1*H*-Azepin-3(2*H*)-ones

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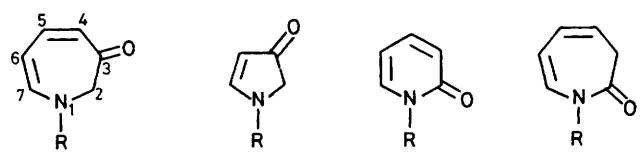
The reactivity of the title compounds (**1**) with acids, bases, and electrophiles, and in pericyclic processes is compared to the chemistry of the structurally related pyrrol-3-ones (**2**), pyridin-2-ones (**3**), and azepin-2-ones (**4**).

In the preceding communication, we reported a convenient synthesis of *N*-substituted-1*H*-azepin-3(2*H*)-ones (**1**).[1] We now describe the chemical properties of this new heterocyclic system, which is structurally related to the pyrrol-3-ones (**2**)[2] (vinylogue) and the pyridin-2-ones (**3**) (homo-analogue) as well as being isomeric with the azepin-2-ones (**4**) which have been studied in detail by Vogel[3] and Paquette.[4]

Typical reactions of the simple azepinones (**1a**) and (**1b**) are summarised in Scheme 1. The electron-rich, push–pull character of the conjugated system is reflected in reactivity towards electrophiles, which includes *O*-protonation, and *O*-alkylation with Meerwein's reagent (reactions a and b) together with deuterium exchange and halogenation† (reactions c—e). The relative reactivity of the ring positions in the latter examples [4>6(>2)] is parallel to that of electronically related sites in open-chain dienaminones[5] and pyridin-2-ones.[6,7]

The electrocyclisation and cycloaddition examples (Scheme 1, reactions f—h) demonstrate the reactivity of the diene unit of the azepin-3-ones (**1**). Such processes are also found in pyridin-2-one[8,9] and azepin-2-one[3,10] chemistry; however, Diels–Alder reactions in these systems take place only under forcing conditions, whereas (**1a**) reacts with maleic anhydride in 2 h at room temperature to give the adduct (**5**; R = Me). The *endo* stereochemistry of (**5**; R = Ph) was established by nuclear Overhauser enhancement experiments. Reaction with acetylenic dienophiles is accompanied by cleavage of the bridge, even at room temperature, to give benzene derivatives in high yield (reaction h), whereas corresponding Diels–Alder adducts of (**4**) are stable at 130 °C.[10]

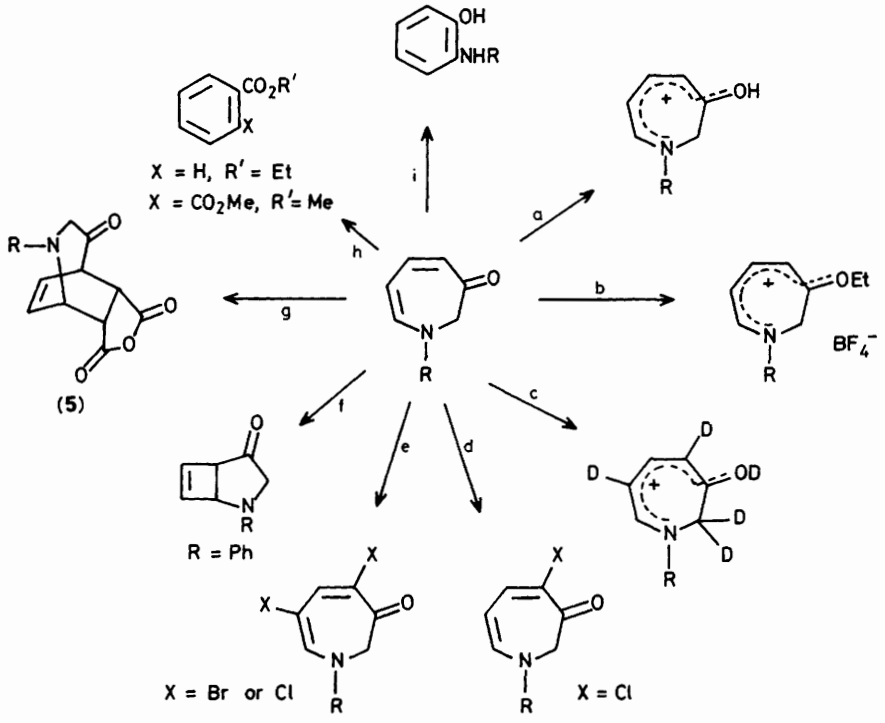
The potential acidic properties of the 2-methylene group of



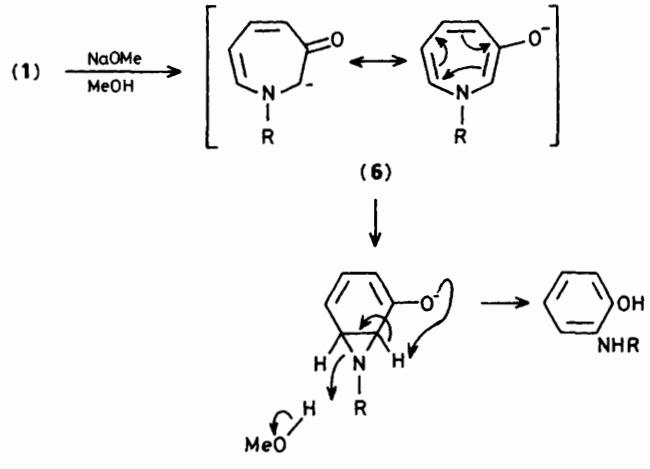
(**1**) (**2**) (**3**) (**4**)

a; R = Me
b; R = Ph

† All new compounds are characterised by their spectra, and by elemental analysis (solids), or exact mass measurement (liquids).



Scheme 1. *Reagents:* a, CF_3CO_2H; b, $Et_3O^+BF_4^-$; c, CF_3CO_2D; d, *N*-chlorosuccinimide; e, *N*-bromo or *N*-chlorosuccinimide (2 equiv.); f, *hν*; g, maleic anhydride; h, $HC{\equiv}CCO_2Et$ or $MeO_2CC{\equiv}CCO_2Me$; i, NaOMe–MeOH, then H^+.



Scheme 2

the azepin-3-ones (**1**) are profoundly influenced by the counter-Hückel (8π-electron) character of the resulting anion (**6**). Thus deuterium exchange does not occur at all under mild basic conditions (*e.g.* NaOMe in CD_3OD), and instead a quantitative ring contraction to *o*-aminophenol derivatives takes place (Scheme 1, reaction i). A possible mechanism is given in Scheme 2. In contrast, the methylene group of the pyrrol-3-ones (**2**) exchanges instantaneously, *via* a 6π-electron species, even under neutral conditions in [$^2H_4$]methanol.[2]

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