Anomalous Cycloadducts from Benzocinnoline *N*-Alkylimides and Acetylenic Esters

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Summary With acetylenedicarboxylic esters benzocinnoline *N*-alkylimides (**1**) give dibenzoimidazolinodihydrodiazepines (**4**), which rearrange to 1-(2′-aminobiphenyl-2-yl) imidazoles (**5**) with acid; the latter undergo novel internuclear cyclisations upon attempted deamination.

BENZOCINNOLINE *N*-ETHOXYCARBONYLIMIDES give azomethine imines with acetylenedicarboxylic esters by 1,5-dipolar cycloaddition and ring opening.[1] With olefinic dipolarophiles, benzocinnoline is formed under the vigorous conditions necessary to effect reaction. In a search for more reactive benzocinnoline *N*-imides we have studied benzocinnoline alkylimides (**1**), readily obtained by alkylation of benzocinnoline *N*-imide. These react with acetylenic esters to give anomalous 1:1 adducts, the formation of which can now be readily rationalised following the elucidation of the novel rearrangement found for benzocinnoline *N*-alkylbenzaminimides (**7**).[2]

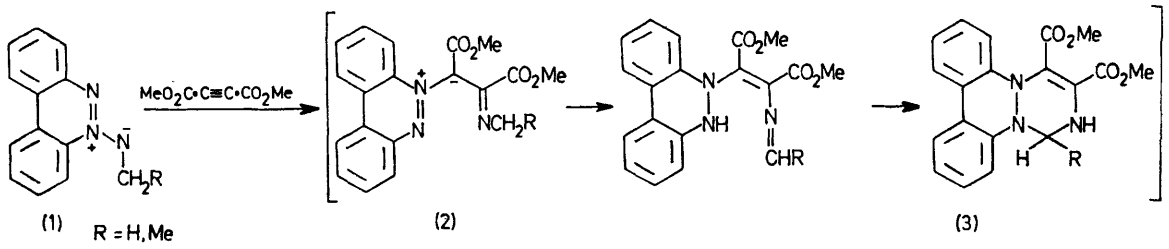
Reaction of the *N*-methyl imide (**1**; R = H), m.p. 92°, with dimethyl acetylenedicarboxylate in dimethylformamide at room temperature is rapid and exothermic. When the resulting solution is poured into water a colourless 1:1 adduct (80%), m.p. 156—157°, is precipitated; spectral data are consistent with structure (**4**; R = H):† δ ($CDCl_3$) 7·6—6·8 (8H, m, ArH), 5·2 (1H, d, *J* 16 Hz), 4·8 (1H, d, *J* 16 Hz), 4·5 (1H, s, removed by addition of D_2O, NH), 3·94 (3H, s, CO_2Me) and 3·76 (3H, s, CO_2Me); ν_{max} (KBr) 3340 (NH), 1760 and 1740 (CO_2Me), and 1650 (C=N) cm^{-1}. Chemical support for structure (**4**; R=H) comes from its quantitative rearrangement in cold sulphuric acid to the aminoimidazole (**5**; R = H), m.p. 164—165°. Structure (**5**; R = H) was fully supported by spectral data and by the following chemical correlation. Diazotisation of (**5**; R = H) followed by treatment with hypophosphorous acid, in an attempt to effect deamination, gave the internuclear cyclisation product (**6**), which on hydrolysis and decarboxylation gave imidazo[1,2,-*f*]phenanthridine, m.p. 135—136°. This was identical with the product of manganese dioxide oxidation of its known 2,3-dihydro derivative.[3]

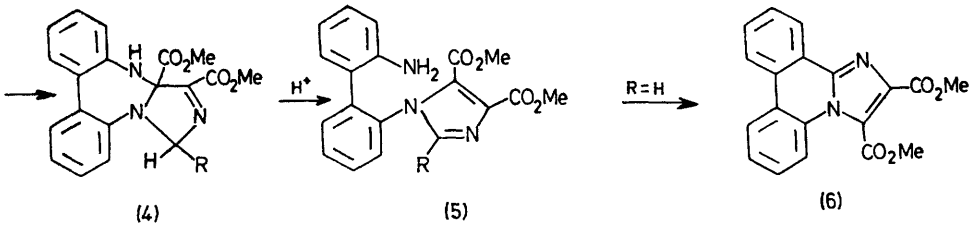
The proposed reaction sequence shown in the Scheme involves a rearrangement of the expected azomethine imine (**2**) which is directly analogous to that observed for the isoelectronic imidoazimine (**7**).[2] In the latter case the intermediate corresponding to (**4**) aromatised spontaneously without acid catalysis, presumably because cleavage of an NH rather than CH bond is involved.

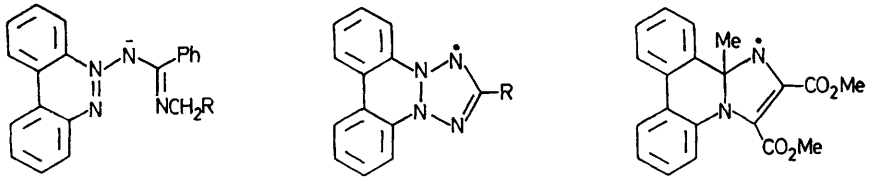
Analogous cycloadditions were observed for the ylide (**1**; R = H) and diethyl acetylenedicarboxylate and for the ethyl ylide (**1**; R = Me) with dimethyl and diethyl acetylenedicarboxylate.

The cyclisation observed upon attempted deamination of the amine (**5**; R = H) presumably involves hitherto unobserved radical attack on an imidazole nucleus. Similar attempted deamination of the amine (**5**; R = Me) surprisingly gave

† The alternative structure (**3**; R = H) for this product is considered unlikely since inversion about ring nitrogens would render the two methylene protons equivalent. The AB quartet remains sharp up to 160° when irreversible decomposition occurs.







6-methylphenanthridine. A possible analogy for this intriguing reaction is to be found in the formation of benzocinnoline by reduction of radical (**8**).[4] A similar radical (**9**) may be involved in our reaction, and under the reducing conditions the corresponding anion could be formed and undergo retro-1,3-dipolar cycloaddition.

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[3] R. F. Cookson and R. E. Rodway, *J.C.S. Chem. Comm.*, 1972, 511; H.-L. Pan and T. L. Fletcher, *J. Heterocyclic Chem.*, 1972, **9**, 859,
[4] F. A. Neugebauer, *Angew. Chem. Internat. Edn.* 1973, **12**, 455.