Synthesis of Dibenzo[*c,f*]-1,2-oxazepines as Primary Stable Photo-products in the Photolyses of Acridine 10-Oxides

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Summary The dibenzo[*c,f*]-1,2-oxazepines (**2a** and **2b**) were obtained as the major products from 9-cyano- and 9-chloro-acridine 10-oxides by irradiation in benzene.

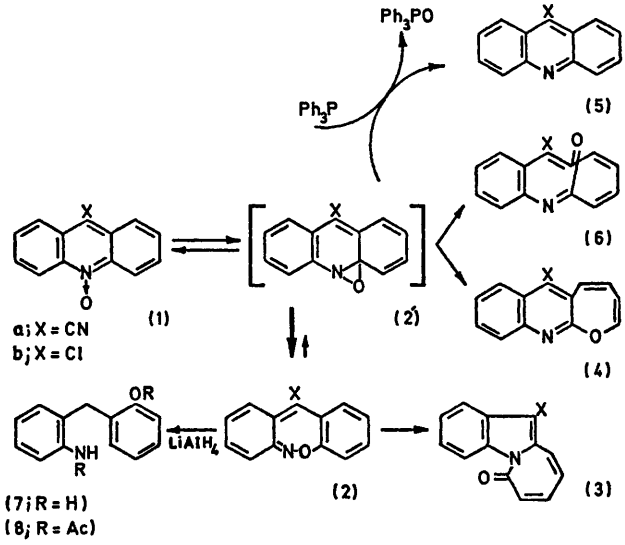
THOUGH the intermediacy of a 1,2-oxazepine species has frequently been suggested in the photo-isomerization reaction of aromatic amine oxides (*e.g.*, pyridine,[1] acridine,[2] and benzo[*a*]phenazine *N*-oxides[3]), actual isolation of such a species has not been achieved as yet. Recent identification[4] of such a species (existing only in solution) in the irradiated solution of acridine and 9-methylacridine 10-oxides prompted us to irradiate a variety of acridine 10-oxides in attempt to obtain an isolable 1,2-oxazepine derivative. As a result, we now report the synthesis, isolation, and properties of two dibenzo[*c,f*]-1,2-oxazepines, these being the first examples of stable 1,2-oxazepines.

Irradiation of a solution of 9-cyanoacridine 10-oxide in benzene (0·01 mol l^{-1}) with a Hanovia high-pressure mercury arc (450 W) using a Pyrex filter followed by repeated extraction with pentane gave an orange-red crystalline solid (**2a**) (59%), m.p. 105—109°, ν_{max} (KBr) 2220, 1600, 760, and 740 cm^{-1}, λ_{max} (log ϵ) (cyclohexane) 224(4·50) and 400 nm (3·68), and τ (C_6D_6) 4·15 (t, 7 Hz, 1H), 4·0 (t, 7 Hz, 1H), 2·7—3·4 (m, 5H), and 2·5 (d, 8 Hz, 1H). The pentane insoluble portion was chromatographed on silica gel affording 11-cyano-6-oxo-6*H*-azepinoindole (**3a**), 11-cyano-oxepino[2,3-*b*]quinoline (**4a**), 9-cyanoacridine (**5a**), and (**1a**) in respective yields of 9, 3, 1, and 13%.†

Compound (**2a**) underwent a variety of isomerization reactions under mild conditions. Thus, for example, it isomerized to 1-cyanobenzo[*c*]-2-aza-1,6-oxido[10]annulene (**6a**),† (**3a**), and (**4a**) in respective yields of 15, 3, and 65%

† The rearrangement products (**3a**, **4a**, and **6a**) were obtained by photolysis of (**1a**) followed by chromatography on silica gel, and their structures were determined unequivocally.[5]

by column chromatography on either silica gel or alumina. The g.l.c. chromatogram (OV-17 at 220°) of (**2a**) showed four peaks whose relative retention times were the same as those of (**5a**), (**4a**), (**6a**) [and/or (**3a**)],‡ and (**1a**).



Scheme

9-Chloroacridine 10-oxide (**1b**) also gave orange needles (**2b**; m.p. 51—54°) as a main product (*ca.* 50%) from the pentane soluble portion of the products. Compound (**2b**) showed almost the same spectroscopic and chemical properties as (**2a**) but readily isomerized to the starting *N*-oxide (**1b**). Thus, (**2b**) gave (**1b**) in 90% yield on heating in an aprotic solvent. $LiAlH_4$ reduction of (**2b**) gave an oily hydroxyamino-compound (**7**) in 20—25% yield, which was characterized as 2-(2′-aminobenzyl)phenol by conversion into the known diacetate (**8**; m.p. 119—120°).[4]

All of the reactions of (**2a**) and (**2b**) indicate that they have the dibenzo[*c*,*f*]-1,2-oxazepine structure (**2**).

It should be noted that both (**2a**) and (**2b**) were deoxygenated quantitatively to the corresponding acridines, (**5a**) and (**5b**), by triphenylphosphine in acetonitrile at room temperature. This and some reactions of (**2**), *e.g.*, (**2b**)→(**1b**) and (**2a**)→(**4a**) and (**6a**), can be satisfactorily explained if we assume that minor equilibration of (**2**) with the corresponding oxaziridine (**2′**) exists under these conditions, though so far the formation of the latter species could not be detected from u.v. and other spectra of (**2a**) and (**2b**).

The present direct isolation of (**2a**) and (**2b**) not only constitutes the first synthesis of 1,2-oxazepine derivatives but also lends experimental support to the previously suggested mechanism (Scheme) for the photolyses of acridine 10-oxides[2–4] and the related *N*-oxides.[1]

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‡ Compounds (**3a**) and (**6a**) showed the same relative retention time.

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[4] S. Yamada, M. Ishikawa, and C. Kaneko, *Tetrahedron Letters*, 1972, 977.
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