Dibenzo[*d,f*][1,2,3]triazepine and the Attempted Generation of 2,2'-Didehydrobiphenyl [1]

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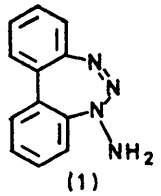
Dibenzo[*d,f*][1,2,3]triazepine, the first reported 1,2,3-triazepine, has been prepared in high yield by addition of ammonia to bis-diazotised 2,2'-diaminobiphenyl. Various mechanisms are considered for this reaction since complexities are revealed when ammonia is replaced by methylamine.

The instability of the triazepine ring and its tendency to act as a masked diazonium compound accounts for the complexity of diazotisation of 2,2'-diaminobiphenyl which, under various conditions, gives carbazole, benzocinnoline, 2-amino-2'-azidobiphenyl, benzocinnoline *N*-imide, 1,3-bis-(2-aminobiphenyl-2-yl)triazene, and 9,20-dihydrotetrabenzo[*d,f,k,m*][1,2,3,8,9,10]hexa-azacyclotetradecine, a new heterocyclic system (Scheme 1). The dibenzotriazepine reacts as a masked diazonium compound with hydrobromic acid and copper, hydriodic acid, hydrazine, diethyl malonate, and on catalytic hydrogenation (Scheme 2).

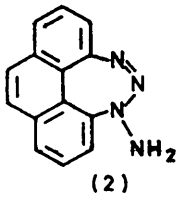
The *N*(5)-methyl derivative of the triazepine is formed by methylation but attempts to introduce other *N*-substituents have so far been unsuccessful. In particular, failure to isolate the unstable *N*(5)-amino-derivative has precluded the generation of 2,2'-didehydrobiphenyl.

SEVERAL years ago we generated 1,8-didehydronaphthalene by oxidation of 1-aminonaphtho[1,8-*de*]triazine.[2] Our observation that this species underwent stereospecific 1,2-addition to monoenes was, in part, the stimulus for Hoffmann and his co-workers to carry out calculations for a variety of didehydroarenes.[3] These calculations indicated that through-bond interaction between the component dehydro orbitals was important as well as direct through-space interaction. For certain geometrical arrangements of the component dehydro orbitals through-bond interaction led to an inversion of the expected symmetric-below-antisymmetric ordering for the delocalised dehydro molecular orbitals. 1,8-Didehydronaphthalene was just such a case, the calculated antisymmetric HOMO explaining the observed, apparently concerted 1,2-addition. Because of the problems associated with both the generation of, and interception of non-*ortho*-didehydroarenes, particularly under conditions where the symmetry of the HOMO might be revealed (*e.g.* cycloaddition), no experimental tests of Hoffmann's predictions for them have been reported. Of those didehydroarenes for which calculations were available, 4,5-didehydrophenanthrene and 2,2'-didehydrobiphenyl seemed the most amenable to experimental investigation.

Precursors (1) and (2) would be required by analogy



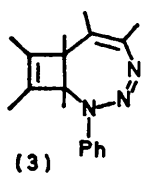
(1)



(2)

with our generation of 1,2-didehydrobenzene [4] and 1,8-didehydronaphthalene,[2] and they do not appear unreasonable synthetic goals. Furthermore interception of the didehydro-species in cycloadditions seems geometrically feasible. Indeed these are particularly attractive cases for study since calculations indicate symmetric HOMOs for both didehydro-species so that 1,4-addition to dienes is allowed whereas the sterically more reasonable addition to monoenes is disallowed unless the latter acts in an antarafacial mode. Thus orbital symmetry and stereochemical intuition lead to opposite predictions.

We therefore set out to synthesise the desired *N*-aminotriazepine derivatives by amination of the unsubstituted heterocycles. At the outset of this work, no 1,2,3-triazaheterocycles with more than six ring atoms were known. Since then a dihydrotriazepine (3) has



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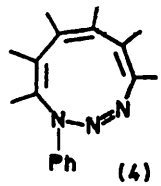


(4)

been reported as a pyrolysis product of the hexamethyl-(Dewar benzene)–phenyl azide cycloadduct.[5] Convincing evidence for this structure is lacking however, and the structural assignment was made largely on the basis of its n.m.r. spectrum and ready rearrangement to the 1,2,3-triazonine (4). The surprising stability of the latter can be attributed to aromaticity. This is not possible for the 8 π-electron triazepine system which we anticipated to be a reactive, strained, acid-sensitive 'cyclic triazene.'

Because of the greater accessibility of appropriate 2,2'-disubstituted biphenyls compared with 4,5-disubstituted phenanthrenes and because of the greater flexibility of this system we chose to concentrate initially on the synthesis of dibenzo[*d,f*][1,2,3]triazepine (5). An obvious route to this compound is diazotisation of 2,2'-diaminobiphenyl; this reaction proved, however, to be quite complex.†

† This complexity is apparent from early reports of the diazotisation of 2,2'-diaminobiphenyl; see, for example, L. Mascarelli and D. Gatti, *Gazzetta*, 1929, **59**, 858.

[1] Preliminary communication, S. F. Gait, M. E. Peek, C. W. Rees, and R. C. Storr, *J.C.S. Chem. Comm.*, 1972, 482.

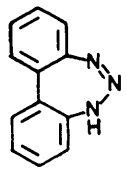
[2] C. W. Rees and R. C. Storr, *J. Chem. Soc.* (*C*), 1969, 765.

[3] R. W. Hoffmann, A. Imamura, and W. J. Hehre, *J. Amer. Chem. Soc.*, 1968, **90**, 1499.

[4] C. D. Campbell and C. W. Rees, *J. Chem. Soc.* (*C*), 1969, 742.

[5] L. A. Paquette and R. J. Haluska, *J. Amer. Chem. Soc.*, 1972, **94**, 534.

Treatment of the diamine in aqueous acetic acid gave carbazole (7) (55%) as the only recognisable product. This was not unexpected and presumably arose by intramolecular displacement in the amino-diazonium



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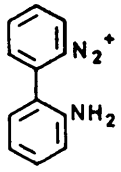
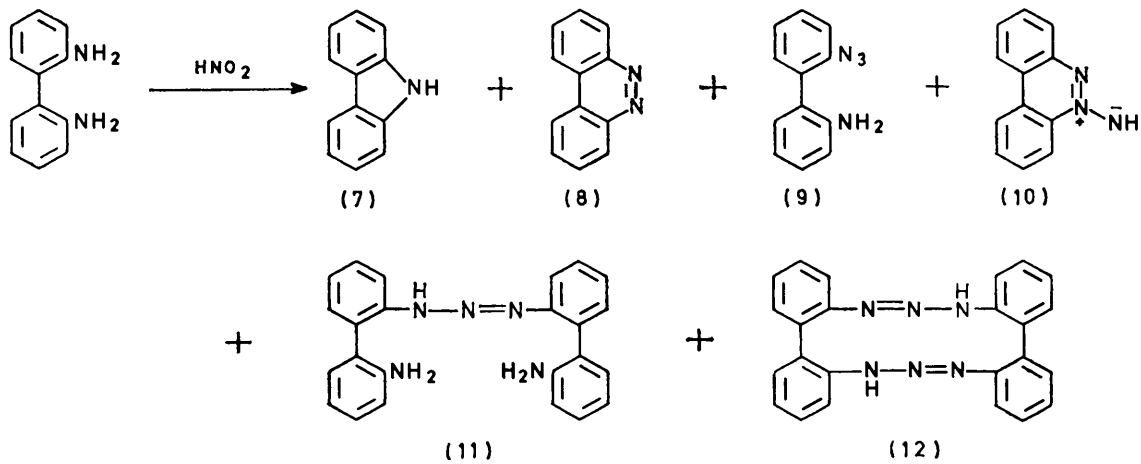


(6)

species (6). Diazotisation in aqueous 2N-hydrochloric acid followed by basification with ammonia and chromatographic work-up on alumina gave the products shown in Scheme 1. Discussion of the structural evidence for, and the chemistry of the benzocinnoline *N*-imide (10) is deferred until a later paper;[6] 2-amino-2′-azidobiphenyl (9) was identified spectroscopically and by its conversion into the known 2,2′-diazidobiphenyl;[7] spectral, mass spectral and analytical data were all in accord with the diaminotriazene structure (11).



(7) (8) (9) (10) (11) (12)

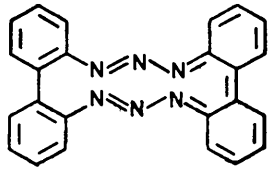
SCHEME 1

The bis-triazene (12) showed typical linear aryltriazene (u.v. and i.r.) and biphenyl (u.v.) spectral characteristics, very similar to those of 1,3-bis(biphenyl-2-yl)triazene synthesised for comparison.[8] The bis-triazene (12) was also obtained by diazotisation of the diaminotriazene (11), and this is presumably how it arose in the diazotisation of 2,2′-diaminobiphenyl. The mass spectrum of (12) did not show a molecular ion, but an ion corresponding to the loss of two molecules of nitrogen was observed; the base peak corresponded to carbazole. Heating (12) in refluxing bis-(2-methoxyethyl) ether gave carbazole (77%), presumably by stepwise loss of two molecules of nitrogen; u.v. irradiation also gave carbazole (36%), together with much polymeric material.

Further proof for structure (12) came from the formation of 2,2′-diaminobiphenyl by hydrogenation over Adams catalyst. The bis-triazene (12), which represents a new heterocyclic system, can be considered as a dihydrohexa-aza[14]annulene, and oxidation might have been expected to give the aromatic hexa-aza[14]annulene (13) or various products resulting from transannular interaction between the nitrogen atoms. However treatment with lead tetra-acetate, potassium permanganate, pentyl nitrite, and dichlorodicyanobenzoquinone gave bicarbazolyl, carbazole, and benzocinnoline as the only recognisable products.

Aprotic diazotisation of 2,2′-diaminobiphenyl with pentyl nitrite or diphenylnitrosamine in refluxing benzene gave carbazole (7), the *N*-imide (10), and the amino-azide (9). Similar results were obtained by using as solvent methylene chloride from which all traces of acid had been removed, but in the absence of such precautions the bis-triazene (12) was formed rather than the *N*-imide (10).

It is apparent that all the above products can be rationalised in terms of decomposition, disproportionation, or rearrangement of initially formed dibenzotriazepine (5) or its ring-opened conjugate acid (6). In



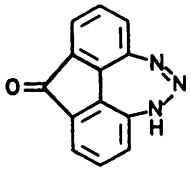
(13)

particular, in the aprotic diazotisation in the absence of acid, the *N*-imide (10) presumably arises by a mild thermal rearrangement of the triazepine. Attempts were therefore made to form dibenzotriazepines for which the isomeric ylides would be destabilised.

Introduction of 6- and 6′-substituents into the biphenyl system should severely destabilise the planar

[6] S. F. Gait, C. W. Rees, and R. C. Storr, in preparation.
[7] P. A. S. Smith, B. B. Brown, R. K. Putney, and R. F. Reinisch, *J. Amer. Chem. Soc.*, 1953, **75**, 6335.
[8] H. H. Richmond, U.S.P. 2,448,155/1948.

N-imide. However when 2,2′-diamino-6,6′-dinitrobiphenyl [9] was refluxed with pentyl nitrite in benzene only the linear diaminotriazene analogous to (11) was obtained (73%). Incorporation of the 6- and 6′-positions into a five membered ring as in fluorenone was also considered since this should greatly favour the triazepine over the *N*-imide; however diazotisation of 4,5-diaminofluorenone (obtained from 4-nitrofluorenone-5-carboxylic acid [10] by a Schmidt reaction and reduction) proved to be equally complex. No triazepine (14) was observed although the isoelectronic diazepinone (15) was formed readily from 4,5-diaminofluorenone and triethyl orthoacetate, and was stable. Aprotic diazotisation of the diamine in benzene gave 4-phenylfluorenone and 4-aminofluorenone as the only identified products. The tendency for both amino-groups to be lost even when exactly 1 mol. equiv. of diazotising agent was used (unchanged diamine was always recovered) was also noted in diazotisation in aqueous hydrochloric acid where dichloro- and chlorohydroxy-fluorenones were formed. The high reactivity of fluorenone diazonium compounds is almost certainly due to steric destabilisation which would be relieved either by loss of nitrogen (radical or cation formation) or by attack by nucleophiles to give electronically stabilised tetrahedral intermediates such as (16). The higher reactivity of the monoaminofluorenones than of diaminofluorenone towards diazotisation is less easy to explain but may result from particularly favourable hydrogen bonding in the protonated diamine (17).



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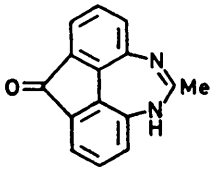

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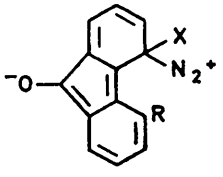

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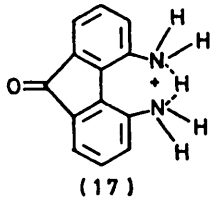
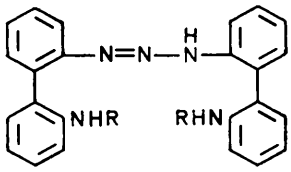


(17)

Since it seemed possible that a mobile tautomeric N–H system was necessary for isomerisation of the triazepine (5) to the *N*-imide (10) (see a later paper [6] for a full discussion of the mechanism of this rearrangement) attempts were made to produce an *N*-substituted triazepine by diazotisation of a monosubstituted diaminobiphenyl. However 2-amino-2′-methylaminobiphenyl with pentyl nitrite in either benzene or methylene chloride gave only *N*-methylcarbazole,* and 2-acetamido-2′-aminobiphenyl gave 2-acetamido-*o*-terphenyl in benzene and 1,3-bis-(2-′acetamidobiphenyl-2-yl)triazene (18; R = MeCO) in methylene chloride.

In an attempt to apply our modification [4] of the route used by Trave and Bianchetti [11] for the synthesis of 1-aminobenzotriazole to the present problem we also studied the diazotisation of the amino-hydrazone (19). This was obtained from 2-amino-2′-nitrobiphenyl by diazotisation and coupling with diethyl malonate, followed by catalytic hydrogenation. With pentyl nitrite in benzene, and in methylene chloride, a mixture of the *N*-substituted carbazole (20) and the triazene



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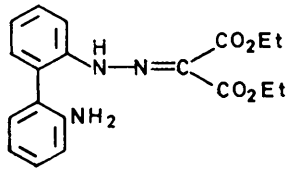

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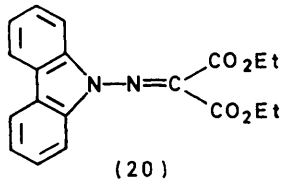

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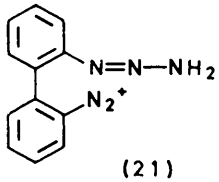


(21)

[18; R = N:C(CO$_2$Et)$_2$] was produced. Both aqueous diazotisation and treatment with diphenylnitrosamine in benzene gave only the *N*-substituted carbazole (20).

In view of the failure of all attempts to produce a triazepine by formation of a ' triazene N–N bond ' we turned our attention to syntheses where an intact triaza unit might be transformed into a triazepine. Although Grignard reagents react with azides to give triazenes [12] in high yield we were unable to achieve this reaction intramolecularly by treatment of 2-azido-2′-bromobiphenyl with magnesium in ether or with butyl-lithium. It was, however, thinking along these lines which led us to treat biphenyl-2,2′-bisdiazonium dichloride with ammonia in the hope that a triazeno-diazonium species such as (21) would undergo intramolecular displacement of nitrogen to give the triazepine. Although this reasoning may, in retrospect, have been based on too simple a view of the reaction mechanism this procedure was highly successful. Bis-diazotisation in dilute hydrochloric acid at 0° and careful basification with ammonia at 0° gave dibenzotriazepine (5) as a yellow precipitate (77%) from the basic solution. It crystallised from ether–petroleum as a surprisingly stable solid, m.p. 99—100°.

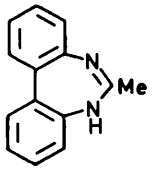
Similar results were obtained when the known pure crystalline biphenyl-2,2′-bisdiazonium bistetrafluoro-

* Subsequently *N*-methyldibenzotriazepine was isolated in low yield (20%) from a carefully controlled diazotisation in aqueous solution (see later).

[9] P. F. Holt and A. N. Hughes, *J. Chem. Soc.*, 1960, 3216.
[10] F. J. Moore and E. H. Huntress, *J. Amer. Chem. Soc.*, 1927, **49**, 1324.
[11] R. Trave and G. Bianchetti, *Att. Accad. naz. Lincei, Rend. Classe Sci. fis. mat. nat.*, 1960, **28**, 652.
[12] O. Dimroth, *Ber.*, 1903, **36**, 909; 1905, **38**, 670; O. Dimroth, M. Eble, and W. Gruhl, *Ber.*, 1907, **40**, 2390.

borate [13] was treated with aqueous ammonia, indicating that bis-diazotisation is indeed essential.

The triazepine structure was supported by both spectral and chemical evidence. The i.r. spectrum showed a sharp N–H stretching absorption at 3270 cm^{-1} characteristic of diaryltriazenes and no indication of a diazonium cation absorption even in solution. The u.v. spectrum [$\lambda_{max.}$ 239 (ε 27,300), 265 (9750), and 294 (5850) nm] is comparable to that of the isoelectronic diazepine (22), which shows a typical twisted biphenyl chromophore [$\lambda_{max.}$ 251 nm (ε 18,500)].[14] The hypsochromic shift of the main biphenyl chromophore in the triazepine indicates that conjugation along the biphenyl axis is less effective than for the diazepine; this is probably a consequence of more pronounced conjugation with the triaza-bridge. Chemical support came from the analogous formation of the known naphtho[1,8-*de*]-triazine (23) by similar treatment of bis-diazotised 1,8-diaminonaphthalene.



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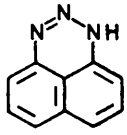
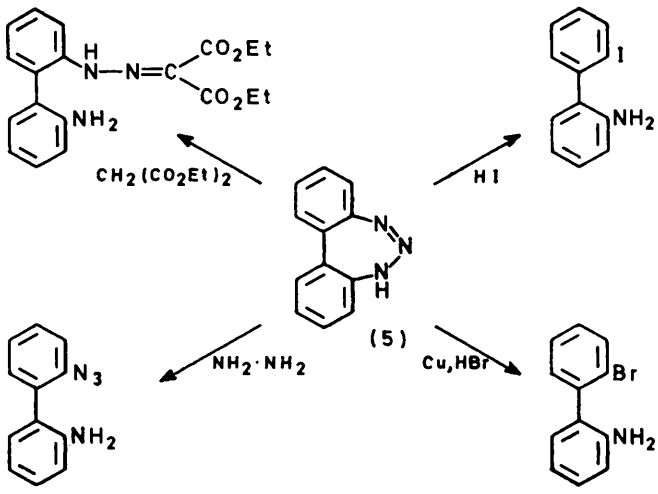


(23)

The triazepine (5) was converted quantitatively into the *N*-imide (10) on heating in benzene, indicating that the triazepine was almost certainly formed as the initial product in aprotic diazotisation. Indeed, subsequently, careful t.l.c. examination of the aprotic diazotisation reaction mixture at room temperature showed the triazepine (5) to be present. More vigorous heating in refluxing bis-(2-methoxyethyl) ether gave carbazole.

Irradiation of dibenzotriazepine in the presence of benzophenone as sensitiser gave only an 8% yield of carbazole, the major product being benzocinnoline. In the absence of a sensitiser benzocinnoline and the *N*-imide (10) were produced. Since benzocinnoline is a product of irradiation of the *N*-imide (10), these results suggest that the predominant photochemical reaction of triazepine (5) is isomerisation to the *N*-imide. This contrasts with observations for the diazepine system [15] where pyridine *N*-imides have been shown to be converted into diazepines by irradiation, the reverse reaction being thermally induced.

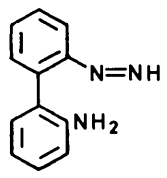
The masked diazonium character of the triazepine (5) was demonstrated by the reactions shown in Scheme 2. Catalytic reduction gave 2-aminobiphenyl. This contrasts with the normal behaviour of linear triazenes which are reduced to amines and hydrazines,[16] and is presumably the result of attack on the exceptionally weak N–N bond in this cyclic system. The amino-diimide (24) is a likely intermediate. 3-Methyl- and 3-methoxy-5(7)*H*-dibenzotriazepines (25; R = Me or OMe) were similarly obtained from the corresponding diaminobiphenyl by bis-diazotisation and treatment with ammonia. The n.m.r. spectra of the crude triazepines



SCHEME 2

showed only one methyl or methoxy-absorption indicating that dibenzotriazepines undergo rapid prototropy as expected. In line with this, both compounds gave the two possible monoamines on catalytic reduction. 3,9-Dimethoxydibenzotriazepine was also prepared by this method.

The chemical characteristics of dibenzotriazepine (5) are therefore as anticipated; it is a reactive cyclic triazene with a high degree of masked diazonium character. The heterocyclic ring cannot attain full stabilisation by conjugation since this would involve an 8 π-electron system. The triazepine is therefore somewhat more reactive than typical diaryltriazenes and



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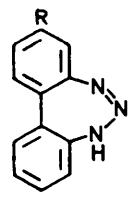


(25)

considerably more labile than naphtho[1,8-*de*]triazine (23).

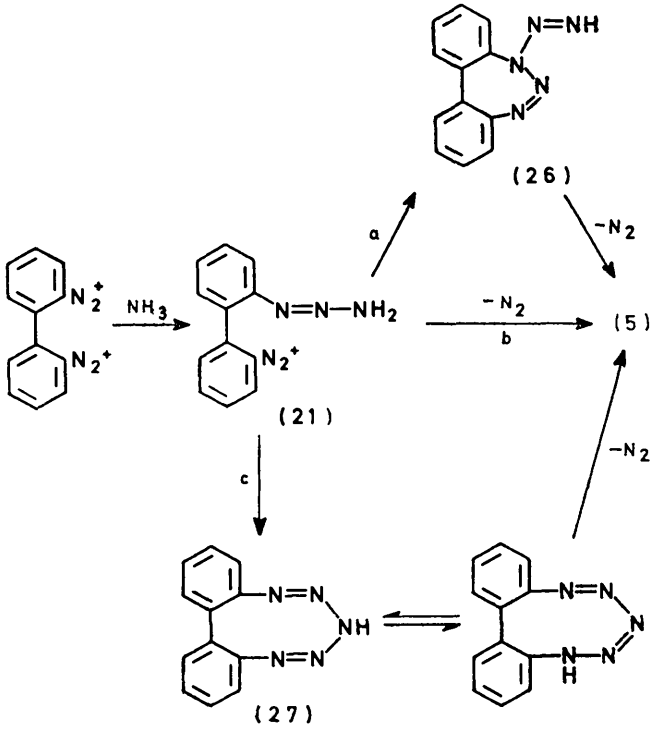
Its reactivity accounts for the complexity of the diazotisation reaction of 2,2′-diaminobiphenyl and control experiments show that in principle all the observed products can be obtained when the dibenzotriazepine is subjected to the appropriate reaction conditions. The mild thermal rearrangement to the *N*-imide (10), which occurs under the conditions of aprotic diazotisation, has already been mentioned. In aqueous acid the triazepine is converted into the *N*-imide, the amino-azide (9), benzocinnoline, and carbazole.

[13] G. Schiemann and R. Roselius, *Ber.*, 1932, **65**, 737.
[14] Y. A. Levin, A. P. Mokhova, and V. A. Kukhtin, *Zhur. obshchei Khim.*, 1961, **31**, 1573.
[15] J. Streith and J.-M. Cassal, *Angew Chem. Internat. Edn.*, 1968, **7**, 129; T. Sasaki, K. Kanematsu, and A. Kakehi, *Chem. Comm.*, 1969, 432.
[16] T. W. Campbell and B. F. Day, *Chem. Rev.*, 1951, **48**, 299.

This indicates that the triazepine isomerises to the *N*-imide in the presence of an acid catalyst. Under these conditions *N*-imide and triazepine interact to give amino-azide and benzocinnoline, the *N*-imide transferring NH to the amino-diazonium cation (6). In accord with this, phenyl azide is formed from the *N*-imide and benzenediazonium chloride.[6] Benzocinnoline and the amino-azide (9) are always formed whenever the *N*-imide and amino diazonium species such as (6) are present together, as, for example, in the aprotic diazotisation of diaminobiphenyl but not in the thermal uncatalysed rearrangement of triazepine to *N*-imide.

Coupling of the triazepine with diaminobiphenyl gives the diaminotriazene (11), which on further diazotisation gives the bis-triazene (12), thus explaining the formation of these two products. In acetic acid, carbazole is formed rapidly *via* the amino-diazonium species (6). Surprisingly dibenzotriazepine can be recovered unchanged from its solution in concentrated sulphuric acid, presumably because diprotonation renders the amino-group non-nucleophilic.

The mechanism for the formation of dibenzotriazepine from bis-diazotised 2,2′-diaminobiphenyl and ammonia is of interest. Almost certainly the diazonium triazene (21) is involved, and basically three routes to the triazepine from this precursor can be envisaged (Scheme 3a—c).



SCHEME 3

The complexity of the reaction was only revealed when ammonia was replaced by methylamine. This reaction gave the triazepine, although in much reduced yield, together with carbazole, benzocinnoline, the *N*-imide (10), benzocinnoline *N*-methylimide,[6] and the *N*-methyltriazepine. Particularly surprising is the preponderance of non-methylated products. The fate of the methyl group was established when diazomethane was detected in the reaction mixture by sweeping through with nitrogen and passing the effluent gases through an ethereal solution of 2-amino-3-naphthoic acid to give methyl 2-amino-3-naphthoate.

Formation of only small amounts of *N*-methyldibenzotriazepine suggests that simple nucleophilic displacement of diazonium ion (pathway b) does not occur to a major extent. Formation of dibenzotriazepine is therefore more likely to involve either of the intermediates (26) and (27). Breakdown of the methylated species (28) and (29) corresponding to (26) and (27) could well be considerably affected by substitution of the mobile hydrogen atom, thus allowing other processes, leading to the products observed, to intervene. Possible routes are tentatively outlined in Scheme 4.

Analogies for the interesting and rare type of cycloreversion with rearrangement proposed for (30) are provided by the high temperature decomposition of the oxatriazolone (31) [17] and fragmentation of the stable radical (32),[18] on reduction, to give benzocinnoline.

Addition to bis-diazotised 2,2′-diaminobiphenyl of amines other than methylamine which make diazo-compound formation impossible failed to shed further light on this problem. Thus aniline gave only the bis-triazene (33) and t-butylamine gave intractable mixtures. Furthermore, addition of hydrazine gave 2,2′-diazidobiphenyl rather than 5-aminodibenzo[*d*,*f*]-[1,2,3]triazepine (1) or products derived therefrom (see later).

Only limited success has so far been achieved in functionalising dibenzotriazepine. The 5-methyl derivative was obtained by treatment of the lithium or thallium salt of the triazepine with methyl iodide. The sodium salt could not be utilised in this reaction since the free (anti- or non-aromatic) anion readily rearranges to the more stable benzocinnoline *N*-imide anion and only benzocinnoline *N*-methylimide is formed. We associate the greater stability of the lithium salt towards rearrangement with the greater degree of covalent character of the *N*–metal bond. The *N*-methyltriazepine has a u.v. spectrum very similar to that of the unsubstituted triazepine and, like the latter, is a typical masked diazonium compound. Heating and u.v. irradiation gave *N*-methylcarbazole, though significantly [6] not benzocinnoline *N*-methylimide, and catalytic reduction gives 2-methylaminobiphenyl.

Treatment of the lithium salt of dibenzotriazepine with benzoyl chloride and ethyl chloroformate gave (34; R = COPh or CO_2Et, respectively), indicating that an electron-withdrawing substituent on nitrogen increases the diazonium character, as anticipated.

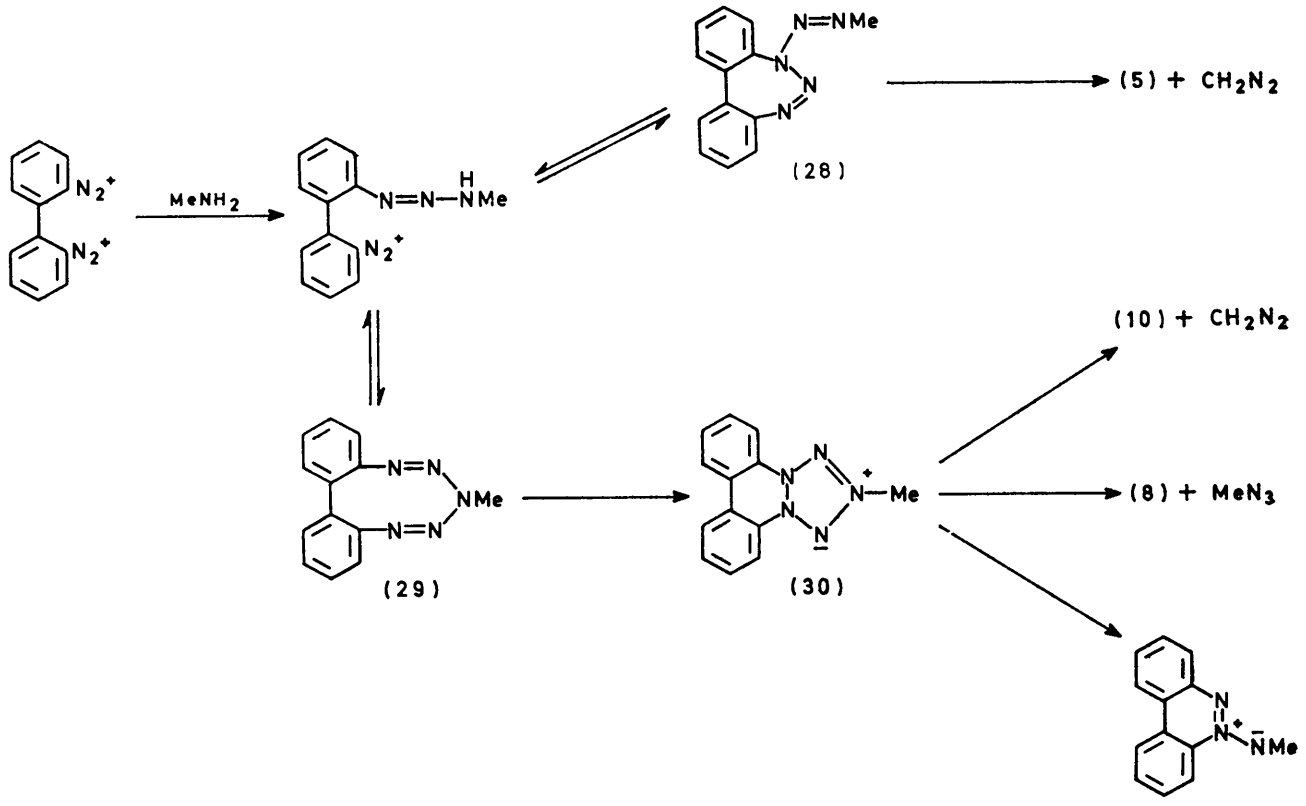
All attempts to aminate the triazepine (5) to give the

[17] R. Huisgen, H. Gotthardt, and R. Grashey, *Chem. Ber.*, 1968, **101**, 536.

[18] F. A. Neugebauer, *Angew. Chem. Internat. Edn.*, 1973, **12**, 455.

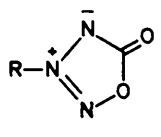
desired *N*-aminotriazepine have so far failed although there is evidence that the latter is formed but is extremely labile. Hydroxylamine *O*-sulphonic acid under aqueous, neutral, or basic conditions gave carbazole and the amino-azide (9). Chloramine and *O*-(2,4-dinitrophenyl)hydroxylamine did not react with borate with sodium borohydride in an attempt to obtain the *N*-amino-compound by cyclisation of the hydrazino-diazonium compound also gave 2-amino-2′-azidobiphenyl.

These two products could well be formed from the required 5-aminodibenzotriazepine if this, too, exhibits

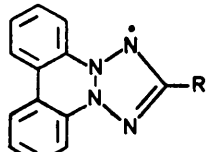


SCHEME 4

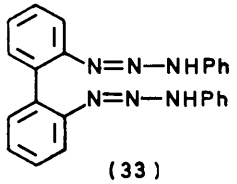
the lithium, sodium, or thallium salt of (5). With *O*-mesitylsulphonylhydroxylamine, even at low temperature, these salts gave nitrogen and a mixture of the



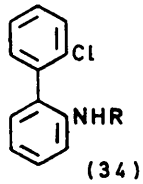
(31)



(32)



(33)



(34)

amino-azide (9) (30%) and *N*-aminocarbazole (40%). Reduction of biphenyl-2,2′-bisdiazonium bistetrafluoro-

masked diazonium character. Nucleophilic displacement of nitrogen in the ring-opened form would give *N*-aminocarbazole, whilst intramolecular (or intermolecular) reaction between the diazonium and hydrazine groups would give the amino-azide, as in the well known reaction between arenediazonium compounds and hydrazines. Indeed we have previously reported a close analogy for this reaction in the mild acid-catalysed rearrangement of 1-aminonaphtho[1,8-*de*]triazine to 1-amino-8-azidonaphthalene.[19]

Since failure to isolate the required *N*-amino-compound precluded the oxidative route to didehydrobiphenyl, dibenzotriazepine was treated with Angeli's salt [20] in the hope that the *N*-nitrene (diazene), which would have been involved in oxidation of the *N*-amino-compound, would be formed directly.[21] In water, in aqueous dimethylformamide, and in aqueous ethanol, biphenyl was formed together with a small amount of benzocinnoline. Although formation of biphenyl could be rationalised in terms of hydrogen abstraction by

[19] C. W. Rees and R. C. Storr, *J. Chem. Soc.* (*C*), 1969, 756.
[20] A. Angeli, *Chem. Zentr.*, 1896, **67**, I, 799; H. R. Hunt, J. R. Cox, and J. D. Ray, *Inorg. Chem.*, 1962, **1**, 938.
[21] D. M. Lemal in 'Nitrenes,' ed. W. Lwowski, Interscience, New York, 1970, p. 345.

2,2′-didehydrobiphenyl it is more likely to arise from a sequence of abstraction by intermediates formed by stepwise loss of nitrogen. No biphenylene, expected from electrocyclic ring closure of didehydrobiphenyl, was detected and generation of the diazene in the presence of tetraphenylcyclopentadienone or dimethyl acetylenedicarboxylate gave no trace of any adduct.

Although we failed to generate didehydrobiphenyl, this work on the unknown 1,2,3-triazepine system was additionally rewarding in that it led to the isomeric azimines (benzocinnoline *N*-imides [6]), whose cycloaddition reactions proved to be very fruitful.[22]

EXPERIMENTAL

Common reaction products such as carbazole, benzocinnoline, 2,2′-diaminobiphenyl, benzocinnoline *N*-imide, and *N*-methylcarbazole were always characterised by mixed m.p. determination and i.r. spectral comparison; literature m.p.s for these are not recorded. U.v. spectra are for solutions in ethanol and n.m.r. spectra for solutions in deuteriochloroform unless otherwise stated.

Diazotisation of 2,2′-Diaminobiphenyl.—(i) *With sodium nitrite in aqueous acetic acid.* 2,2′-Diaminobiphenyl (1·24 g, 10 mmol) was dissolved in 1 : 1 glacial acid–water maintained at 0°. Sodium nitrite (0·69 g, 10 mmol) in water (20 ml) was added dropwise and the mixture was stirred for 30 min at 0°. After several hours at room temperature the solution was basified and extracted with chloroform. The extracts were dried (Na_2SO_4), filtered, and evaporated, and the residue was chromatographed on basic alumina. Elution with 40% ether–petroleum gave carbazole (49%), m.p. and mixed m.p. 245—246°.

(ii) *With sodium nitrite in* 2N-*hydrochloric acid.* 2,2′-Diaminobiphenyl (368 mg, 2 mmol) was dissolved in 2N-hydrochloric acid (20 ml) at 0—5°. Sodium nitrite (132 mg, 2 mmol) in water (5 ml) was added dropwise with stirring. After 30 min the mixture was basified with aqueous 5% ammonia and extracted with ether (3 × 50 ml), and the extracts were washed with water, dried (Na_2SO_4), and evaporated. The residue was chromatographed on basic alumina. Elution with 10% ether–petroleum gave 9,20-*dihydrotetrabenzo*[d,f,k,m][1,2,3,8,9,10]-*hexa-azacyclotetradecine* (12) (28 mg, 7%), bright yellow crystals from ether–petroleum, m.p. 210° (decomp.) (Found: C, 73·5; H, 4·9; N, 21·3. $C_{24}H_{18}N_6$ requires C, 73·8; H, 4·6; N, 21·5%); $\lambda_{max.}$ 228 (ε 15,250) and 353 (12,300) nm; $\nu_{max.}$ 3305 (N–H), 1585, 1515, 1485, 1260, 1230, 1190, 780, and 760 cm^{-1}; τ 2·0—3·6 (m), *m/e* 334 ($M - 2N_2$), 180, 167, and 152. Further elution gave carbazole (21 mg, 6%). Elution with 15% ether–petroleum gave *benzocinnoline* N-*imide* (10) (37 mg, 10%), yellow needles from ether–petroleum, m.p. 126° (Found: C, 73·6; H, 4·7; N, 21·6. $C_{12}H_9N_3$ requires C, 73·8; H, 4·6; N, 21·5%), $\lambda_{max.}$ 254 (ε 37,600), 297 (8930), 310 (7700), 323 (6900), and 367 (9120) nm; $\nu_{max.}$ 3160 (N–H), 1595, 1490, 1470, 1400, 1330, 1268, 1205, 1140, 778, 724, and 683 cm^{-1}; τ 1·0—1·4 (2H, m; 1H after D_2O shake) and 1·75—3·0 (7H, m); *m/e* 195, 180, 167, and 152 (*m** 143 and 118). Elution with 20% ether–petroleum gave 2-amino-2′-azidobiphenyl (132 mg, 31%) as an oil which rapidly decomposed to give benzocinnoline; *m/e* 210 (M^+), 182 ($M - N_2$), 180, and 152; $\lambda_{max.}$ 233 (ε 28,400), 273 (6500), 287 (6000), and 364 (5800) nm; $\nu_{max.}$ 3410 and 3350 (N–H), 2107 (N_3), 1612, 1000, and 750 cm^{-1}; τ 2·5—3·1br (8H, m, aromatic) and 6·4 (2H, s, NH_2). Ether–petroleum (50%) eluted benzocinnoline (62 mg, 17%), m.p. and mixed m.p. 155—156°. Finally, elution with ether gave 1,3-*bis*-(2′-*aminobiphenyl-2-yl*)*triazene* (91 mg, 24%) as yellow needles from ether, m.p. 179—182° (Found: C, 75·5; H, 6·1; N, 18·4. $C_{24}H_{21}N_5$ requires C, 76·0; H, 5·5; N, 18·5%), $\nu_{max.}$ 3350 and 3295 (N–H), 1613, 1582, 1380, 1222, 1178, and 750 cm^{-1}; τ 2·4—3·2 (8H, m, aromatic) and 6·2—6·5br (4H, s, NH_2); *m/e* 351 ($M - N_2$), 183, 182, 166, and 152.

(iii) *With pentyl nitrite in dichloromethane containing a trace of acid.* Pentyl nitrite (1·17 g, 10 mmol) was added slowly to a solution of 2,2′-diaminobiphenyl (1·84 g, 10 mmol) in dichloromethane (150 ml) containing one drop of concentrated hydrochloric acid. The mixture was heated under reflux for 16 h, then evaporated, and the residue was chromatographed on basic alumina. Elution with 30% ether–petroleum gave the bis-triazene (12) (455 mg, 23%), m.p. 210°. Elution with 35% ether–petroleum gave carbazole (168 mg, 10%).

(iv) *With pentyl nitrite in refluxing benzene.* 2,2′-Diaminobiphenyl (2·0 g, 11 mmol), pentyl nitrite (1·3 g, 11 mmol), and benzene (150 ml) were heated under reflux for 16 h. The benzene was removed by rotary evaporation and the residue was chromatographed on basic alumina (eluant in parentheses) to give carbazole (320 mg, 17·5%) (30% ether–petroleum), 2-amino-2′-azidobiphenyl (75 mg, 4%) (30% ether–petroleum), benzocinnoline *N*-imide (1·1 g, 52%), m.p. 126° (60% ether–petroleum), benzo[*c*]cinnoline (68 mg, 3·4%) (ether), and unchanged 2,2′-diaminobiphenyl (193 mg, 9·6%) (20% ethyl acetate–ether).

(v) *With pentyl nitrite in refluxing dichloromethane.* 2,2′-Diaminobiphenyl (1·0 g, 6·5 mmol) was dissolved in dichloromethane (100 ml) which had previously been passed through a basic alumina column to remove any traces of acid. Pentyl nitrite (0·76 g, 6·5 mmol) and sodium hydrogen carbonate (1·0 g) were added to the solution which was then heated under reflux for 16 h. Work-up and chromatography as above gave benzocinnoline *N*-imide (165 mg, 13%).

(vi) *With diphenylnitrosamine in refluxing benzene.* 2,2′-Diaminobiphenyl (1·84 g, 10 mmol) and diphenylnitrosamine (1·98 g, 10 mmol) were dissolved in benzene (150 ml) containing glacial acetic acid (0·2 ml) and the resulting solution was heated under reflux for 17 h. Evaporation, followed by chromatography of the residue on basic alumina (eluant in parentheses) gave diphenylamine (1·3 g, 77%), m.p. and mixed m.p. 54° (5% ether–petroleum), a mixture of diphenylamine and an unidentified red compound (0·34 g) (10% ether–petroleum), carbazole (72 mg, 4·3%) (20% ether–petroleum), and benzocinnoline *N*-imide (600 mg, 31%) (50% ether–petroleum).

(vii) *With pentyl nitrite in cold benzene.* 2,2′-Diaminobiphenyl (184 mg, 1 mmol) and pentyl nitrite (117 mg, 1 mmol) were kept in benzene (30 ml) at room temperature for 12 h. Evaporation followed by chromatography of the residue on basic alumina (eluant in parentheses) gave 2-amino-2′-azidobiphenyl (8 mg, 4%) (30% ether–petroleum), benzocinnoline *N*-imide (28 mg, 14%), m.p. 126° (50% ether–petroleum), 5*H*-dibenzo[*d*,*f*][1,2,3]triazepine (see later) (34 mg, 17%), m.p. and mixed m.p. 99° (50% ether–petroleum), benzocinnoline (7 mg, 4%) (ether), and un-

[22] S. F. Gait, M. J. Rance, C. W. Rees, and R. C. Storr, in preparation.

changed 2,2′-diaminobiphenyl (43 mg, 23%) (5% ethyl acetate–ether).

Diazotisation of 4,5-*Diaminofluorenone*.—(i) 4,5-*Diaminofluorenone*. 4-Nitro-9-oxofluorene-5-carboxylic acid [10] was prepared from phenanthraquinone *via* 4-nitrophenanthraquinone [23] and 6-nitrodiphenic acid.[10] 4-Nitro-9-oxofluorene-5-carboxylic acid (20 g) was heated under reflux for 4 h in the minimum quantity of freshly distilled thionyl chloride. The thionyl chloride was removed by distillation leaving 4-*nitro*-9-*oxofluorene*-5-*carbonyl chloride* (23·7 g, 100%), crystallised from ethanol as pale yellow needles, m.p. 150—152° (Found: C, 58·4; H, 2·0; N, 4·9. $C_{14}H_6ClNO_4$ requires C, 58·4; H, 2·1; N, 4·9%), $\lambda_{max.}$ 252 (ε 19,300), 280 (13,500) and 317 (4800) nm; $\nu_{max.}$ 1742 (C=O) and 1722 (C=O) cm^{-1}; *m/e* 289 and 287 (M^+). 4-Nitro-9-oxofluorene-5-carbonyl chloride (8 g) and an excess of sodium azide (2·3 g) were heated under reflux for 12 h in acetone (200 ml). After cooling, the mixture was poured into water (2 l) to give a red precipitate. This was extracted with chloroform and the extracts were dried (Na_2SO_4) and evaporated to give a mixture of 4-nitro-9-oxofluorene-5-carbonyl azide, 4-nitro-5-isocyanatofluorenone, and 4-amino-5-nitrofluorenone. This mixture was heated under reflux in benzene (300 ml) for 2 h; aqueous 50% potassium hydroxide (200 ml) was then added, and the mixture was boiled for a further 2 h. After cooling, the benzene layer was separated and the aqueous layer was further extracted with hot benzene. The combined extracts were dried (Na_2SO_4) and evaporated to give 4-*amino*-5-*nitrofluorenone* (5·5 g, 86%) as red needles from ethanol, m.p. 201—204° (Found: C, 64·7; H, 3·4; N, 11·4. $C_{13}H_8N_2O_3$ requires C, 65·0; H, 3·4; N, 11·7%), $\lambda_{max.}$ 229 (ε 17,800) and 259sh nm; $\nu_{max.}$ 3410 and 3350 (N–H), and 1690 (C=O) cm^{-1}; *m/e* 240 (M^+). Sodium sulphide (37·5 g) was added during 2 h to refluxing ethanol (350 ml) containing 4-amino-5-nitrofluorenone (7·5 g) and ammonium chloride (4 g). After addition was complete the solution turned purple and the mixture was refluxed for a further 1 h, cooled, and poured into water (3 l). The resulting mixture was extracted with ether until the extracts were colourless. These were then extracted with 20% hydrochloric acid to give a yellow solution which on neutralisation with dilute ammonia gave a purple solid. This was filtered off, washed with water and dried to give 4,5-*diaminofluorenone* (4·7 g, 71%) as red needles, m.p. 230—232° (from ethanol) (Found: C, 74·1; H, 5·0; N, 13·1. $C_{13}H_{10}N_2O$ requires C, 74·3; H, 4·8; N, 13·3%); $\lambda_{max.}$ 236 (ε 13,300), 250 (10,600), and 294 (4500) nm; $\nu_{max.}$ 3400 and 3340 (N–H), and 1683 (C=O) cm^{-1}; τ [$(CD_3)_2SO$] 3·0 (6H, s, aromatic) and 6·45br (4H, s, NH_2); *m/e* 210 (M^+), 182, and 154.

(ii) *Diazotisation with sodium nitrite in* 2N-*hydrochloric acid*. Sodium nitrite (350 mg, 5 mmol) in water (10 ml was added dropwise to a finely divided suspension of 4,5-diaminofluorenone (1·05 g, 5 mmol) in 2N-hydrochloric acid and maintained at 0—5°. After 1 h the resulting solution was allowed to warm to room temperature and gas was evolved. After several hours the solution was basified with ammonia and extracted with chloroform, and the extracts were chromatographed on silica gel. Elution with 5% ether–petroleum gave 4,5-*dichlorofluorenone* (10 mg, 8%) as yellow needles, m.p. 149—152°; *m/e* 250 (M^+), 248, 222, 220, 185, and 150; $\lambda_{max.}$ 252 (ε 10,400), 259 (16,800), and 268 (17,900) nm; $\nu_{max.}$ 1720 (C=O) cm^{-1}. Elution with 10% ether–petroleum gave 4-*chloro*-5-*hydroxyfluorenone* (164 mg, 14%) as orange needles from petroleum (b.p. 60—80°), m.p. 207—208° (Found: C, 67·3; H, 3·4. $C_{13}H_7ClO_2$ requires C, 67·7; H, 3·0%); $\lambda_{max.}$ 251 (ε 12,000), 256 (14,600), and 276 (6800) nm; $\nu_{max.}$ 3250 (OH) and 1690 (C=O) cm^{-1}; *m/e* 232 (M^+), 230, 195, 167, and 150. Further elution gave a trace of 4,5-dihydroxyfluorenone, *m/e* 212 (M^+), 184, 167, and 150; $\nu_{max.}$ 3280 (O–H) and 1696 (C=O) cm^{-1} Elution with 50% ether–petroleum gave unchanged 4,5-diaminofluorenone (38 mg, 4%).

(iii) *Diazotisation with pentyl nitrite in benzene*. 4,5-Diaminofluorenone (1·05 g, 5 mmol) was suspended in benzene (120 ml) containing pentyl nitrite (700 mg, 6 mmol) and the mixture was heated under reflux for 73 h. Evaporation and chromatography of the residue on silica gel (eluant in parentheses) gave 4-phenylfluorenone (128 mg, 10%), m.p. 110—111° (lit.,[24] 112°) (5% ether–petroleum), 4-aminofluorenone (152 mg, 15%), m.p. and mixed m.p. 138—139° (lit.,[25] 138°) (50% ether–petroleum), and unchanged 4,5-diaminofluorenone (52 mg, 5%) (ether).

(iv) *Diazotisation with pentyl nitrite in dichloromethane*. 4,5-Diaminofluorenone (105 mg, 0·5 mmol) and pentyl nitrite (59 mg, 0·5 mmol) were heated under reflux in dichloromethane (20 ml). The resulting mixture was evaporated and separated by preparative t.l.c. on silica gel with 50% ether–petroleum to give fluorenone (36 mg, 42%), m.p. and mixed m.p. 81—82°, and 4-aminofluorenone (22 mg, 22%), m.p. and mixed m.p. 138°.

4-*Phenylfluorenone*.—4-Aminofluorenone (98 mg, 0·5 mmol) was heated under reflux with pentyl nitrite (70 mg, 0·6 mmol) in benzene (30 ml) for 1 h. Preparative t.l.c. on silica gel gave, on elution with 20% ether–petroleum, 4-phenylfluorenone (76 mg, 59%), m.p. and mixed m.p. 111°.

Fluorenone.—4-Aminofluorenone (20 mg, 0·1 mmol) was heated under reflux for 1 h in methylene chloride containing 2 drops of pentyl nitrite. Evaporation followed by preparative t.l.c. on silica gel with 50% ether–petroleum as eluant gave fluorenone (14 mg, 76%), m.p. and mixed m.p. 82—83°.

5-*Methylfluoreno*[4,5-def][1,3]*diazepin*-10-*one* (15).—4,5-Diaminofluorenone (105 mg, 0·5 mmol) was heated at 140° for 2 min with an excess of triethyl orthoacetate. The mixture was poured into 50% hydrochloric acid (100 ml) to give an orange hydrochloride. This was neutralised with aqueous 5% ammonia to give a deep purple solid which was filtered off, dried, and sublimed at 250° and 0·2 Torr to give the *diazepinone* (105 mg, 90%) as purple needles, m.p. 227—230° (decomp.) (from ethanol) (Found: C, 76·7; H, 4·3; N, 11·9. $C_{15}H_{10}N_2O$ requires C, 77·0; H, 4·3; N, 12·0%); $\lambda_{max.}$ 227 (ε 21,300), 283 (8800), 290 (9500), and 314 (1600) nm; τ 1·8—2·6 (6H, m, aromatic) and 6·4 (3H, s, CH_3); *m/e* 234 (M^+), 219, 205, and 150.

Diazotisation of 2,2′-*Diamino*-6,6′-*dinitrobiphenyl*.[9]—Pentyl nitrite (0·22 ml) in benzene (250 ml) was added dropwise over 1 h to a refluxing solution of 2,2′-diamino-6,6′-dinitrobiphenyl (500 mg) in benzene (500 ml). After 5 h t.l.c. indicated disappearance of starting material. Evaporation followed by chromatography of the residue on basic alumina (elution with ethyl acetate) gave 1,3-*bis*-(2′-*amino*-6,6′-*dinitrobiphenyl*-2-*yl*)*triazene* (372 mg, 73%), m.p. 165—169° (from ethanol) (Found: C, 51·9; H, 3·3; N, 21·9. $C_{24}H_{17}N_9O_8$ requires C, 51·5; H, 3·0; N, 22·6%);

[23] J. Schmidt and O. Spoun, *Ber.*, 1922, **55**, 1194.
[24] K. Alder, J. Haydn, K. Heimbach, and K. Neufang, *Annalen*, 1954, **586**, 110.
[25] C. Graebe and P. Schestakow, *Annalen*, 1895, **284**, 311.

$\nu_{max.}$ 3410 and 3350 (N–H) cm^{-1}; *m/e* 531 ($M^+ - N_2$) 257, 211, 181, and 183.

Diazotisation of 2-Acetamido-2′-aminobiphenyl.[26]—(i) *With pentyl nitrite in benzene.* Pentyl nitrite (0·66 ml) in benzene (75 ml) was added dropwise over 1 h to a refluxing solution of 2-acetamido-2′-aminobiphenyl in benzene (125 ml). Heating was continued for 16 h after which evaporation and chromatography of the residue on silica gel (elution with 60% ether–petroleum) gave *2-acetamido-o-terphenyl*, m.p. 117—119° (from petroleum) (Found: C, 83·9; H, 6·2; N, 4·4. $C_{20}H_{17}NO$ requires C, 83·6; H, 6·0; N, 4·9%); $\nu_{max.}$ 3220 (N–H) and 1655 (C=O) cm^{-1}; τ 1·65—2·95 (13H, m, aromatic) and 8·08 (3H, s, CH_3); *m/e* 287 (M^+), 211, 180, 169, and 152.

(ii) *With pentyl nitrite in dichloromethane.* The foregoing procedure was repeated with dichloromethane as solvent. Chromatography on silica gel (elution with ether) gave *1,3-bis-(2′-acetamidobiphenyl-2-yl)triazene* (18; R = MeCO) (65%), yellow crystals from benzene–petroleum, m.p. 194—195° (decomp.) (Found: C, 72·3; H, 5·5; N, 14·5. $C_{28}H_{25}N_5O_2$ requires C, 72·6; H, 5·4; N, 15·1%); $\nu_{max.}$ 3200 (N–H) and 1655 (C=O) cm^{-1}; τ 1·9—2·1 (16H, m, aromatic H) and 8·15 (6H, s, CH_3).

Diazotisation of 2-Amino-2′-methylaminobiphenyl.—2-Amino-2′-methylaminobiphenyl was obtained by hydrogenation of 2-methylamino-2′-nitrobiphenyl over 10% palladium–charcoal, as crystals, m.p. 79—81°. 2-Methylamino-2′-nitrobiphenyl was obtained from 2-amino-2′-nitrobiphenyl by trifluoroacetylation, methylation, and hydrolysis as in the procedure described by Johnstone and his coworkers [27] for monomethylation of amines.

(i) *With pentyl nitrite in benzene.* Pentyl nitrite (0·32 ml) in benzene (150 ml) was added dropwise over 30 min to a refluxing solution of 2-amino-2′-methylaminobiphenyl (450 mg) in benzene (200 ml). After heating for 24 h the solvent was removed and the residue was chromatographed on basic alumina. Elution with 10% ether–petroleum gave *N*-methylcarbazole (125 mg, 35%), m.p. and mixed m.p. 85—87°.

(ii) *With pentyl nitrite in dichloromethane.* The foregoing procedure was repeated with dichloromethane as solvent and a total reaction time of 48 h to give *N*-methylcarbazole (72%).

(iii) *With sodium nitrite in* 2N-*hydrochloric acid.* Sodium nitrite (70 mg, 1 mmol) in water was added dropwise, with stirring, to a solution of 2-amino-2′-methylaminobiphenyl (198 mg, 1 mmol) in 2N-hydrochloric acid (10 ml) at 0—5°. After 30 min the resulting solution was allowed to warm to room temperature and was basified with sodium carbonate. The mixture was extracted with ether and the extracts were dried ($MgSO_4$) and evaporated. The residue was chromatographed on basic alumina. Elution with 10% ether–petroleum gave *N*-methylcarbazole (62 mg, 34%). Elution with 20% ether–petroleum gave 5-methyldibenzotriazepine (41 mg, 20%), identical with that obtained by methylation of dibenzotriazepine (see later).

Diazotisation of Diethyl Mesoxalate 2′-Aminobiphenyl-2-ylhydrazone (19).—(i) *Diethyl mesoxalate 2′-nitrobiphenyl-2-ylhydrazone.* 2-Amino-2′-nitrobiphenyl (6·5 g, 30 mmol) was stirred with concentrated hydrochloric acid (20 ml). After dilution with water (50 ml) the resulting suspension was cooled to 0° and sodium nitrite (2·5 g, 35 mmol) in water (10 ml) was added dropwise. After stirring for 30 min the diazonium solution was added slowly to a rapidly stirred suspension of diethyl malonate (4·8 g, 30 mmol) in water (20 ml). Sodium acetate was added in portions during addition of the diazonium compound to buffer the solution. The resulting oily precipitate was extracted into chloroform and adsorbed on neutral alumina for chromatography. Elution with 30% ether–petroleum gave *diethyl mesoxalate 2′-nitrobiphenyl-2-ylhydrazone* (4·8 g, 42%) as yellow crystals from ether–petroleum, m.p. 79—80° (Found: C, 59·2; H, 5·0; N, 10·8. $C_{19}H_{19}N_3O_6$ requires C, 59·2; H, 5·0; N, 10·9%); $\nu_{max.}$ 3250 (NH) and 1722 (C=O) cm^{-1}; τ 1·9—3·1 (8H, m, aromatic), 5·77 and 5·92 (4H, 2 overlapping q, *J* 7 Hz, CH_2), and 8·7 and 8·80 (6H, 2 overlapping t, *J* 7 Hz, CH_3).

(ii) *Diethyl mesoxalate 2′-aminobiphenyl-2-ylhydrazone* (19). The foregoing nitrohydrazone (1·5 g) in methanol was hydrogenated at 0° over 10% palladium–carbon. Removal of the solvent left a yellow oil which solidified. Crystallisation from ether–petroleum gave the *aminohydrazone* (19) (1·2 g, 87%) as yellow prisms, m.p. 105—107° (Found: C, 64·2; H, 5·7; N, 11·6. $C_{19}H_{21}N_3O_4$ requires C, 64·2; H, 5·9; N, 11·8%); $\nu_{max.}$ 3450, 3380, and 3200 (NH_2 and NH) and 1718 (C=O) cm^{-1}; τ 2·12—3·26 (8H, m, aromatic), 5·75 and 5·90 [6H, 2 overlapping q (4H after D_2O shake), *J* 7 Hz, CH_2 and NH_2], and 8·68 and 8·80 (6H, 2 overlapping t, *J* 7 Hz, CH_3).

(iii) *Diazotisation with diphenylnitrosamine.* A solution of the amino-hydrazone (19) (500 mg), glacial acetic acid (0·2 ml), and diphenylnitrosamine (300 mg) in benzene (15 ml) was heated under reflux for 3 h, then evaporated. The residue was chromatographed on silica gel. Elution with 10% ether–petroleum gave diphenylamine (172 mg, 68%), m.p. and mixed m.p. 54°. Elution with 15% ether–petroleum gave *diethyl carbazol-9-yliminomalonate* (20) (242 mg, 51%), m.p. 72—73·5° (from petroleum) (Found: C, 67·9; H, 5·5; N, 8·5. $C_{19}H_{18}N_2O_4$ requires C, 67·4; H, 5·4; N, 8·3%); *m/e* 338 (M^+), 166. The finely ground hydrazone (20) was stirred in concentrated hydrochloric acid for 16 h until the mixture became homogeneous. Basification gave *N*-aminocarbazole (96%), m.p. and mixed m.p. 150° (lit.,[28] 151°).

(iv) *Diazotisation with pentyl nitrite.* A mixture of the amino-hydrazone (19) (500 mg, 1·4 mmol) and pentyl nitrite (250 mg, 2 mmol) in benzene was heated under reflux for 16 h, then evaporated. The residue was chromatographed on silica gel. Elution with 15% ether–petroleum gave diethyl carbazol-9-yliminomalonate (20) (122 mg, 25%). Elution with 50% ether–petroleum gave *1,3-di-(2′-bisethoxycarbonylmethylenehydrazinobiphenyl-2-yl)triazene* [18; R = $N{:}C(CO_2Et)_2$] (290 mg, 58%) as bright yellow crystals, m.p. 172—174° (from ethanol) (Found: C, 63·4; H, 5·5; N, 13·6. $C_{38}H_{39}N_7O_8$ requires C, 63·3; H, 5·4; N, 13·6%); $\nu_{max.}$ 3250 (NH) and 1735 (C=O) cm^{-1}; τ 2·17—3·0 (16H, m, aromatic), 5·74 and 5·89 (8H, 2 overlapping q, *J* 7 Hz, CH_2), and 8·67 and 8·81 (12H, 2 overlapping t, *J* 7 Hz, CH_3). When the reaction was carried out in dichloromethane the same products were obtained in similar yields.

(v) *Diazotisation with sodium nitrite.* The amino-hydrazone (19) (335 mg, 1 mmol) in N-hydrochloric acid (10 ml) was treated with sodium nitrite (69 mg, 1 mmol) in water (5 ml) at 0—5°. After 30 min the diazonium solution

[26] S. Sako, *Mem. Coll. Eng. Kyushu Imp. Univ.*, 1932, **6**, 263 (*Chem. Abs.*, 1932, **26**, 3246).

[27] R. A. W. Johnstone, D. W. Payling, and C. Thomas, *J. Chem. Soc.* (*C*), 1969, 2223.

[28] A. V. Blom, *J. prakt. Chem.*, 1916, **94**, 77.

was neutralised with aqueous 5% ammonia and extracted with ether. The extracts were washed, dried, and evaporated, and the residue was subjected to preparative t.l.c. on silica gel to give diethyl carbazol-9-yliminomalonate (20) (207 mg, 60%).

5H-*Dibenzo*[d,f][1,2,3]*triazepine* (5).—A cold solution of 2,2′-diaminobiphenyl (1·84 g, 10 mmol) in 2N-hydrochloric acid (80 ml) was added over 2 min to a stirred solution of sodium nitrite (2·07 g, 30 mmol) in water (50 ml) at 0—5°. The mixture was stirred for 10 min and then basified with ice-cold aqueous 5% ammonia. A buff solid separated and was extracted from the cold solution with ether (3 × 50 ml). The extracts were washed with water, dried ($MgSO_4$), and evaporated to give 5H-*dibenzo*[d,f][1,2,3]-*triazepine* (1·42 g, 77%) as a brown oil which solidified on trituration with light petroleum. Recrystallisation from ether–petroleum gave yellow crystals, m.p. 98—99° (decomp.) (Found: C, 73·4; H, 4·6; N, 21·5. $C_{12}H_9N_3$ requires C, 73·8; H, 4·6; N, 21·5%); $\lambda_{max.}$ 239 (ε 27,300), 265 (9750), and 294 (5850) nm; $\nu_{max.}$ 3271 (N–H), 1618, 1595, 1270, 765, 750, and 720 cm^{-1}; τ 2·4—2·95 (aromatic H), *m/e* 195 (M^+), 167 ($M - N_2$), and 152.

By using the same procedure the following dibenzotriazepines were obtained as unstable oils which decomposed on attempted distillation. They were therefore characterised by conversion into their isomeric benzocinnoline *N*-imides.[6] 3-*Methoxy*-5H-*dibenzo*[d,f][1,2,3]*triazepine*, from 2,2′-diamino-4-methoxybiphenyl [29] (62%), showed *m/e* 225 (M^+) and 197 ($M - N_2$); $\lambda_{max.}$ 232 (ε 18,400), 262sh, and 290 (5100) nm; $\nu_{max.}$ 3335 (NH), 1608, 1282, 1021, and 757 cm^{-1}; τ 2·4—3·3 (7H, m, aromatic) and 6·08 (3H, s, OMe). 3-*Methyl*-5H-*dibenzo*[d,f][1,2,3]*triazepine*, from 2,2′-diamino-4-methylbiphenyl [29] (74%), showed *m/e* 209 (M^+) and 181 ($M - N_2$); $\lambda_{max.}$ 236 (ε 20,600), 264 (12,250), and 292 (5500) nm; $\nu_{max.}$ 3280 (N–H), 1618, 1280, 1206, 1098, 772, and 715 cm^{-1}; τ 2·5—3·0 (7H, m, aromatic) and 7·6 (3H, s, Me). 3,9-*Dimethoxy*-5H-*dibenzo*[d,f][1,2,3]*triazepine*, from 2,2′-diamino-4,4′-dimethoxybiphenyl (obtained by reduction of 4,4′-dimethoxy-2,2′-dinitrobiphenyl [29]) (62%), showed *m/e* 255 (M^+) and 227 ($M - N_2$); $\lambda_{max.}$ 235 (ε 23,900), 268 (12,000), and 300 (6100) nm; $\nu_{max.}$ 3300 (N–H), 1618, 1280, 1250, 1045, and 816 cm^{-1}; τ 2·5—3·3 (6H, m, aromatic) and 6·12 (6H, s, OMe).

5H-*Dibenzo*[d,f][1,2,3]*triazepine from Biphenyl-2,2′-bisdiazonium Bistetrafluoroborate*.—2,2′-Diaminobiphenyl dihydrochloride (1·29 g, 5 mmol) in water (15 ml) and 2N-hydrochloric acid (10 ml) at 0° was added dropwise to a stirred solution of sodium nitrite (1·04 g, 15 mmol) in water (15 ml), also at 0°. After 15 min sodium tetrafluoroborate (1·0 g, 3 mmol) in water (10 ml) was added and the mixture was stirred for 2 h. The resulting precipitate was filtered off and washed with water, ethanol, and ether to give biphenyl-2,2′-bisdiazonium bistetrafluoroborate (1·62 g, 85%), m.p. 138° (lit.,[13] 133—134°). The bistetrafluoroborate (380 mg, 1 mmol) was suspended in water (10 ml) at room temperature. This stirred suspension was basified with aqueous 5% ammonia whereupon gas was evolved. After 1 h, extraction with ether gave 5*H*-dibenzo[d,f][1,2,3]-triazepine (115 mg, 60%).

Naphtho[1,8-de]*triazine* (23).—1,8-Diaminonaphthalene (1·58 g, 10 mmol) in dichloromethane was converted into its dihydrochloride with hydrogen chloride gas. The salt was filtered off, dried, and suspended in N-hydrochloric acid (100 ml) at 0—5°, and sodium nitrite (1·73 g, 25 mmol) in water (20 ml) was added rapidly. The solution was stirred for 15 min and basified with aqueous 5% ammonia to give naphtho[1,8-*de*]triazine (1·1 g, 65%), m.p. and mixed m.p. 236—237° (lit.,[30] 236—237°) (from ethanol).

Reactions of 5H-*Dibenzo*[d,f][1,2,3]*triazepine* (5).—(i) *Thermolysis in benzene*. A solution of dibenzotriazepine (1·95 g) in dry benzene (50 ml) was heated under reflux for 1 h, cooled, and evaporated to give benzocinnoline *N*-imide (1·71 g, 88%), m.p. and mixed m.p. 126°.

Similar treatment of 3-methyl- and 3-methoxy-dibenzo-[*d,f*][1,2,3]triazepine gave 3-methyl- and 3-methoxybenzocinnoline 6-imides.[6]

(ii) *Thermolysis in bis-(2-methoxyethyl) ether*. Dibenzotriazepine (195 mg) in bis-(2-methoxyethyl) ether (15 ml) was added dropwise to the refluxing ether (15 ml). After 0·5 h, the solution was cooled, poured into water (500 ml), and extracted with ether. The extracts were dried (Na_2SO_4) and evaporated to give carbazole (165 mg, 100%).

Similar pyrolysis of 3-methyldibenzo[*d,f*][1,2,3]triazepine gave 2-methylcarbazole (84%), m.p. and mixed m.p. 256—258° (lit.,[31] 259°). 3-Methoxydibenzo[*d,f*][1,2,3]triazepine gave 2-methoxycarbazole (89%), m.p. 231—233° (lit.,[32] 234°).

(iii) *Reaction with hydriodic acid*. Hydriodic acid (10 ml; 55% w/w) was added to dibenzotriazepine (195 mg) to give an immediate effervescence. After stirring for 2 h the solution was diluted with water (50 ml), basified, and extracted with ether. Evaporation of the dried extracts gave a yellow gum which was purified by preparative t.l.c. on silica gel with ether–petroleum as eluant. This gave 2-amino-2′-iodobiphenyl (210 mg, 77%), m.p. 129—130° (from ether) (lit.,[33] 129—130°).

(iv) *Reaction with hydrobromic acid*. Dibenzotriazepine (195 mg) was treated with an excess of 48% hydrobromic acid (10 ml). A few copper turnings were added and the solution was stirred overnight. The resulting mixture was diluted with water (100 ml) and heated under reflux for 30 min. The almost clear solution was filtered, cooled, basified with ammonia and extracted with ether. Evaporation of the dried extracts gave 2-amino-2′-bromobiphenyl (210 mg, 85%), which solidified on trituration with petroleum; m.p. 45—48° (lit.,[34] 46—50°).

(v) *Reaction with hydrazine*. Dibenzotriazepine (195 mg, 1 mmol) and hydrazine hydrochloride (67 mg, 1 mmol) were stirred overnight in water (15 ml). The mixture was diluted with water and extracted with ether, and the extracts were dried and evaporated to give 2-amino-2′-azidobiphenyl (204 mg, 96%). In a similar procedure using hydrazine hydrate, the extracts were chromatographed on basic alumina to give, on elution with 20% ether–petroleum, carbazole (17 mg, 10%), followed by 2-amino-2′-azidobiphenyl (147 mg, 70%).

(vi) *Reaction with diethyl malonate*. Diethyl malonate (176 mg, 1·1 mmol) was added dropwise to a stirred solution of dibenzotriazepine (195 mg, 1 mmol) in aqueous sodium acetate. After 24 h the product was extracted with ether

[29] W. Baker, J. W. Barton, and J. F. W. McOmie, *J. Chem. Soc.*, 1958, 2658.
[30] H. Sieper, *Chem. Ber.*, 1967, **100**, 1646.
[31] W. Borsche, *Annalen*, 1908, **359**, 75.
[32] J. A. Cummins and M. L. Tomlinson, *J. Chem. Soc.*, 1955, 3475.
[33] L. Mascarelli and D. Gatti, *Att. accad. naz. Lincei, Rend. Classe Sci. fis. mat. nat.*, 1931, **13**, 887.
[34] L. Mascarelli and G. Benati, *Gazzetta*, 1908, **38**, 624.

and purified by preparative t.l.c. on silica gel with 50% ether–petroleum as eluant to give diethyl mesoxalate 2′-aminobiphenyl-2-ylhydrazone (210 mg, 60%), m.p. and mixed m.p. 106—108°.

(vii) *Catalytic reduction.* Dibenzotriazepine (195 mg) in methanol (30 ml) was shaken under hydrogen at room temperature in the presence of 10% palladium–charcoal. No apparent uptake of hydrogen was observed. After 3 h, the solution was filtered and evaporated to give 2-aminobiphenyl (160 mg, 96%), m.p. and mixed m.p. 50°.

Similar reduction of 3-methoxydibenzo[*d*,*f*][1,2,3]triazepine gave an inseparable mixture of 2-amino-4-methoxybiphenyl and 2-amino-4′-methoxybiphenyl (90%), *m/e* 199 (M^+); $\nu_{max.}$ 3420 and 3372 (N–H) cm^{-1}; τ 2·6—3·4 (8H, m, aromatic), 6·2 (1·5H, s, MeO), 6·25 (1·5H, s, MeO), and 6·5 (2H, s, NH_2). The mixture of amines (90 mg) in 2N-sodium hydroxide (8 ml) was shaken with benzoyl chloride (2 drops) for 15 min, then extracted with ether; the extracts were washed, dried and subjected to preparative t.l.c. on silica gel with 70% ether–petroleum as eluant to give 2-benzamido-4′-methoxybiphenyl (26 mg, 29%), m.p. 84—86° (lit.,[35] 84—85°), and 2-benzamido-4-methoxybiphenyl (41 mg, 46%), m.p. 141—144° (lit.,[35] 144—145°).

Reduction of 3-methyldibenzo[*d*,*f*][1,2,3]triazepine gave an inseparable mixture of 2-amino-4-methylbiphenyl and 2-amino-4′-methylbiphenyl (78%), *m/e* 183 (M^+); $\nu_{max.}$ 3430 and 3380 (N–H) cm^{-1}; τ 2·5—2·8 (8H, m, aromatic), 6·4—6·6br (2H, s, NH_2), 7·6 (1·5H, s, Me), and 7·7 (1·5H, s, Me).

(viii) *Irradiation.* A solution of dibenzotriazepine (5) (195 mg) in acetonitrile (200 ml) was irradiated with a Hanovia medium-pressure 125 W lamp with a quartz filter. The resulting mixture was concentrated and chromatographed on alumina. Elution with 5% ether–petroleum gave a trace of 2-aminobiphenyl (t.l.c.); 20% ether–petroleum gave carbazole (10 mg, 6%); 40% ether–petroleum gave benzocinnoline *N*-imide (60 mg, 36%); ether gave benzocinnoline (58 mg, 32%).

A similar procedure with benzophenone (2 g) as sensitiser gave carbazole (8%) and benzocinnoline (57%).

Control Experiments with 5H-*Dibenzo*[d,f][1,2,3]*triazepine* (5).—(i) *Chromatography.* Dibenzotriazepine (195 mg, 1 mmol) was adsorbed on and chromatographed on silica gel. Elution with 20% ether–petroleum gave carbazole (36%); 30% ether–petroleum gave benzocinnoline *N*-imide (40%) followed by a mixture of this and unchanged dibenzotriazepine. Ether gave benzocinnoline (10%). A similar procedure with an alumina column gave carbazole (14%), benzocinnoline *N*-imide (30%), and an inseparable mixture of the *N*-imide and unchanged dibenzotriazepine.

(ii) *Acetic acid.* Dibenzo[*d*,*f*][1,2,3]triazepine (195 mg) was stirred for 2·5 h with 50% acetic acid (50 ml). The solution was then poured into water (100 ml), basified with ammonia, and extracted with ether to give carbazole (130 mg, 78%).

(iii) *Hydrochloric acid.* Repetition of the foregoing procedure with 5N-hydrochloric acid gave carbazole (112 mg, 67%). Repetition with 2N-hydrochloric acid and a reaction time of 24 h gave a dark solution which was basified with ammonia and extracted with ether. Evaporation followed by preparative t.l.c. of the residue on silica gel with 50% ether–petroleum as eluant gave carbazole (22 mg, 12%), 2-amino-2′-azidobiphenyl (34 mg, 16%), unchanged dibenzotriazepine, and benzocinnoline *N*-imide (46 mg, 23%), and benzocinnoline (15 mg, 8%).

Repetition of the foregoing procedure with concentrated hydrochloric acid gave unchanged triazepine (95%).

(iv) 2,2′-*Diaminobiphenyl.* A mixture of dibenzotriazepine (195 mg, 1 mmol) and 2,2′-diaminobiphenyl (184 mg, 1 mmol) in 2N-hydrochloric acid (10 ml) and ethanol (5 ml) was stirred overnight at room temperature. The mixture was diluted with water, basified, and extracted with ether. The dried extracts were evaporated and the residue was subjected to preparative t.l.c. on silica gel with ether as eluant. This gave carbazole (17 mg, 10%) and 1,3-bis-(2′-aminobiphenyl-2-yl)triazene (11) (306 mg, 81%), m.p. 178—182° (decomp.).

(v) *Benzocinnoline N-imide* (10). A mixture of dibenzotriazepine (195 mg, 1 mmol) and benzocinnoline *N*-imide (195 mg, 1 mmol) in 2N-hydrochloric acid was stirred overnight, basified with dilute ammonia, and extracted with ether. The extracts were dried and evaporated and the residue was chromatographed on alumina. Elution with 20% ether–petroleum gave carbazole (16 mg, 10%) followed by 2-amino-2′-azidobiphenyl (120 mg, 30%). Elution with ether gave benzocinnoline (74 mg, 25%).

5-*Methyldibenzo*[d,f][1,2,3]*triazepine.*—(i) n-Butyl-lithium in hexane (6 mmol) was added dropwise to a solution of 5*H*-dibenzo[*d*,*f*][1,2,3]triazepine (980 mg, 5 mmol) in dry tetrahydrofuran (40 ml) maintained at −30° under nitrogen. The resulting purple solution was stirred for 15 min and then a large excess of methyl iodide was added. The mixture was allowed to warm slowly to room temperature, was stirred overnight, and then was evaporated onto alumina and chromatographed. Elution with 10% ether–petroleum gave 5-*methyldibenzo*[d,f][1,2,3]*triazepine* (730 mg, 67%) as a bright yellow solid, m.p. 66—67° (decomp.) (from ether–petroleum) (Found: C, 74·4; H, 5·2; N, 20·0. $C_{13}H_{11}N_3$ requires C, 74·6; H, 5·3; N, 20·1%); $\lambda_{max.}$ 242 (ε 23,000) and 295 (6500) nm; $\nu_{max.}$ 1599, 1537, 1430, 1276, 1250, 1043, 882, 857, 812, 761, and 726 cm^{-1}; τ 2·5—2·7 (8H, m, aromatic) and 6·5 (3H, s, CH_3); *m/e* 209 (M^+), 181 ($M - N_2$), 167, and 152.

(ii) Thallium ethoxide (1·2 g) was added to a stirred solution of dibenzotriazepine (390 mg) in dry dimethylformamide (10 ml) and ether (5 ml). After 30 min an excess of methyl iodide was added. The mixture was set aside overnight, then poured into water (500 ml), and extracted with ether. The dried extracts were evaporated and chromatographed on alumina. Elution with 5% ether–petroleum gave 2-dimethylaminobiphenyl (28 mg, 7%), m.p. and mixed m.p. 226—228° (lit.,[36] 228°); 10% ether–petroleum gave 5-methyldibenzo[*d*,*f*][1,2,3]triazepine (171 mg, 40%), m.p. 66—67°.

Reactions of 5-*Methyldibenzo*[d,f][1,2,3]*triazepine.*—(i) *Thermolysis.* (a) *In benzene.* The triazepine was recovered (96%) after 48 h from its solution in refluxing benzene.

(b) *In bis-(2-methoxyethyl) ether.* The triazepine (209 mg) in bis-(2-methoxyethyl) ether (20 ml) was added dropwise to the refluxing ether (15 ml). After 1 h the mixture was cooled, poured into water, and extracted with ether. Evaporation of the dried extracts followed by crystallisation from ether–petroleum gave *N*-methylcarbazole (100%).

(ii) *Hydrogenation.* The triazepine (209 mg) in methanol (30 ml) was shaken under hydrogen in the presence of 10%

[35] I. G. M. Campbell and D. J. Morrill, *J. Chem. Soc.*, 1955, 1662.

[36] D. H. Hey and E. R. B. Jackson, *J. Chem. Soc.*, 1934, 645.

palladium–charcoal at room temperature. No change in gas volume was observed, and after 3 h the solution was filtered and the methanol removed to give 2-methylaminobiphenyl (141 mg, 77%), identical with a specimen synthesised by methylation of 2-aminobiphenyl.[36]

(iii) *Irradiation.* 5-Methyldibenzotriazepine (209 mg) in dry ether (200 ml) was irradiated with a Hanovia medium pressure 125 W lamp (quartz filter). Evaporation of the solution left *N*-methylcarbazole (178 mg, 100%).

3-Methoxy-5- and 7-methyldibenzo[d,f][1,2,3]*triazepines.* Methylation of 3-methoxydibenzotriazepine (300 mg) by the procedure (i) described for methylation of dibenzotriazepine (5) gave an inseparable mixture of 3-methoxy-5-methyldibenzo[*d,f*][1,2,3]triazepine and 3-methoxy-7-methyldibenzo[*d,f*][1,2,3]triazepine (243 mg, 76%) as an oil, b.p. 142—146° at 0·1 mmHg (Found: C, 70·2; H, 5·3; N, 17·7. $C_{14}H_{13}N_3O$ requires C, 70·3; H, 5·4; N, 17·6%); τ 2·3—3·0 (7H, m), 6·10 (2·2H, s, OMe), 6·15 (0·8H, s, OMe), 6·45 (2·2H, s, NMe), and 6·47 (0·8H, s, NMe); *m/e* 239 (M^+), 211 ($M - N_2$), 196, 182, 168, 167, and 152.

Benzoylation of 5H-*Dibenzo*[d,f][1,2,3]*triazepine* (5).—n-Butyl-lithium in hexane (4 mmol) was added dropwise to a solution of the triazepine (585 mg, 3 mmol) in dry tetrahydrofuran (30 ml) at −50°. After 15 min benzoyl chloride (490 mg, 3·5 mmol) was added and the mixture was allowed to warm to room temperature and left overnight. Evaporation followed by chromatography on alumina gave, with 10% ether–petroleum, a trace of carbazole and, with 20% ether–petroleum, *2-benzamido-2′-chlorobiphenyl* (645 mg, 70%) as yellow prisms, m.p. 60—61° (from ether–petroleum) (Found: C, 74·4; H, 4·8; N, 4·8. $C_{19}H_{14}ClNO$ requires C, 74·2; H, 4·6; N, 4·6%); $\nu_{max.}$ 1725 (C=O) cm^{-1}; *m/e* 309 (M^+) and 307 (M^+).

Ethoxycarbonylation of 5H-*Dibenzo*[d,f][1,2,3]*triazepine* (5).—The triazepine (585 mg) was converted into its lithium salt as before. Treatment with ethyl chloroformate followed by a similar work-up gave *2-chloro-2′-ethoxycarbonylaminobiphenyl* (520 mg, 63%) as an oil, b.p. 168—173° at 0·1 mmHg (Found: C, 66·1; H, 4·8; N, 5·1. $C_{15}H_{14}ClNO_2$ requires C, 65·3; H, 5·1; N, 5·1%); $\nu_{max.}$ 3420 (N–H) and 1740 (C=O) cm^{-1}; $\lambda_{max.}$ 223 (ε 15,000) and 245 (8900) nm; τ 2·5—2·7 (8H, m, aromatic), 5·75 (2H, q, CH_2), and 8·6 (3H, t, CH_3); *m/e* 277 (M^+) and 275 (M^+).

Attempted Preparation of 5-Aminodibenzo[d,f][1,2,3]*triazepine* (1).—(i) *By amination with hydroxylamine O-sulphonic acid (HOS).* Sodium hydride (50% dispersion in oil; 96 mg, 2 mmol) was added to a stirred solution of dibenzotriazepine (5) (390 mg, 2 mmol) in dry ether (20 ml) at room temperature. After 3 h, the ether was evaporated off and the residue was dissolved in dry dimethylformamide. HOS (678 mg, 6 mmol) was added over 1 h with stirring and the mixture was poured into water and extracted with ether. The dried extracts were evaporated and chromatographed on alumina. Elution with 15% ether–petroleum gave carbazole (102 mg, 31%). Elution with 25% ether–petroleum gave 2-amino-2′-azidobiphenyl (186 mg, 44%) and with ether gave benzocinnoline (13 mg, 4%). A similar procedure using dimethylformamide containing an excess of sodium hydrogen carbonate gave carbazole (2%) and 2-amino-2′-azidobiphenyl (67%). Similar mixtures of carbazole and 2-amino-2′-azidobiphenyl were obtained on treatment of the lithium salt of dibenzotriazepine with HOS.

(ii) *By amination with O-(mesitylsulphonyl)hydroxylamine (MSH).* (*a*) n-Butyl-lithium (2 mmol) was added slowly to the dibenzotriazepine (5) (390 mg, 2 mmol) in dry tetrahydrofuran at −50° under nitrogen. After 15 min, MSH (430 mg, 2 mmol) in dry tetrahydrofuran (8 ml) was added dropwise and the mixture was allowed to warm to room temperature and left for 24 h. The tetrahydrofuran was removed and the residue was subjected to preparative t.l.c. on silica gel with 50% ether–petroleum as eluant. This gave 2-amino-2′-azidobiphenyl (168 mg, 40%), *N*-aminocarbazole (25 mg, 8%), m.p. and mixed m.p. 150—151° (lit.,[28] 151°), and benzocinnoline (18 mg, 5%).

(*b*) Dibenzotriazepine (5) (195 mg, 1 mmol) in dry ether (15 ml) was converted into its sodium salt by stirring with sodium hydride (50% dispersion in oil; 48 mg, 1 mmol) for 15 min. MSH (215 mg, 1 mmol) was added over 30 min, vigorous effervescence being noted. After a further 30 min the mixture was filtered and concentrated and the products were separated by preparative t.l.c. on silica gel with 50% ether–petroleum. This gave 2-amino-2′-azidobiphenyl (63 mg, 30%) and *N*-aminocarbazole (75 mg, 14%), m.p. and mixed m.p. 149—151°.

(iii) *From biphenyl-2,2′-bisdiazonium bistetrafluoroborate with hydrazine.* Hydrazine hydrate was added to a stirred suspension of biphenyl-2,2′-bisdiazonium bistetrafluoroborate (380 mg) in water (15 ml). After 30 min, the products were extracted with ether and chromatographed on alumina. Elution with 5% ether–petroleum gave 2,2′-diazidobiphenyl (182 mg, 77%); 10% ether–petroleum gave carbazole (6 mg, 4%); and ether gave benzocinnoline (9 mg, 5%).

(iv) *By reduction of biphenyl-2,2′-bisdiazonium bistetrafluoroborate.* Sodium borohydride (61 mg, 1·65 mmol) was added slowly to a stirred suspension of the bisdiazonium salt (570 mg, 1·5 mmol) in methanol at 5°. After 30 min the mixture was poured into ice-cold 2N-hydrochloric acid and extracted with chloroform, and the extracts were dried and evaporated. Preparative t.l.c. on silica gel (50% ether–petroleum) gave 2-amino-2′-azidobiphenyl (30 mg, 10%), *N*-aminocarbazole (33 mg, 12%), and benzocinnoline (57 mg, 21%).

Reaction of 5H-*Dibenzo*[d,f][1,2,3]*triazepine* (5) *with Angeli's Salt.*[20]—Freshly prepared Angeli's salt ($Na_2N_2O_3$; 240 mg, 2 mmol) was added to a solution of dibenzotriazepine in 70% aqueous ethanol (30 ml). The mixture was stirred for 60 h and then diluted with water (200 ml). Extraction with ether followed by preparative t.l.c. of the extracts on alumina with petroleum as eluant gave biphenyl (48 mg, 62%), m.p. and mixed m.p. 70—71°. A mixture of dibenzotriazepine and benzocinnoline *N*-imide (5 mg, 5%) and benzocinnoline (15 mg, 17%) were recovered from the base line and separated by further preparative t.l.c. on alumina with 50% ether–petroleum as eluant.

Repetition of the foregoing procedure with solutions of dibenzotriazepine containing tetraphenylcyclopentadienone or dimethyl acetylenedicarboxylate gave similar yields of biphenyl. Biphenylene was not detected in any of these reactions.

9,20-Dihydrotetrabenzo[d,f,k,m][1,2,3,8,9,10]*hexa-azacyclotetradecine* (12).—Pentyl nitrite (20 mg) and 1,3-bis-(2′-aminobiphenyl-2-yl)triazene (90 mg) were heated under reflux for 15 min in dichloromethane (50 ml) containing one drop of hydrochloric acid. The resulting solution was evaporated and the residue was chromatographed on alumina. Elution with 30% ether–petroleum gave compound (12) (59 mg, 63%), m.p. and mixed m.p. 208—210°.

Reactions of 9,10-*Dihydrotetrabenzo*[d,f,k,m][1,2,3,8,9,10]-*hexa-azacyclotetradecine* (12).—(i) *Pyrolysis.* The bis-triazene (12) (116 mg) was heated under reflux for 16 h in bis-(2-methoxyethyl) ether (19 ml). The resulting mixture was poured into water to give a precipitate of carbazole (25 mg). Further carbazole (52 mg) was obtained by extraction of the aqueous mixture with dichloromethane (total yield 77%).

(ii) *Irradiation.* The bis-triazene (12) (200 mg) in acetonitrile (200 ml) and dichloromethane (25 ml) was irradiated with a Hanovia medium-pressure 125 W lamp (quartz jacket). After 22 h, no triazene remained. The mixture was concentrated and chromatographed on alumina. Elution with 50% ether–petroleum gave carbazole (61 mg, 36%). The remainder of the mixture appeared to be polymeric.

(iii) *Reduction.* The bis-triazene (12) (150 mg) in ethyl acetate (100 ml) was stirred under hydrogen in the presence of Adams catalyst for 24 h. Although hydrogen uptake had not ceased the mixture was filtered, concentrated, and chromatographed on alumina. Elution with 30% ether–petroleum gave unchanged bis-triazene (12) (90 mg, 66%); ethyl acetate gave 2,2′-diaminobiphenyl (42 mg, 30%).

(iv) *Oxidation.* (a) *With lead tetra-acetate.* Lead tetra-acetate (500 mg) was added in portions to a stirred solution of the bis-triazene (12) (195 mg) in dichloromethane (30 ml). When gas evolution had ceased, the mixture was filtered to remove lead salts and the filtrate was concentrated and chromatographed on alumina. Elution with petroleum gave *NN′*-bicarbazolyl (49 mg, 30%), m.p. and mixed m.p. 217—221 (lit.,[37] 221°). Elution with 30% ether–petroleum gave carbazole (27 mg, 16%) and with 75% ether–petroleum gave benzocinnoline (36 mg, 20%).

(b) *With* 2,3-*dichloro*-5,6-*dicyano*-1,4-*benzoquinone* (*DDQ*). The bis-triazene (12) (100 mg) and DDQ (50 mg) were heated under reflux in benzene for 30 min. This gave a brown precipitate (104 mg) which appeared to be a complex between the reactants. Chromatography of the mixture on alumina, with petroleum as eluant, gave *NN′*-bicarbazolyl (11 mg, 13%).

(c) *With pentyl nitrite.* The bis-triazene (12) (200 mg) and pentyl nitrite (0·5 ml) were heated under reflux in benzene (60 ml) for 2·5 h. The benzene was removed by distillation and the residue was chromatographed on alumina to give *NN′*-bicarbazolyl (20 mg, 13%) and carbazole (45 mg, 27%).

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