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α-KETOCARBONIUM IONS - EVIDENCE FOR A NOVEL OXO-TRANSFER

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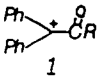
Abstract - Evidence from a specifically labelled acylcarbenium ion of an oxo-transfer reaction is reported.

There has been a considerable interest recently in the study of carbocations directly bonded to electron-withdrawing substituents[1-3,8]. Direct nmr spectral evidence for α-cyanodiphenylmethyl cation has been obtained[2] and we have reported nmr spectral data of diphenylmethyl cations bearing an α-carbonyl group under stable ion conditions[4]. These ions appear to be discrete tertiary bis benzilic cations 1 rather than cyclic ions 2 as suggested by ab initio MO calculations for the parent formylmethyl cation[5].

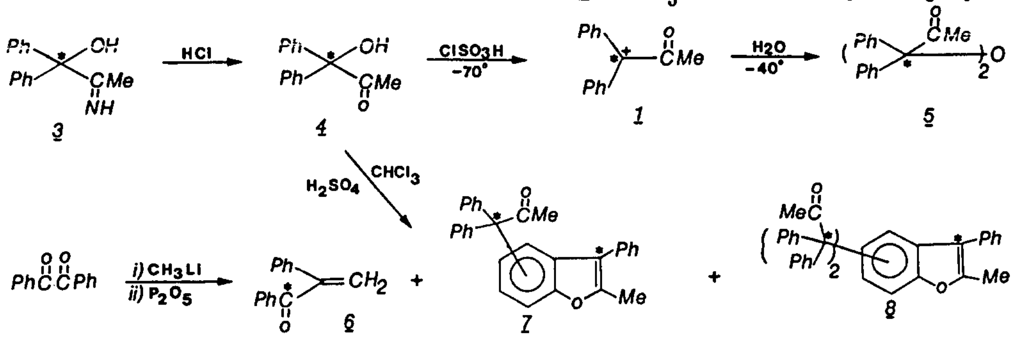


1

2

We now report the first example of an oxo transfer from a specific α-ketocarbonium ion 1 ($R=CH_3$) implying ion 2 as an intermediate or transition state as substantiated by labelling experiments.

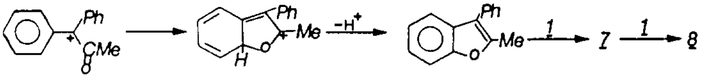
Hydroxyketone 4 was prepared from hydroxyimine 3 obtained by condensation of benzophenone and acetonitrile as described by Ioffe[6]. The carbonium ion 1 ($R=CH_3$) was obtained by mixing a precooled solution of hydroxyketone 4 with $ClSO_3H$ at -70°. The ^{13}C nmr spectrum of 1 exhibits two low field signals at 209 and 202 ppm representing the carbonyl and cationic carbons respectively. The assignments were based on specific labelled substrate 4 with 90% enriched C-13 at the benzilic carbon. When labelled 4 was mixed with $ClSO_3H$ at -70° an identical ^{13}C nmr spectrum was obtained except that the signal at 202 ppm was enhanced by about 90 times relative to the other peaks. Quenching of this solution with ice and solid $NaHCO_3$ gave exclusively the dimeric ether 5. Warming the $ClSO_3H$ solution of 1 to room temperature and then quenching with ice gave mainly water soluble materials and a small amount of an intractable material. On the other hand neutralization of a conc. $H_2SO_4/CHCl_3$ two phase system produced three products 6, 7 and 8 in 20, 20 and 52% respectively. The structure of



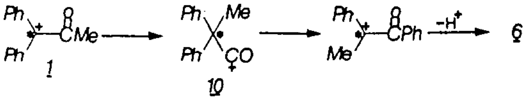
enone 6 was assigned on the basis of synthesis from benzil. Reaction of benzil with methyl lithium followed by dehydration with P_2O_5 in reflux benzene gave 6 identical in all respects with a previous sample.

Dimer 7 and trimer 8 are postulated as being formed from subsequent reaction of one or two equivalents ion 7 with one equivalent of benzofuran 9 formed by intramolecular cyclization of 1 (Scheme 1). Such cyclizations have been previously observed for related systems[7]. The formation of enone 6 can be rationalized by the following mechanisms. Formation of acylium ion 10 by 1,2-methyl shift is followed by phenyl migration (Scheme 2) or alternatively formation of an oxiranyl ion 11 followed by a phenyl shift and deprotonation (Scheme 3). The labelling experiment rules out the double migration as shown in Scheme 2.

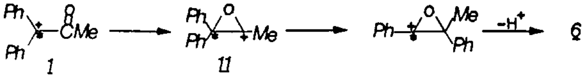
Scheme 1



Scheme 2



Scheme 3



^{13}C labelled 4 (at benzilic carbon) gave enone 6 exclusively labelled at the carbonyl carbon as shown by ^{13}C nmr spectroscopy suggesting an oxo migration occurs via an oxiranyl cation 11. The specific sites of ^{13}C label in dimer 7 and trimer 8 are as shown above as deduced from signal enhancement in their ^{13}C nmr spectra.

Although Wagner-Meerwein rearrangements have been observed for α-acylcarbenium ions[1], to our knowledge this is the first example of a carbonyl oxygen transfer in such cations. Further studies are in progress to establish the nature of such cyclic oxiranyl cations 2 as intermediates in these rearrangements.

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