Reactions of Condensed *N*-Heteroaromatic Molecules. Part II.[1] Electrophilic Substitution of *N*-Acetylcarbazole, *N*-Acetyl-10,11-dihydrodibenz[*b*,*f*]azepine, and Derivatives

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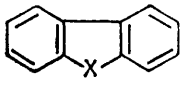
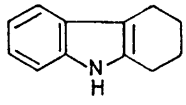
N-Acetylation of carbazole and 10,11-dihydrodibenz[*b*,*f*]azepine deactivates the aromatic nuclei to electrophilic substitution. However, Friedel–Crafts acylation, catalysed by aluminium trichloride, proceeds smoothly to give high yields of the ring substitution products acylated *meta* to the nitrogen atom. Specific complexation of the *N*-acetyl derivative, aluminium trichloride, and acetyl chloride is thought to be involved, and the reaction appears to be general for a variety of *N*-heteroaromatic molecules. In contrast, the corresponding *N*-alkyl derivatives readily undergo electrophilic substitution *para* to the nitrogen atom.

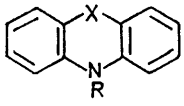
ACYLATION of the nitrogen atom of the condensed heteroaromatic molecules (1), (3), (4), and (5) is known to affect profoundly its directing influence towards electrophiles. Carbazoles, *N*-alkylcarbazoles,[2] and their tetrahydro-derivatives[3] are attacked by electrophiles *para* to the nitrogen atom, *cf.* aniline;[4] also under different conditions, the 10,11-double bond of tetrahydrocarbazole is susceptible to electrophilic attack.[5] However *N*-acyl[6] and *N*-benzoyl derivatives[7] undergo substitution *meta* to the nitrogen atom. A possible explanation of this behaviour is that electron withdrawal from the nitrogen atom by the acyl group renders the nitrogen atom electron-deficient and non-directing. Thus incoming electrophiles are directed *para* to the biphenyl linkage, *cf.* fluorene (2).[8]



(1) X = NH
(1a) X = NAc
(2) X = CH_2



(3)



(4) X = S, R = H
(4a) X = S, R = Ac
(5) X = O, R = H
(5a) X = O, R = Ac
(6) X = CH=CH, R = H
(7) X = CH_2·CH_2, R = H

The differing behaviour towards electrophiles of *N*-acylated as compared to *N*-alkylated derivatives is a feature of electrophilic substitution of other ring systems, *e.g.* indole,[9] phenothiazine (4),[10] and phenoxazine (5).[11]

The anomalous behaviour of an *N*-acylated amine towards electrophilic attack is well illustrated by diphenylamine and its *N*-acetyl derivative; whereas the former readily undergoes nitration[12] and, under Friedel–Crafts conditions, alkylation, and benzoylation,[13] the latter is unreactive towards nitration[12] and acylation. This lack of reactivity promoted a re-examination of related electrophilic substitution reactions of *N*-acyl derivatives of the ring systems (1), (4), and (5).

Electrophilic substitution of the *N*-acetyl derivatives (1a), (4a), and (5a) is apparently confined to Friedel–Crafts acylation, the one reported exception being chlorination,[14] by chlorine–acetic acid, of *N*-acetylcarbazole, which affords, contrary to the foregoing generalisations, *N*-acetyl-3-chlorocarbazole, the product of substitution *para* to the nitrogen atom.

The electrophilic chlorination of carbazoles at room temperature under aprotic conditions by 1-chlorobenzotriazole has been shown to afford the same nuclear-chlorinated products as obtained by chlorination with molecular chlorine in acidic media.[15] We have found that in the reaction of *N*-acetylcarbazole with 1-chlorobenzotriazole in dichloromethane at room temperature, no chlorination occurs. This result is taken as evidence that *N*-acetyl-3-chlorocarbazole isolated from the reaction of *N*-acetylcarbazole with chlorine in acetic acid, does not arise *via* electrophilic substitution of *N*-acetylcarbazole. We suggest an alternative interpretation of the results for the chlorination of *N*-acetylcarbazole by chlorine–acetic acid. Hydrolysis of *N*-acetylcarbazole by adventitious water impurity in acetic acid would produce an equilibrium concentration of carbazole, as evidenced by the rapid growth of carbazole absorptions (336 and 323 nm) in the u.v. spectrum of a solution of *N*-acetylcarbazole in acetic acid containing a few drops

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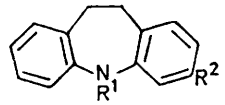
of 5M-hydrochloric acid. Carbazole, being very much more reactive to electrophiles than the *N*-acetyl derivative, would react preferentially to afford 3-chlorocarbazole, which under the conditions of the reaction would be reacetylated to produce the observed product, *N*-acetyl-3-chlorocarbazole.

N-Acetylcarbazole was found to be unreactive also towards formylation (Vilsmeier conditions), and, more interestingly, to acetylation by acetylium perchlorate [16] generated *in situ* from silver perchlorate and acetyl chloride. Under identical conditions the latter reagent acetylates *N*-ethylcarbazole to give 3-acetyl-*N*-ethylcarbazole, and it is apparent from the foregoing that, generally, *N*-acyl compounds are deactivated towards electrophilic substitution. The failure of *N*-acetylcarbazole and the structurally related 5-acetyl-10,11-dihydrodibenz[*b*,*f*]azepine (*N*-acetyliminobibenzyl) to react with acetylium perchlorate * suggests that the Friedel–Crafts acylation of these molecules is a fortuitous consequence of the formation of a substrate–aluminium trichloride complex [17] which ensures the proximity of the substrate and the active acylating species.

Absorption spectroscopy reveals that in dichloromethane, aluminium trichloride and *N*-acetylcarbazole form a red complex ($\lambda_{max.}$ *ca.* 550 nm), whereas *N*-acetyldiphenylamine does not form coloured complexes under these conditions. Other workers have isolated 1 : 1 complexes of aluminium bromide and aromatic hydrocarbons,[18] 1 : 1 : 1 complexes of aluminium bromide, aromatic hydrocarbons, and acyl halides,[19] and also complexes have been proposed as intermediates in the *ortho*-alkylation of aromatic amines with aluminium trichloride–ethylene.[20]

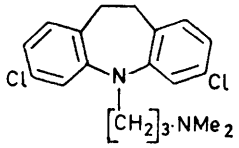
Acylation and alkylation [1] of *N*-heteroaromatic molecules is important in the context of the synthesis of new vinyl compounds for studies of cation radical reactivity [21] and polymerisation,[22,23] and as part of a continuing interest in dibenz[*b*,*f*]azepine (6), and 10,11-dihydrodibenz[*b*,*f*]azepine (7) (iminobibenzyl), we sought to discover whether the differing directing influence towards electrophiles of *N*-alkyl as compared with *N*-acyl derivatives operated in the latter ring system. Many examples of 5-substituted dibenz[*b*,*f*]azepines and iminobibenzyls have been synthesised and screened for possible biological activity, but the fundamental chemistry of these systems has been largely overlooked.

Studies of the electrophilic substitution of 10,11-dihydrodibenz[*b*,*f*]azepine have been restricted to the Friedel–Crafts acylation of the *N*-acetyl derivative (10), which affords 3,5-diacetyl-10,11-dihydrodibenz[*b*,*f*]azepine (15); [24] and to the bromination of the parent compound (7), with bromine–acetic acid, to give 2,4,6,8-tetrabromo-10,11-dihydrodibenz[*b*,*f*]azepine (19).[25] In the former case the position occupied by the acetyl



(8) R^1 = Me, R^2 = H
(9) R^1 = Et, R^2 = H
(10) R^1 = COMe, R^2 = H
(11) R^1 = COEt, R^2 = H
(12) R^1 = CO·CH_2Cl, R^2 = H
(13) R^1 = COPh, R^2 = H
(14) R^1 = H, R^2 = COMe
(15) R^1 = R^2 = COMe
(16) R^1 = COEt, R^2 = COMe
(17) R^1 = CO·CH_2Cl, R^2 = COMe
(18) R^1 = COPh, R^2 = COMe

(19) R^1 = H, R^2 = R^3 = Br
(20) R^1 = R^2 = H, R^3 = Br
(21) R^1 = Me, R^2 = H, R^3 = Br
(22) R^1 = Me, R^2 = H, R^3 = COMe



(23)

substituent was established by hydrolysis to the 3-acetyl compound (14) and subsequent reduction to the known 3-ethyl-10,11-dihydrodibenz[*b*,*f*]azepine.[26]

The ability of an *N*-acyl substituent to direct incoming electrophiles into the 3-position of the iminobibenzyl nucleus is also displayed by *N*-propionyl (11), *N*-chloroacetyl (12), and *N*-benzoyl-10,11-dihydrodibenz[*b*,*f*]-azepine (13), which under Friedel–Crafts conditions afford the 3-acetyl derivatives (16)—(18), respectively. However unlike the *N*-acetyl derivative (10), these compounds (11)—(13) only underwent acetylation after prolonged reaction with a large excess of acetyl chloride–aluminium trichloride. In no case was any diacetylated product isolated, and despite repeated attempts an acetyl group could not be introduced into the unsubstituted ring of the 3,5-diacetyl compound (15).

One possible explanation of this observed lack of reactivity is apparent upon inspection of space-filling molecular models of the 3,5-diacetyl compound (15). The iminobibenzyl ring is puckered and the most reasonable conformation of (15) is one in which the *N*-acetyl group is coplanar and conjugated with the unsubstituted aromatic ring, thus deactivating this ring, *cf.* *N*-acetyldiphenylamine.

Friedel–Crafts acetylation of the *N*-methyl compound (8) afforded 2,8-diacetyl-10,11-dihydro-5-methyldibenz-

* The referees have pointed out that, owing to differing electrophilic reactivities, acetylium perchlorate and acetyl chloride–aluminium trichloride are not strictly comparable.

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[26] J. R. Geigy A.G., Belg. P. 591,293 and 585,356.

[*b*,*f*]azepine (22); no monoacetylated material was isolated from the reaction. The positions occupied by the acetyl groups were established by the 100 MHz n.m.r. spectrum. By analogy with the model compound *p*-aminoacetophenone (protons *ortho* to the nitrogen τ 3·29; protons *ortho* to the acetyl group τ 2·23 [27]) the absorptions in the aromatic region at higher field are assigned to the 4- and 6-protons (*ortho* to nitrogen). These occur as a doublet at τ 2·90 (*J* 8 Hz), appropriate to an *ortho*-coupled aromatic proton. For the 3,7-isomer these protons would also give a doublet, but the coupling constant would be much smaller (< 3 Hz).

Bromination of the *N*-methyl compound with molecular bromine in acetic acid afforded the dibromo-compound (21); a similar reaction employing carbon tetrachloride as solvent and the *N*-acetyl derivative (10) as substrate, afforded only unchanged starting material.

10,11-Dihydro-*N*-methyldibenz[*b*,*f*]azepine (8), required for these acylation studies, was synthesised from the free base (7) and n-butyl-lithium–iodomethane. This method was superior to the literature recipes employing dimethyl sulphate or phenyl-lithium–iodomethane.[28] An analogous reaction with iodoethane afforded the *N*-ethyl derivative (9). All attempts to prepare the *N*-n-propyl homologue were unsuccessful, even when a powerful Lewis base, *NNN'N'*-tetramethylethylenediamine, was used to convert the n-butyl-lithium aggregate into the more reactive co-ordinated monomeric reagent.[29] This lack of reactivity may be a consequence of the low temperature employed, and the steric hindrance associated with the introduction of a bulky substituent at the nitrogen atom. At higher temperatures, typically that of refluxing toluene, and with an alkali metal or alkali metal amide as the base, a bulky group, *e.g.* 3-dimethylaminopropyl may be introduced at the nitrogen atom, but at these elevated temperatures iminobibenzyl may adopt a more amenable conformation.

N.m.r. spectra of iminobibenzyl derivatives have not previously been reported but are invaluable in the present work as an aid to structural identification. Appropriate data are collected in the Table and interest attaches to the protons of the ethano bridge, which for the parent compound and *N*-alkyl derivatives are all equivalent and appear as a sharp singlet in the region τ 6·9—7·17. An increase in the size of the nitrogen substituent *e.g.* 3-dimethylaminopropyl does not alter the equivalence of the ethano-bridge protons. However, when the nitrogen atom carries an acyl substituent the ethano-bridge protons are no longer equivalent and appear as a broad complex multiplet in the region τ 6·1—7·5. Presumably conjugation of the nitrogen atom and acyl substituent freezes the conformation of the molecule, thus rendering the protons of the ethano-bridge non-equivalent.

Conclusions.—Friedel–Crafts acylation of *N*-acetylcarbazole and *N*-acetyliminobibenzyl is facilitated by complex formation between the *N*-acetyl compound and aluminium trichloride or aluminium trichloride–acetyl chloride complex. The reaction appears to be general for *N*-acetyl derivatives of several heteroaromatic molecules and specifically orients acylation *meta* to the nitrogen atom.

^{1}H N.m.r. spectra (τ values) of iminobibenzyl derivatives

Compound	$[CH_2]_2$	ArH	Other
(7)	7·17 (4H, s)	3·0—3·6 (8H, m)	4·4br (1H, NH)
(8)	7·00 (4H, s)	2·9—3·4 (8H, m)	6·85 (3H, s, N·CH_3)
(9)	6·90 (4H, s)	2·6—3·1 (8H, m)	6·24 (2H, q, *J* 8 Hz, N·CH_2), 8·87 (3H, t, CH_3)
(10)	6·6—7·5 (4H, m)	2·8—3·1 (8H, m)	8·10 (3H, s, CO·CH_3)
(11)	6·5—7·5 (4H, m)	2·6—3·1 (8H, m)	7·5—8·1 (2H, m, CO·CH_2), 8·95 (3H, t, *J* 7 Hz, CH_3)
(12)	6·5—7·5 (4H, m)	2·9—3·1 (8H, m)	6·17 (2H, s, N·CO·CH_2Cl)
(13)	6·4—7·5 (4H, m)	2·6—3·2 (13H, m)	
(14)	7·14 (4H, s)	2·2—3·2 (7H, m)	7·60 (3H, s, CO·CH_3)
(15)	6·5—7·5 (4H, m)	2·0—2·8 (7H, m)	7·45 (3H, s, CO·CH_3), 7·99 (3H, s, N·CO·CH_3)
(16)	6·6—7·5 (4H, m)	2·0—2·8 (7H, m)	7·55 (3H, s, CO·CH_3), 7·8br (2H, CO·CH_2), 8·85 (3H, t, *J* 8 Hz, CH_3)
(17)	6·5—7·4 (4H, m)	1·9—2·6 (7H, m)	6·00 (2H, s, CO·CH_2Cl), 7·32 (3H, s, CO·CH_3)
(18)	6·1—7·2 (4H, m)	2·0—2·7 (12H, m)	7·55 (3H, s, CO·CH_3)
(19) †	7·24 (4H, s)	2·8—3·3 (6H, m)	
(21)	6·95 (4H, s)	2·5—3·2 ((6H, m)	6·75 (3H, s, N·CH_3)
(22)	6·95 (4H, s)	2·2—3·1 (6H, m)	6·69 (3H, s, N·CH_3), 7·60 (6H, s, CO·CH_3)
(23) ‡	6·92 (4H, s)	2·6—3·1 (6H, m)	6·28 (2H, t, *J* 7 Hz, N·CH_2), 7·8br (2H, N·CH_2), 7·85 (6H, s, N·CH_3), 8·3br (2H, CH_2)

† In $(CD_3)_2SO$. ‡ Supplied by Smith Kline and French Ltd.

EXPERIMENTAL

^{1}H N.m.r. spectra were measured at 60 MHz for solutions in deuteriochloroform with tetramethylsilane as internal standard. I.r. spectra were recorded for Nujol mulls. Mass spectra were measured by the Physico-Chemical Measurements Unit, Harwell. Alumina for chromatography was Brockmann grade I neutral (B.D.H.).

N-Acetylcarbazole, m.p. 68—69° (lit.,[30] 68—69°), *N*-acetyldiphenylamine, m.p. 101—103° (lit.,[31] 103°), and

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5-acetyl-10,11-dihydrodibenz[*b,f*]azepine, m.p. 85—86° * (lit.,[24] 98°) were prepared by acetylation of the corresponding amine, as reported.

10,11-Dihydro-5-methyldibenz[*b,f*]azepine (70%), m.p. 106—107° (lit.,[28] 107—108°) was prepared by treatment of an ethereal solution of iminobibenzyl with n-butyl-lithium, and subsequent reaction *in situ* of the lithium salt with iodomethane. A similar procedure employing iodoethane afforded 5-*ethyl*-10,11-*dihydrodibenz*[b,f]*azepine* (65%), m.p. 52—53° [from methanol–benzene (9 : 1 v/v)] (Found: C, 85·9; H, 7·5; N, 6·2. $C_{16}H_{17}N$ requires C, 86·0; H, 7·7; N, 6·3%), $\nu_{max.}$ 1602, 1580, 1500, 1330, 1250, 1130, 1110, 775, and 760 cm^{-1}, *m/e* 223 (M^+, 58%), 224 (M + 1, 9), 209 (16), 208 (M − Me, 100), 194 (M − Et, 37), and 193 (46), *m** 194 (223 ⟶ 208) and 179 (208 ⟶ 194).

5-Chloroacetyl-10,11-dihydrodibenz[*b,f*]azepine, m.p. 96—98° (lit.,[32] 97—100°) was prepared [32] by refluxing a solution of iminobibenzyl in benzene with an excess of chloroacetyl chloride. Similarly, propionyl chloride and benzoyl chloride gave 10,11-*dihydro*-5-*propionyldibenz*[b,f]-*azepine* (67%), m.p. 71—72° (Found: C, 81·3; H, 6·9; N, 5·7. $C_{17}H_{17}NO$ requires C, 81·2; H, 6·8; N, 5·6%), $\nu_{max.}$ 1670br (C=O), 1610, 1580, 1500, 1300, 1270, 1180, 1075, 915, 810, 780, and 760 cm^{-1}, *m/e* 251 (M^+, 28%), 196 (21), 195 (M − C_3H_4O, 100), 194 (M − COEt, 53), 193 (14), 180 (21), 168 (9), and 57 ($EtCO^+$, 24); and 5-*benzoyl*-10,11-*dihydrodibenz*[b,f]*azepine* (72%), m.p. 130—131° [from ether–petroleum (b.p. 40—60°) (8 : 2 v/v)] (Found: C, 84·2; H, 5·9; N, 4·7. $C_{21}H_{17}NO$ requires C, 84·3; H, 5·7; N, 4·7%), $\nu_{max.}$ 1650br (C=O), 1605, 1580, 1500, 1300, 1280, 1250, 965, 800, 782, 755, and 720 cm^{-1}, *m/e* 299 (M^+, 46%), 195 (12), 194 (M − COPh, 13), 105 ($PhCO^+$, 100), and 77 (25).

3-Acetyl-10,11-dihydrodibenz[*b,f*]azepine (11%), m.p. 154—156° (lit.,[24] 156—157°) was prepared as described by Schindler and Blattner.[24]

Reaction of N-*Acetylcarbazole with* 1-*Chlorobenzotriazole*.—1-Chlorobenzotriazole (1·6 g) in dichloromethane (20 ml) was added to a solution of *N*-acetylcarbazole (2·0 g) in dichloromethane (20 ml). The mixture was stirred at room temperature overnight, repeatedly extracted with aqueous sodium hydroxide, and then washed with water and dried ($MgSO_4$). Evaporation afforded an oil which crystallised from ethanol to give *N*-acetylcarbazole (1·5 g, 75% recovery), m.p. 68—69° (lit.,[30] 68—69°).

Attempted Formylation of N-*Acetylcarbazole*.—*N*-Acetylcarbazole (10 g) was treated with phosphoryl chloride (5 ml) in dimethylformamide (35 ml) as described by Burghardt *et al.*[33] Work-up afforded unchanged starting material (80% recovery).

Acetylation of N-*Ethylcarbazole*.—A solution of acetyl chloride (2·34 g) in acetonitrile (20 ml) was added to a stirred ice-cooled mixture of *N*-ethylcarbazole (5·85 g) and silver perchlorate (6·21 g) in acetonitrile (150 ml). The ice cooled mixture was then stirred for a further 0·75 h, and poured on ice. Silver chloride was filtered off and the aqueous layer extracted with dichloromethane; the combined extracts were washed and dried ($MgSO_4$). Evaporation afforded an oil, which was dissolved in benzene (10 ml) and chromatographed on a column of neutral alumina (*ca.* 300 g) made up in petroleum. Elution with petroleum–benzene mixtures afforded unchanged starting material (1·8 g). Benzene–ether mixtures eluted 3-acetyl-*N*-ethylcarbazole (2·8 g, 57%), m.p. 112—114°, (lit.,[34] 114—115°). *N*-Acetylcarbazole, *N*-acetyldiphenylamine, *N*-acetyliminobibenzyl and 3,5-diacetyliminobibenzyl (14) all proved unreactive towards acetylium perchlorate, under the foregoing conditions.

Friedel–Crafts Acetylation of 5-*Acetyl*-10,11-*dihydrodibenz*[b,f]*azepine* (*Typical Procedure*).—Powdered aluminium trichloride (65 g) was added with stirring to a solution of 5-acetyl-10,11-dihydrodibenz[*b,f*]azepine (12·0 g) in carbon disulphide (100 ml) cooled in ice–water. Acetyl chloride (30 g) was then added dropwise during 1 h and then the mixture was refluxed for 6 h. After cooling the upper layer of carbon disulphide was discarded and the lower viscous layer treated cautiously with cracked ice and then repeatedly extracted with dichloromethane. The extract was washed with water and dried ($MgSO_4$). Evaporation afforded an oil which was chromatographed on a column of neutral alumina (250 g) made up in petroleum. Elution with petroleum–benzene mixtures and with benzene gave, after evaporation, 3,5-diacetyl-10,11-dihydrodibenz[*b,f*]azepine (5·4 g, 30%), m.p. 140—142° (lit.,[24] 143—144°), *m/e* 237 (M^+, 100%), 238 (M + 1, 16), 236 (20), 222 (M − Me, 13), 194 (M − MeCO, 29), 193 (10), and 112 (11), *m** 208 (237 ⟶ 222) and 159 (237 ⟶ 194).

Further elution with benzene–ether mixtures and with ether gave only intractable oils.

Similarly prepared were 3-*acetyl*-10,11-*dihydro*-5-*propionyldibenz*[b,f]*azepine* (26%), m.p. 93—94° [from petroleum (b.p. 40°)–benzene (1 : 1 v/v)] (Found: C, 77·7; H, 6·6; N, 4·8. $C_{19}H_{19}NO_2$ requires C, 77·8; H, 6·5; N, 4·8%), $\nu_{max.}$ 1680br (C=O), 1620, 1500, 1280br, 1180, 978, 830, and 755 cm^{-1}, *m/e* 293 (M^+, 10%), 288 (24), 237 (M − C_2H_2O, 100), 209 (16), 208 (M − C_2H_2O − Et, 71), 195 (34), 194 (45), 193 (37), 85 (50), and 83 (40), *m** 192 (293 ⟶ 237) and 182 (237 ⟶ 208); 3-*acetyl*-5-*chloroacetyl*-10,11-*dihydrodibenz*[b,f]*azepine* (57%), m.p. 145—146° [from benzene–ethanol (1 : 1 v/v)] (Found: C, 68·8; H, 5·2; Cl, 11·2; N, 4·6. $C_{18}H_{16}NO_2$ requires C, 68·9; H, 5·2; Cl, 11·3; N, 4·5%), $\nu_{max.}$ 1685 (C=O), 1618, 1500, 1250br, 830, 780, and 755 cm^{-1}, *m/e* 315/313 (M^+, 10/32%), 277 (M − HCl, 12), 271 (18), 238 (12), 237 (M − $CO{\cdot}CH_2Cl$, 92), 236 (36), 222 (12), 208 (13), 195 (60), 194 (M − $CO{\cdot}CH_2Cl$ − C_2H_2O, 100), 193 (36), 179 (10), and 165 (10); 3-*acetyl*-5-*benzoyl*-10,11-*dihydrodibenz*[b,f]*azepine* (34%), m.p. 155—156° [from petroleum (b.p. 40°)–benzene (2 : 1 v/v)] (Found: C, 80·8; H, 5·7; N, 4·0. $C_{23}H_{19}NO_2$ requires C, 80·9; H, 5·6; N, 4·1%), $\nu_{max.}$ 1685 and 1660 (C=O), 1618, 1595, 1505, 1290, 1270, 970, 840, 760, and 730 cm^{-1}, *m/e* 341 (M^+, 14%), 105 ($PhCO^+$, 100), and 77 (40).

Acetylation of 10,11-*Dihydro*-5-*methyldibenz*[b,f]*azepine*.—10,11-Dihydro-5-methyldibenz[*b,f*]azepine (5 g), aluminium trichloride (12 g), and acetyl chloride (6 g) were treated in carbon disulphide (50 ml) according to the general procedure outlined previously. The crude product was repeatedly extracted with petroleum (b.p. 40—60°); evaporation of the extract gave starting material (2·9 g). The petroleum-insoluble material was recrystallised from benzene to give 2,8-*diacetyl*-10,11-*dihydro*-5-*methyldibenz*[b,f]*azepine* (1·3 g, 30% conversion) as pale yellow crystals, m.p. 124—125°

* The m.p. of this material could not be raised despite chromatography and repeated recrystallisation.

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(Found: C, 77·6; H, 6·4; N, 4·8. $C_{19}H_{19}NO_2$ requires C, 77·8; H, 6·5; N, 4·8%), $\nu_{max.}$ 1670 (C=O), 1600, 1592, 1502, 1500, 1305, 1295, 1230, 1125, 964, 840, and 820 cm^{-1}, *m/e* 293 (M^+. 100%), 294 (M + 1, 21), 279 (18), 278 (M − Me, 94), and 83 (10), *m** 264 (293 ⟶ 278).

2,8-*Dibromo*-10,11-*dihydrodibenz*[b,f]*azepine*.— Bromine (4·0 g) in glacial acetic acid (10 ml) was added to a solution of iminobibenzyl (5·0 g) in glacial acetic acid (60 ml) and the mixture stirred at room temperature for 3 h. The pale pink precipitate (7·0 g) was filtered off, washed with glacial acetic acid, and dried. The i.r. spectrum showed absorptions at 2500, 2650, and 2710 cm^{-1} appropriate to an ammonium salt, and in daylight the material developed a green colouration. Treatment of a solution of the salt (6·5 g) in dioxan (15 ml) with warm aqueous potassium hydroxide liberated the free amine, 2,8-dibromo-10,11-dihydrodibenz-[*b,f*]azepine (2·2 g, 23%), m.p. 173—174° (decomp., green melt) [lit.,[25] 167° (decomp.)] (Found: M^+ 350·9233; C, 47·8; H, 3·2; Br, 45·1; N, 4·2%. Calc. for $C_{14}H_{11}N^{79}Br_2$: M^+ 350·9259; C, 47·6; H, 3·1; Br, 45·3; N, 4·0%), $\nu_{max.}$ 3400 (NH), 1615, 1580, 1530, 1500, 1250, 1125, 900, 885, and 810 cm^{-1}, *m/e* 355/353/351 (M^+, 49/100/51%), 356/354/352 (M + 1, 7/9/18), 273/271 (M − HBr, 14/11), 193 (M − 2Br, 22), 192 (12), 191 (M − 2HBr, 10), 99 (9), and 97 (12), *m** *ca.* 210 (355/353/351 ⟶ 273/271) and 136 (273/271 ⟶ 191).

2,8-*Dibromo*-10,11-*dihydro*-5-*methyldibenz*[b,f]*azepine*.— 5-Methyl-10,11-dihydrodibenz[*b,f*]azepine (3·1 g) and bromine (4·8 g) were stirred together in glacial acetic acid at room temperature for 12 h. The yellow precipitate was filtered off, dissolved in dioxan, and treated with warm aqueous potassium hydroxide. The mixture was poured into water and extracted with dichloromethane; the extracts were dried ($MgSO_4$). Evaporation gave an oil which was recrystallised from petroleum (b.p. 40°) to afford 2,8-*dibromo*-10,11-*dihydro*-5-*methyldibenzo*[b,f]*azepine* (1·0 g, 18%), m.p. 108—109° (Found: C, 49·2; H, 3·6; Br, 43·4; N, 3·8. $C_{15}H_{13}NBr_2$ requires C, 49·1; H, 3·6; Br, 43·5; N, 3·8%), $\nu_{max.}$ 1500br, 1285, 1240, 1130br, 895, and 825 cm^{-1}, *m/e* 369/367/365 (M^+, 50/100/53%), 370/368/366 (M + 1, 7/20/14), 354/352/350 (M − Me, 20/37/17), 273/271 (M − Me − Br, 11/10), and 195 (14), *m** 336br (369/367/365 ⟶ 354/352/350).

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