

THE GENERATION OF VINYL CATIONS BY BECKMANN FRAGMENTATION

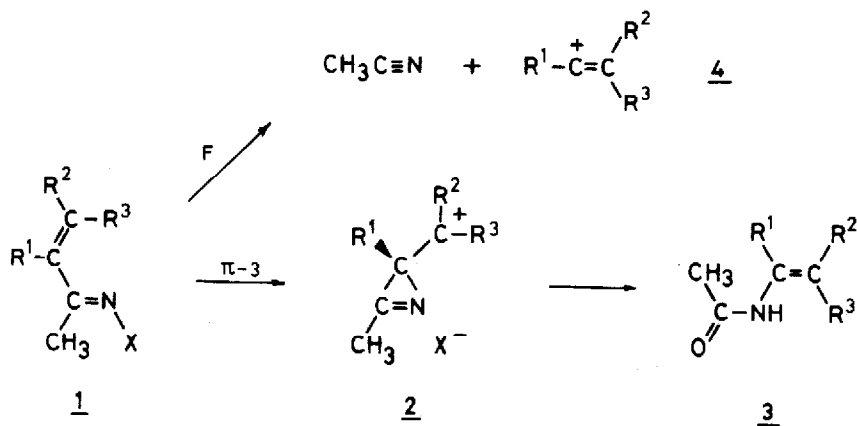
OF α,β -UNSATURATED KETOXIME DERIVATIVES

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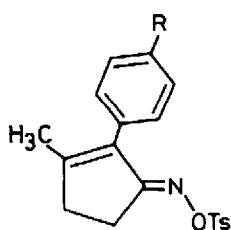
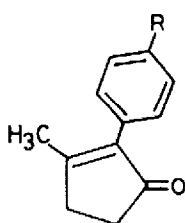
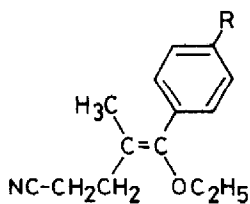
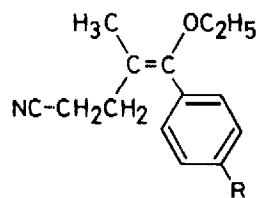
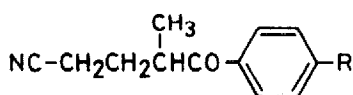
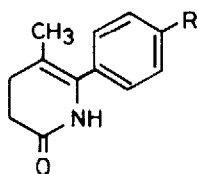
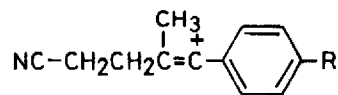
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As shown in the preceding communication ¹ derivatives of acyclic anti-vinyl-methylketoximes 1 (e.g. X = p-CH₃C₆H₄SO₃) bearing electron releasing substituents R² and R³ readily undergo π -3 assisted Beckmann rearrangement to enamides 3 by way of the azirine cation 2. This mechanism requires that the planes of the C=C and C=N groups intersect at an angle of ca. 90° during activation. Fragmentation to a nitrile and a vinyl cation 4 (route F) was not detected even when the latter should be relatively stable, as when R¹ = p-(CH₃)₂NC₆H₄ ².



On this basis fragmentation would be expected to occur if π -3 participation were suppressed for structural reasons. This has now been confirmed by the following study of the rates and products of the p-toluenesulfonates (tosylates) of 3-methyl-2-aryl-2-cyclopenten-1-one oximes 5a, 5b and 5c, the C=C and C=N groups of which are practically coplanar.

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a) R=H

b) R=OCH₃c) R=N(CH₃)₂

In 80 % ethanol at 110° the p-unsubstituted tosylate 5a reacted slowly affording the apparent hydrolysis product, i.e. the cyclic ketone 6a, in 83 % yield beside tarry material. Under the same conditions the p-CH₃O-derivative 5b yielded 11 % of fragmentation products, i.e. the Z- and E-enol ethers 7b beside their hydrolysis product 8b. In addition, 61 % of the cyclic ketone 6b beside tar were formed. At 80° the more reactive p-(CH₃)₂N-derivative 5c afforded 63 % of fragmentation products, i.e. equal amounts of the Z- and E-enol ethers 7c and their hydrolysis product 8c beside 10 % of the cyclic ketone 6c and tar. As expected, no rearranged lactams 9 were formed. The configuration of the enol ethers 7 follows from their NMR-spectra, the singlet due to the CH₃C=C group appearing at lower field in the E-isomer.

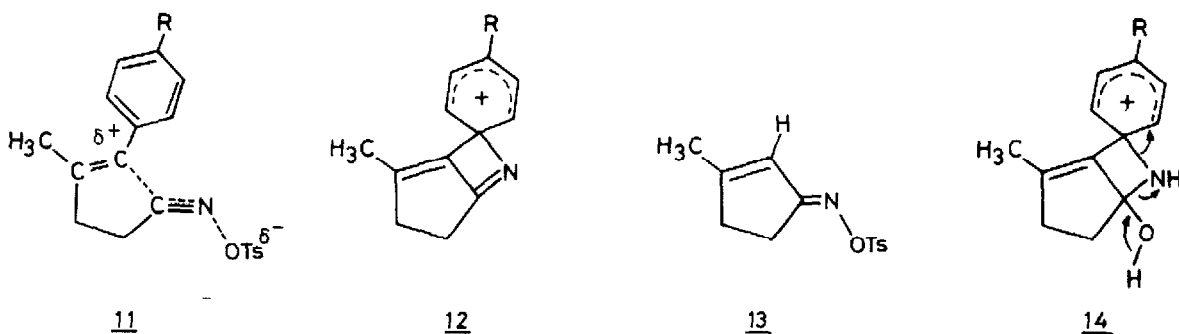
Table. First order rate constants in 80 vol.% ethanol at 90.00° C ^a.

| | k_{obs} (s^{-1}) | k_{rel} | k_{f} | k_{h} |
|-----------|--------------------------------------|------------------|-----------------------|-----------------------|
| <u>5a</u> | 4.07×10^{-6} | 1 | -- | 3.26×10^{-6} |
| <u>5b</u> | 2.72×10^{-5} | 7 | 2.72×10^{-6} | 1.63×10^{-5} |
| <u>5c</u> | 7.61×10^{-3} | 1870 | 5.33×10^{-3} | 5.33×10^{-4} |

a) with 1.5 equiv. of triethylamine

The observed first order rate constants (k_{obs}) for the tosylates 5 in 80 vol.% ethanol (Table) are the sum of the rate constants for fragmentation (k_{f}), hydrolysis (k_{h}) and resinification. Since the ratios of the latter rate constants are proportional to the known yields of the corresponding products, k_{f} and k_{h} can be calculated approximately (Table).

Surprisingly, hydrolysis of the oxime tosylates 5 competes with fragmentation. Furthermore both reactions are accelerated by electron releasing p-substituents, especially the latter reaction. This indicates a concerted fragmentation mechanism involving cleavage of the N-OTs and C(1)-C(2) bonds in the transition state 11 leading to the vinyl cations 10b and 10c, respectively ³. These reactions appear to be the first examples of vinyl cation formation by heterolytic fragmentation ⁴.



The ready hydrolysis of the oxime tosylates 5 cannot be explained by a conventional mechanism involving nucleophilic addition of water to the C=N group ⁵. Rather, the increase of the hydrolysis rates k_h caused by electron releasing p-substituents (Table) indicates aryl-4-participation in the transition state with formation of phenonium ions 12 ⁶. This is strikingly confirmed by the observation that 5a reacts ca. 75 times as fast as its analogue 13 in which the 2-phenyl group is absent. Addition of water to the strained C=N bond in 12 should lead to 14 which in turn could decompose to a cyclic ketone 6 and to imine (NH), a possible participant in the formation of the tarry material which is formed in the solvolysis of all the oxime tosylates 5.

REFERENCES

- 1) C.A. Grob & P. Wenk, Tetrahedron Letters
- 2) C.A. Grob & G. Cseh, Helv. chim. acta 47, 194 (1964); C.A. Grob & H.R. Pfändler, *ibid.* 54, 2060 (1971).
- 3) α -Aryl-substituted vinyl cations were first obtained by solvolysis of α -bromostyrenes ².
- 4) C.A. Grob & P.W. Schiess, Angew. Chemie, internat. Edit., 6, 1 (1967).
- 5) The oximes 5 (H for Ts) are not hydrolyzed under the reaction conditions.
- 6) Aryl-4-participation is usually considered to be unimportant, cf. B. Capon, Quarterly Reviews 18, 45 (1964).