the alkynes and modifying the vinyl cation chemistry.

In the above discussion we have disregarded the possibility of writing the 1,2-dimethylvinyl cation as a non-classical species X:



X

Our reasons for doing so were as follows:

(i) Of the two modes of attack of carbon monoxide in the plane of ion X only mode (b) will lead to the observed products I and II. In the non-classical norbornyl ion the attack of carbon monoxide in the kinetically determined process is from the (a) side[16].

(ii) The dependence of the ratio of I to II on the carbon monoxide concentration is not explained by structure X.

(iii) In the case of propyne it is the (Z)-3-methylpropenoyl ion rather than the observed 2-methylpropenoyl ion that is expected to be the product.

Finally, it is worth noting that in the metal-carbonyl-catalysed hydrocarboxylation of alkynes ("Reppe reaction") almost exclusively cis addition of the elements of H-COOH is found[17], as opposed to the trans addition of the elements of H-CO$^{\oplus}$ reported in this paper.

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