Further Examination of the Reactions between Arenesulphonyl Azides and Tetrahydrocarbazoles

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The nature of the product formed by treating 1-*p*-tolylsulphonylaminotetrahydrocarbazole with acid has been determined. 9-Methyl-4a-*p*-tolylsulphonylamino-2,3,4,4a-tetrahydrocarbazole has been isolated and shown to be an intermediate in the reaction of tosyl azide with 9-methyltetrahydrocarbazole. Good yields of cyclopentenoquinolines may be obtained by carrying out these reactions under basic conditions.

The products formed by heating 4a-arylsulphonylaminotetrahydrocarbazoles have been characterised, the effect of substituents at the 1-position on the nature of the product obtained when tetrahydrocarbazoles react with azides has been studied, and the kinetics of the acid-catalysed rearrangement of 1-methyl-3-*p*-tolylsulphonyliminoindoline-2-spirocyclopentane have been examined.

FIVE compounds (I—V; Z = Ts) have been isolated [1] from the reaction between 9-methyltetrahydrocarbazole and toluene-*p*-sulphonyl azide (tosyl azide) and we suggested that all were derived from the zwitterion (VI) as shown. Further work on the reactions of azides with tetrahydrocarbazoles and some properties of the products are now reported.

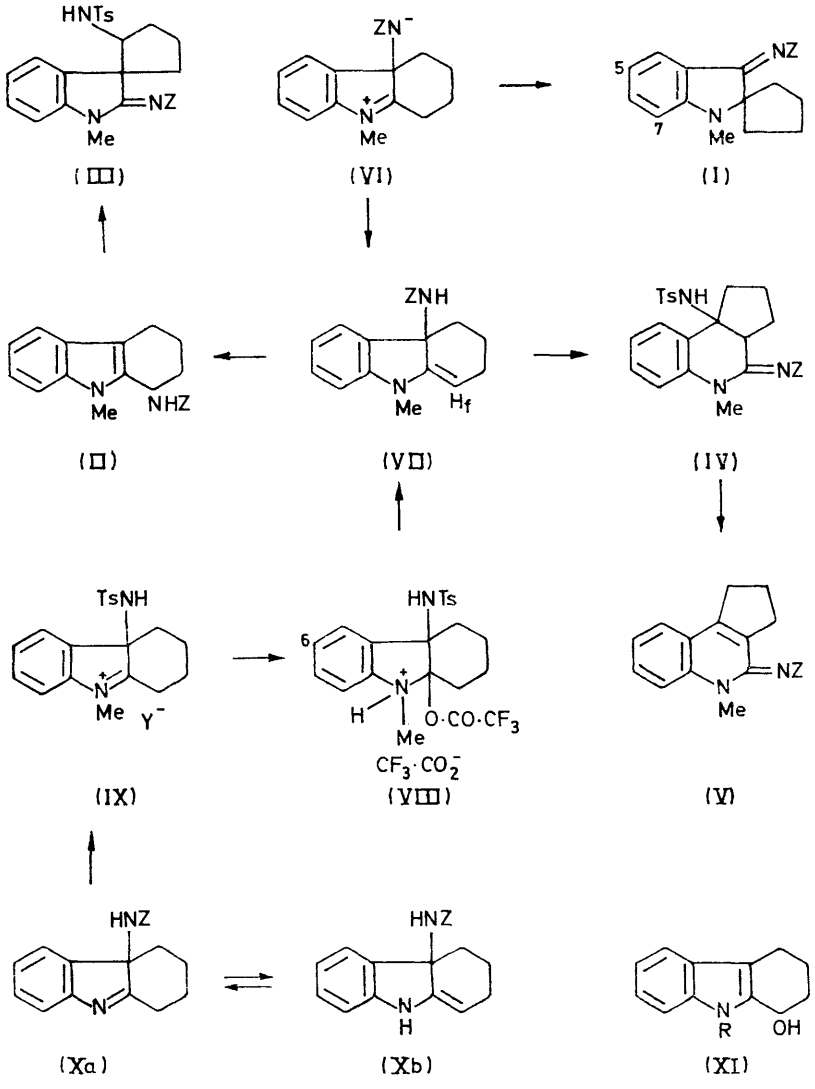
Dissolving the orange-coloured compound (I; Z = Ts) in trifluoroacetic acid (TFA) afforded a colourless water-soluble salt to which we assigned structure (VIII) [1] and which yielded 9-methyl-1-tosylaminotetrahydrocarbazole (II; Z = Ts) on treatment with base. This colourless salt was not derived from (II) since solutions of (II; Z = Ts) in TFA are bright purple and (II) cannot be recovered from these solutions. The action of acid on compound (II) has now been examined in more detail. From the solution of (II; Z = Ts) in TFA a very high yield of toluene-*p*-sulphonamide was isolated but the other component of the mixture was an amorphous polymeric material, m.p. over 300°. On boiling a solution of (II; Z = Ts) in acetic acid for 10 h under reflux, toluene-*p*-sulphonamide was again isolated and the other component was a mixture of 9-methylcarbazole and 9-methyl-1,2,3,4-tetrahydrocarbazole. The mass spectrum of the mixture contained peaks at *m/e* 181 and 185 but no peak at *m/e* 183. The intensities of the two *N*-methyl n.m.r. signals showed that the mixture contained 84% of 9-methylcarbazole (τ 6·32) and 16% of 9-methyltetrahydrocarbazole (τ 6·54). These results suggest that (II; Z = Ts) eliminates toluene-*p*-sulphonamide and the resulting dihydrocarbazole polymerises in the presence of TFA, disproportionates in acetic acid solution and is oxidised by air. Compound (II; Z = Ts) is best prepared in acetic acid solution [1] at room temperature; the mother liquors from this preparation were examined and found to contain toluene-*p*-sulphonamide and 9-methylcarbazole. Attempted dehydrogenation of (II; Z = Ts) with tetrachloro-*p*-benzoquinone gave 9-methylcarbazole. Bruck [2] has recently reported that Vilsmeier–Haack formylation of 9-methyltetrahydrocarbazole yielded a fully aromatic product. Finally, a sample of 1-hydroxy-9-methyl-1,2,3,4-tetrahydrocarbazole (XI; R = Me) [3] was dissolved in TFA yielding a bright purple solution; evaporation gave an amorphous solid, m.p. over 300°, presumably the same polymer that was obtained from (II; Z = Ts) and TFA.

In our previous [1] paper we suggested that the salt formed by dissolving compound (I) in TFA had structure (VIII) rather than the alternative structure (IX; Y = $CF_3{\cdot}CO_2$) plus one molecule of TFA in the crystal. We have now demonstrated that this transformation is general by dissolving 5-bromo-1-methyl-3-*p*-tolylsulphonyliminoindoline-2-spirocyclopentane [1] and 1,5-dimethyl-3-*p*-tolylsulphonyliminoindoline-2-spirocyclopentane [1] in TFA. The resulting salts were crystallised from ethyl acetate and dried for several hours at 60°; the analytical data showed that two molecules of TFA were contained in each compound, supporting structures of type (VIII). If the second molecule of TFA were present as in acid salt of type (IX) and not chemically combined it should have been lost during crystallisation and drying, since the b.p. of TFA (72°) is lower than that of ethyl acetate (77°). 4a,9-Dimethyl-1,2,3,4-tetrahydro-4a*H*-carbazolium iodide readily adds methanol [4] and it has recently been shown that trifluoroacetic acid adds to the C=C bond of indenone.[5]

A key intermediate in the proposed [1] reaction scheme is the indolenine (VII; Z = Ts); intermediates of this type have been suggested to explain the formation of compounds obtained by the reactions of indoles with azides and supported by the structures of the products formed by the reactions of tosyl azide with 1,3,3-trimethyl-2-methyleneindoline [1] and with 2-isopropylidene-1,3,3-trimethylindoline.[6] When sodium carbonate solution was added to an ice-cold solution of the salt (VIII) an unstable solid was obtained which was not (II; Z = Ts); however attempts to purify this material yielded (II; Z = Ts). The u.v. spectrum of the compound was very similar to those published [4,7,8] for indolenines in both $\lambda_{max.}$ value and general shape. The n.m.r. spectrum of the compound included signals at τ 7·22 (NMe), and 5·36br (t, C=CH), and some of the

[1] A. S. Bailey, R. Scattergood, and W. A. Warr, *J. Chem. Soc.* (*C*), 1971, 2479; I. J. Tickle and C. K. Prout, *ibid.*, p. 3401.
[2] P. Bruck, *Chem. Comm.*, 1970, 1690.
[3] L. J. Dolby and D. L. Booth, *J. Org. Chem.*, 1965, **30**, 1550.
[4] H. Fritz and E. Stock, *Annalen*, 1969, **721**, 82.
[5] P. H. Lacy and D. C. C. Smith, *J. Chem. Soc.* (*C*), 1971, 41.
[6] A. S. Bailey, R. Scattergood, and W. A. Warr, *J. Chem. Soc.* (*C*), 1971, 3769.
[7] F. Berlage and P. Karrer, *Helv. Chim. Acta*, 1957, **40**, 736.
[8] C. W. Rees and C. E. Smithen, *J. Chem. Soc.*, 1964, 945.

signals from the aromatic protons appeared in the region τ 3·4—3·8, typical of indolines. The spectrum was very similar to that of 4a,9-dimethyl-2,3,4,4a-tetrahydrocarbazole.[1] It contained a signal at τ 6·50 (NMe) due to the presence of *ca.* 15% of compound (*II*; Z = Ts). After the solution had been left for 1 h the signal at τ 7·2 had almost disappeared and the signal at τ 6·5 had greatly increased. After 24 h the spectrum was that of compound (II; Z = Ts). These observations indicate that the unstable compound is the intermediate (VII; Z = Ts) and that the transformation (VII) ⟶ (II) is rapid. A sample of compound (VII; Z = Ts) was prepared and immediately extracted into chloroform which contained tosyl azide. From this solution were isolated compounds (II; Z = Ts) and (V; Z = Ts). From a second reaction using *p*-chlorobenzenesulphonyl azide (CbsN$_3$) in the chloroform solution were isolated compounds (II; Z = Ts), (III; Z = Cbs), (IV; Z = Cbs), and (V; Z = Cbs). The isolation of compounds (II; Z = Ts), (IV; Z = Cbs), and (V; Z = Cbs) shows that the second molecule of azide involved in the reaction of an arenesulphonyl azide with 9-methyltetrahydrocarbazole becomes attached to the 2-position of the quinoline ring, and fully supports the proposed scheme.[1] The structure of compound (IV; Z = Cbs) was confirmed by its mass spectrum, which contained important peaks at *m/e* 543 (M^+, 2%), 372 (M — TsNH$_2$, 7%), 308 (372 — SO$_2$, 9%), 307 (12%), and 197 (372 — Cbs, 100%). There was no signal corresponding to (M — CbsNH$_2$).



The products obtained by treating indole, 1-methylindole, and 1,3-dimethylindole with tosyl azide[9,10] under neutral conditions are different from those obtained in the presence of base; it was therefore of interest to examine the reactions of tetrahydrocarbazoles with azides in basic solvents. From the reaction of

[9] A. S. Bailey, A. J. Buckley, and W. A. Warr, *J.C.S. Perkin I*, 1972, 1626.

[10] A. S. Bailey, A. J. Buckley, W. A. Warr, and J. J. Wedgwood, *J.C.S. Perkin I*, 1972, 2411.

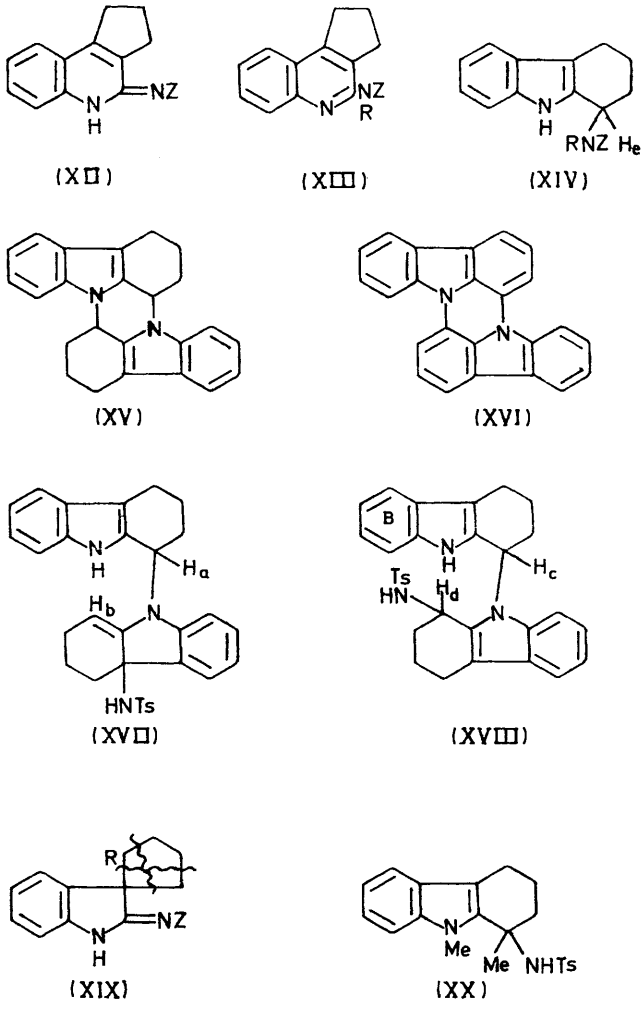
9-methyl-1,2,3,4-tetrahydrocarbazole and Cbs azide in pyridine solution, compound (V; Z = Cbs) was isolated in 80% yield. This contrasts with the 2% yield of (V; Z = Ts) obtained [1] under neutral conditions. The base probably catalyses the transformation (VI; Z = Cbs) ⟶ (VII; Z = Cbs) and reduces the yield of (I); it also catalyses the elimination step (IV) ⟶ (V). The fact that $CbsN_3$ is more reactive than TsN_3 will increase the rate of step (VII) ⟶ (IV) relative to the rate of the migration (VII) ⟶ (II). In the experiments described earlier in this paper the yield of compound (II; Z = Ts) was smaller when (VII; Z = Ts) was treated with $CbsN_3$ than when it was treated with TsN_3 (see Experimental section). The structure of compound (V; Z = Cbs) was fully supported by spectroscopic data. The u.v. spectrum was almost identical with that published [1] for (V; Z = Ts) and the molecular ion peak *m/e* 372 (2%) was smaller than the (*M* − SO_2 − H) peak [307 (12%)], the base peak being *m/e* 197 (*M* − Cbs). In the light of this result the reaction of tetrahydrocarbazole with tosyl azide in pyridine was examined. From this reaction compound (X; Z = Ts) [1] was isolated (30% yield), along with an 8% yield of (XII; Z = Ts). When this reaction was repeated using $CbsN_3$ rather than TsN_3 the yield of (XII; Z = Cbs) was 75%, showing again the value of $CbsN_3$ in this type of reaction. In contrast, tetrahydrocarbazole reacts with $CbsN_3$ under neutral conditions yielding (X; Z = Cbs) in 70% yield. These results suggest that compound (Xa) exists in equilibrium with (Xb), although (Xb) cannot be detected spectroscopically in (X). A sample of compound (X; Z = Ts) was treated with $CbsN_3$ under basic conditions, affording (XII; Z = Cbs) in agreement with this hypothesis.

The u.v. spectra of compounds (XII; Z = Ts) and (XII; Z = Cbs) in ethanol were very similar to those of (V; Z = Ts) and (V; Z = Cbs), supporting structure (XII) rather than the tautomeric structure (XIII; R = H).[11] A sample of compound (XII; Z = Ts) was shaken with dimethyl sulphate, aqueous potassium hydroxide, and acetone (a two-phase system since the compound was insoluble in aqueous alkali) in an attempt to prepare (V; Z = Ts).[1] Although this product (m.p. 213°) [1] could be detected by t.l.c. there was insufficient for isolation, the major product being the isomeric compound (XIII; R = Me, Z = Ts) (m.p. 153°). This structure is supported by the n.m.r. spectrum [τ 6·83 (NMe); *cf.* 6·15 (NMe) [1] for structure (V; Z = Ts)]; the u.v. spectrum was different from that of (V).[1] This result is in striking contrast to the methylation of 2-*p*-tolylsulphonylaminoquinoline [1] in aqueous alkali to form the 1-methyl derivative. The influence of various solvent systems and reagents on the proportions of the products formed by alkylating 2-arylsulphonylaminopyridines has been reported.[12]

[11] Yu. N. Sheinker, E. M. Peresleni, N. P. Zosimova, and Yu. I. Pomerantsev, *Russ. J. Phys. Chem.*, 1959, **33**, 306.

[12] E. Klingsberg 'The Chemistry of Heterocyclic Compounds. Pyridine and Derivatives,' Interscience, New York, 1962, Part 3, p. 26.

It was observed that when a sample of compound (X; Z = Ts) was recrystallised from boiling n-propanol the hot solution became pale green and highly fluorescent, properties characteristic of structure (I).[1] A solution of compound (X; Z = Ts) in propanol was boiled for 24 h in an attempt to isolate (I; NH replacing



NMe). The amount of fluorescent material formed was less than 1 mg (prep. t.l.c.) but all the starting material had disappeared and three other compounds were isolated. One was the rearrangement product (XIV; R = H, Z = Ts), clearly distinguished from structures of type (I) by lack of colour and fluorescence and from the isomer (XIX; R = H, Z = Ts) by n.m.r. and i.r. spectra which show the presence of two NH groups; the mass spectral cracking pattern of structures of type (XIX) is different from those of type (XIV) (see later). The second product to be identified was the dihydrocarbazole dimer (XV); [13,14] the compound was characterised as the fully aromatic pyrazinodicarbazole (XVI),

[13] S. G. P. Plant and M. L. Tomlinson, *J. Chem. Soc.*, 1950, 2127; A. E. J. Herbert and M. L. Tomlinson, *ibid.*, 1958, 4492.

[14] B. Witkop and J. B. Patrick, *J. Amer. Chem. Soc.*, 1950, **72**, 633; 1951, **73**, 2188.

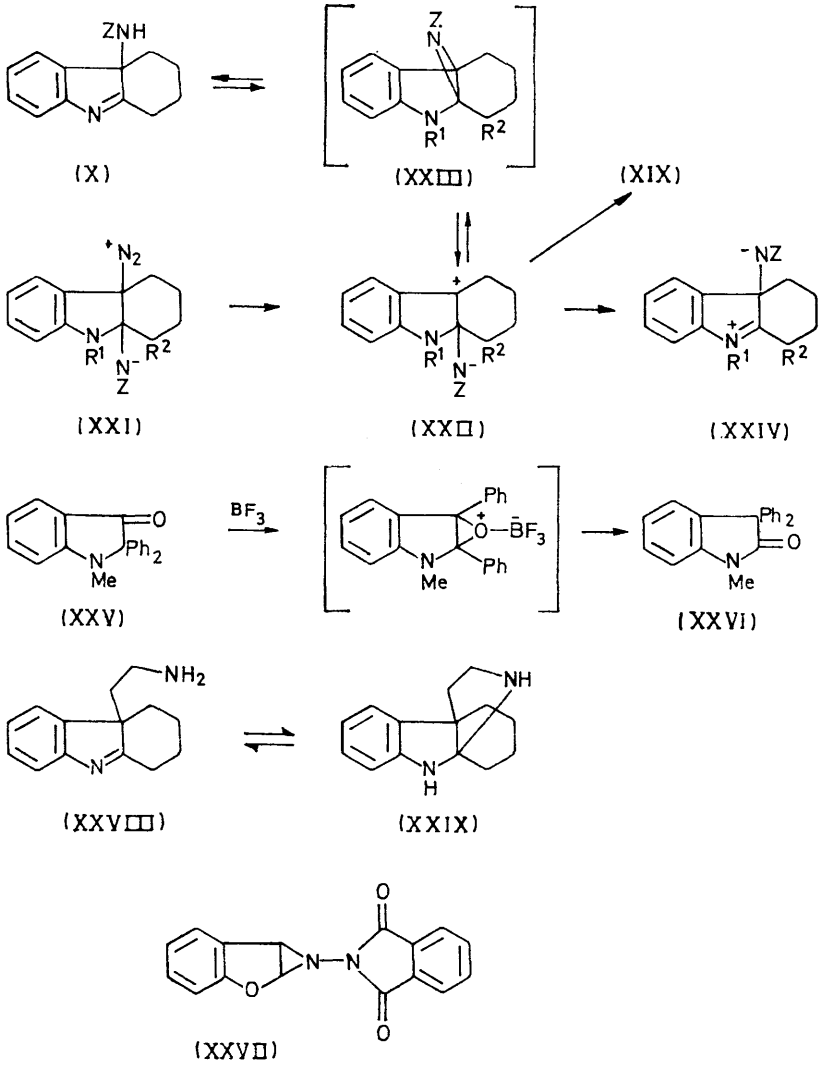
identical with a sample kindly provided by Dr. M. L. Tomlinson; the dimer (XV) is readily formed from (XI; R = H) by loss of water, and the samples isolated in our reaction may arise *via* the rearrangement product (XIV; R = H, Z = Ts). The third product was an insoluble material (A), the analytical and mass spectroscopic data supporting the molecular formula $C_{31}H_{31}N_3O_2S$ [(XV) + 1 molecule of toluene-*p*-sulphonamide]. This product readily decomposed in solution giving (XV) and toluene-*p*-sulphonamide, and two structures, (XVII) and (XVIII), appear reasonable. If the former (XVII) is correct it must be formed by one molecule of (XIV; R = H, Z = Ts) eliminating toluene-*p*-sulphonamide and the resulting dihydrocarbazole being attacked by a molecule of (Xb; Z = Ts). We have observed that a pure sample of (XIV; R = H, Z = Ts) when kept in acetic acid solution for a week at room temperature yields toluene-*p*-sulphonamide, compounds (XV) and (XVI), and compound (A). If (XVII) is the correct structure for (A) this implies that a compound of type (XIV) must revert to the 4a-substituted structure (X), which seems unlikely. This seems to support structure (XVIII) for (A). The u.v. spectrum of (A) contained a weak band at 340 nm, at longer wavelength than one might expect for the two isolated indole chromophores in (XVIII) (the molecule will be non-planar). In the n.m.r. spectrum of (A) a broad signal (2H) appeared at τ 5·42; this must be either due to $H_a + H_b$ in (XVII) or $H_c + H_d$ in (XVIII). The signal for H_e in compound (XIV; R = H, Z = Ts) appears at τ 5·49 and that for H_f in compound (VII) at τ 5·36; these values are too close together to allow a clear distinction between (XVII) and (XVIII). In the aromatic region of the n.m.r. spectrum the signals covered the range τ 2·3—3·7, at higher field than might be expected for the aromatic protons of an indole such as (XVIII), and are similar to those observed for the aromatic protons in the n.m.r. spectrum of (VII); this observation could be taken to support structure (XVII). However in the non-planar structure (XVIII) the benzene ring in the tosyl group will be close to ring B of (XVIII) and cause an upfield shift of the aromatic proton signals. Such upfield shifts have been reported [15] for arylsulphonylaminoindole derivatives. This type of interaction would also account for the weak band in the u.v. spectrum. We therefore prefer to assign structure (XVIII) to compound (A). The mass spectrum of the compound contained a small molecular ion peak at *m/e* 509 (3%) and a signal at *m/e* 338 ($M - TsNH_2$, 18%). This ion has the same constitution as (XV) but cannot have the same structure since the main peaks are *m/e* 170 (100%) and 168 (33%), formed by cleavage of the bond joining the two tetrahydrocarbazole units. In contrast the mass spectrum of (XV) contains peaks at *m/e* 338 (M^+, 16%), 157 (100%), and 110 (66%). When compound (X; Z = Cbs) was boiled in propanol the proportion of ' dimer ' found was smaller but it proved impossible to separate the main product (XIV; R = H, Z = Cbs) from the mixture. The crude product was therefore methylated, yielding (XIV; R = Me, Z = Cbs); the position of the NMe signal (τ 7·33) in the n.m.r. spectrum showed that methylation had occurred on the NCbs group [16] and not at the indolic nitrogen atom. For comparison a sample of (II; Z = Ts) was also methylated. Since a pure sample of compound (XIV; R = H, Z = Ts) had yielded compounds (XV), (XVI), and (XVIII) when dissolved in acetic acid, we examined the reaction between tetrahydrocarbazole and Cbs azide in acetic acid at room temperature. After 3 weeks compound (XV) had separated from the solution in 50% yield; this represents a simple route to this compound from tetrahydrocarbazole.

When a sample of compound (X; Z = Cbs) was heated at 210° for 1 min an isomeric compound was obtained to which we ascribe structure (XIX; R = H, Z = Cbs). There is no similar simple structure known in the 9-methyl series, but compound (III) is a more elaborate example. The absence of colour and fluorescence eliminated structures of type (I), although in the n.m.r. spectrum of the new compound the shape of the envelope containing the methylene proton signals was very similar to that of the aliphatic protons in the spectrum of (I); the i.r. spectrum of the compound contained bands at 3285 (NH) and 1590 cm^{-1} (C=N), eliminating structure (XIV; R = H, Z = Cbs). The most valuable spectral evidence came from the mass spectrum. In the mass spectra of molecules of types (II) and (XIV) no strong peaks appear above *m/e* 200, apart from the molecular ion; this contrasts with the mass spectra of structures of type (III) in which fragmentation of the spiro ring occurs [see detail of spectrum of (III) [1]]. The mass spectrum of (XIX; R = H, Z = Cbs) contained signals at *m/e* 360 (M^+, 45%), 319 ($M - C_3H_5$, 100%), 185 (M — Cbs, 67%), 168 ($M - CbsNH_2$ — H, 32%), and 144 (319 — Cbs, 55%). In the mass spectrum of (X; Z= Cbs) a peak appears at *m/e* 319 ($M - 41$, 36%) of greater intensity than the molecular ion [*m/e* 360 (24%)], suggesting that some isomerisation may be occurring in the spectrometer inlet. In contrast, in the mass spectrum of (X; Z = Ts) the molecular ion [*m/e* 340 (34%)] is far more intense than the peak at $M - 41$ [*m/e* 299 (2%)]. In striking contrast to the behaviour of (X; Z = Cbs) on melting, a sample of (X; Z = Ts) darkened and rapidly decomposed at the m.p. yielding a tar from which nothing crystalline could be isolated.

The effect on the reaction of substitution at the 1-position of tetrahydrocarbazole has been examined; from the reaction of 1-methyltetrahydrocarbazole with Ts azide and Cbs azide, compounds (XIX; R = Me, Z = Ts) and (XIX; R = Me, Z = Cbs) have been isolated. The u.v. spectra showed that the compounds were not of type (X) and n.m.r. and mass spectra showed that they were not of type (XIV); the mass spectrum of (XIX; R = Me, Z = Ts) included peaks at *m/e* 354

[15] A. S. Bailey, A. G. Holton, and J. F. Seager, *J.C.S. Perkin I*, 1972, 1003.
[16] R. M. Moriarty, *J. Org. Chem.*, 1965, **30**, 600.

(M^+, 30%), 313 ($M - C_3H_5$, 50%), 299 ($M - C_4H_7$, 100%), and 199 (M — Ts, 22%). In contrast, 1,9-dimethyltetrahydrocarbazole reacted with tosyl azide affording the 1-substituted compound (XX). In the mass spectrum of (XX) the base peak appeared at *m/e* 197 ($M - TsNH_2$), showing clearly the difference in cracking pattern between the two structures (XIX; R = Me) and (XX).



These results show that the nature of products obtained by the reactions of arenesulphonyl azides with tetrahydrocarbazoles is markedly affected by substituents at positions 1 and 9. When in the intermediate (XXI) R^1 and R^2 are both H, the fastest step at room temperature is the formation of (X) *via* (XXII) and (XXIII) rather than the formation of the spiro-compound (XIX; R = H) by C–C migration. The formation of compound (XIX; R = H, Z = Cbs) on melting (X; Z = Cbs) shows that the step (X) ⟶ (XXII) is reversible, and this transformation is similar in many ways to the conversion (XXV) ⟶ (XXVI).[17,18] Although no example of an azirine structure such as (XXIII) is known, a derivative of benzofuroazirine (XXVII) [19] has recently been isolated and the equilibrium (XXVIII) ⇌ (XXIX) has been studied.[20] When in the intermediate (XXI) R^2 is Me and R^1 is H C–C migration forming spiro-compounds (XIX; R = Me) becomes important at room temperature. This parallels the order of migratory aptitudes in the pinacol transformation [21] and in the rearrangements of glyceric esters.[22] When R^1 and R^2 are both Me the zwitterion (XXIV) is favoured; the structure (XXIV) is similar to the protonated form of an indole and it is known (ref. 8, p. 5) that 1-methylindole is a stronger base than indole.

We have examined the kinetics of the acid-catalysed

[17] B. Witkop and A. Ek, *J. Amer. Chem. Soc.*, 1951, **73**, 5664.
[18] R. J. Sundberg, 'The Chemistry of Indoles,' Academic Press, New York, 1970, pp. 316—331.
[19] D. W. Jones, *J.C.S. Perkin I*, 1972, 225.
[20] H. Fritz and O. Fischer, *Tetrahedron*, 1964, **20**, 1737, 2047.
[21] C. J. Collins, *Quart. Rev.*, 1960, **14**, 359.
[22] J. Kagan, D. A. Agdeppa, and S. P. Singh, *Helv. Chim. Acta*, 1972, **55**, 2253.

transformation (I; Z = Ts) ⟶ (VIII). Since the use of neat TFA proved difficult the rates of the reaction of the spiro-compound with acid were determined by following the disappearance of the band at *ca.* 470 nm in the u.v. spectrum, with trifluoroacetic acid as the catalyst and carbon tetrachloride as the solvent. The solvent was purified by passing through an alumina column and solutions containing 4—10 mg of the compound under investigation in *ca.* 40 ml of the solvent

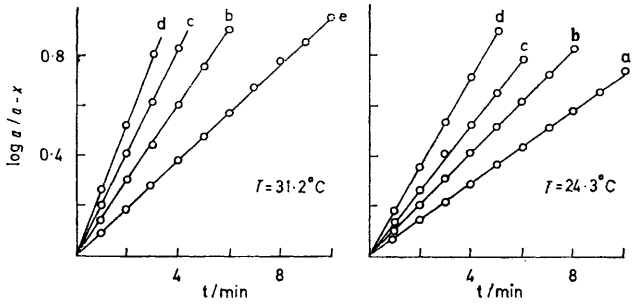


FIGURE 1 Reaction of compound (I; Z = Ts) in CCl_4 + TFA; acid concns. (mol l^{-1}): (a) 0·0845, (b) 0·106, (c) 0·132, (d) 0·158, (e) 0·0792

were made up. A known weight of TFA was then added, followed by solvent to give a total volume of 50 ml, and the change of intensity of the band at 470 nm was followed using a Unicam SP 800 spectrometer fitted with 1 cm cells. The temperature was maintained constant within ±0·1 °C. An excess of TFA was used, giving pseudo-first-order kinetics, and good straight line plots were obtained (see Figure 1).

Since TFA is highly associated in non-polar solvents,[23] it is impossible to calculate a true rate. Therefore we

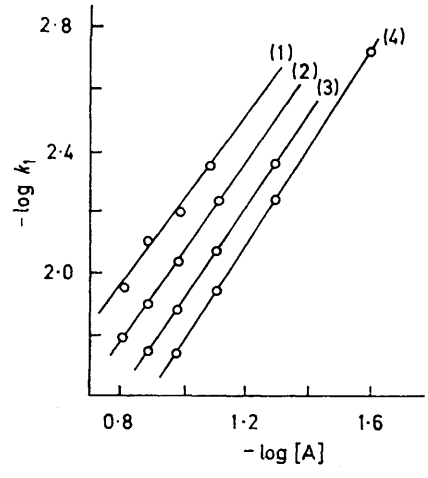


FIGURE 2 Plot of $-k_1$ against $-\log[A]$ for reaction of compound (I; Z = Ts) with TFA in CCl_4; temperatures (°C): (1) 24·3, (2) 31·2, (3) 38·5, (4) 45·6

assumed an ' apparent ' order in TFA such that $dx/dt = k[C][A]^n$, where [C] is the concentration of spiro-compound and [A] that of TFA, k is the true rate constant, and n is the apparent order in TFA. The corresponding equation for pseudo-first-order conditions is then $dx/dt = k_1[C]$, where k_1 is the pseudo-first-order constant. Combining the foregoing equations we have $k_1 = k[A]^n$ and hence

$$-\log k_1 = -\log k + n(-\log[A]) \qquad \text{(i)}$$

By plotting $-\log k_1$ against $-\log[A]$ the true rate constant may be found (when [A] = 1), and the value of n at any given temperature. Four experiments were carried out at each of four temperatures using different amounts of TFA, and four values of k_1 were determined at each temperature. Equation (i) was then applied to these results (see Figure 2), giving k and four values of n (Table 1) (n would be expected to vary with temperature).

The kinetic measurements were repeated with four substituted spiro-compounds (for preparations see ref. 1) at the four temperatures for which values of n had been obtained (Table 2), and the values of k were calculated (Table 3). When the values of log k were plotted against $1/T$ good straight-line plots were obtained from which values of E, $\Delta H^{\ddagger}$, and $\Delta S^{\ddagger}$ were deduced (Table 4).

TABLE 1

Rate constants for the acid-catalysed transformation of compound (I; Z = Ts)

T/°C	24·3	31·2	38·5	45·6
n	1·375	1·487	1·542	1·635
10^3k/s^{-1}	84·8	161	258	452

TABLE 2

Pseudo-first-order rate constants for the acid-catalysed transformations of derivatives of compound (I; Z = Ts)

T/°C		24·3	31·2	38·5	45·6
10^3k_1/s^{-1}	5-Me	2·87 [a]	4·02 [a]	5·69 [a]	7·83 [a]
	5-Br	1·36 [b]	1·78 [b]	2·52 [b]	3·51 [b]
	5-SCN	3·40 [c]	2·57 [d]	4·18 [d]	6·29 [d]
	5-NO_2	0·79 [c]	1·18 [c]	2·07 [c]	3·09 [c]

Concn. of TFA mol l^{-1}: [a] 0·0528, [b] 0·0792, [c] 0·792, [d] 0·528.

TABLE 3

Rate constants calculated from data in Table 2

T/°C		24·3	31·2	38·5	45·6
10^3k/s^{-1}	5-Me	164	318	529	958
	5-Br	44	77	126	221
	5-SCN	4·6	6·7	11·2	17·8
	5-NO_2	1·1	1·7	3·0	4·6

TABLE 4

Thermodynamic parameters

5-Substituent	E/kJ mol^{-1}	$\Delta H^{\ddagger}$/ kJ mol^{-1}	$\Delta S^{\ddagger}$/ J deg^{-1} mol^{-1}
H	60·6	58·1	−69·4
Me	64·4	61·9	−52·3
Br	58·5	56·0	−82·3
SCN	55·2	52·7	−113
NO_2	53·5	51·0	−130

The results show that electron-withdrawing groups decrease the rate of reaction; the main cause of the

[23] G. C. Hood, O. Redlich, and C. A. Reilly, *J. Chem. Phys.*, 1955, **23**, 2229; F. Thyrion and D. Decroocq, *Compt. rend.*, 1965, **260**, 2797.

decrease appears to be changes in $\Delta S^{\ddagger}$. A plot of $\log k/k_0$ against σ (Figure 3) gave a good line through four points if a value of 1·24 was used for the NO_2 group.[24] The point for SCN is off this line but the value of σ used (0·52) is that obtained from the ionisation constant of

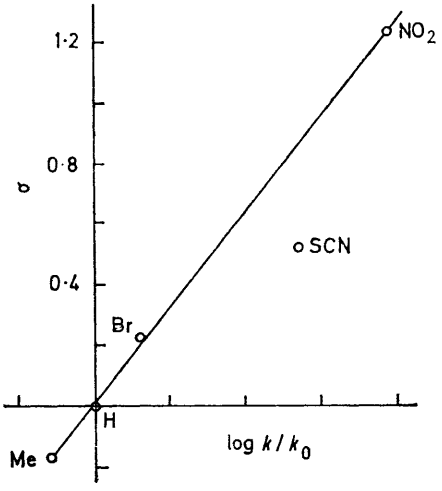


FIGURE 3 Plot of $\log k/k_0$ against σ

benzoic acid,[24,25] and it has been suggested [26] that there is mesomeric interaction between the SCN group and *p*-hydroxy- or *p*-amino-groups.

EXPERIMENTAL

General directions and instruments used have been reported.[1,6] U.v. spectra were determined for solutions in ethanol and n.m.r. spectra for solutions in [^{2}H]chloroform unless stated otherwise. I.r. spectra were measured either for Nujol mulls (N) or for solutions in chloroform (C).

Action of Acid on 9-*Methyl*-1-p-*tolylsulphonylamino*-1,2,3,4-*tetrahydrocarbazole* (II; Z = Ts).—(*a*) The tetrahydrocarbazole (200 mg) was dissolved in TFA (2 ml) and after 5 min the acid was removed *in vacuo*; the residue was recrystallised from benzene yielding toluene-*p*-sulphonamide, m.p. 137—138° (identified by i.r. and t.l.c.) (85 mg, 88%) (Found: C, 48·9; H, 5·1; N, 8·2. Calc. for $C_7H_9NO_2S$: C, 49·1; H, 5·3; N, 8·2%). T.l.c. of the benzene mother liquors (alumina; benzene–ethyl acetate, 9 : 1) showed two components, R_F 0·14 (toluene-*p*-sulphonamide) and 0·78. Column chromatography [silica; benzene–petroleum (b.p. 60—80°)] gave an off-white solid (90 mg) decomposing above 300° without melting.

(*b*) A solution of the tetrahydrocarbazole (500 mg) in acetic acid (4 ml) was heated (100°) under reflux for 10 h. The acid was removed *in vacuo* and the residue recrystallised from benzene yielding toluene-*p*-sulphonamide (identified by m.p. and i.r.) (206 mg). The mother liquors were chromatographed (silica; benzene–petroleum, 1 : 9). The first fractions were recrystallised from ethanol yielding a mixture of 9-methylcarbazole and 9-methyltetrahydrocarbazole. Spectroscopic data for this mixture are reported in the Discussion section.

(*c*) The acetic acid mother liquors from several preparations [1] of compound (II; Z = Ts) were combined and evaporated, and the tarry residue was taken up in hot benzene. On cooling, toluene-*p*-sulphonamide separated; chromatography of the benzene mother liquors yielded 9-methylcarbazole, m.p. 85—86°.

1-Hydroxy-9-methyltetrahydrocarbazole (XI; R = Me) [3] was dissolved in TFA and the acid was then evaporated off *in vacuo*. The resulting non-crystalline material decomposed above 300° without melting.

Compound (II; Z = Ts) (500 mg) and tetrachloro-*p*-benzoquinone (750 mg) were boiled together in benzene for 5 h. The mixture was cooled and the solid collected. From the solid, toluene-*p*-sulphonamide was separated chromatographically, and from the benzene mother liquor 9-methylcarbazole (identified by m.p., i.r., and n.m.r.) was isolated (silica; benzene).

1,2,3,4,4a,9a-*Hexahydro*-6,9-*dimethyl*-4a-p-*tolylsulphonylamino*-9a-*trifluoroacetoxycarbazolium Trifluoroacetate* (VIII; 6-Me).— 1,5-Dimethyl-3-*p*-tolylsulphonyliminoindoline-2-spirocyclopentane [1] (200 mg) was dissolved in the minimum of TFA. When the red colour of the solution had disappeared the acid was evaporated off and the residue recrystallised from ethyl acetate to give *crystals*, m.p. 124—126° (220 mg) (Found after drying at 60°: C, 50·6; H, 4·6; N, 4·8; S, 5·5. $C_{25}H_{26}F_6N_2O_6S$ requires C, 50·3; H, 4·4; N, 4·7; S, 5·4%); $\nu_{max.}$ (N) 1646, 1770, and 3210 cm^{-1}; τ (TFA) 2·3—2·6 (2H, m, Ar), 2·82 (4H, s, Ar), 3·31 (1H, s, Ar), 5·84 (3H, s, NMe), 6·5br (2H), 6·9—7·5 (2H, m), 7·56 (3H, s, tosyl Me), 7·85 [3H, s, C(6)Me], and 7·6—8·5 (4H, m). Similarly, 5-bromo-1-methyl-3-*p*-tolylsulphonyliminoindoline-2-spirocyclopentane (200 mg) [1] yielded 6-*bromo*-1,2,3,4,4a,9a-*hexahydro*-9-*methyl*-4a-p-*tolylsulphonylamino*-9a-*trifluoroacetoxycarbazolium trifluoroacetate* (VIII; 6-Br), m.p. 109—112° (from ethyl acetate) (198 mg) (Found for sample dried at 60°: C, 43·7; H, 3·5; N, 4·4; S, 4·5. $C_{24}H_{23}BrF_6N_2O_6S$ requires C, 43·6; H, 3·5; N, 4·2; S, 4·8%); $\nu_{max.}$ (N) 1650, 1775, and 3220 cm^{-1}; τ (TFA) 2·1—2·5 (2H, m, Ar), 2·8 (4H, s, Ar), 3·04 (1H, s, Ar), 5·82 (3H, s, NMe), 6·48br (2H), 6·9—7·4 (2H, m), 7·50 (3H, s, tosyl Me), and 7·6—8·4 (4H, m).

2,3,4,4a-*Tetrahydro*-9-*methyl*-4a-p-*tolylsulphonylamino*-*carbazole* (VII; Z = Ts).—The first preparations of this compound used samples of (VIII) made by dissolving (I; Z = Ts) in TFA, since the methiodide (IX; Y = I),[1] which is readily obtained by methylation of (X; Z = Ts), is insoluble in water. However, boiling the methiodide under reflux in TFA yielded the water-soluble trifluoroacetate and this is the most convenient route. 2,3,4,4a-Tetrahydro-4a-*p*-tolylsulphonylamino-1*H*-carbazole (X; Z = Ts) (5 g) [1] and methyl iodide (21 g) were heated for 5 h under reflux in benzene (75 ml) and methyl cyanide (75 ml). Next day the solid was collected (5·25 g). This salt (2 g) was boiled under reflux for 3 h in TFA (20 ml). The solvent was removed, the residue was triturated with methanol, the methanol was removed *in vacuo*, and the residue was recrystallised from ethyl acetate (yield 1·9 g); the product was identical (m.p., i.r. spectrum) with the sample obtained [1] by dissolving (I; Z = Ts) in TFA. This salt (500 mg) was dissolved in water (40 ml), the solution was cooled to 0°, and sodium carbonate solution (0·1M; 9 ml) was added dropwise. The white precipitate was collected and dried at room temperature (295 mg); $\nu_{max.}$ (N) 3305 cm^{-1}; $\lambda_{max.}$ (Et_2O) 271 (log ε 4·02) and 308sh nm (3·26);

[24] J. Clark and D. D. Perrin, *Quart. Rev.*, 1964, **18**, 302.
[25] D. H. McDaniel and H. C. Brown, *J. Org. Chem.*, 1958, **23**, 420.
[26] F. G. Bordwell and P. J. Boutan, *J. Amer. Chem. Soc.*, 1956, **78**, 856; T. W. Campbell and M. T. Rogers, *ibid.*, 1948, **70**, 1029.

Rees [8] reports $\lambda_{max.}$ 278 (log ε 4·15) and 310sh nm (3·36) for 4a-dichloromethyl-2,3,4,4a-tetrahydro-9-methylcarbazole. The compound (100 mg) was recrystallised from boiling ethanol yielding 70 mg of material, identified by m.p. and i.r. spectrum as compound (II; Z = Ts).

A solution of compound (VIII) (2 g) in water (80 ml) was added to a solution of tosyl azide (0·72 g) in chloroform (40 ml); the mixture was cooled in an ice–salt bath and stirred vigorously while aqueous sodium carbonate (0·36 g in 20 ml) was added dropwise. The mixture was stirred for 10 min. The organic phase was then separated, the aqueous phase was extracted with chloroform (2 × 100 ml), and the combined extracts were dried ($MgSO_4$) and filtered. After 18 h the solvent was removed and the residue triturated with methanol yielding compound (II; Z = Ts) (t.l.c., m.p., i.r.) (225 mg). The mother liquors were evaporated and the residue was chromatographed on silica (benzene–ethyl acetate) giving, in order of elution, tosyl azide (510 mg), compound (II; Z = Ts) (190 mg), and an oil which would not crystallise. This oil was taken up in TFA (10 ml). After 3 days the solution was poured into water, the acid was neutralised (Na_2CO_3), and the mixture was extracted with chloroform. The dried ($MgSO_4$) extract was evaporated and the residue was filtered through silica gel in benzene–ethyl acetate (9 : 1). The solvent was removed and the residue recrystallised from methyl cyanide giving fine needles of compound (V; Z = Ts) (t.l.c., m.p., i.r.) (60 mg). In a separate series of experiments (Seager, unpublished work) it was shown that compound (IV; Z = Ts) is smoothly converted into (V; Z = Ts) by TFA.

The foregoing experiment was repeated with *p*-chlorobenzenesulphonyl azide (0·8 g) instead of tosyl azide. The chloroform extract was evaporated after 20 h and the residue was triturated with methanol. The insoluble material was separated into two compounds by preparative t.l.c. (silica; benzene–ethyl acetate, 9 : 1). The faster running component (30 mg) was compound (III; Z = Cbs) [1] (t.l.c., i.r.) and the slow moving fraction was (IV; Z = Cbs), m.p. 222—225° (50 mg). The methanolic liquors from the trituration were evaporated and the residue was chromatographed on silica (benzene–ethyl acetate mixtures), yielding, in order of elution, $CbsN_3$ (460 mg), (II; Z = Ts) (140 mg), (V; Z = Cbs) (250 mg) [identical with an authentic specimen (see later)], and (IV; Z = Cbs) (200 mg), (identical by t.l.c. with the sample obtained earlier).

4-p-*Chlorophenylsulphonylimino*-2,3,3a,4,5,9b-*hexahydro*-5-*methyl*-9b-p-*tolylsulphonylamino*-1H-*cyclopenta*[c]*quinoline* (IV; Z = Cbs) formed prisms, m.p. 220—224° (decomp.) (from methyl cyanide) (Found: C, 57·2; H, 4·8; N, 7·5; S, 12·1. $C_{26}H_{26}ClN_3O_4S_2$ requires C, 57·5; H, 4·8; N, 7·7; S, 11·8%); $\nu_{max.}$ (N) 1542 (C=N) and 3245 cm^{-1} (NH); $\lambda_{max.}$ 224 and 283 nm (ε 36,500 and 24,800), τ [$(CD_3)_2SO$] 7·4—9·10 (6H, m), 7·74 (3H, s, tosyl Me), 6·64 (3H, s, NMe), 5·77 (1H, m), 2·8—3·3 (8H, m, Ar), 2·79 (1H, NH, exchanged D_2O), 2·34 (2H, d, *J* 8 Hz, low-field half of tosyl signal), and 2·02 (2H, d, *J* 8 Hz, low-field half of Cbs signal).

4-(p-*Chlorophenylsulphonylimino*)-2,3,4,5-*tetrahydro*-5-*methyl*-1H-*cyclopenta*[c]*quinoline* (V; Z = Cbs).—9-Methyltetrahydrocarbazole (1·85 g) and Cbs azide (4·3 g) were mixed with pyridine (1 ml). A white crystalline solid separated. After 4 days ethanol (10 ml) was added and the solid collected (3·5 g). Recrystallisation from methyl cyanide gave white *needles* (3·0 g), m.p. 218—220° (Found: C, 61·4; H, 4·7; Cl, 9·4; N, 7·6; S, 8·6. $C_{19}H_{17}ClN_2O_2S$ requires C, 61·2; H, 4·6; Cl, 9·5; N, 7·5; S, 8·6%); $\nu_{max.}$ (N) 1535, 1610, and 1628w cm^{-1}; $\lambda_{max.}$ 216, 263, 293, 304, 342sh, 351, and 362 nm (ε 35,700, 26,900, 5620, 5760, 12,700, 15,100, and 11,300); τ 7·75 (2H, quint, *J* 8 Hz), 6·76 (2H, t, *J* 8 Hz), 6·32 (2H, t, *J* 8 Hz), 6·17 (3H, s, NMe), 2·2—2·8 (6H, m, Ar), and 1·97 (2H, d, *J* 8 Hz, low-field half of Cbs signal) [see published [1] values for (V; Z = Ts)].

2,3,4,5-*Tetrahydro*-4-(p-*tolylsulphonylimino*)-1H-*cyclopenta*[c]*quinoline* (XII; Z = Ts).—A solution of tetrahydrocarbazole (8·6 g) and tosyl azide (18·5 g) in pyridine (20 ml) was heated at 60°. After 5 days the mixture was cooled and the solid collected. Recrystallisation from n-propanol afforded (X; Z = Ts) [1] (5·0 g), m.p. 204—206° (Found: C, 66·9; H, 6·0; N, 8·2; S, 9·5. Calc. for $C_{19}H_{20}N_2O_2S$: C, 67·1; H, 5·9; N, 8·2; S, 9·4%). The pyridine mother liquors were concentrated to half volume and an equal volume of methanol was added. Next day the solid was collected, washed with methanol, and recrystallised from methyl cyanide, yielding the *quinoline* (XII; Z = Ts) as fine white needles, m.p. 223—224° (1·4 g) (Found: C, 67·2; H, 5·3; N, 8·3; S, 9·5. $C_{19}H_{18}N_2O_2S$ requires C, 67·5; H, 5·3; N, 8·3; S, 9·5%); $\nu_{max.}$ (N) 1542, 1590, 1628, and 3230 cm^{-1}; $\lambda_{max.}$ 213, 222sh, 262, 330sh, 341, and 350 nm (ε 40,200, 28,500, 23,100, 13,300, 18,400, and 13,000); τ 7·81 (2H, quint, *J* 8 Hz), 7·5 (3H, s, tosyl Me), 7·05 (2H, t, *J* 8 Hz), 6·82 (2H, t, *J* 8 Hz), 2·3—2·9 (6H, m, Ar), 2·09 (2H, d, *J* 8 Hz, low-field half of tosyl signal), and −1·60 (1H, NH, exchanged D_2O); *m/e* 338 (M^+, 7%), 183 (M − Ts, 100%), and 91 (C_7H_7, 35%).

4-(p-*Chlorophenylsulphonylimino*)-2,3,4,5-*tetrahydro*-1H-*cyclopenta*[c]*quinoline* (XII; Z = Cbs).—(*a*) Tetrahydrocarbazole (5·7 g) and Cbs azide (15·0 g) were dissolved in pyridine (30 ml) and after 6 h the solution was heated (55°) for 5 days. The solid which had separated was collected, washed with methanol, and recrystallised from acetic acid giving compound (XII; Z = Cbs) (9·1 g), m.p. 212—214°, identical (m.p., i.r., t.l.c.) with the compound described later.

(*b*) Compound (X; Z = Ts) (3·4 g) and Cbs azide (2·2 g) were dissolved in pyridine (20 ml) and 10M-sodium hydroxide (5 ml) was added. The mixture was heated (50°) for 5 days then cooled, and methanol (10 ml) was added. After 1 h the solid (1·1 g) was collected. Recrystallisation gave white *needles* (0·85 g), m.p. 212—214°, identical with the compound prepared in (*a*) (Found: C, 60·2; H, 4·2; Cl, 9·9; N, 7·7; S, 9·0. $C_{18}H_{15}ClN_2O_2S$ requires C, 60·2; H, 4·2; Cl, 9·9; N, 7·8; S, 8·9%); $\nu_{max.}$ (N) 1542w, 1594, 1630, and 3270w cm^{-1}; $\lambda_{max.}$ 213, 223sh, 262, 330sh, 340, and 355 nm (ε 38,200, 28,200, 20,900, 12,900, 17,700, and 14,000); τ 7·88 (2H, quint, *J* 8 Hz), 7·14 (2H, t, *J* 8 Hz), 6·80 (2H, t, *J* 8 Hz), 2·3—2·7 (6H, m, Ar), 2·07 (2H, d, *J* 8 Hz, low-field half of Cbs signal), and −1·83 (1H, NH, exchanged D_2O) [the compound gave the same spectrum in $(CD_3)_2SO$]; *m/e* 358 (M^+, 19%) and 183 (M − Cbs, 100%).

4a-(p-*Chlorophenylsulphonylamino*-2,3,4,4a-*tetrahydro*-1H-*carbazole* (X; Z = Cbs).—Tetrahydrocarbazole (1·71 g) and Cbs azide (2·15 g) were mixed and heated (50°) for 2 days. Methanol (5 ml) was then added and the solid (3 g) collected. Recrystallisation from n-propanol gave *compound* (X; Z = Cbs) (2·5 g, 70%) as white crystals, m.p. 200—202° (Found: C, 59·7; H, 4·9; Cl, 10·1; N, 7·7; S, 9·2. $C_{18}H_{17}ClN_2O_2S$ requires C, 59·9; H, 4·7; Cl, 9·9; N, 7·8; S. 8·9%); $\nu_{max.}$ (N) 1587, 1612w, and 3080br cm^{-1}; $\lambda_{max.}$ 216, 220, 233sh, and 260sh nm (ε 16,300, 16,700, 8700, and

3000) [this spectrum was similar to that published [1] for (X; Z = Ts)]; τ [$(CD_3)_2SO$] 6·4—9·4 (8H, m), 3·2—3·6 (2H, m, Ar), 2·5—3·1 (6H, m, Ar), and 1·28 (1H, NH, exchanged D_2O); *m/e* 360 (M^+, 24%), 319 ($M - C_3H_5$, 36%), 185 (M — Cbs, 66%), 169 (M — $CbsNH_2$, 49%), 168 (100%), and 144 (319 — Cbs, 26%).

2,3-*Dihydro*-4-(N-*methyl*-p-*tolylsulphonylamino*)-1H-*cyclopenta*[c]*quinoline* (XIII; R = Me, Z = Ts).—To a solution of potassium hydroxide (2 g) in water (10 ml) was added compound (XII; Z = Ts) (0·5 g). Acetone (20 ml) was then added, followed, with stirring, by dimethyl sulphate (4 × 0·5 ml at 2 min intervals). After a further 0·5 h stirring the mixture was filtered; the acetone was evaporated off *in vacuo* and water (10 ml) was added. An oil separated which solidified on cooling (0·4 g, 77%); t.l.c. showed the presence of two components, one of which appeared to be (V; Z = Ts). Recrystallisation from methyl cyanide did not effect separation. A sample (0·2 g) was separated by t.l.c. From the band corresponding to (V; Z = Ts) less than 1 mg of material was obtained. The material from the other band afforded *compound* (XIII; R = Me, Z = Ts) (180 mg), m.p. 153—154° (from methanol) (Found: C, 68·0; H, 5·6; N, 7·8; S, 9·1. $C_{20}H_{20}N_2O_2S$ requires C, 68·2; H, 5·7; N, 8·0; S, 9·1%); $\nu_{max.}$ (N) 1585 cm^{-1}; $\lambda_{max.}$ 225, 240sh, 310, and 324 nm (ε 50,000, 22,800, 4400, and 5200); τ 7·71 (2H, quint, *J* 8 Hz), 7·57 (3H, s, tosyl Me), 6·83 (3H, s, NMe), 6·67 (2H, t, *J* 8 Hz), 6·60 (2H, t, *J* 8 Hz), and 2·1—2·8 (8H, m, Ar).

Action of Heat upon 4a-(*Arylsulphonylamino*)-2,3,4,4a-*tetrahydro*-1H-*carbazoles*.—Compound (X; Z = Ts) (20 g) was dissolved in boiling n-propanol (150 ml) and heated under reflux for 24 h. The precipitate (P) (7 g) was filtered from the hot mixture and the solution was allowed to cool, depositing white needles. These were collected and recrystallised from acetic acid affording 1,2,3,4-*tetrahydro*-1-(p-*tolylsulphonylamino*)*carbazole* (XIV; R = H, Z = Ts) (5 g) as white needles, m.p. 208—210° (Found: C, 66·9; H, 5·9; N, 7·9; S, 9·2. $C_{19}H_{20}N_2O_2S$ requires C, 67·1; H, 5·9; N, 8·2; S, 9·4%); $\nu_{max.}$ (N) 1591, 3230, and 3485 cm^{-1}; $\lambda_{max.}$ 202, 227, 276, 284, and 294 nm (ε 59,300, 50,300, 8990, 9190, and 6480); τ 7·2—8·8 (6H, m), 7·55 (3H, s, tosyl Me), 5·49 [1H, m, C(1)H], 5·15 (1H, NH, exchanged D_2O), 2·3—3·0 (6H, m, Ar), 2·22 (2H, d, *J* 8 Hz, low-field half of tosyl signal), and 1·64 (1H, NH, indole, exchanged D_2O) [values are similar to those recorded for (II; Z = Ts) [1]]; *m/e* 340 (M^+, 6%), 91 (70%), and 43 (100%). The precipitate (P) (7 g) was boiled for 10 min with acetone (100 ml) and the solution was filtered hot; the insoluble fraction (2 g) (XV) had m.p. 241—243° (decomp.) (slow heating) [the m.p. of (XV) varies between 250 and 290° depending on the rate of heating [12,13]]. This sample of (XV) was identical with samples prepared in other ways (see later). A sample of (XV) was heated at 250° for 5 min. The melt resolidified as needles, m.p. 335°, identical with an authentic specimen of (XVI) supplied by Dr. M. L. Tomlinson. T.l.c. of the original propanolic liquors showed traces of (XVI). The hot acetone solution was concentrated to 50 ml and allowed to cool; 1,2,3,4-*tetrahydro*-9-(1,2,3,4-*tetrahydrocarbazol*-1-*yl*)-1-(p-*tolylsulphonylamino*)*carbazole* (XVIII) separated as fine white needles (0·25 g), m.p. 300—302° (Found: C, 73·4; H, 6·3; N, 8·1; S, 6·5. $C_{31}H_{31}N_3O_2S$ requires C, 73·1; H, 6·1; N, 8·2; S, 6·3%); $\nu_{max.}$ (N) 1684w and 3320w cm^{-1}; $\lambda_{max.}$ ($CHCl_3$) 240, 286, 293, and 340 nm (ε 30,850, 15,700, 14,700, and 400); τ [$(CD_3)_2SO$] −0·12 (1H, NH, indole), 2·3—3·7 (12H, m, Ar), 5·42br (2H), 7·0—8·4 (12H, m), 7·5—7·6 (tosyl Me, partially obscured by solvent signal) (the tosyl NH signal could not be detected in the weak solution used: it may have been obscured by the water peak); *m/e* 509 (M^+, 3%), 338 (18%), 170 (100%), 169 (24%), and 168 (23%). Compound (XIV; R = H, Z = Ts) (0·5 g) was dissolved in hot acetic acid (100 ml) and the solution was allowed to cool to room temperature. After 1 week t.l.c. in three separate solvent systems showed the presence of toluene-*p*-sulphonamide and compounds (XV), (XVI), and (XVIII).

4a-(*p*-Chlorophenylsulphonylamino)-2,3,4,4a-tetrahydrocarbazole (X; Z = Cbs) (1 g) was boiled for 4 h in n-propanol (100 ml); half the solvent was removed *in vacuo* and the solution was allowed to cool. The white prisms (0·64 g) which separated could not be purified and were suspended in aqueous potassium hydroxide (2 g in 10 ml). Acetone was added until all the solid disappeared and the two-phase system was stirred while dimethyl sulphate (4 × 0·5 ml) was added. After 30 min the acetone was removed and the solid collected and washed with water. Recrystallisation from chloroform–methanol (1 : 1) gave white needles of 1,2,3,4-*tetrahydro*-1-(N-*methyl*-p-*chlorophenylsulphonylamino*)*carbazole* (0·48 g), m.p. 198° (Found: C, 61·2; H, 5·3; Cl, 9·3; N, 7·3; S, 8·8. $C_{19}H_{19}ClN_2O_2S$ requires C, 60·9; H, 5·1; Cl, 9·5; N, 7·5; S, 8·6%); $\nu_{max.}$ (C) 3460 cm^{-1}; $\lambda_{max.}$ (204, 227, 276, 283, and 295 nm) (ε 25,900, 41,600, 9680, 9530, and 7130); τ 7—8·5 (6H, m), 7·33 (3H, s, NMe), 4·77 [1H, t, *J* 9 Hz, C(1)H], 2·3—3·1 (6H, m, Ar), 2·12 (2H, d, *J* 8 Hz, low-field half of Cbs signal), and 1·87 (1H, NH, exchanged D_2O); *m/e* 374 (M^+, 3%), 170 (M — CbsNMe, 55%), 169 (55%), 168 (90%), and 167 (100%). A sample of (II; Z = Ts) (1·0 g) was similarly methylated, yielding 1,2,3,4-*tetrahydro*-9-*methyl*-1-(N-*methyl*-p-*tolylsulphonylamino*)*carbazole* as crystals (from n-propanol) (0·7 g), m.p. 153—155° (Found: C, 68·5; H, 6·8; N, 7·5; S, 9·1. $C_{21}H_{24}N_2O_2S$ requires C, 68·5; H, 6·5; N, 7·6; S, 8·7%); $\lambda_{max.}$ 203, 231, 279, and 287 nm (ε 30,200, 49,000, 8500, and 8500); τ 7·2—8·5 (6H, m), 7·56 (3H, s, tosyl Me), 7·42 (3H, s, $NMeSO_2$), 6·29 (3H, s, NMe indole), 4·53br [1H, s, C(1)H], 2·4—3·1 (6H, m, Ar), and 2·20 (2H, d, *J* 8 Hz, low-field half of tosyl signal; *m/e* 368 (M^+, 20%), 213 (M — Ts, 50%), 184 (M — TsNMe, 100%), and 91 (34%).

A solution of tetrahydrocarbazole (2 g) in acetic acid (20 ml) containing Cbs azide (5·2 g) was kept at room temperature in the dark for 3 weeks. The material which separated formed crystals of 5a,6,7,8,13a,14,15,16-octahydropyrazino[1,2,3-*jk*:4,5,6-*j'k'*]dicarbazole (XV), m.p. 240—243° (from chloroform) (1 g), identical with the material described before (Found: C, 84·9; H, 6·3; N, 8·2. Calc. for $C_{24}H_{22}N_2$: C, 85·2; H, 6·5; N, 8·3%); no significant i.r. bands between 1400 and 3800 cm^{-1}; $\lambda_{max.}$ 241, 297, and 412 nm (ε 46,500, 16,600, and 400).

2-(p-*Chlorophenylsulphonylimino*)*indoline*-3-*spirocyclopentane* (XIX; R = H; Z = Cbs).—Compound (X; Z = Cbs) (0·5 g) was heated (210°) for 1 min. The melt was cooled and the solid recrystallised from n-propanol to give white *needles*, m.p. 195° (0·3 g) (Found: C, 60·3; H, 4·9; Cl, 10·1; N, 7·9; S, 8·9. $C_{18}H_{17}ClN_2O_2S$ requires C, 59·9; H, 4·7; Cl, 9·9; N, 7·8; S, 8·9%); $\nu_{max.}$ (N) 1590br and 3285 cm^{-1}, $\nu_{max.}$ (C) 1600br and 3365 cm^{-1}; $\lambda_{max.}$ 227 and 280 nm (ε 27,300 and 14,100); τ 7·2—8·5br (envelope, 8H, 2·4—3·1 (6H, m, Ar), and 2·13 (2H, d, *J* 8 Hz, low-field half of Cbs signal).

2'-Methyl-2-p-*tolylsulphonyliminoindoline*-3-*spirocyclopentane* (XIX; R = Me, Z = Ts).—1-Methyltetrahydrocarbazole (8·0 g) (m.p. 65°; lit.,[27] 65°) and tosyl azide (8·0 g) were mixed and heated (50°) for 5 days. Petroleum was added and 7 days later the solid was collected (15·5 g). The material tended to revert to an oil on recrystallisation but from a large volume of ethanol white *rhombs* (5 g), m.p. 185—186°, were obtained (Found: C, 67·8; H, 6·3; N, 7·9; S, 9·1. $C_{20}H_{22}N_2O_2S$ requires C, 67·8; H, 6·2; N, 7·9; S, 9·1%); $\nu_{max.}$ (N) 1592br and 3275 cm^{-1}; $\lambda_{max.}$ 222, 282, and 291sh nm (ε 23,100, 14,100, and 11,000); τ 9·53 (3H, d, *J* 8 Hz, HC·C*H*$_3$), 7·2—8·6 (7H, m), 7·59 (3H, s, tosyl Me), 2·6—3·1 (6H, m, Ar), 2·12 (2H, d, *J* 8 Hz, low-field half of tosyl signal), and −0·08 (1H, NH, exchanged D_2O). Similarly, 1-methyltetrahydrocarbazole (3 g) and Cbs azide (3·6 g) yielded 2-p-*chlorophenylsulphonylimino*-2'-*methylindoline*-3-*spirocyclopentane* (XIX; R = Me, Z = Cbs) (3 g), m.p. 170—172° (from ethanol) (Found: C, 61·1; H, 5·1; Cl, 9·8; N, 7·5; S, 8·7. $C_{19}H_{19}ClN_2O_2S$ requires C, 60·9; H, 5·1; Cl, 9·5; N, 7·5; S, 8·6%); $\nu_{max.}$ (N) 1600br and 3305 cm^{-1}; $\lambda_{max.}$ 225, 279, and 290sh nm (ε 26,500, 16,400, and 12,900); τ 9·55 (3H, d, *J* 8 Hz, HC·C*H*$_3$), 7·2—8·6 (7H, m), 2·4—3·1 (6H, m, Ar), 2·06 (2H, d, *J* 8 Hz, low-field half of Cbs signal), and −0·12 (1H, NH, exchanged D_2O); *m/e* 374 (M^+, 27%), 333 ($M - C_3H_5$, 45%), 319 ($M - C_4H_7$, 100%), 199 (M — Cbs, 52%), and 144 (319 — Cbs, 45%).

1,2,3,4-*Tetrahydro*-1,9-*dimethyl*-1-(p-*tolylsulphonylamino*)-*carbazole* (XX).—1,9-Dimethyltetrahydrocarbazole,[28] prepared by methylating (in sodium–liquid ammonia)[29] 1-methyltetrahydrocarbazole, had m.p. 50° (Found: C, 84·1; H, 8·3. Calc. for $C_{14}H_{17}N$: C, 84·4; H, 8·6%); τ 8·76 (3H, d, *J* 8 Hz, HC·C*H*$_3$), 6·8—7·4 (7H, m), 6·47 (3H, s, NMe), and 2·6—3·3 (4H, m, Ar). When this compound (5·0 g) was mixed with tosyl azide (5 g) at 55° the reaction became vigorous; the mixture was cooled, kept at room temperature for 12 h, and then heated (55°) for 48 h. Methanol (20 ml) was added and the solid collected and recrystallised from ethanol to give white *needles*, m.p. 200—203° (3 g) (Found: C, 68·8; H, 6·7; N, 7·6; S, 8·7. $C_{21}H_{24}N_2O_2S$ requires C, 68·5; H, 6·5; N, 7·6; S, 8·7%); $\nu_{max.}$ (N) 1595w and 3255 cm^{-1}; $\lambda_{max.}$ 203, 229, and 288 nm (ε 30,700, 57,000, and 8600); τ 8·27 (3H, s, C·C*H*$_3$), 7·60 (3H, s, tosyl Me), 7·5—8·5 (4H, m), 7·37 [2H, m, C(4)H], 5·11 (1H, NH, exchanged D_2O), 2·4—3·1 (6H, m, Ar), and 2·31 (2H, d, *J* 8 Hz, low-field half of tosyl signal); *m/e* 368 (M^+, 18%), 198 (M — TsNH, 78%), 197 (M — $TsNH_2$, 100%), 196 (58%), and 182 (197 — Me, 38%).

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5,7-*Dibromo*-N-*methyl*-3-p-*tolylsulphonyliminoindoline*-2-*spirocyclopentane*.—Compound (I; Z = Ts) (200 mg) was dissolved in pyridine (5 ml), pyridinium bromide perbromide (450 mg) was added, and the mixture was warmed (45°) for 6 h. T.l.c. (silica; benzene–ethyl acetate, 9 : 1) showed two spots, the monobromo-compound [1] (R_F 0·50) and another compound, R_F 0·61. The mixture was poured into water and extracted with chloroform. The dried extract was evaporated and the residue chromatographed over silica. Elution with benzene yielded the faster-moving compound (125 mg), which formed bright orange-coloured *needles*, m.p. 193—196° (decomp.) (from chloroform–methanol) (Found: C, 47·0; H, 4·1; Br, 31·7; N, 5·4; S, 6·5. $C_{20}H_{20}Br_2N_2O_2S$ requires C, 46·9; H, 3·9; Br, 31·2; N, 5·5; S, 6·3%); $\lambda_{max.}$ 258 and 481 nm (ε 13,600 and 4320); τ 8·0—8·2br (8H), 7·57 (3H, s, tosyl Me), 6·57 (3H, s, NMe), 2·64 [2H, d, *J* 8 Hz, tosyl C(3)H and C(5)H], 2·23 [1H, d, *J* 2 Hz, C(6)H], 2·05 [2H, d, *J* 8 Hz, tosyl C(2)H and C(6)H], and 1·26 [1H, d, *J* 2 Hz, C(4)H] (note the effect of the 7-Br atom on the NMe signal [30]). At 195° the bright orange colour of the melt rapidly faded. When the sample of 5-bromo-*N*-methyl-3-*p*-tolylsulphonyliminoindoline-2-spirocyclopentane (m.p. 174—175°) [1] was heated (190°; 5 min) a white solid was formed. Recrystallisation from acetic acid gave 6-bromo-1,2,3,4-tetrahydro-9-methyl-1-*p*-tolylsulphonylaminocarbazole as white crystals, m.p. 230—232°; τ 8·28br (4H), 7·56 (3H, s, tosyl Me), 7·37 [2H, m, C(4)H], 6·48 (3H, s, NMe), 5·23br [2H, NH and C(1)H], 2·7—3·1 (2H, m, Ar), 2·69 (2H, d, *J* 8 Hz, high-field half of tosyl signal), 2·41 [1H, s, C(5)H], and 2·02 (2H, d, *J* 8 Hz, low-field half of tosyl signal).

1-*Methyl*-5-*thiocyanato*-3-p-*tolylsulphonyliminoindoline*-2-*spirocyclopentane*.—To a solution of compound (I; Z = Ts) (200 mg) in chloroform (10 ml) was added a solution of ammonium thiocyanate (170 mg) in acetic acid (20 ml). The mixture was cooled to 0° and stirred, and a solution of bromine (180 mg) in acetic acid (2 ml) was added. After 1 h the mixture was diluted with water and extracted with chloroform. The product was isolated by chromatography (silica; benzene) and gave orange-coloured *needles* (from chloroform–methanol), m.p. 181—183° (130 mg) (Found: C, 61·8; H, 5·0; N, 9·9; S, 15·2. $C_{21}H_{21}N_3S_2O_2$ requires C, 61·3; H, 5·1; N, 10·2; S, 15·6%); $\nu_{max.}$ (N) 2175 cm^{-1} (NCS); τ 8·10br (8H), 7·56 (3H, s, tosyl Me), 6·98 (3H, s, NMe), 3·30 [1H, d, *J* 8 Hz, C(7)H], 2·70 (2H, d, *J* 8 Hz, high-field half of tosyl signal), 2·30—2·47 [1H, dd, *J* 8 and 2 Hz, C(6)H], 2·11 (2H, d, *J* 8 Hz, low-field half of tosyl signal), and 1·27 [1H, d, *J* 2 Hz, C(4)H].

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