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Acridone Studies. XIII*
The Nature of Hexabromoacridone

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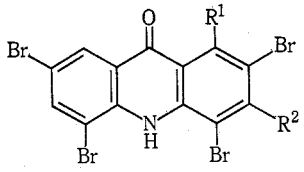
Abstract

Acheson's 'hexabromoacridone'[1] 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[1] 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, δ 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.



	R^1	R^2
(1)	Br	Br
(2)	H	H
(3)	$C_5H_{10}N$	$C_5H_{10}N$
(4)	$C_5H_{10}N$	Br

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[T] in methanol[2] 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,[3] 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).

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[1] Acheson, R. M., and Robinson, M. J. T., *J. Chem. Soc.*, 1953, 232.
[2] Hodgeman, D. K. C., and Prager, R. H., *Aust. J. Chem.*, 1972, **25**, 585.
[3] Gream, G. E., Hodgeman, D. K. C., and Prager, R. H., *Aust. J. Chem.*, 1972, **25**, 569.

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[4] 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 $C_{13}H_5Br_4NO$: C, 30·5; H, 1·0%).

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

10-Methyl-9-acridone-[1-T] and -[3-T] were prepared as detailed previously.[2] The activity of the 10-methyl-9-acridone[*1-T*] was $2·5 \times 10^6$ d min^{-1} mmol^{-1} and that of the [*3-T*] isomer $2·65 \times 10^7$ 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 $1·35 \times 10^6$ d min^{-1} mmol^{-1} and that from 10-methyl-9-acridone[*3-T*] $1·25 \times 10^7$ d min^{-1} mmol^{-1}.

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

Hexabromo-9-acridone (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, 3·7; N, 6·2. $C_{23}H_{23}Br_4N_3O$ 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, Me_2SO) 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. $C_{18}H_{13}Br_5N_2O$ requires N, 4·2%).

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[4] See Prager, R. H., and Thredgold, H. M., *Aust. J. Chem.*, 1969, **22**, 1511, and previous papers.
[5] Prager, R. H., and Hodgeman, D. K. C., *Aust. J. Chem.*, 1972, **25**, 1761.