# Azoniaazulenes. Part 7.[1] Functionalisation of 10*H*-Azepino[1,2-*a*]indoles

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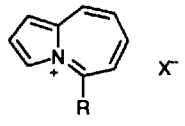
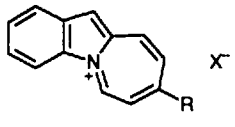
Direct functionalisation of azepinoindole **7** is described. Electrophilic attack by bromine, and by the Vilsmeier, Mannich, and Friedel–Crafts reagents gives 11-substituted azepinoindoles **8** and **11–14**. From the bromo compound **8** an 11-lithioazepinoindole was obtained. With *tert*-butyllithium the azepinoindole **7** gave an allylic anion **36**, which with trimethylsilyl (TMS) chloride gave the 8*H*-8-TMS derivative **16** and the 10*H*-8,10-bis-TMS derivative **17**, for which an X-ray structure is provided. Alkylation of anion **36** gave mixtures of 8*H*-8-alkyl- and 10*H*-10-alkyl derivatives **18–25**, while further lithiation of compound **16** and alkylation gave mixtures of 8,8- and 8,10-disubstituted compounds **26–33**. Decomposition of azide **43** gave eight identified products **44**, **45**, **47–51** and **54**.

We have had, as a long standing objective, the synthesis of the aromatic pyrrolo[1,2-*a*]azepinium ion **1** or its benzologue the



**1** R = H
**3** R = OH
**5** R = $CH_2CN$

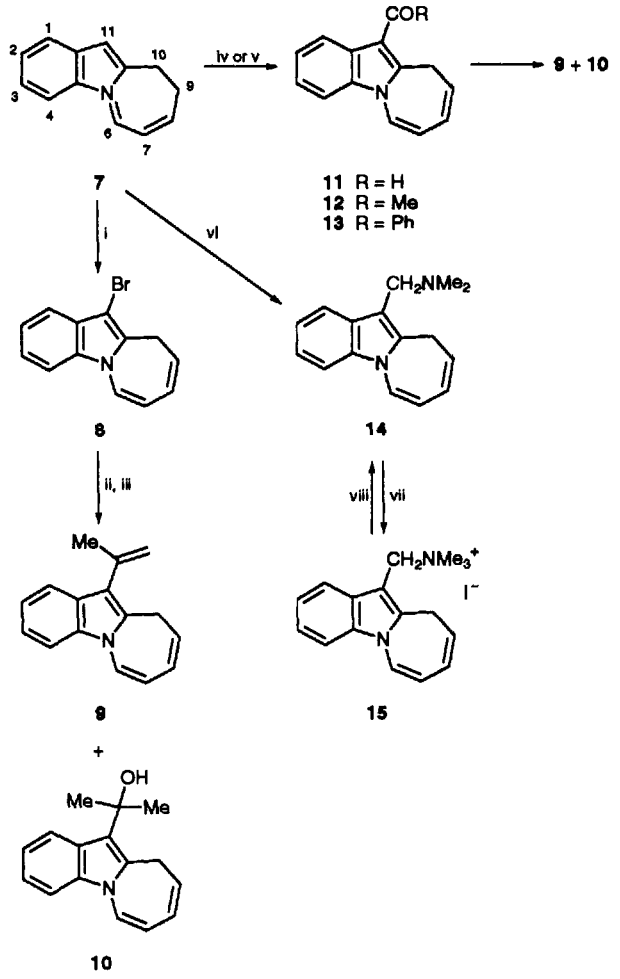


**2** R = H
**4** R = OH, X = $HSO_4^-$
**6** R = OEt, X = $BF_4^-$

azepino[1,2-*a*]indolium ion **2**. Hydroxy- and ethoxy-substituted ions such as compounds **3**, **4** and **6** have been obtained by protonation or ethoxylation [2,3] of the corresponding azepinones but the only alkyl derivative remains the cyanomethyl compound **5**.[2] We report here further approaches to azepinoindolium salts, which, though unsuccessful have produced methods to functionalize azepinoindoles directly, a process not previously achieved.

A number of 10*H*-azepinoindoles have been made from a standard nitrene insertion reaction, starting from 2-azidodiphenylmethanes,[1,3–6] and we have improved the synthesis of the parent **7** to 70% after three stages from the readily available 2-aminobenzophenone (2-aminodiphenylmethanone). Attempts to remove hydride directly from compound **7** have previously failed, possibly because of electrophilic attack by the carbocation on the reactive indolic 11 position. We tried hydride abstraction from 11-methylazepinoindole using the triphenylmethyl carbocation and the potentially more hindered 1,2,4,6-tetramethylcycloheptatrienylium tetrafluoroborate, but without success. Feeling that a better leaving group was required, we next studied the bromination of azepinoindole **7**, using *N*-bromosuccinimide under a variety of conditions, the best yields of a monobrominated product being obtained in carbon tetrachloride solution at room temperature in an ultrasonic bath. The mass spectrum showed the compound to be a monobromo derivative, but it proved too unstable for consistent microanalysis. The only significant change in the $^1H$ NMR spectrum from that of compound **7** was the absence of the singlet at $\delta$ 6.20 diagnostic for the indole proton 11-H, and hence bromination had not taken place at the allylic position as required for ionisation. We confirmed that the substitution was electrophilic since the bromination was unaffected by the presence of glacial acetic acid as a radical trap. A short investigation of the potential in synthesis of this 11-bromo derivative **8** was made (Scheme 1). Treatment with butyllithium, followed by acetone, gave two products, one unstable to heat, when it was converted into the other. The more stable product had the formula $C_{16}H_{15}N$ from its mass spectrum and microanalysis, and the $^1H$ NMR spectrum showed, in addition to the normal azepinoindole signals, a methyl singlet at $\delta$ 2.20 and two alkene multiplets (each 1 H) at $\delta$ 5.00 and 5.30, indicating that the product was an 11-isopropenylazepinoindole, **9**. The second product was shown by microanalysis and $^1H$ NMR spectroscopy to be the alcohol **10**. Other carbonyl compounds gave uncharacterised products.

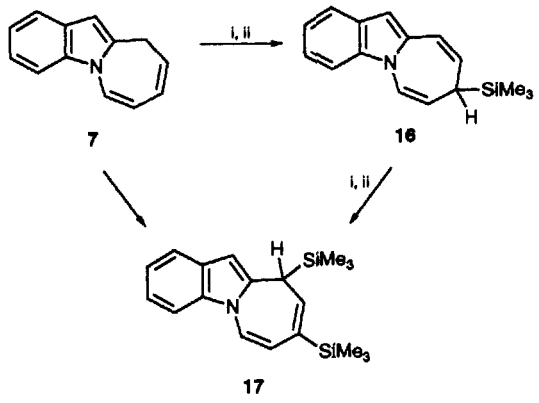
The generality of electrophilic attack at position 11 was tested with other reagents. Vilsmeier–Haack formylation gave a single product, the 11-formyl derivative, **11**, in 76% yield. The absence of a signal at $\delta$ 6.20 confirmed 11 substitution, and there was an aldehyde signal at $\delta$ 10.15. The modified Vilsmeier reaction with dimethylacetamide gave 11-acetylazepinoindole **12**. Reaction with *N*-benzoylmorpholine and phosphoryl chloride gave a very small yield of the 11-benzoylazepinoindole **13**, identical with a sample prepared by treating compound **7** with benzoyl chloride and tin(IV) chloride (41% yield). The acetyl derivative **12** gave with methylmagnesium iodide the same mixture of alkene **9** and alcohol **10** as was obtained from the 11-lithio derivative and acetone. A Mannich reaction gave 11-dimethylaminomethylazepinoindole **14** (79% yield), which gave the methiodide **15** in quantitative yield. Thermolysis of the quaternary hydroxide gave only the amine **14**. The instability of the bromo compound **8** limited our access to 11-substituted azepinoindoles, so we investigated the possibility of direct lithiation. No anion was formed when azepinoindole **7** was treated with butyllithium, lithium diisopropylamide (LDA) or butyllithium–*N*,*N*,*N*′,*N*′-tetramethylethylenediamine (TMEDA), but with *tert*-butyllithium at −78 °C a deep green solution formed, and subsequent treatment with trimethylsilyl chloride gave a single crystalline product in 82% yield. Microanalysis and its mass spectrum showed it to be a monotrimethylsilyl derivative, but the $^1H$ NMR spectrum revealed considerable differences from that of the 10*H*-azepinoindole **7**. In addition to the singlets at $\delta$ 0.0 (9 H, $Me_3Si$) and 6.30 (1 H, 11-H) there was only a single proton (pseudotriplet) at $\delta$ 2.55, well upfield of the normal 10-H position. The presence of two doublets, each 1 H, at $\delta$ 6.15 and




**Scheme 1** *Reagents and conditions:* i, *N*-Bromosuccinimide, $CCl_4$; ii, BuLi; iii, MeCOMe; iv, $R'_2CONR$, $POCl_3$, or v, RCOCl, $SnCl_4$; vi, $Me_2NH$, HCHO, AcOH; vii, MeI; viii, $Ag_2O$, heat

6.65 (assigned to 6-H and 10-H), allows only one structure, the 8-substituted 8*H*-azepinoindole **16** (Scheme 2). We have previously seen only one 8*H*-compound, among those formed when 2-azido-2′,4′,6′-trimethyldiphenylmethane was decomposed,[3] and it is notable that the 8-methylazepinoindole prepared by nitrene insertion has the 10*H*-structure. Compound **16** was relithiated with *tert*-butyllithium and, with excess trimethylsilyl (TMS) chloride gave a single product with two TMS substituents. From the $^1$H NMR spectrum this was shown to be the 8,10-disubstituted 10*H*-azepinoindole **17** (all NMR spectra for 10*H*-azepinoindoles are collected in Table 1, all 8*H* in Table 2). An X-ray structure on compound **17** confirmed the assignment (Fig. 1).

Compound **17** could also be prepared directly from azepinoindole **7** by using a large excess of *tert*-butyllithium, the TMS chloride being added before or after lithiation. No further lithiation occurred and no trisubstituted products were ever observed. The lithiation reaction provides the first direct functionalisation of the seven-membered ring in azepinoindoles, and we next examined the reaction of the lithiated azepinoindole **7** with alkyl halides. Quenching the anion with methyl iodide gave a mixture of equal amounts of two products, both monomethylazepinoindoles. Their behaviour on chromatography was very similar; pure samples could only be obtained by crystallisation of fractions from the front and rear of a single broad band from a Chromatotron. The less polar product had an NMR spectrum identical with that of 10-methyl-10*H*-azepinoindole **18**, while the more polar material had an NMR




**Scheme 2** *Reagents and conditions:* i, Bu$^t$Li, THF, −78 °C; ii, $Me_3SiCl$

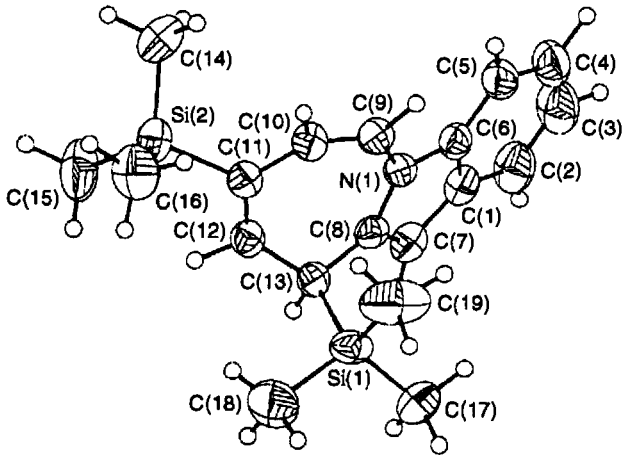
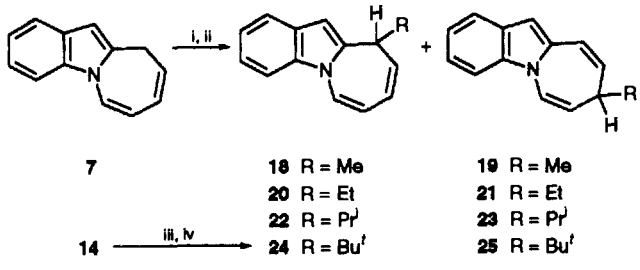



**Fig. 1** X-Ray crystal structure of compound **17**

spectrum very similar to that of compound **16** and was the 8-methyl-8*H* isomer **19** (Scheme 3). The spectrum of this isomer showed a number of small long-range couplings, from 6-H and 10-H to 8-H, and from 7-H to 9-H, similar to those shown by azepinoindol-8-one.[3]




**Scheme 3** *Reagents and conditions:* i, Bu$^t$Li, THF, −78 °C; ii, R–X; iii, BuLi; iv, Bu$^t$I

Further experiments using ethyl iodide, isopropyl bromide or iodide, and *tert*-butyl bromide or iodide, gave in all cases equal mixtures of the 10*H* isomers **20**, **22** and **24** with the 8*H* isomers **21**, **23** and **25**. Only compound **25** was not obtained analytically pure, but all isomers were separated by GC–MS, and mass spectra determined for all.

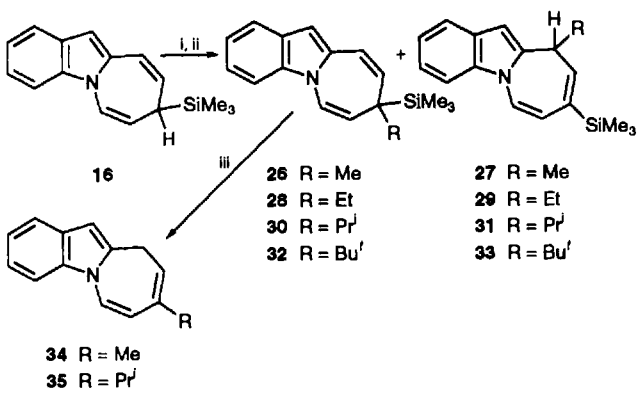
The observation that the anion from the 8-trimethylsilyl derivative **16** gave only one product with TMS chloride suggested that similar clean reactions might be achieved with alkyl halides, but this was not so. When the anion from compound **16** was treated with methyl iodide, a mixture of two compounds of very similar behaviour on chromatography was obtained. From the mixture only one compound could be

**Table 1** $^1$H NMR shifts (ppm) and coupling constants of new 10*H*-azepinoindoles

| Comp. | 1-H | 2-H | 3-H | 4-H | 6-H | 7-H | 8-H | 9-H | 10-H | 11-H | Other | *J*/Hz |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| **8** | 7.15–7.60 (m) | | | | | 5.75 (m) | 6.10 (m) | 5.90 (m) | 3.50 (2 H, d) | — | — | $J_{9,10}$ 8 |
| **9** | 7.10–7.70 (m) | | | | | 5.80 (m) | 6.05 (m) | 5.90 (m) | 3.55 (2 H, d) | — | 2.20 (3 H, s), 5.00 (1 H, m), 5.30 (1 H, m) | $J_{9,10}$ 6 |
| **10** | 7.00–7.90 (m) | | | | | 6.05 (m) | 5.80 (m) | 5.95 (m) | 2.70 (2 H, d) | — | 1.75 (6 H, s), 1.85 (1 H, br s, OH) | $J_{9,10}$ 6 |
| **11** | 8.30 (m) | 7.20–7.40 (m) | | | | 6.10 (m) | | 5.85 (m) | 3.65 (2 H, d) | — | 10.15 (s, CHO) | $J_{9,10}$ 6.4 |
| **12** | 8.00 (m) | 7.25–7.50 (m) | | | | 6.15 (m) | | 6.00 (m) | 3.90 (2 H, d) | — | 2.70 (3 H, s, $CH_3CO$) | $J_{9,10}$ 6.4 |
| **13** | 7.20–7.80 (m) | | | | | 6.15 (m) | | 5.80 (m) | 3.40 (2 H, d) | — | 7.20–7.80 (m, $C_6H_5$) | $J_{9,10}$ 6.3 |
| **14** | 7.00–7.60 (m) | | | | | 5.65 (m) | 5.95 (m) | 5.80 (m) | 3.40 (2 H, d) | — | 2.20 [6 H, s $(CH_3)_2N$], 3.50 (2 H, s, $CH_2N$) | $J_{9,10}$ 6.6 |
| **17** | 7.00–7.45 (m) | | | | 6.96 (d) | 5.55 (d) | — | 6.00 (d) | 3.35 (1 H, d) | 5.95 (s) | 0.05 (9 H, s), 0.15 (9 H, s) | $J_{9,10}$ 8.6, $J_{6,7}$ 9.3 |
| **18** | 7.10–7.55 (m) | | | | | 5.80 (m) | 5.95 (m) | 5.60 (m) | 3.35 (1 H, d) | 6.15 (s) | 1.60 (3 H, d) | $J_{10,CH_3}$ 6.9 |
| **20** | 7.11–7.25 (m) | | | | 6.90 (d) | 5.50 (m) | 5.75 (m) | 5.40 (m) | 3.05 (1 H, d) | 6.00 (s) | 0.95 (3 H, overlapping t), 1.78 (2 H, m) | $J_{6,7}$ 10, $J_{CH_3,CH_2}$ 7 |
| **22** | 7.10–7.60 (m) | | | | | | | | | 6.15 (s) | 0.80, 1.10 (3 H, overlapping d), 2.30 (1 H, m) | $J_{CH_3,CH}$ 7 |
| **24** | 7.40 (m) | 7.10–7.30 (m) | | | 7.55 (m) | 5.85 (m) | 6.00 (m) | 5.60 (m) | 3.50 (1 H, m) | 6.25 (s) | 1.05 (9 H, s) | |
| **31** | 7.00–7.50 | | | | | 5.90 (d) | — | 6.10 (d) | 3.20 (1 H, m) | 6.20 (s) | 0.00 (9 H, s) | |
| **35** | 6.90–7.10 (m) | | | 7.40 (m) | 6.80 (d) | 5.25–5.35 (m) | — | 5.25–5.35 (m) | 3.00 (1 H, m) | 5.90 (s) | 0.80 (6 H, d), 2.05 (1 H, hept) | $J_{CH_3,CH}$ 5.8, $J_{9,10}$ 6.6, $J_{6,7}$ 9.5 |
| **39** | 7.40 (m) | 7.10–7.30 (m) | | 7.55 (m) | 7.10–7.30 (m) | 5.85 (d) | — | 6.25 (t) | 3.45 (2 H, d) | 6.20 (s) | | |
| **44** | 7.60 (d) | — | 7.60 (d) | — | 8.85 (d) | — | — | — | 3.55 (2 H, s) | 6.50 (s) | 3.50 (3 H, s) | $J_{6,7}$ 9.5 |
| **45** | 7.50 (d) | — | 7.60 (d) | — | 8.55 (s) | — | — | 5.15 (t) | 3.30 (2 H, d) | 5.90 (s) | 3.65 (3 H, s) | $J_{9,10}$ 6.8 |
| **48** | 7.75 (d) | — | 7.55 (s) | — | 8.25 (d) | 5.80 (d) | — | 4.95 (t) | 3.30 (2 H, d) | 6.10 (s) | 3.50 (3 H, s) | $J_{9,10}$ 6.5, $J_{6,7}$ 9.0 |

**Table 2** $^1$H NMR shifts (ppm) and coupling constants of new 8*H*-azepinoindoles

| Compound | 1-H | 2-H | 3-H | 4-H | 6-H | 7-H | 8-H | 9-H | 10-H | 11-H | Other | *J*/Hz |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| **16** | 7.00–7.25 (m) | | | 7.50 (m) | 6.65 (d) | 4.9 (m) | 2.55 (m) | 5.60 (m) | 6.15 (d) | 6.30 (s) | 0.05 (9 H, s) | $J_{6,7}$ 11.7, $J_{7,8}$ 7.2, $J_{8,9}$ 7.1, $J_{9,10}$ 9.8, $J_{7,9}$ 1.2 |
| **19** | 7.10–7.60 (m) | | | | 6.85 (d) | 5.05 (m) | 3.25 (m) | 5.65 (m) | 6.45 (d) | 6.50 (s) | 1.25 (3 H, d) | $J_{6,7}$ 9.1, $J_{9,10}$ 10.5, $J_{8,CH_3}$ 8 |
| **21** | 7.10–7.60 (m) | | | | 6.90 (d) | 5.05 (m) | 3.05 (m) | 5.65 (m) | 6.50 (d) | 6.45 (s) | 1.00 (3 H, t), 1.60 (2 H, m) | $J_{CH_3,CH_2}$ 6.5, $J_{6,7}$ 9, $J_{9,10}$ 10.8, |
| **23** | 7.15–7.55 (m) | | | | 6.95 (d) | 5.05 (m) | 2.95 (m) | 5.70 (m) | 6.50 (d) | 6.45 (s) | 0.95 (6 H, d), 1.85 (1 H, m) | $J_{6,7}$ 9.5, $J_{9,10}$ 11.8 |
| **26** | 7.10–7.50 (m) | | | | 6.80 (d) | 4.55 (dd) | — | 5.25 (dd) | 6.15 (d) | 6.30 (s) | 0.00 (9 H, s), 1.30 (3 H, s) | $J_{6,7}$ 10, $J_{9,10}$ 12, $J_{7,9}$ 1.7 |
| **28** | 7.00–7.50 (m) | | | | 6.70 (d) | 4.50 (dd) | — | 5.20 (dd) | 6.20 (d) | 6.30 (s) | 0.00 (9 H, s), 1.00 (3 H, t), 2.00 (2 H, m) | $J_{6,7}$ 10, $J_{9,10}$ 12.2, $J_{7,9}$ 2.1 |
| **30** | 7.00–7.50 (m) | | | | 6.70 (d) | 4.55 (dd) | — | 5.30 (dd) | 6.20 (d) | 6.30 (s) | 0.00 (9 H, s) | $J_{6,7}$ 10.2, $J_{9,10}$ 12.2, $J_{7,9}$ 2.2 |
| **51** | 7.75 (d) | — | 7.85 (d) | — | 9.20 (dd) | 5.95 (dd) | — | 6.40 (dd) | 7.25 (dd) | 6.95 (s) | | $J_{6,7}$ 10.5, $J_{9,10}$ 11.0, $J_{1,3}$ 1.7, $J_{6,10}$ 0.5, $J_{7,9}$ 2.5 |
| **54** | 7.55 (d) | — | 7.65 (d) | — | 8.70 (d) | 5.75 (d) | — | 3.20 (2 H, m) | 2.85 (2 H, m) | 6.40 (s) | | $J_{6,7}$ 10.5, $J_{1,3}$ 1.5 |

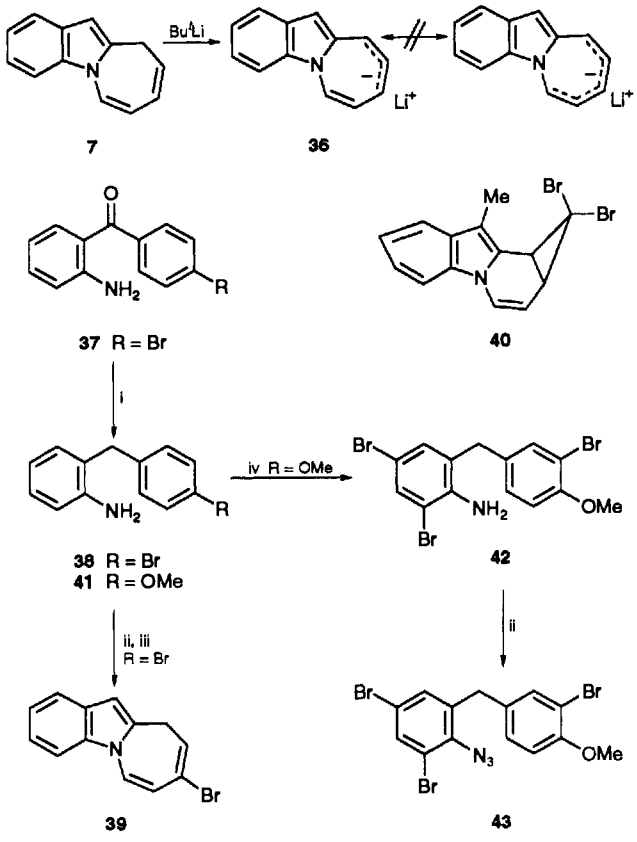



**Scheme 4** *Reagents and conditions:* i, Bu'Li, THF, −78 °C; ii, R–X; iii, $Bu_4N^+F^-$

isolated crystalline, and the NMR spectrum showed a singlet methyl signal at $\delta$ 1.30 and the TMS signal, but no other $sp^3$ protons. The similarity of the rest of the spectrum to that of the 8*H* isomers shows that this compound is the 8,8-disubstituted derivative **26** (Scheme 4). Inspection of the NMR spectrum of the mixture shows a pair of overlapping triplets at $\delta$ 3.45, which can be confidently assigned to the 8,10-disubstituted 10*H* isomer **27**. Ethyl iodide gave also a mixture of approximately equal amounts of two products, of which the 8,8-disubstituted isomer **28** could be isolated, and the 8,10 isomer **29** identified from the NMR spectrum of the mixture. Isopropyl iodide and *tert*-butyl iodide gave mixtures that could not be separated, but linked GC–MS showed the presence of two isomers in each case, compounds **30**–**33** (with mass spectra for each), and the NMR spectra left no doubt that they had the structures proposed.

Treatment of compound **26** with tetrabutylammonium fluoride (TBAF) at room temperature gave very rapidly the known 8-methylazepinoindole **34**;[1] under similar conditions compound **30** gave 8-isopropylazepinoindole **35**. We have reported that flash vacuum pyrolysis of azepinoindole gave a mixture containing the 6*H* isomer;[7] we have heated the three 8*H* tautomers **16**, **19** and **21**, and the 10*H* tautomers **17**, **22** and **24**, for extended periods in deuteriated toluene at 105 °C, but no changes were observed. Attempts to obtain an 8*H* or 10*H* bromo- or chloro-azepinoindole by reaction between the lithiated compound **7** and bromine, or 1,2-dibromotetrachloroethane, or hexachloroethane were unsuccessful. Dialkylamino groups have been used to direct lithiation.[8] The Mannich compound **14** reacted more easily with lithiating agents than compound **7**, butyllithium causing rapid formation of a lithium derivative, but treatment of the lithium derivative with *tert*-butyl iodide again gave a mixture of 8- and 10-substituted compounds, with no degree of regioselectivity. We believe that deprotonation of compound **7** gives the allylic anion **36**, and that the tautomer which forms when this anion is attacked by an electrophile is stable under the conditions of reaction and work-up. We see no indication of further extension of delocalisation to position 6; no 6-substituted products have been observed and such a fully delocalised azepine would be anti-aromatic if planar. Our anion **36** is stable up to 0 °C. The only unexplained discrepancy is the regiospecificity shown by TMS chloride, but this may indicate kinetic control.

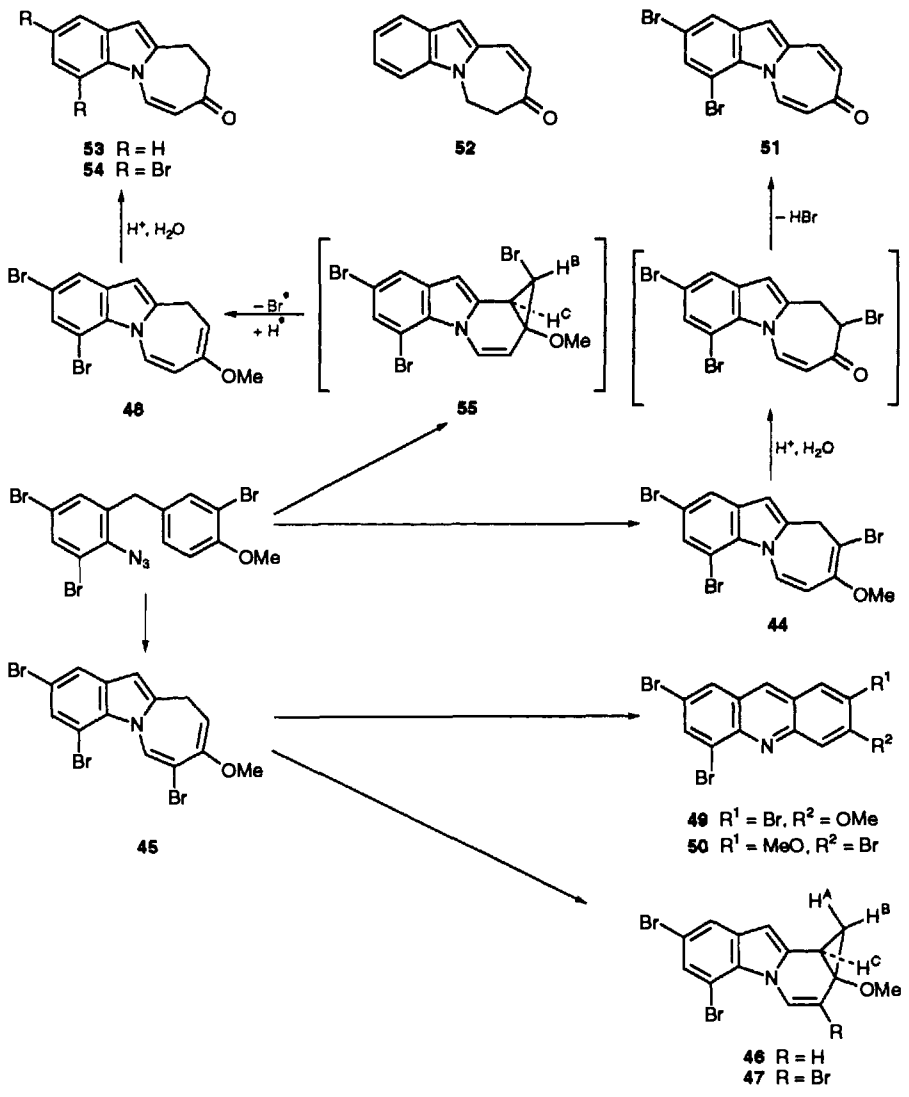
Our final efforts to produce the azepinoindolium carbocation were aimed at the synthesis of bromoazepinoindoles with the bromine in the seven-membered ring, starting from suitable brominated aminobenzophenones. The 4′-bromo derivative **37** was prepared from acetanthranil and the mono Grignard reagent from 1,4-dibromobenzene.[9] Reduction of benzophenone **37** by our usual procedure (sodium in ethanol) removed the




**Scheme 5** *Reagents and conditions:* i, $LiAlH_4$, $AlCl_3$; ii, $HNO_2$, $NaN_3$; iii, TCB, 165 °C; iv, $Br_2$, 3 mol

bromine to give 2-aminodiphenylmethane, but reduction with lithium aluminium hydride and aluminium chloride gave the amine **38** (Scheme 5), converted into the azide by a standard procedure. Pyrolysis of the azide in boiling trichlorobenzene gave a single crystalline product, which from its analysis, mass spectrum, and NMR spectrum was the expected 8-bromo-10*H*-azepinoindole **39**. We were unable to remove bromide, using antimony(V), so the amount of tautomeric 8*H* isomer must be vanishingly small. A second possibility seemed to be to use tetracyclic compounds of type **40** similar to products which we have found from some of our nitrene insertions; attempts to add dibromocarbene to 10-methylpyridoindole[10] under a number of different conditions failed.

We have made a single attempt to obtain a suitable cyclopropapyridoindole *via* a nitrene insertion. Bromination of 2-amino-4′-methoxydiphenylmethane **41** in concentrated hydrobromic acid gave three products; increasing the amount of bromine maximized the yield of one product, a tribromo derivative. The $^1H$ NMR spectrum showed that there were no hydrogen atoms *ortho*- or *para*- to the amino group, and that the third bromine atom was in position 3′, giving formula **42**. Since substitution on the aniline ring does not affect the final nitrene insertion we converted the amine **42** into the azide **43** and decomposed the azide at 165 °C in trichlorobenzene, giving a mixture of at least seven compounds, and some high molecular weight material. By careful chromatography it was possible to obtain three main bands (A, B and C), and from these to isolate three compounds analytically pure, and another four in sufficient purity to allow identification by spectroscopy. The first pure compound from band A was a tribromomethoxyazepinoindole. The $^1H$ NMR spectrum showed an intact methylene group (10-H) at $\delta$ 3.75 as a singlet, indicating substitution, presumably by bromine, at C-9, confirmed by a pair of doublets at $\delta$ 8.40 and 5.90 ($J$ 9.5 Hz) assigned to 6-




Scheme 6

and 7-H. Hence this compound is the 2,4,9-tribromo derivative **44**. The second crystalline compound from band A was an isomer of compound **44**, with a methylene doublet at $\delta$ 3.30 and a singlet (1 H) at $\delta$ 8.85 assigned to 6-H and hence establishing structure **45**. The third compound in the fast moving band A was identified as the cyclopropapyridoindole **47**, by its very characteristic set of three NMR signals (each 1 H) at $\delta$ 0.90 ($H^A$), 1.95 ($H^B$) and 5.00 ($H^C$), very similar to those in compound **46**,[6] but with a downfield shift in $H^C$. This, and the absence of long range coupling in $H^C$, proves the presence of the bromine at C-7. From band B two compounds were isolated. The first, obtained pure, was a dibromoazepinoindole, **48**, with an NMR spectrum very similar to that of 8-methoxyazepinoindole,[3] the two remaining bromine atoms being on the benzene ring. The second compound from band B was bright yellow, and highly fluorescent in ultraviolet light. In the NMR spectrum all signals were in the aromatic region apart from the methoxy singlet. This product is formulated as an acridine, although we cannot distinguish between structures **49** and **50**. From band C two compounds were obtained; the first was bright orange, and had a pattern of signals in the NMR spectrum very similar to that of azepinoindol-8-one[3] modified only by the presence of two bromine atoms on the benzene ring; hence this compound is the azepinoindol-8-one **51**. The last compound isolated was a dibromodihydroazepinoindol-8-one. Models are available in the 6,7-dihydro **52** and in the 9,10-dihydro derivative **53**.[3] Comparison of the chemical shifts of the two methylene signals in our new compound with those reported showed it to be compound **54**. These compounds are summarized, together with our interpretation of their mode of formation in Scheme 6.

Some brief comment on Scheme 6 is necessary. No bromo derivative **55** suitable for conversion into an aromatic system was obtained. Insertion of the intermediate nitrene into the adjacent ring could give a spirodiene intermediate,[11] from which either acridine **49** or **50** could be obtained. Ring expansion gives azepinoindoles **44** and **45** and hydrolysis of compound **44** during work-up produces a bromo ketone well set up for elimination of hydrogen bromide to give azepinoindolone **51**.

We have postulated radical intermediates during formation of azepinoindoles from cyclopropapyridoindoles.[6] The isomer **55** which we sought, is well set up for radical abstraction of bromine, to give an azepinoindolyl radical (centred on C-8 and C-10), which by hydrogen abstraction produces compound **48** and hence, by hydrolysis the dihydro derivative **54**.

*X-Ray Crystal Structure of Compound* **17**.—The first report[12] of the formation of an azepinoindole by nitrene insertion from an azidodiphenylmethane wrongly ascribed an 11*H* structure,

corrected [3] to the accepted 10*H* structure **7** on the basis of $^1$H NMR data.

Until now there has been no confirmation of the structure by X-ray diffraction, but with the bis-TMS compound **17** (Fig. 1) it can clearly be seen that the previous suggestion was correct. The axial position of the trimethylsilyl group in the 10 position appears unusual, but there are in fact no bad non-bonded interactions.

## Experimental

M.p.s were determined on a Kofler heated stage, and are uncorrected. NMR spectra were determined on a JEOL 270 MHz spectrometer, for solutions in $CDCl_3$, from tetramethylsilane (TMS) as standard. $\delta$ Values are in ppm and $J$ values in Hz. Linked GC–MS determinations were performed on a Hewlett-Packard HP5890 chromatograph coupled to an HP5970 mass sensitive detector, controlled by an HP series 300 computer and HP5970C Chemstation software. UV and visible spectra were recorded on a Varian DMS100 spectrometer for solutions in 95% ethanol. Chromatography was performed on Aldrich alumina, deactivated to Brockmann grade IV, and Chromatotron separations used plates with 2 mm of PF254 silica gel. Solvent mixtures were of petroleum (b.p. 60–80 °C) and ethyl acetate, proportions given thus (60:40). Ether refers to diethyl ether.

10H-*Azepino*[1,2-a]*indole* **7**.—The overall procedure was as described previously [12] but it was observed that crude material from the reduction of 2-aminobenzophenone (2-aminodiphenylmethanone) was sufficiently pure to use in the preparation of azide, which in turn could be used crude for pyrolysis [boiling trichlorobenzene (TCB) under argon]. Thus, from 20 g of aminobenzophenone 13 g of azepinoindole **7** (72% yield) was obtained after chromatography but before recrystallisation. The product was pure by $^1$H NMR, and could be used as such in most reactions.

11-*Bromo*-10H-*azepino*[1,2-a]*indole* **8**.—A solution of azepinoindole **7** (0.4 g) in carbon tetrachloride (25 cm$^3$) with *N*-bromosuccinimide (0.4 g) was stirred in an ultrasonic bath under nitrogen. Progress of the reaction was monitored by NMR spectroscopy (disappearance of the signal at $\delta_H$ 6.15). When the reaction was complete the solution was filtered through Celite and the solvent removed under reduced pressure, keeping the temperature below 20 °C to give 0.44 g of product; any attempt at purification or increase in temperature led to decomposition; *m/z* 261 ($M^+ + 2$, 84%) and 259 ($M^+$, 84), 180 ($M^+ - Br$, 100), 165 (39), 152 (34) and 143 (49).

11-*Isopropenyl*-10H-*azepino*[1,2-a]*indole* **9** *and* 11-(2-*Hydroxypropan*-2-*yl*)-10H-*azepino*[1,2-a]*indole* **10**.—To a stirred solution of the bromide **8** (0.44 g) in anhydrous ether (25 cm$^3$) at −50 °C, under argon, was added, dropwise, butyllithium (1.2 mol dm$^{-3}$ in hexane; 2 cm$^3$). After a further 20 min, anhydrous acetone was added, and the mixture allowed to warm to room temperature and then treated with saturated ammoniacal ammonium chloride (10 cm$^3$). The organic layer was separated, the aqueous layer further extracted with ether (3 × 25 cm$^3$), the organic extracts dried ($MgSO_4$), filtered, and then evaporated. The residual oil (0.33 g), was chromatographed; elution with petroleum (b.p. 60–80 °C) gave the *isopropenyl compound* **9**, b.p. 160 °C/0.02 mmHg (bulb to bulb) (Found: C, 86.6; H, 6.8; N, 6.55. $C_{16}H_{15}N$ requires C, 86.85; H, 6.85; N, 6.35%); *m/z* 221 ($M^+$, 68%), 180 ($M^+ - C_3H_5$, 100), 165 (44) and 143 (42). Further elution (85:15) gave the *alcohol* **10**. Attempts to distill the alcohol gave mixtures of alkene and alcohol (Found: C, 80.05; H, 7.2; N, 4.55. $C_{16}H_{17}NO$ requires C, 80.4; H, 7.1; N, 5.85%).

11-*Formyl*-10H-*azepino*[1,2-a]*indole* **11**.—Phosphoryl chloride (3.1 g, 22 mmol) was added dropwise over 10 min to stirred anhydrous dimethylformamide (DMF) (10 cm$^3$), at −5 °C, under nitrogen. The mixture was stirred (15 min) and then a solution of azepinoindole **7** (3.3 g, 18.5 mmol) in DMF (5 cm$^3$) was added dropwise over 20 min, keeping the temperature below 5 °C. The red solution was heated at 40 °C (3 h) and then evaporated under reduced pressure to reduce the volume by 70%. A large excess (~ 150 cm$^3$) of saturated aqueous sodium carbonate was added to the mixture to give a precipitate. The mixture was extracted with ether, dried ($MgSO_4$), decolourised with charcoal and then filtered to give, after evaporation, a pale yellow solid. Recrystallisation from ethanol gave the *aldehyde* **11**, m.p. 130 °C (Found: C, 80.2; H, 5.05; N, 6.6. $C_{14}H_{11}NO$ requires C, 80.35; H, 5.3; N, 6.9%); $\nu_{max}(CCl_4)$/cm$^{-1}$ 1664, 1462, 1180 and 1052; $\lambda_{max}$/nm 321 ($\log_{10}\varepsilon$ 4.19), 244 (4.42) and 219 (4.65); *m/z* 209 ($M^+$, 91%), 208 (53), 180 ($M^+ - CHO$, 100) and 152 (20).

11-*Acetyl*-10H-*azepino*[1,2-a]*indole* **12**.—Phosphoryl chloride (3.1 g, 22 mmol) was added dropwise over 10 min to stirred, anhydrous *N*,*N*-dimethylacetamide (DMA) (15 cm$^3$) at −10 °C under nitrogen. After 20 min azepinoindole **7** (2.5 g, 14 mmol) in anhydrous DMA (10 cm$^3$) was added dropwise, keeping the temperature below 0 °C, and the mixture then stirred at 40 °C (48 h). The cooled mixture was quenched with approx. 100 cm$^3$ of saturated aqueous sodium carbonate, giving a dense white precipitate. The mixture was extracted with chloroform (3 × 75 cm$^3$), dried ($MgSO_4$) and then evaporated to give a yellow solid. Chromatography, eluting with petroleum, b.p. 60–80 °C gave starting material (1.6 g) and the *acetyl compound* **12**, m.p. 116 °C (0.5 g after sublimation, 16% based on unrecovered starting material) (Found: C, 80.6; H, 5.9; N, 6.1. $C_{15}H_{13}NO$ requires C, 80.75; H, 5.8; N, 6.25%); $\nu_{max}(CCl_4)$/cm$^{-1}$ 1650, 1460, 1410 and 716; $\lambda_{max}$/nm 321 ($\log_{10}\varepsilon$ 4.05), 241 (4.29) and 224 (4.28); *m/z* 223 ($M^+$, 88%), 208 ($M^+ - CH_3$, 44), 180 ($M^+ - CH_3CO$, 100) and 166 (25).

11-*Benzoyl*-10H-*azepino*[1,2-a]*indole* **13**.—(*a*) A solution of *N*-benzoylmorpholine (2.5 g, 13 mmol) in phosphoryl chloride (3 cm$^3$) was stirred at 0 °C (24 h). A solution of indoloazepine **7** (2.0 g, 11 mmol) in 1,2-dichloroethane (40 cm$^3$) was added to it, stirring continued (3 h), and then saturated aqueous sodium carbonate (75 cm$^3$) added. The resultant green–black suspension was shaken (15 min) and then boiled (15 min). Aqueous sodium hydroxide (2 mol dm$^{-3}$; 50 cm$^3$) was added to the hot solution, and the mixture stirred until it reached room temperature. Ether was added to the mixture and then it was filtered. The aqueous phase was extracted with further ether and the combined organic extracts were worked-up as described for compound **12**. Recrystallisation from ethanol gave the *benzoyl derivative* **13** (0.13 g, 3%), m.p. 223 °C (Found: C, 84.2; H, 5.3; N, 4.75. $C_{20}H_{15}NO$ requires C, 83.9; H, 5.6; N, 4.9%); $\lambda_{max}$/nm 338 ($\log_{10}\varepsilon$ 3.99), 311 (3.85), 250 (4.36) and 220 (4.48).

(*b*) A solution of benzoyl chloride (1.35 g, 9.5 mmol) and compound **7** (1.5 g, 8.5 mmol) in carbon disulfide (30 cm$^3$) was added dropwise to a cooled (−20 °C) stirred solution of stannic chloride (4 g, 16 mmol) in $CS_2$ (10 cm$^3$) under nitrogen. After 45 min a further portion of benzoyl chloride (0.7 g, in 5 cm$^3$ $CS_2$) was added. After a further 15 min the reaction mixture was added carefully to methanol (125 cm$^3$) and then water added until a precipitate formed. The aqueous mixture was extracted with chloroform (3 × 150 cm$^3$), the organic extracts dried and

the solvent removed to give a residue (3.9 g) which was chromatographed on a column (100 g, 9:1) to give the benzoyl derivative (1.0 g, 41%).

*11-Dimethylaminomethyl-10H-azepino[1,2-a]indole* **14**.—A mixture of purified dioxane (15 $cm^3$), glacial acetic acid (15 $cm^3$), aqueous formaldehyde (1.1 $cm^3$ of a 36% solution) and aqueous dimethylamine (3.2 $cm^3$ of a 25% solution) was placed in a flask fitted with a rubber septum and under a positive pressure of nitrogen. The mixture was stirred in an ice bath (10 min) and then azepinoindole **7** (2.5 g, 13.8 mmol) in dioxane (15 $cm^3$) was added *via* a syringe (25 min), and the mixture was left overnight at room temperature. The mixture was poured into water (150 $cm^3$), filtered through Celite, basified (aq. NaOH) and then extracted with ether (3 × 75 $cm^3$). The combined organic extracts were dried ($MgSO_4$), filtered and evaporated, to give a pale yellow oil (2.8 g), Distillation (Kugelrohr) gave the *amine* **14**, b.p. 150 °C/0.5 mmHg (2.6 g, 79%) (Found: C, 80.55; H, 7.55; N, 11.85. $C_{16}H_{18}N_2$ requires C, 80.7; H, 7.55; N, 11.75%); $\nu_{max}$(film)/$cm^{-1}$ 2946, 2762, 1634, 1412, 1172 and 1040; $\lambda_{max}$/nm 310 ($\log_{10}$ $\varepsilon$ 3.89), 273 (4.18) and 227 (4.40). The *methiodide*, **15**, was prepared in acetone and crystallised from methanol, m.p. 219 °C (decomp.) (Found: C, 53.9; H, 5.4; N, 7.15. $C_{17}H_{21}IN_2$ requires C, 53.7; H, 5.55; N, 7.35%); $\nu_{max}$(Nujol mull)/$cm^{-1}$ 1580, 1560, 858 and 726; $\lambda_{max}$/nm 271 ($\log_{10}$ $\varepsilon$ 4.20) and 221 (4.46).

*General Procedure for the Direct Lithiation of Azepinoindole* **7**.—To a cooled (−78 °C) stirred solution of compound **7** (0.7 g, 3.8 mmol) in anhydrous THF under argon, was added *tert*-butyllithium (1.5 mol $dm^{-3}$ in pentane; 2.6 $cm^3$). A dark green colour developed over 20 min, and then the co-reagent was added dropwise *via* a syringe and septum. The reaction mixture was allowed to come to room temperature, quenched with saturated ammonium chloride in methanol (20 $cm^3$) and extracted with ether (3 × 40 $cm^3$). The dried ($MgSO_4$) ether extracts were filtered, evaporated, and the residue purified as described for each product.

*8-Trimethylsilyl-8H-azepino[1,2-a]indole* **16**. The residue was crystallised from ethanol to give the *trimethylsilyl derivative* **16**, m.p. 91.5–92.5 °C (82%) (Found: C, 76.2; H, 7.7; N, 5.4. $C_{16}H_{19}NSi$ requires C, 75.9; H, 7.5; N, 5.55%); $\nu_{max}$($CCl_4$)/$cm^{-1}$ 1665, 1517, 1204, 740 and 634; $\lambda_{max}$/nm 310 ($\log_{10}$ $\varepsilon$ 4.22), 263 (4.43) and 224 (4.37); *m/z* 253 ($M^+$, 78%), 180 [$M^+$ − $(CH_3)_3Si$, 100] and 73 [$Si(CH_3)_3$, 100].

*10-Methyl-10H-azepino[1,2-a]indole* **18** *and* *8-methyl-8H-azepino[1,2-a]indole* **19**. The co-reagent was methyl iodide and separation was by Chromatotron (petroleum, b.p. 60–80 °C). The early fractions gave the *10-methyl derivative* **18**, which was recrystallised from ethanol, m.p. 59 °C (lit.,[3] m.p. 59 °C). Recombination of the later bands from the Chromatotron, followed by a further passage across the Chromatotron, gave later fractions sufficiently pure for purification by distillation (Kugelrohr) to give the *8-methyl derivative* **19**, b.p. 160 °C/0.04 mmHg (Found: C, 86.55; H, 6.65; N, 6.8. $C_{14}H_{13}N$ requires C, 86.15; H, 6.65; N, 7.15%); $\lambda_{max}$/nm 323 ($\log_{10}$ $\varepsilon$ 4.09), 261 (4.16) and 222 (4.34); *m/z* 195 ($M^+$, 66%) and 180 ($M^+$ − $CH_3$, 100).

*10-Ethyl-10H-azepino[1,2-a]indole* **20** *and* *8-ethyl-8H-azepino[1,2-a]indole* **21**. The co-reagent was ethyl iodide. The separation procedure was as described for compounds **18** and **19** to give the *10-ethyl derivative*, m.p. 53 °C (from ethanol) (Found: C, 86.15; H, 7.3; N, 6.55. $C_{15}H_{15}N$ requires C, 86.1; H, 7.15; N, 6.7%); $\lambda_{max}$/nm 275 ($\log_{10}$ $\varepsilon$ 4.24) and 230 (4.33); *m/z* 209 ($M^+$, 44%), 180 ($M^+$ − $C_2H_5$, 100%). From the later Chromatotron fractions the *8-ethyl derivative* was isolated, b.p. 140 °C/0.05 mmHg (Kugelrohr) (Found: C, 86.1; H, 7.5; N, 6.5. $C_{15}H_{15}N$ requires C, 86.1; H, 7.15; N, 6.7%), $\lambda_{max}$/nm 323 ($\log_{10}$ $\varepsilon$ 4.12), 265 (4.20) and 219 (4.40); *m/z* 209 ($M^+$, 58%) and 180 ($M^+$ − $C_2H_5$, 100).

*10-Isopropyl-10H-azepino[1,2-a]indole* **22** *and* *8-isopropyl-8H-azepino[1,2-a]indole* **23**. The co-reagent was isopropyl bromide or iodide. The separation procedure was as described for compounds **18** and **19** to give the *10-isopropyl derivative* **22**, m.p. 56 °C (from ethanol) (Found: C, 85.9; H, 7.7; N, 6.4. $C_{16}H_{17}N$ requires C, 86.1; H, 7.6; N, 6.3%); $\lambda_{max}$/nm 311sh, 277 ($\log_{10}$ $\varepsilon$ 4.21) and 228 (4.31); *m/z* 223 ($M^+$, 25%) and 180 ($M^+$ − $C_3H_7$, 100). From later fractions the *8-isopropyl derivative* **23** was isolated, b.p. 145 °C/0.04 mmHg (Found: C, 85.75; H, 7.7; N, 6.35. $C_{16}H_{17}N$ requires C, 86.1; H, 7.6; N, 6.3%); *m/z* 223 ($M^+$, 20%) and 180 ($M^+$ − $C_3H_7$, 100).

*10-tert-Butyl-10H-azepino[1,2-a]indole* **24** *and* *8-tert-butyl-8H-azepino[1,2-a]indole* **25**. The co-reagent was *tert*-butyl bromide or *tert*-butyl iodide. The lithiation mixture had to be raised to room temperature to complete reaction. The separation procedure was as described for compounds **18** and **19** to give the *10-tert-butyl derivative* **24**, m.p. 141–142 °C (Found: C, 86.3; H, 8.4; N, 5.9. $C_{17}H_{19}N$ requires C, 86.05; H, 8.05; N, 5.8%); $\lambda_{max}$/nm 319 ($\log_{10}$ $\varepsilon$ 3.90), 274 (4.23) and 228 (4.37); *m/z* 237 ($M^+$, 9%), 180 ($M^+$ − $C_4H_9$, 100) and 152 (7). The *8-tert-butyl derivative* **25** was characterised only from its NMR spectrum and mass spectrum, *m/z* 237 ($M^+$, 10%) and 180 ($M^+$ − $C_4H_9$, 100).

*General Procedure for the Lithiation of 8-Trimethylsilyl-8H-azepino[1,2-a]indole* **16**.—To a stirred, cooled (−78 °C) solution of the trimethylsilylazepinoindole **16** (0.5 g, 2 mmol) in anhydrous THF (7 $cm^3$) was slowly added *tert*-butyllithium (1.5 mol $dm^{-3}$ in pentane; 6 mmol). After 15 min alkyl halide (10 mmol) was added dropwise, and stirring continued while the flask reached room temperature. Following work-up with methanolic ammonium chloride, the crude product was passed across a Chromatotron, giving a single broad band. In the case of the methyl and ethyl derivatives, collection of early portions of this broad band gave one component sufficiently pure to allow crystallisation from ethanol. In the case of the isopropyl and *tert*-butyl derivatives no single pure fraction was obtained. The mixture of isomers was distilled (Kugelrohr) and individual components identified by $^1H$ NMR and by GC–MS.

*8,10-Bis(trimethylsilyl)-10H-azepino[1,2-a]indole* **17**. *Compound* **17** was obtained in 88% yield by the general procedure, m.p. 125–127 °C (from ethanol) (Found: C, 70.05; H, 8.6; N, 4.15. $C_{19}H_{27}NSi_2$ requires C, 70.15; H, 8.3; N, 4.3%); $\lambda_{max}$/nm 261 ($\log_{10}$ $\varepsilon$ 4.19) and 230 (4.32); *m/z* 325 ($M^+$, 4%) and 252 ($M^+$ − $C_3H_8Si$, 100).

*8-Methyl-8-trimethylsilyl-8H-azepino[1,2-a]indole* **26**. Recrystallised from ethanol, m.p. 140–144 °C (Found: C, 75.9; H, 8.1; N, 5.0. $C_{17}H_{21}NSi$ requires C, 76.3; H, 7.85; N, 5.25%); $\lambda_{max}$/nm 308 ($\log_{10}$ $\varepsilon$ 4.26), 266 (4.36) and 222 (4.39); *m/z* 267 ($M^+$, 5%), 252 ($M^+$ − $CH_3$, 4) and 195 ($M^+$ − $C_3H_8Si$, 100).

*8-Ethyl-8-trimethylsilyl-8H-azepino[1,2-a]indole* **28**. Recrystallised from ethanol, m.p. 140–144 °C (Found: C, 76.4; H, 8.25; N, 5.15. $C_{18}H_{23}NSi$ requires C, 76.85; H, 8.2; N, 5.0%); *m/z* 281 ($M^+$, 4%) and 209 ($M^+$ − $C_3H_8Si$, 100).

*8-Isopropyl-8-trimethylsilyl-8H-azepino[1,2-a]indole* **30** *and* *10-isopropyl-8-trimethylsilyl-10H-azepino[1,2-a]indole* **31**. Formed as an inseparable mixture, which on distillation (Kugelrohr) gave microanalytical figures C, 76.8; H, 8.15; N, 4.9. $C_{19}H_{25}NSi$ requires C, 77.3; H, 8.45; N, 4.75%. Two peaks on GC yielded *m/z* values of 295 ($M^+$, 4%) and 223 ($M^+$ − $C_3H_8Si$, 100) and 295 ($M^+$, 9) and 223 ($M^+$ − $C_3H_8Si$, 100), respectively.

*8-tert-Butyl-8-trimethylsilyl-8H-azepino[1,2-a]indole* **32** *and* *10-tert-butyl-8-trimethylsilyl-10H-azepino[1,2-a]indole* **33**. Obtained as a mixture, inseparable by chromatography. A sample

distilled (Kugelrohr) had microanalytical figures C, 77.35; H, 8.75; N, 4.6. $C_{20}H_{27}NSi$ requires C, 77.3; H, 8.45; N, 4.75%. Two peaks on GC yielded *m/z* values of 309 ($M^+$, 2%), 252 ($M^+ - C_4H_9$, 75) and 236 ($M^+ - C_3H_9Si$, 100) and 309 ($M^+$, 4), 252 ($M^+ - C_4H_9$, 70) and 236 ($M^+ - C_3H_9Si$, 100), respectively.

8-*Methyl*-10H-*azepino*[1,2-a]*indole* **34**.—A solution of tetrabutylammonium fluoride (1 mol $dm^{-3}$ in THF; 0.05 mmol) was added to a solution of compound **26** (0.05 mmol) in anhydrous THF (2 $cm^3$) at −78 °C. After 1 min the reaction mixture was taken up in ether (15 $cm^3$), washed with water (3 $cm^3$), dried ($MgSO_4$), filtered, and then evaporated. The residue was almost pure 8-methyl derivative **34**, identified by comparison of its spectra with those of an authentic specimen.[1] Similarly, from compound **28**, was obtained the 8-isopropyl derivative **35** (NMR spectrum in Table 1).

2-*Amino*-4'-*bromodiphenylmethanone* **37**.—The Grignard reagent from 1,4-dibromobenzene (78 g, 0.3 mol) and magnesium (8 g, 0.3 mol) prepared as described by Schiemenz[9] was slowly added to a vigorously stirred suspension of acetanthranil (53 g, 0.3 mol) in a mixture of toluene (400 $cm^3$) and ether (300 $cm^3$) at 0 °C. The mixture was warmed at 30 °C with stirring (2 h). Dilute hydrochloric acid (2 mol $dm^{-3}$; 500 $cm^3$) was added slowly and the mixture stirred (10 min) and then the organic layer was separated. Extraction (ether, 2 × 200 $cm^3$) was followed by evaporation of the combined organic layers to give a yellow oil, which was dissolved in a mixture of concentrated hydrochloric acid (150 $cm^3$) and ethanol (300 $cm^3$). The solution was boiled (2.5 h), cooled, and then basified with 10% aqueous sodium hydroxide. Extraction with ether (4 × 250 $cm^3$) and removal of the solvent from the dried, filtered solution, gave a red oil, which solidified and was recrystallised from ethanol, to give the title compound **37** (44 g, 48%). (Bergmann and Barshai reported a 25% yield of the *N*-acetyl derivative).[13]

2-*Amino*-4'-*bromodiphenylmethane* **38**.—Lithium aluminium hydride (8 g) was added slowly to an ethereal solution of freshly sublimed aluminium chloride (40 g in 150 $cm^3$), stirred under a nitrogen atmosphere. A solution of benzophenone **37** (20 g) in the minimum amount of anhydrous ether was added dropwise to the hydride solution, and the mixture vigorously stirred (1 h). Careful addition of damp ether, then water (200 $cm^3$) was followed by separation of the ether layer, and further extraction of the aqueous layer with ether (3 × 100 $cm^3$). The combined extracts were dried ($MgSO_4$) and after evaporation of the filtered solution the residue was chromatographed. Elution with petroleum (b.p. 60–80 °C) gave as the slower running of two bands the bromo amine **38** (9.7 g, 47%), sufficiently pure for conversion into the bromoazepinoindole **39**.

8-*Bromo*-10H-*azepino*[1,2-a]*indole* **39**.—(*a*) Sulfuric acid (4 mol $dm^{-3}$; 50 $cm^3$) was added slowly to a solution of bromo amine **38** (4.1 g, 15 mmol) in dioxane (50 $cm^3$), and the resultant solution was cooled to −10 °C. A solution of sodium nitrite (1.2 g, 17 mmol) in water (10 $cm^3$) was added to the reaction mixture at −10 °C, and stirring was continued (20 min) before slow addition of sodium azide (1.3 g, 20 mmol in 10 $cm^3$ of water). The reaction mixture was stirred at 30 °C (10 min), diluted with water (300 $cm^3$), and then extracted with ether (3 × 100 $cm^3$). The combined ether extracts were washed with sodium hydroxide (50 $cm^3$ of 5% aqueous solution), dried ($MgSO_4$), and evaporated, keeping the temperature below 35 °C. The azide was decomposed directly in boiling TCB (400 $cm^3$). Removal of solvent and column chromatography gave 8-*bromoazepinoindole* **39**, m.p. 137.5–138.5 °C (2.3 g, 56% from the amine **38**) (Found: C, 60.1; H, 3.75; N, 5.15. $C_{13}H_{10}BrN$ requires C, 60.0; H, 3.85; N, 5.4%); $\lambda_{max}$/nm 322 ($\log_{10}\varepsilon$ 4.00), 269 (4.34), 224 (4.50) and 205 (4.44); *m/z* 261 ($M^+ + 2$, 20%), 259 ($M^+$, 20) and 180 ($M^+ - Br$, 100).

2-*Amino*-3,3',5-*tribromo*-4'-*methoxydiphenylmethane* **42**.—To a solution of the amine **41** (6.3 g, 30 mmol) in concentrated hydrobromic acid (50 $cm^3$) was added bromine (15.1 g, 90 mmol). The reaction mixture was stirred in the dark (48 h) at which point a sample basified showed a single major product. The whole reaction mixture was basified (4 mol $dm^{-3}$ NaOH) and extracted with ether (3 × 75 $cm^3$), the combined extracts were dried ($MgSO_4$), and the filtrate decolourised using charcoal. Removal of solvent gave a yellow oil, which slowly solidified and was crystallised from ethanol to give the *tribromo amine* **42**, m.p. 178–183 °C (Found: C, 37.75; H, 2.65; N, 3.05. $C_{14}H_{12}Br_3NO$ requires C, 37.35; H, 2.65; N, 3.10%); *m/z* 453 ($M^+ + 6$, 33%), 451 ($M^+ + 4$, 100), 449 ($M^+ + 2$, 100), 447 ($M^+$, 32), 372 (28), 370 (66), 368 ($M^+ - Br$, 35), 210 (58), 195 (35), 167 (67), 139 (48), 105 (47) and 77 (64).

2-*Azido*-3,3',5-*tribromo*-4'-*methoxydiphenylmethane* **43**.—Prepared from amine **42** as described in the preparation of 8-bromoazepinoindole (above) to give the *azide* **43**, m.p. 74–75 °C (from ethanol) (Found: C, 35.2; H, 2.0; N, 8.75. $C_{14}H_{10}Br_3N_3O$ requires C, 35.30; H, 2.10; N, 8.85%); $\nu_{max}$(KCl disc)/$cm^{-1}$ 2112, 1490, 1436 and 1254; $\lambda_{max}$/nm 209 ($\log_{10}\varepsilon$ 4.09).

*Decomposition of* 2-*Azido*-3,3',5-*tribromo*-4'-*methoxydiphenylmethane* **43**.—A solution of the azide **43** (1.0 g) in TCB (5 $cm^3$) was added dropwise to stirred TCB (150 $cm^3$) at 165 °C under argon. Heating at 165 °C was continued (4 h), and then the cooled solution was evaporated under reduced pressure. The residue was adsorbed on to alumina, applied to a column of alumina, and eluted with petroleum (b.p. 60–80 °C) and then with mixed solvent containing ethyl acetate (up to 40%). All the fractions were combined and evaporated to give total non-polymeric products (0.48 g). Passage across a Chromatotron gave three broad bands A, B and C (eluted with petroleum, b.p. 60–80 °C and mixtures with up to 15% of ethyl acetate). Each band was collected in several fractions. Some compounds were crystallised from enriched fractions; compounds are reported in order of elution.

*Band A*.—2,4,9-*Tribromo*-8-*methoxy*-10H-*azepino*[1,2-a]*indole* **44**. Recrystallised from petroleum (b.p. 60–80 °C), m.p. 179–182 °C (Found: C, 37.5; H, 2.15; N, 3.05. $C_{14}H_{10}Br_3NO$ requires C, 37.55; H, 2.25; N, 3.15%); $\nu_{max}$(KCl disc)/$cm^{-1}$ 1624, 1384, 1230 and 780; $\lambda_{max}$/nm 314 ($\log_{10}\varepsilon$ 3.85), 266 (4.16), 237 (4.28) and 205 (4.32).

2,4,7-*Tribromo*-8-*methoxy*-10H-*azepino*[1,2-a]*indole* **45**. Recrystallised from petroleum (b.p. 60–80 °C), m.p. 162–165 °C (Found: C, 37.9; H, 2.2; N, 3.05%); $\nu_{max}$(KCl disc)/$cm^{-1}$ 1638, 1442, 1394, 1134 and 764; $\lambda_{max}$/nm 313 ($\log_{10}\varepsilon$ 3.78), 275 (4.06), 237 (4.15) and 205 (4.27).

The cyclopropapyridoindole **47** had $\delta$ 0.90 (1 H, m, *J* 5.5 and 7.0, $H^A$), 1.95 (1 H, m, *J* 5.5 and 8.2, $H^B$), 3.40 (3 H, s, $OCH_3$), 5.00 (1 H, m, *J* 7.0 and 8.2, 9-H), 6.35 (1 H, s, 10-H), 6.90 (1 H, s, 6-H), 7.50 (1 H, d, *J* 1.5, 1-H) and 7.65 (1 H, d, *J* 1.5).

*Band B*.—2,4-*Dibromo*-8-*methoxy*-10H-*azepino*[1,2-a]*indole* **48**. Recrystallised from ethanol, m.p. 144–147 °C (Found: C, 45.45; H, 2.95; N, 3.6. $C_{14}H_{11}Br_2NO$ requires C, 45.55; H, 3.0; N, 3.60%); $\nu_{max}$(KCl disc)/$cm^{-1}$ 1648, 1444, 1398, 1228, 1154 and 776; $\lambda_{max}$/nm 313 ($\log_{10}\varepsilon$ 3.74), 264 (4.08), 229 (4.10) and 210 (4.16).

Acridine **49** or **50** had $\delta$ 4.15 (3 H, s, $OCH_3$), 7.65 (1 H, s), 8.10 (1 H, d, *J* 1.8), 8.20 (1 H, d, *J* 1.8), 8.25 (1 H, s) and 8.50 (1 H, s, 9-H).

*Band C.*—2,4-Dibromo-8*H*-azepino[1,2-*a*]indol-8-one **51**, $\delta$ 5.95 (1 H, dd, *J* 1.5 and 10.5, 7-H), 6.40 (1 H, dd, *J* 1.5 and 11.0, 9-H), 6.95 (1 H, s, 11-H), 7.25 (1 H, dd, *J* 1.5 and 11.0, 10-H), 7.75 (1 H, d, *J* 2.0, 1-H), 7.85 (1 H, d, *J* 2.0, 3-H) and 9.20 (1 H, dd, *J* 1.5 and 10.5, 6-H).

2,4-Dibromo-9,10-dihydro-8*H*-azepino[1,2-*a*]indol-8-one **54**, $\delta$ 2.85 (2 H, m, 10-H), 3.20 (2 H, m, 9-H), 5.75 (1 H, d, *J* 10.5, 7-H), 6.40 (1 H, s, 11-H), 7.55 (1 H, d, *J* 1.7, 1-H), 7.65 (1 H, d, *J* 1.7, 3-H) and 8.70 (1 H, d, *J* 10.5, 6-H).

*X-Ray Crystallography.*—Crystals of compound **17** suitable for X-ray work were grown from ethanol. Unit cell and intensity data were recorded using a Delft Instruments FAST TV area detector diffractometer positioned at the window of a rotating anode generator with Mo-K$\alpha$ radiation ($I$ = 0.710 69 Å) following previously described procedures.[14] The structures were solved by direct methods (SHELX-S),[15] and refined by full-matrix least-squares on $F$ using SHELX-76.[16] Hydrogen atoms were included in idealised positions with C–H = 0.96 Å. Non-hydrogens were refined anisotropically. Details are as follows.

*Crystal data.* $C_{19}H_{27}NSi_2$, $M$r = 325.60, monoclinic, $a$ = 6.293(1), $b$ = 23.000(3), $c$ = 13.851 Å, $\beta$ = 97.00(2)°, $U$ = 1988 Å$^3$, monoclinic, space group $P2_1/c$, $Z$ = 4, $D_c$ = 1.088 g cm$^{-1}$, $F$(000) = 704, $m$ – 1.70 cm$^{-1}$. Total data measured 11 843 giving 4842 unique ($R_{int}$ 0.06) and 2400 observed [$F_o$ > 3 s ($F_o$)]. $R$ = 0.050, $R_w$ = 0.052 with unit weights and 221 refined parameters. Atomic fractional coordinates, thermal parameters and bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre.*

* For details of the deposition scheme, see 'Instructions for Authors', *J. Chem. Soc., Perkin Trans. 1*, 1995, Issue 1.

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