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RING-CONTRACTION REACTIONS OF BICYCLIC NITRONIC ESTERS

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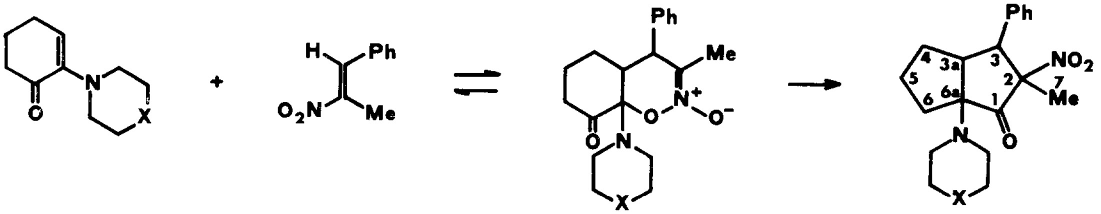
Abstract: Hexahydro-4H-1,2-benzoxazine N-oxide derivatives rearrange into 1(2H)-hexahydropentalenone systems.

Enaminones have been largely used as synthetic tools in the chemistry of functionalized enamines.[1] On the contrary, ketoenamines of the type 1 (Scheme) have received little attention.[2] The present paper deals with the reactivity of 1a,b,c with 1-phenyl-2-nitropropene (1P2NP). When the reactants are mixed thoroughly in the absence of solvent, the 1,2-oxazine N-oxide systems 2[3] are formed within few hours, in quantitative yields, whereas the reaction does not proceed in solution.

SCHEME

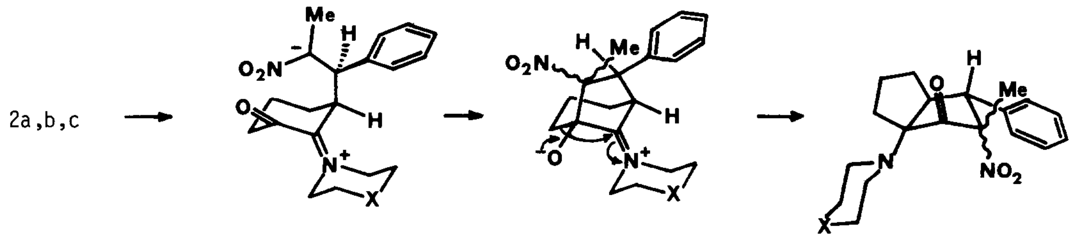


1a,b,c 2a,b,c 3a,b,c

a: X=O; b: X=CH_2; c: X=—

Of the heterocyclic systems, 2a and 2b are stable in the solid state, as they can be kept at r.t. for a long time, whereas 2c must be stored at -20°C. Instead, when 2 are dissolved in a solvent, they partially revert to the reactants and partially undergo an isomerization reaction into 3[4], the conversion being achieved rapidly and completely under more forcing conditions.

The products 3 have been assigned the structure of 1(2H)-hexahydro-pentalenone derivatives. The configuration around C-2 is uncertain, while those around C-3, C-3a and C-6a have been tentatively assigned. The phenyl group in fact is likely to be *exo* with respect to the carbocyclic ring,[5] and the attributed *cis* fusion is a consequence of the proposed mechanism. The mechanism in fact would involve the nucleophilic ring fission of 2 to give the dipolar intermediates 4, followed by collapse of the carbon anion onto the carbonyl carbon atom, to give 5. Finally, a 1,2-shift of the methylene group adjacent to the carbon bearing the negatively charged oxygen would lead to 3.



4a,b,c 5a,b,c 3a,b,c

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[3] 2a: IR (nujol) 1615 ($C=\overset{+}{N}-$), 1727 cm^{-1} (CO); PMR (80 MHz,$CDCl_3$) δ 1.70 (d, J = 1.5 Hz, Me), 3.40 (bd, C*H*Ph). 2b: IR (nujol) 1620 ($C=\overset{+}{N}-$), 1730 cm^{-1} (CO); PMR (80 MHz, $CDCl_3$) δ 1.70 (d, J = 1.5 Hz, Me), 3.30 (bd, C*H*Ph). 2c: IR (nujol) 1620 ($C=\overset{+}{N}-$), 1720 cm^{-1} (CO); PMR (80 MHz, $CDCl_3$) δ 1.60 (d, J = 1.5 Hz, Me).

[4] 3a: IR (nujol) 1750 (CO), 1545 cm^{-1} (NO_2); PMR (300 MHz, $CDCl_3$) δ 1.70 (s, Me), 3.0 (d, J = 12.0 Hz, C*H*Ph); CMR ($CDCl_3$) δ 21.2 (C-7), 46.7 (C-3), 55.8 (C-3a), 81.8 (C-6a), 95.4 (C-2), 207.4 (C-1). 3b: IR (nujol) 1750 (CO), 1542 cm^{-1} (NO_2); PMR (300 MHz, $CDCl_3$) δ 1.47 (s, Me), 2.90 (d, J = 10.0 Hz, C*H*Ph), 3.60 (bdd, H-3a); CMR ($CDCl_3$) 21.7 (C-7), 46.2 (C-3), 55.8 (C-3a), 82.6 (C-6a), 82.6 (C-6a), 95.4 (C-2), 207.2 (C-1). 3c: IR (nujol) 1750 (CO), 1545 cm^{-1} (NO_2); PMR (300 MHz, $CDCl_3$) δ 1.60 (s, Me), 2.95 (d, J = 9.0 Hz, C*H*PH), 3.70 (bdd, H-3a).

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