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MECHANISM OF THE BECKMANN REARRANGEMENT OF α,β-UNSATURATED KETOXIMES

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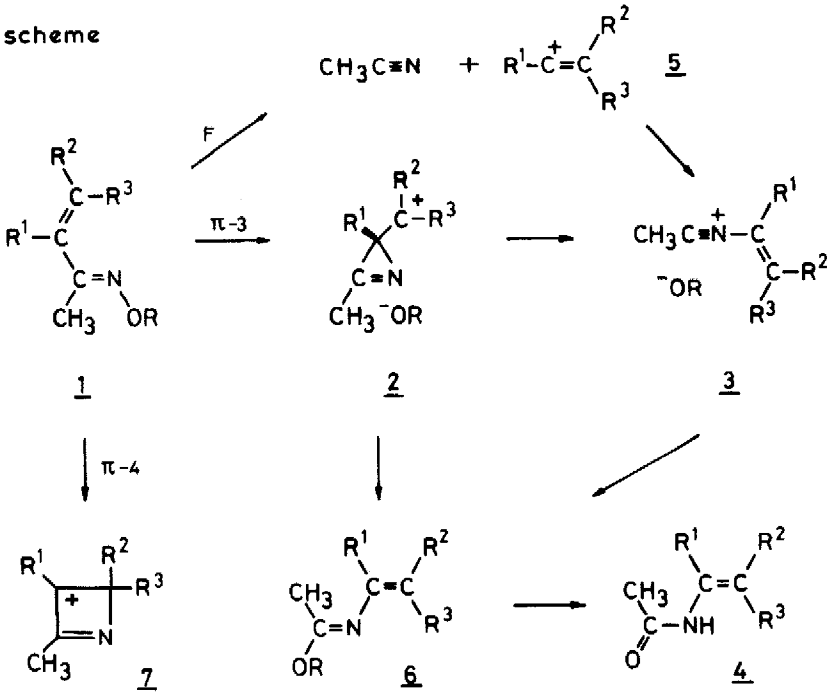
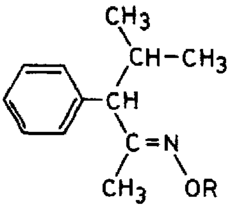
Recent studies indicate that anti-vinyl ketoxime derivatives, such as 1 (R = $ArSO_2$), do not readily undergo solvolytic Beckmann rearrangement to enamides 4 unless the planes of the C=C and C=N groups intersect at an angle of ca. 90°, for only then is π-3 assisted ionization to a cationic azirin derivative 2 possible [1]. If such participation is excluded for structural reasons, as in five- or six-membered cyclic α,β-unsaturated ketoximes, more drastic reaction conditions, such as conc. H_2SO_4, PCl_5 or PPA, are required to induce vinyl migration, and yields of enamides 4 are as a rule low [1, 2].

scheme



Whereas π-3 participation is well established in aryl migration [3], evidence for a cyclic intermediate 2 in vinyl migration appears to be still lacking. Also, no quantitative data concerning the relative rates of alkyl and vinyl migration are available. Furthermore, in the presence of strongly electron releasing α-substituents R^1 in 1 solvolytic fragmentation [4] leading to a stabilized vinyl cation 5 and a nitrile (scheme, route F) could occur. Recombination of these fragments to a nitrilium ion 3 [5] followed by hydration would also account for the formation of the enamide 4. Finally, electron releasing α-substituents R^1 could also promote the formation of an azetinium ion 7 and its resultant products by π-4 participation. A study of the products and rates of α- and β-substituted anti-vinyl-methylketoxime 2,4-dinitrophenyl (DNP) ethers 1a-1i including the saturated analogue of 1a, i.e. 8 ($R = 2,4\text{-}(NO_2)_2C_6H_3$), has now resolved these questions.



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$R^1COCHR^2R^3$

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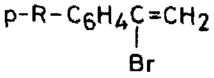

$p\text{-}R\text{-}C_6H_4C(Br){=}CH_2$

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With the exception of 1e [6], the DNP-ethers 1a-1i underwent practically quantitative rearrangement to the enamides 4 which were hydrolysed to the corresponding ketones 9 by 4N acid. In no case could products derived from the azetinium ion 7 be detected.

That vinyl migration occurs with π-3 participation follows from the rate comparisons in the Table. Thus, DNP-ether 1a reacts 2370 times as fast as the saturated analogue 8, but the rate is drastically reduced when the β-methyl groups are replaced by hydrogen, as in 1b, 1c and 1d. This demonstrates that considerable positive charge is generated at C(β) in the transition state.

On the other hand 1a reacts only 15 times faster than 1e which lacks the α-phenyl group. Furthermore, the electron-donating p-substituents CH_3, CH_3O and $(CH_3)_2N$ in 1f, 1g and 1h increase the rate by factors of only 1.2, 1.6 and 9, respectively, while

Table

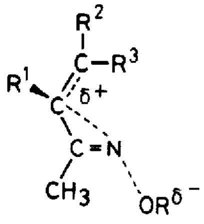
First order rate constants for 2,4-DNP-ethers in 80 vol.% ethanol (90.00°) [a]

	R^1	R^2	R^3	$k(s^{-1})$	k_{rel}
1a	C_6H_5	CH_3	CH_3	2.90×10^{-2} [b]	2370
1b	C_6H_5	H	CH_3	2.60×10^{-4}	21.3
1c	C_6H_5	CH_3	H	8.80×10^{-5}	7.2
1d	C_6H_5	H	H	1.12×10^{-5}	0.92
1e	H	CH_3	CH_3	1.89×10^{-3} [b]	155
1f	$p\text{-}CH_3C_6H_4$	CH_3	CH_3	3.43×10^{-2} [b]	2810
1g	$p\text{-}CH_3OC_6H_4$	CH_3	CH_3	4.62×10^{-2} [b]	3790
1h	$p\text{-}(CH_3)_2NC_6H_4$	CH_3	CH_3	2.60×10^{-1} [b]	21300
1i′	$p\text{-}NO_2C_6H_4$	CH_3	CH_3	2.74×10^{-3} [b]	225
8	--	--	--	1.22×10^{-5}	1

a) Containing three equivalents of triethylamine

b) Extrapolated from measurements at three other temperatures

the NO_2 group in 1i lowers it by a factor of 10. These relatively small effects disprove the generation of a sizable positive charge at C(α) in the transition state, a conclusion supported by the excellent correlation of log k of 1a and 1f-1i with Hammett's σ_p constants and by the resultant ρ value of -1.18. As shown previously [7] solvolysis rates of p-substituted α-bromostyrenes 10 correlate well with Brown's σ_p^+ constants, ρ being -6.6. Concerted fragmentation to vinyl cations 5 as well as π-4 participation are therefore precluded.



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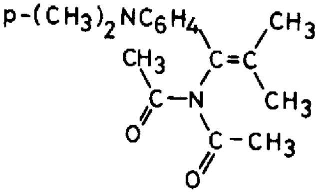

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These findings indicate that π-3 participation in the transition state 11 of the ionization of the DNP-ethers 1 leads to the ion pairs 2, the early stage of the reaction being somewhat facilitated by α-aryl substituents with +M-effects, presumably because these increase the electron density in the vinyl group. The subsequent fast steps leading to enamides 4 can be rationalized in different ways: a) The cation in 2 isomerizes to the nitrilium ion 3 [8] which adds water to form the iminol tautomer 6 (R = H) of the enamide 4. b) Nucleophilic attack on 2 by water leads directly to 6 (R = H) whereas attack by weakly nucleofugal and therefore strongly nucleophilic counter ions RO^- affords iminol ethers or esters 6. The latter possibility is clearly demonstrated by the oxime acetate 1h ($R = COCH_3$) which in refluxing 80 % ethanol furnishes the diacetylimide 12 in 71 % yield. As is well known these compounds are formed by a Mumm rearrangement [9] of an acyl imidate 6 ($R = COCH_3$) which is therefore a true intermediate in this case. The latter in turn could arise by attack of acetate ion on the azirin[illegible] cation in 2 or the nitrilium ion in 3 ($R = COCH_3$). The fact that acetate ion competes successfully with the nucleophilic solvent points to the intermediacy of ion pairs 2 or 3 ($R = COCH_3$).

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