

An Easy Route to Dibenz[*c,e*]azepines via Nitrile Ylide Cyclisation: the Electrocyclic Equivalent of a Bischler–Napieralski Reaction

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N-(2-Arylbenzyl)benzimidoyl chlorides (**9**) are converted into dibenz[*c,e*]azepines (**6**) by treatment with potassium *t*-butoxide, *via* cyclisation of nitrile ylides (**4**).

Recent work has established that the 1,7-cyclisation of diene-conjugated 1,3-dipolar intermediates can provide effective routes to a variety of monocyclic and fused seven-membered heterocyclic systems such as azepines,^{1,2} diazepines,^{3,4} triazepines,⁵ and oxepines.⁶ This communication is concerned with the reactions of systems of types (**3**) and (**4**) in which both α,β - and γ,δ -double bonds of the diene are aromatic. In earlier work on diazo compound cyclisations it was found that systems incorporating a benzene or heteroaromatic ring in the α,β - or γ,δ -position, for example (**1a**)⁷ and (**1b**),⁸ cyclised to give benzo-fused 1,2-diazepines (**2a**) and (**2b**), respectively, but that the inclusion of *two* aromatic rings as in (**3**) (or thiophene-containing analogues) completely precluded cyclisation: such diazo compounds reacted only *via* loss of nitrogen to give carbene-derived products.⁹ We now report that, in contrast, nitrile ylides (**4**), of the same type as (**3**), undergo rapid cyclisation to provide an easy and effective new route to the dibenz[*c,e*]azepine system (**6**)[†] (Scheme 1

and Table 1). Examples of this system are known to be useful as anxiolytics.¹⁰ The nitrile ylides (**4**) were generated at 0 °C or room temperature by the reaction of the imidoyl chlorides (**9**) with potassium *t*-butoxide in tetrahydrofuran; their presence was indicated in some cases by a transient purple colour. An attraction of this route is the ease of preparation of the amide

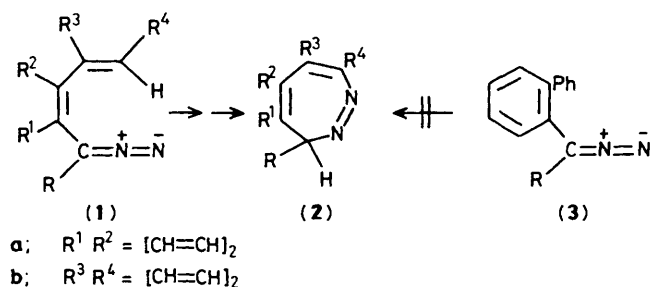
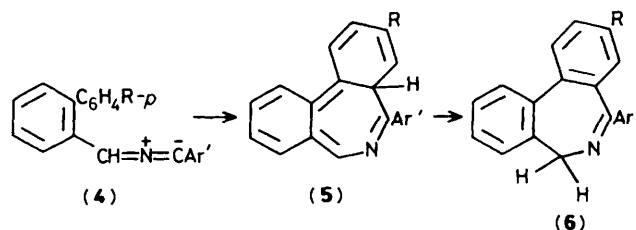


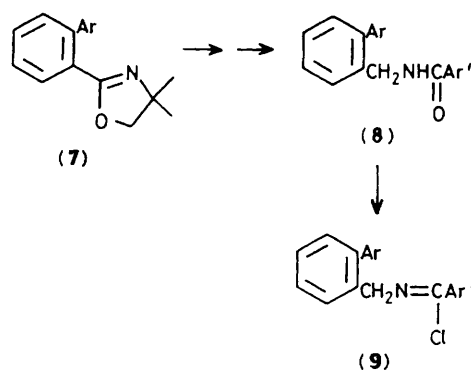
Table 1. Yields of dibenzazepines (**6**).

(6)	R	Ar'	Yield (%)
a	H	Ph	69
b	Cl	Ph	77
c	Cl	<i>o</i> -ClC ₆ H ₄	72
d	Cl	<i>o</i> -FC ₆ H ₄	65
e	Cl	3,4-(MeO) ₂ C ₆ H ₃	78

[†] The products had lit.¹⁰ m.p.s for known examples (**6a**, **b**, **d**) or were identified by elemental analysis and n.m.r. spectroscopy.



Scheme 1



Scheme 2

precursors (8) by conventional methods under mild conditions, for example as shown in Scheme 2 utilising as the key step Meyer's oxazoline route to biaryls¹¹ (7) followed by conversion of the oxazoline ring into CHO, CH=NOH, CH₂NH₂, and CH₂NHCOAr'. The imidoyl chlorides (9) were prepared by conventional routes¹² or by the use of dimethylformamminium chloride as reagent (prepared *in situ* by reaction of thionyl chloride with *N,N*-dimethylformamide). This synthesis thus permits the incorporation of a wide range of substituents into the dibenzazepine ring and the 7-aryl group (Ar').

Overall the conversion of the amide (8) into the dibenzazepine (6) is equivalent to a Bischler-Napieralski-type reaction, but is achieved under very mild conditions. It apparently proceeds *via* an electrocyclic aromatic substitution process which is intrinsically less sensitive to the polar influence of

substituents in the aromatic ring under attack than the Bischler-Napieralski reaction which involves electrophilic substitution.

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