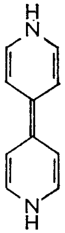
865. *Acridine Syntheses and Reactions. Part VII.*[1] *Some Binuclear Acridines*

By Adrien Albert and Gordon Catterall

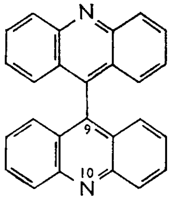
When acridines are heated under reflux with sodium carbonate in ethylene glycol, the corresponding biacridanyls are produced.

The literature provides a few examples of the dimerisation of a heteroaromatic ring, by acid or alkali, to the corresponding biylidene of type (I). Typical monomers giving this reaction are 2- and 6-hydroxypteridine,[2] and ethyl 1,2-dihydro-1-methyl-2-oxo-1,4,5-triazanaphthalene-3-carboxylate.[3]

To extend this reaction, we heated acridine and also *N*-methylacridinium chloride with acid and with alkali. No reaction occurred when acridine was refluxed with N-hydrochloric acid (alone, or in the presence of zinc chloride), or with N-ethanolic potassium hydroxide, in the dark for 12 hr. in an atmosphere of nitrogen. However, refluxing similarly with sodium carbonate in ethylene glycol gave a mixture of acridan (14%) and biacridanyl (9,9′,10,10′-tetrahydro-9,9′-biacridyl) (17%). Biacridanyl was also obtained as a by-product in the reduction of biacridyl (II) with zinc and hydrochloric acid, a reaction hitherto supposed to give 9,9′-biacridylidene exclusively.[4]



(I)



(II)

N-Methylacridinium chloride was unchanged by refluxing with N-hydrochloric acid, whereas N-sodium hydroxide produced *NN*′-dimethylbiacridanyl (3%) as well as *N*-methylacridan (12·5%) and *N*-methylacridone (25%), the last two substances arising by the Pictet–Patry disproportionation [5] of the pseudo-base of the starting material. More interestingly,

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[1] Part VI, A. Albert, preceding Paper.

[2] A. Albert and F. Reich, *J.*, 1960, 1370.

[3] J. W. Clark-Lewis and M. J. Thompson, *J.*, 1957, 430.

[4] H. Decker and W. Petsch, *J. prakt. Chem.*, 1935, **143**, 211.

[5] A. Pictet and E. Patry, *Ber.*, 1902, **35**, 2534.

a 55% yield of *NN'*-dimethylbiacridanyl was obtained by heating *N*-methylacridinium chloride with sodium carbonate in ethylene glycol at 100° (heating in glycol alone produced no change).

The production of biacridanyls (instead of the expected biacridylidenes) from acridines involves a reductive step (one hydrogen atom per acridine nucleus).

Two new reactions of *NN'*-dimethylbiacridanyl were noted: heating in glycol under nitrogen at 200° reduces it to *N*-methylacridan, and refluxing it with iodine in chloroform oxidises it to *N*-methylacridinium iodide.

EXPERIMENTAL

Condensation of Acridine.—Acridine (0·6 g.), heated in 0·25N-sodium carbonate in ethylene glycol (in the dark, under nitrogen, at 150—160°) for 7 hr., formed a colourless deposit. This, filtered off from the cooled suspension, gave biacridanyl (0·1 g.), m. p. 242—245° (decomp.) in an apparatus preheated to 230° (lit.,[6] 247°). It gave a single spot (R_F 0·8) on paper chromatography in butanol–5N-acetic acid (7 : 3). The infrared spectrum [$\nu_{max.}$ 3330; (NH str.), 2875 (non-arom. CH str.) cm.$^{-1}$] was identical with that of a specimen made by the action of Raney nickel on acridine in xylene.[7] The filtrate, on refrigeration, deposited a precipitate which, recrystallised from dilute ethanol, gave material (0·09 g.), m. p. 162—165°, the infrared spectrum of which corresponded to that of an authentic specimen of acridan.

Biacridyl (1·38 g.), prepared by the action of phenylmagnesium bromide on 9-chloroacridine dichlorophosphate,[8] was reduced with zinc and hydrochloric acid;[4] the precipitate was dried and continuously extracted with benzene. Concentration of the extract gave crystals (0·53 g.) which, extracted with 500 parts of boiling ethanol, left biacridanyl (0·08 g.), m. p. 243—244° (decomp.), identical with the above two specimens. The ethanolic filtrate deposited pale orange crystals of 9,9'-biacridylidene, m. p. >350° (lit.,[4] 392°), $\nu_{max.}$ 3200, 3100 (NH str.), 3040, and 2960 cm.$^{-1}$. The infrared spectrum of the crystals from the benzene extract was a combination of those of biacridanyl and biacridylidene.

Condensation of N-*Methylacridinium Chloride.*—The dihydrate of this salt (0·5 g.) and N-sodium hydroxide (40 ml.) were refluxed (in the dark, under nitrogen) for 12 hr. The precipitate was removed from the cooled suspension, washed with water (discarded), then extracted with boiling 5N-hydrochloric acid (30 ml.). The insoluble material (10 mg.) was identified as *NN'*-dimethyl-9,9'-biacridanyl by comparison of the infrared spectrum with that of an authentic specimen.[9]

N-Methylacridinium chloride dihydrate (2 g.) and a 0·25N-solution of sodium carbonate in ethylene glycol (100 ml.) were heated (at 100°, in the dark, under nitrogen) for 8 hr. *NN'*-Dimethylbiacridanyl (0·8 g.), which deposited from the cooled liquid, had m. p. and mixed m. p. 270—271°, and the infrared spectrum was identical with that of an authentic specimen[9] (Found: C, 86·7; H, 6·1; N, 7·1. Calc. for $C_{28}H_{24}N_2$: C, 86·6; H, 6·2; N, 7·2%). The picrate (from ethanol) had m. p. 187—188° (decomp.).

The infrared spectra (KBr discs) were taken with a Unicam S.P. 200 spectrophotometer.

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[6] K. Lehmstedt and H. Hundertmark, *Ber.*, 1930, **63**, 1229.
[7] G. M. Badger and W. H. F. Sasse, *J.*, 1956, 616.
[8] K. Gleu and A. Schubert, *Ber.*, 1940, **73**, 805.
[9] A. M. Grigorovski and A. A. Simeonov, *Zhur. obshchei Khim.*, 1951, **21**, 589.