# *N*-Iminobenzocinnolinium Ylides and Dibenzo-1,2,3-triazepines

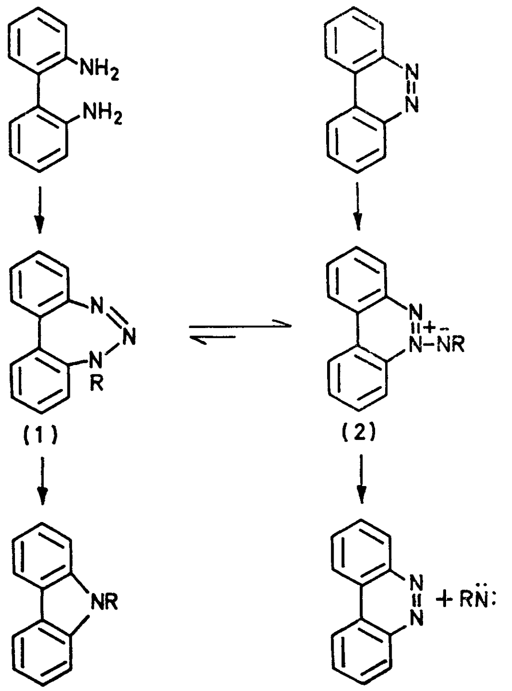
By STEPHANIE F. GAIT, C. W. REES,* and R. C. STORR

(*The Robert Robinson Laboratories, University of Liverpool, P.O. Box* 147, *Liverpool* L69 3BX)

*Summary* Treatment of 2,2′-diaminobiphenyl with pentyl nitrite or *N*-nitrosodiphenylamine gives the ylide (**2**; R = H), possibly *via* the triazepine (**1**; R = H); *N*-substituted derivatives also exist as the ylide (**2**) rather than the triazepine (**1**), and yield benzocinnoline and the nitrene (R–Ṅ:) on photolysis or thermolysis.

WE wished to prepare dibenzo[*d*,*f*]-1,2,3-triazepine (**1**; R = H) as the first example of the 1,2,3-triazepine ring system. Diazotisation of 2,2′-diaminobiphenyl in normal acidic conditions gives carbazole but treatment with pentyl nitrite or *N*-nitrosodiphenylamine in benzene under reflux in the absence of acid gave a stable, bright yellow compound,

$C_{12}H_9N_3$, m.p. 130°. This product was not the desired triazepine (**1**; R = H), however, but the isomeric iminobenzocinnolinium ylide (**2**; R = H). This ylide was readily converted into *N*-substituted derivatives where the substituent is electron withdrawing, *e.g.*, R = acetyl, benzoyl, toluene-*p*-sulphonyl, ethoxycarbonyl, and 2,4-dinitrophenyl.



Spectral data strongly support the suggested ylide structures for (**2**). Thus, all derivatives show the three main u.v. absorption bands characteristic of benzocinnolines and benzocinnoline *N*-oxides. The most intense band occurs at *ca.* 250 nm ($\epsilon$ *ca.* 35,000); the positions of the two lower intensity ($\epsilon$ *ca.* 10,000), higher wavelength absorptions vary as expected with the nature of the *N*-substituent. The aromatic $^1H$ n.m.r. spectra of (**2**) are identical with that of benzocinnoline *N*-oxide. The N–H absorption in the i.r. spectrum of the parent ylide (**2**; R = H) is a sharp singlet (at 3150 $cm^{-1}$) which would not be expected for the prototropic triazepine (**1**; R = H). The low frequency of the carbonyl i.r. absorptions when R = COMe (1590 $cm^{-1}$), COPh (1605 $cm^{-1}$), and $CO_2Et$ (1660 $cm^{-1}$) indicates considerable delocalisation of charge on to oxygen, as expected for the ylide structures. Also, these absorptions show a shift of *ca.* 100 $cm^{-1}$ to higher frequency in the picrate salts of (**2**); a similar effect has been noted for analogous pyridinium ylides.[1] Finally the base peaks in the mass spectra of (**2**) occur at *m/e* 180 (benzocinnoline).

Chemical evidence is also in agreement with the ylide structures. Thus, (**2**; R = H) gives benzocinnoline quantitatively on treatment with pentyl nitrite or sodium nitrite or on catalytic hydrogenation; it forms a very stable hydrochloride which has none of the characteristics of a masked diazonium compound, as would be expected for the triazepine (**1**; R = H). Also, (**2**; R = H) can be formed, in low yield, by amination of benzocinnoline with hydroxylamine *O*-sulphonic acid.

Also in accord with their ylide structure, compounds (**2**) give benzocinnoline (from 60% when R = $CO_2Et$ to 0% when R = 2,4-dinitrophenyl) on photolysis† at room temperature. No trace of carbazoles, which would be expected from the triazepines (**1**), is observed except for a minor amount from the parent compound (**2**; R = H). Benzocinnoline (from 80% when R = $CO_2Et$ to 10% when R = 2,4-dinitrophenyl) is also formed, rather than carbazoles, when the compounds are heated (120—160°) in solution, again except for the parent compound, which gives carbazole quantitatively, and the benzoyl derivative which gives mainly *N*-benzoylcarbazole (50%) together with benzocinnoline (20%).

There is an increasing number of examples of the formation of nitrenes by the (usually photolytic) fragmentation of heterocyclic *N*-imino-ylides.[1,2] We have established that ethoxycarbonyl nitrene is the second fragment in the above thermal, as well as photochemical decompositions of the ylide (**2**; R = $CO_2Et$); expected C–H insertion products of the nitrene have been isolated (*ca.* 30%) after photolysis in cyclohexane and thermolysis in decalin.

Although most of this evidence supports the suggested ylide structures, the formation of ylide (**2**; R = H) by diazotisation of 2,2′-diaminobiphenyl, and the thermal decomposition of (**2**; R = H and COPh) to give carbazoles implies an equilibrium between the benzocinnolinium ylides and dibenzotriazepines in which the triazepine is unstable with respect to the ylide.

(*Received, October* 19*th*, **1971**; *Com.* 1825.)

---

† Direct photolysis in methyl cyanide for 24 h using a 125 W Hanovia medium-pressure mercury lamp with a quartz jacket.

[1] T. Sasaki, K. Kanematsu, A. Kakehi, I. Ichikawa, and K. Hayakawa, *J. Org. Chem.*, 1970, **35**, 426.

[2] V. Snieckus, *Chem. Comm.*, 1969, 831; V. Snieckus and G. Kan, *ibid.*, 1970, 172; T. Shiba, K. Yamane, and H. Kato, *ibid.*, p. 1592; C. W. Bird, D. Y. Wong, G. V. Boyd, and A. J. H. Summers, *Tetrahedron Letters*, 1971, 3187; C. S. Angadiyavar, K. B. Sukumaran, and M. V. George, *ibid.*, p. 633.