Acridone Studies. XIII*
The Nature of Hexabromoacridone

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Abstract
Acheson's 'hexabromoacridone' is shown to be 1,2,3,4,5,7-hexabromo-9-acridone by a combination of n.m.r. spectroscopy and synthesis from specifically tritiated 9-acridones. In boiling piperidine, the bromines at C1 and C3 are replaced.

The bromination of 9-acridone or 10-methyl-9-acridone under vigorous conditions gives a hexabromo-9-acridone which is also obtainable from 2,4,5,7-tetrabromo-9-acridone. Although this compound is insufficiently soluble in most organic solvents to allow its n.m.r. spectrum to be measured, its potassium salt in dimethyl sulphoxide shows two doublets, $\delta$ 8·20 and 7·85 ($J$ 2·0 Hz), and thus the structure is 1,2,3,4,5,7-hexabromo-9-acridone (1). The spectrum was essentially identical with that of 2,4,5,7-tetrabromo-9-acridone (2) taken under the same conditions.

In connection with some other work we have developed a method for the synthesis of specifically labelled 10-methyl-9-acridones and we have used these to confirm the above conclusion. 1-Bromo-10-methyl-9-acridone and 3-bromo-10-methyl-9-acridone were reduced with sodium methoxide in methanol to 1-tritio- and 3-tritio-10-methyl-9-acridone respectively. These compounds were then individually brominated to give hexabromo-9-acridone and the specific radioactivity of the product in each case was essentially half that of the reactant.

In accordance with our previous work, in which it was shown that bromine at C1 and C3 in 9-acridones was displaced by piperidine considerably faster than at C2 and C4, (1) reacts with piperidine at 100° to give a dipiperidino derivative (3).


The substitution pattern for hexabromo-9-acridone is unexpected, as it would be anticipated that substitution of the final bromine would occur in the least electron-deficient ring. An attempt to detect intermediate brominated products led only to the detection and isolation of the tetrabromo-9-acridone (2). Our early work suggests that polysubstituted acridones tend to undergo addition reactions, and it may be that the intermediate pentabromo-9-acridone has the more substituted ring slightly buckled and is therefore susceptible to rapid addition–elimination.

Experimental

General experimental details have been given previously.2,5 Hexabromo-9-acridone was prepared by the method of Acheson and Robinson,1 and was recrystallized from m-cresol, dimethylformamide, and dimethyl sulphoxide, the m.p. remaining unchanged at 346-347°. The n.m.r. spectrum of the potassium salt, generated in dimethyl sulphoxide by potassium t-butoxide, showed the presence of two doublets at δ 7.85 and 8.20 (J 2.0 Hz).

When the reaction was allowed to proceed for 2 h instead of 15 h, fractional crystallization from dimethylformamide allowed the isolation of 2,4,5,7-tetrabromo-9-acridone, m.p. 306° (lit.1 307-308°) (Found: C, 30.3; H, 1.2. Calc. for C13H5Br4NO: C, 30.5; H, 1.0%).

Thin-layer chromatography showed the presence of only the tetrabromo and hexabromo acridones.

10-Methyl-9-acridone-[I-T] and -[3-T] were prepared as detailed previously.2 The activity of the 10-methyl-9-acridone[1-T] was 2.5 x 10⁶ d min⁻¹ mmol⁻¹ and that of the [3-T] isomer 2.65 x 10⁷ d min⁻¹ mmol⁻¹.

Hexabromoacridone[T]

Each of the tritiated 10-methyl-9-acridones above (50 mg) was brominated for 18 h by the method of Acheson and Robinson.1 The hexabromo-9-acridone (140 mg) recrystallized repeatedly from dimethylformamide had m.p. 346-348°. Because of its low solubility in the toluene scintillator solution, samples (c. 0.5 mg) were counted in a mixture of scintillator (3.5 ml), methanol (0.5 ml) and ethanolamine (0.1 ml), which was homogeneous. Sample counts were corrected for quenching; that derived from 10-methyl-9-acridone[1-T] had an activity of 1.35 x 10⁶ d min⁻¹ mmol⁻¹ and that from 10-methyl-9-acridone[3-T] 1.25 x 10⁷ d min⁻¹ mmol⁻¹.

2,4,5,7-Tetrapromono-1,3-dipiperidino-9-acridone

Hexabromo-9-acridine (50 mg) was dissolved in piperidine (4.0 ml), and the mixture heated at 100° for 3 h. On addition of water (0.5 ml) the product precipitated, and was recrystallized from dimethylformamide as yellow crystals, m.p. 203° (Found: C, 40.8; H, 3.8; N, 6.2. Calc. for C26H23Br4N3O requires C, 40.8; H, 3.8; N, 6.2%). The mass spectrum showed no molecular ion; the highest peak, a quintet centred at m/e 511, corresponded to loss of both piperidine groups. Other peaks showed the stepwise loss of each of the four bromine atoms, each with its corresponding peak for m/e-CO. The n.m.r. spectrum (K salt, Me2SO) showed one-proton doublets at δ 8.50 and 8.03 (J 3 Hz) and multiplets at 2.60 (8H) and 1.22 (12H).

On one occasion, after a reaction time of only 1 h, chloroform extraction of the product gave a small amount of a product, m.p. 300°, the n.m.r. spectrum of which suggests it is 2,3,4,5,7-pentabromo-1-piperidino-9-acridone (4) [δ 8.50 (1H) doublet, 3 Hz; 8.03 (1H) doublet, 3Hz; 2.70 (4H) multiplet; 1.30 (6H) multiplet] (Found: N, 4.5. Calc. for C14H13Br5N2O requires N, 4.2%).

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