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BROMINATION OF 1-AMINO-4-FLUORONAPHTHALENE[*]

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In a recent study (1) of substituent effects in naphthalene, we had occasion to prepare a series of substituted fluoronaphthalenes including 2-bromo-4-fluoronaphthalene (I). We accordingly brominated 1-amino-4-fluoronaphthalene (IIa) under the conditions used by Adcock and Wells (2) to effect exclusive monobromination of 1-amino-4-methylnaphthalene (IIb); however in this case we obtained, in addition to the expected monobromo derivative (III), a dibromo derivative (X) of unknown structure, which appeared to be homogeneous to g.l.c.. Since III and X proved difficult to separate, we deaminated the crude mixture and separated the product by fractional distillation; in this way we obtained the required I, together with a dibromofluoronaphthalene (Y) which again proved homogeneous to g.l.c..

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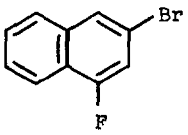
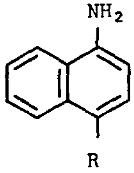
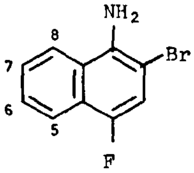


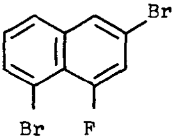
I



II; a, R=F
b, R=CH_3



III



IV

The orientation of Y, and so of X, seemed to us of some interest. Presumably X arises by further bromination of III; since the reaction is so orientationally specific, reactions of this type could be of synthetic importance in other connections. Furthermore, the orientation presents an amusing theoretical problem; reasons could be adduced for supposing that any one of the 5-, 7-, and 8-positions in III might be the most reactive.†

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† The *α*-positions in naphthalene are more reactive than the *β*; this should favor 5- or 8-substitution in III. The 5-position is activated by NH_2, the 8-position by *F* + *Br*; normally NH_2 would win - but here the 5-position will be deactivated by the inductive and/or field effect of the adjacent fluorine. And finally, if this deactivating effect is large, and if at the same time the activating effect of NH_2 is greater than that of *F* + *Br*, the 7-position might end up victorious.

The structure of Y was established to be IV by measurement of its dipole moment. The measured dipole moments of Y, and of the necessary reference compounds, in benzene, were as follows:

1-Fluoronaphthalene	1.51 D
1-Bromonaphthalene	1.70 D
2-Bromonaphthalene	1.74 D
Y	2.39 D

The second bromine in Y must certainly occupy the 5-, 6-, 7-, or 8-position in I; apart from theoretical considerations, this was indicated unambiguously by the proton n.m.r. spectrum of Y which showed the presence of two isolated protons. Using the values listed above, one can then calculate the dipole moments of the four possible isomers; these are as follows:

5-Bromo-I	2.34 D
6-Bromo-I	1.51 D
7-Bromo-I	0.23 D
8-Bromo-I	1.06 D

Evidently Y must be the 5-isomer, IV.

This conclusion was confirmed by a study of the ^{19}F n.m.r. spectrum of Y. Assuming additivity of substituent effects, one can predict from the observed (1) ^{19}F substituent chemical shifts (s.c.s.) of the bromofluoronaphthalenes that the ^{19}F s.c.s. of the 6-, 7-, or 8-bromo derivatives of I should be -4 ±1 p.p.m.. The observed ^{19}F s.c.s. of Y was, however, -11.70 p.p.m., eliminating these as possible structures for Y and leaving IV as the only possible alternative.

References

1. W. Adcock and M.J.S. Dewar, work in the course of publication.
2. W. Adcock and P.R. Wells, *Aust.J.Chem.* *18*, 1351 (1965).