INTERCONVERSIONS OF SOME NITROGEN-CONTAINING HETEROCYCLIC SYSTEMS (REVIEW)

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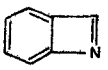
Most of our recent research has been devoted to the synthesis and chemistry of five-, six-, and seven-membered heterocycles containing three adjacent nitrogen atoms: 1,2,3-triazoles, 1,2,3-triazines, and 1,2,3-triazepines. Special attention was directed to their conversion to other heterocyclic systems.

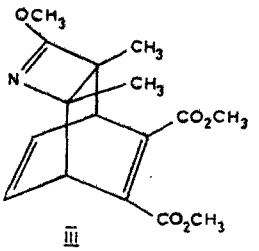
Although these triazaheterocycles are of interest in themselves, our research arose as a result of attempts to create three types of reactive compounds: dehydrogenated aromatic systems, 1H-azirines, and azacyclobutadiene (azete) derivatives (I, II). The last two types are similar to cyclobutadiene and benzocyclobutadiene – highly reactive antiaromatic carbocycles – and are the simplest 4π-electron nitrogen-containing heterocyclic systems. Heterocyclic analogs of this sort which, despite a number of early attempts [1] to obtain them, are still unknown, will have great theoretical and synthetic value.

I

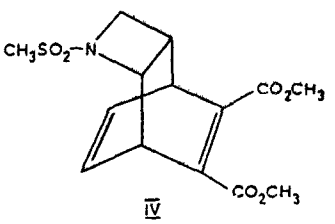


II

Of the very small number of published papers on the preparation of azetes, the method in [2], which was based on reverse Diels–Alder reactions of III and IV, is of interest. A certain amount of dimethyl phthalate was obtained from diester III, but methoxydimethylazete was not detected. Compound IV was also converted to dimethyl phathalate, but the azetine, which might have given strictly the azete on subsequent elimination, was not obtained.



III



IV

We decided to commence our research with a study of benzazete (II), feeling that it would be easier to obtain it and that it would be stabilized by the benzene ring. Our synthesis was based on the following facts. cis,cis-1,4-Dicyanobutadiene (VI) is the stable product of a number of reactions in which o-dinitrenobenzene (V) formally participates: oxidation of o-phenylenediamine [3, 4] or 2-aminobenzotriazole [5] and thermal decomposition of o-diazidobenzene [6]. In contrast to this, cis,cis-octa-3,5-diene-1,7-diyne (VII) is unstable and is readily cyclized to benzocyclobutadiene [7]. In this connection, particles of the o-nitrenophenylcarbene (VIII) type seem of great interest, inasmuch as they may be cyclized to give the required benzazete (II) or may be cleaved to give cyanoacetylene IX. The cyanoacetylene in turn may be thermally or photochemically cyclized in analogy with diacetylene VII to benzazete II.

The apparent precursor of the carbenonitrene of the VIII type is the corresponding diazoazide (for example, XI). It was found that X is obtained with certain difficulties, inasmuch as the usual synthesis of azidohydrazone X from ketone and hydrazine in hot ethanol in the presence of acetic acid gave 3-methylindazole in very high yield. This usual but smooth and, apparently, general reaction is a good method for

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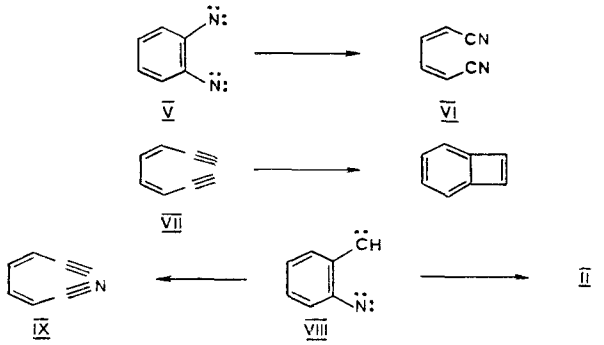
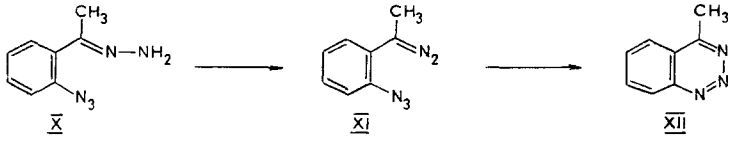
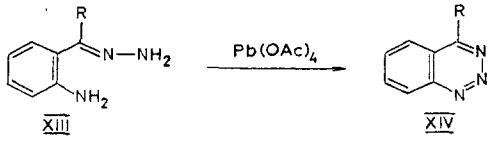


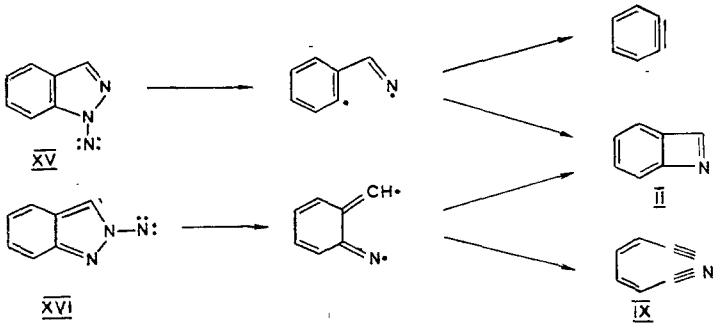
the preparation of indazoles and is worthy of further study. However, azidohydrazone X can be obtained from the azidoketone and hydrazine at room temperature in the presence of iodine as a catalyst. Diazoazide XI, which was converted to 4-methylbenzotriazine (XII) in high yield by thermal decomposition in hot benzene, was obtained by oxidation of the hydrazone with mercuric oxide. Thus, only one mole rather than two moles of nitrogen was split out, but this result is, nevertheless, interesting, inasmuch as simple aromatic 1,2,3-triazines are currently almost unknown [8]. The decomposition of the diazoazide under more severe conditions led to unidentified mixtures. When the methyl group in diazoazide XI was replaced by a hydrogen atom, the diazoazide proved to be unstable, and attempts to replace it by a phenyl group were unsuccessful because cyclization to 3-phenylindazole could not be avoided.



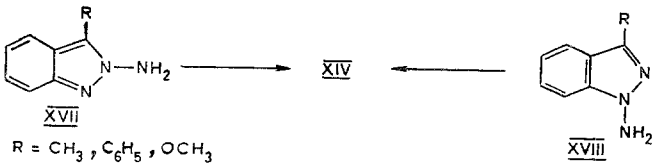
Oxidation of readily accessible o-aminohydrazones XIII (R = CH_3, C_6H_5) [9] with lead tetraacetate in methylene chloride at room temperature proved to be a simpler method for the preparation of the triazines. In this case, triazines XIV were obtained in moderate yields along with the corresponding o-acetamidoketones.



Another approach to the synthesis of compounds with the stoichiometry of a carbenonitrene was based on the results of our investigation of the oxidation of 1-and 2-aminobenzatriazoles [5]. The first of these compounds gave the 1-nitrene, which, on splitting out two moles of nitrogen, was converted to dehydrobenzene; the second compound gave the 2-nitrene, which split out one mole of nitrogen to give dicyanobutadiene VI. The analogous oxidation of 1- and 2-aminoindazoles should have led to N-nitrenes XV and XVI, which would undergo cleavage to give, respectively, dehydrobenzene and (or) benzazete (II) and benzazete and (or) cyanoacetylene IX.

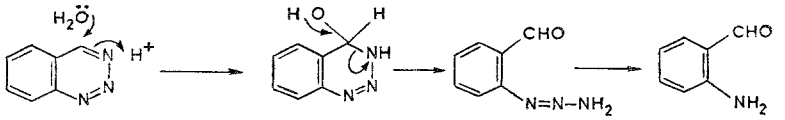


However, aminoindazoles XVII and XVIII [10] are oxidized very rapidly by lead tetraacetate under mild conditions, to give benzotriazines XIV in high yields. They are possibly formed from the intermediate nitrenes with ring expansion.

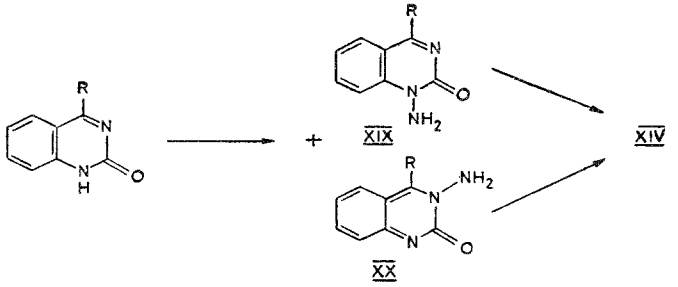


The above-indicated methods for the preparation of benzotriazines are inapplicable when R = H, and the oxidation of unsubstituted N-aminoindazole leads to benzotriazine XIV (R = H) only when absolutely no nucleophilic reagents are present. It is not surprising that the C_4 atom in benzotriazine is very electrophilic and that benzotriazine XIV is hydrated at the 3, 4 bond to give o-aminobenzaldehyde.

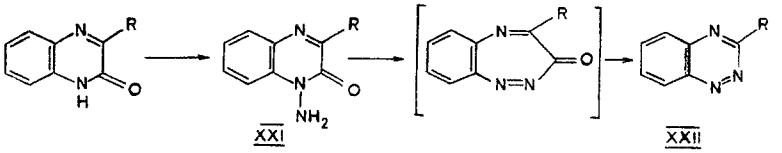
Yet another method for the synthesis of benzotriazines, which also includes rearrangement of nitrenes, is based on the oxidation of 1- and 3-aminoquinazolones XIX and XX. In this case the benzotriazines are



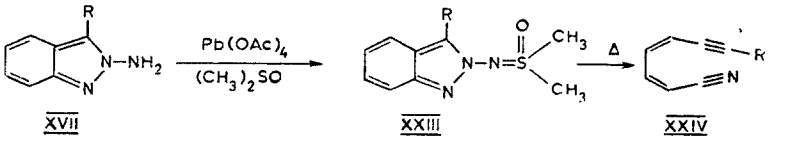
possibly formed from the nitrenes by ring expansion with subsequent splitting out of carbon monoxide (compare XXI and XXII).



This type of reaction was first observed in the monocyclic series during the oxidative transformation of 1-amino-2-pyridones to pyridazines [11]. A similar transformation of 1-aminoquinoxalones XXI to benzo-1,2,4-triazines XXII is also known [12]. This sequence of amination and oxidation reactions is a tempting method for the synthesis of 1,2,4-triazines from the readily accessible starting reagents.

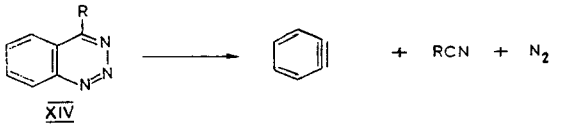


In the attempt to obtain carbenonitrenes VIII from indazolonitrenes XV and XVI, the reaction conditions were evidently insufficiently severe to bring about splitting off of nitrogen up to the point of ring expansion to give benzotriazines. Thus we should have obtained indazolonitrenes under considerably more severe conditions, under which, however, intramolecular transformations would have been suppressed. Instantan-



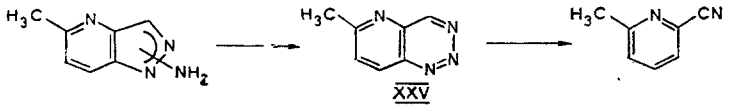
eous pyrolysis in the vapor phase seemed ideal for this purpose, and previous investigations [13] provided a basis for assuming that sulfoximides XXIII are suitable for pyrolysis. The oxidation of 2-aminoindazoles (XVII, R = H, CH_3) with lead tetraacetate in the presence of dimethyl sulfoxide (DMSO) actually gave sulfoximides XXIII. The tying up of the nitrene prevented competitive ring expansion to a triazine. At 450°C (0.01 mm) these sulfoximides, as assumed, were pyrolytically fragmented to DMSO, nitrogen, and conjecturally, to a carbenonitrene, which underwent ring expansion to give a cyanoacetylene (XXIV, R = H, CH_3). However, these cyanoacetylenes are more similar to biscyanides VI than to bisacetylene VII and do not undergo cyclization to benzazete derivatives. The cyanoacetylenes were subjected to thermal and photochemical action under various conditions in the presence of nucleophiles and dienes, which might have recated with the benzazetes if they had formed.

Attention was therefore directed to another source of pyrolytic generation of carbeneonitrenes – to benzotriazines themselves, from which it was necessary to remove a nitrogen molecule.



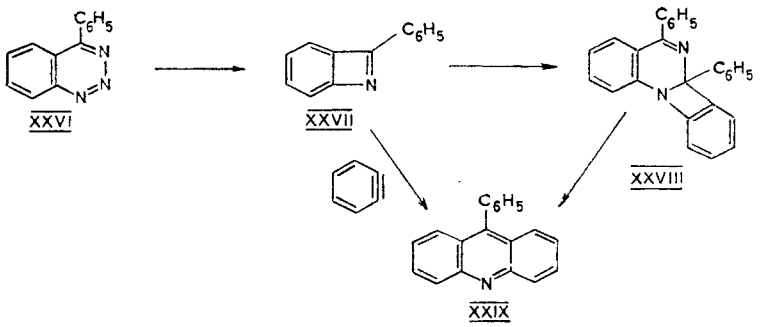
XIV

However, the first experiment showed that triazines XIV are readily cleaved at relatively low temperatures (450-500°C) to give dehydrobenzene and, consequently, diphenylene in yields up to 60%. However, when this reaction was applied to pyridine in order to obtain the difficult-to-prepare diazadiphenylene it was found that N_2 can be split out selectively. The pyrolysis of pyridotriazine XXV gave 2-cyano-6-methylpyridine as a result of splitting out of N_2 and migration of a hydrogen atom. The fragmentation of benzo-



XXV

triazine probably occurs by means of successive splitting out of N_2 and RCN. We therefore made a particularly thorough investigation [14] of the pyrolysis of benzotriazines, particularly of 4-phenylbenzotriazine (XXVI), at 400-450°. At temperatures above 450° the chief product was diphenylene, but at 420°, as a result of the pyrolysis we obtained a bright-red oil containing 20% diphenylene, 15% 9-phenylacridine (XXIX), 5% unchanged benzotriazine XXVI, and 60% of a product that we considered to be the first true azete derivative – red 2-phenylbenzazete XXVII.

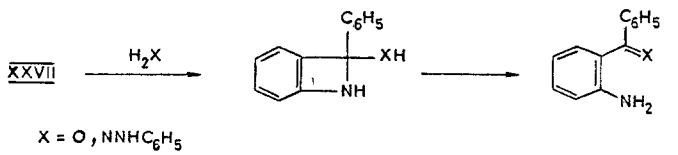


XXVI XXVII XXVIII XXIX

Somewhat unexpectedly, the latter proved to be stable at –80° but was converted on heating to room temperature to a pale-yellow dimer (XXVII) of 2-phenylbenzazete (50%, based on the starting benzotriazine).

The quantitative conversion of this dimer to 9-phenylacridine (thermally or by treatment with a hot alcohol solution of hydrochloric acid) is in agreement with all of the four possible angular dimeric structures of the XXVIII type, which are similar to those formed from benzocyclobutadiene. Two linear dimeric structures – dibenzo-1,2- and dibenzo-1,5-diazocine – would also be possible, but the latter is excluded by comparison with a known sample [15], and the first is incompitable with the conversion to 9-phenylacridine. The 9-phenylacridine formed as a result of the pyrolysis can also be obtained by reaction of the benzazete with dehydrobenzene.

A further confirmation of the fact that the red compound in the pyrolyzate is azete XXVII is offered by its extremely rapid reaction (with decolorization) with nucleophilic reagents and conjugated dienes when they are introduced directly into the cold pyrolyzate at –40° or at lower temperatures. Thus XXVII reacts instantaneously with dilute sulfuric acid in tetrahydrofuran (THF) to give o-aminobenzophenone (50%) or with diphenylhydrazine in THF to give o-aminobenzophenone phenylhydrazone (60%).*

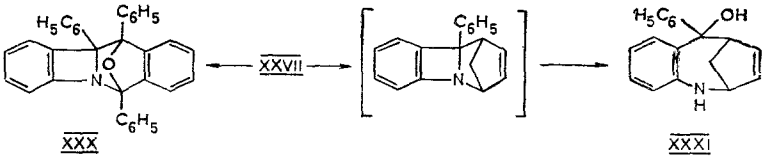


XXVII

X = O, $NNHC_6H_5$

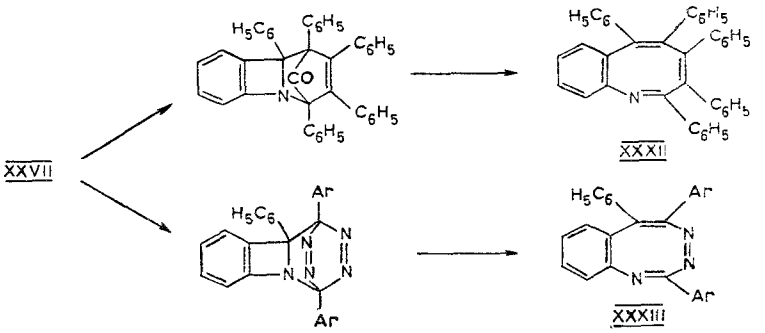
*The yields are given for the starting triazine, and, consequently, we are dealing here with almost quantitative conversion of azete XXVII.

Like benzocyclobutadiene, azete XXVII readily undergoes cycloaddition with various dienes, and this opens up broad possibilities for the synthesis of new heterocyclic systems. Thus it reacts with 1,3-diphenylisobenzofuran to give adduct XXX (55%) with a four-membered azetine ring. However, the strained azetine ring is relatively easily cleaved [16]. For example, reaction with cyclopentadiene leads to amino alcohol XXXI (35%), which is formed by hydration of the Diels–Alder adduct during chromatographic treatment.



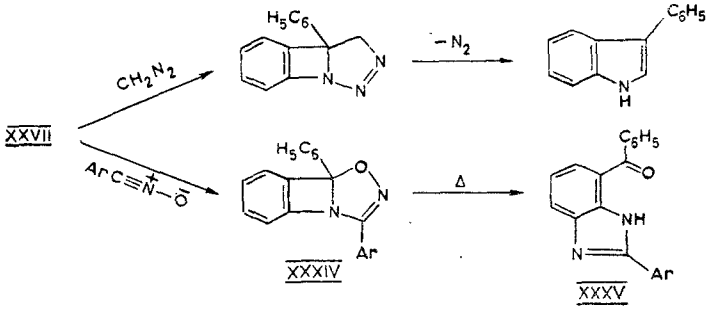
XXX XXXI

Tetraphenylcyclopentadienone and 3,6-diaryltetrazines also give cycloadducts, which are converted to benzazocine XXXII (50%) or benzotriazocine XXXIII (Ar = 2-pyridyl) as a result of splitting out of CO and N_2, respectively.



XXVII XXXII XXXIII

Cycloaddition to benzazete XXVII was also observed with some 1,3-dipoles. Thus XXVII reacts with diazomethane to give 3-phenylindole in very low yield, possibly through splitting out of N_2 from the initial adduct. However, the adduct formed with 4-methylbenzonitrile oxide, viz., oxadiazoline XXXIV, was obtained in 50% yield. Adduct XXXIV underwent a new rearrangement to give benzimidazole XXXV in high yield on heating in solution or during chromatography. The weakening of the strain of the azetine ring, the weakness of the O–N bond, and the stability of the resulting benzophenone carbonyl group possibly promote this rearrangement. An iminonitrene side chain, cyclization with the participation of which subsequently gives benzimidazole XXXV, is formed simultaneously with this carbonyl group.



XXVII XXXIV XXXV

Like benzocyclobutadiene, 2-phenylbenzazete XXVII is almost (or completely) unreactive with dienophiles such as alkenes, alkynes, and enamines. Dimerization and the possible reaction with dehydrobenzene mentioned above constitute exceptions to this.

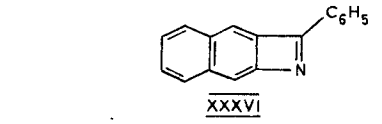
2-Phenylbenzazete proved to be relatively stable: it remained unchanged at −50° for a long time. We decided to attempt to synthesize azetes with greater stability by weakening the antiaromatic character of the four-membered ring by increasing the electron density in the imine bond or by the introduction of another condensed benzene ring. The former was achieved as a result of pyrolysis of 4-(p-methoxyphenyl)-benzotriazine, which formed 2-(p-methoxyphenyl)azete. Although it underwent the same transformations as the 2-phenyl derivative (XXVII), it was considerably more stable in solution and reacted appreciably more slowly with tetraphenylcyclopentadiene and diphenylisobenzofuran.

Stabilization by condensation with a benzene ring was convincingly demonstrated during the flash pyrolysis of 4-phenyl-1,2,3-naphtho[2,3-b]triazine (XXXVIII). It gave 2-phenylnaphtho[2,3-b]azete (XXXVI) as

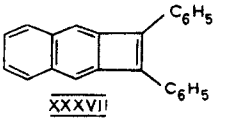
an orange-red crystalline substance that was stable for several hours at room temperature, even when it had access to the air. Azete XXXVI very readily dimerizes in solution, and, like the benzazetes, reacts with nucleophilic reagents and dienes. The yields of adducts decrease as the length of time that azete XXXVI is stored prior to the reaction is increased. This azete can be compared with the analogous carbocyclic compound (XXXVII), which can also be isolated [17].

The facts set forth above constitute almost indisputable evidence that we have synthesized azetes for the first time, and we hope that they will find sufficient application in the chemistry of heterocyclic system.

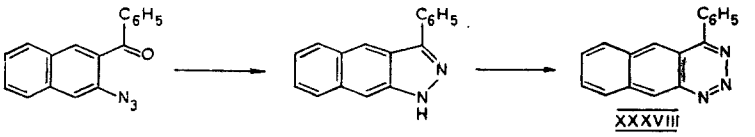
The following portion of our paper is devoted to research with seven-membered 1,2,3-triazepines. These heretofore unknown heterocycles were required for the synthesis of special dehydrogenated aromatic compounds. Very little is presently known about non-ortho-dehydrogenated aromatic systems. We have



XXXVI

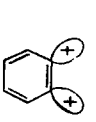


XXXVII

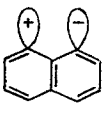


XXXVIII

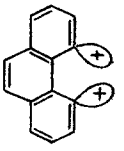
shown [18, 19] that o-dehydrobenzene derivatives add sterospecifically to dienes, while "meta"-dehydrogenated 1,8-dehydronaphthalene adds sterospecifically to monoenes [20]. This difference was explained by the fact that dehydrobenzene has a symmetrical higher filled MO (XXXIX), while 1,8-dehydronaphthalene has an antisymmetrical MO (XL) [21]. Furthermore, Hoffmann [21] has predicted that 4,5-dehydrophenanthrene (XLI) and 2,2'-dehydrodiphenyl will have symmetrical higher filled MOs. Consequently, these compounds will add to dienes in the 1, 4 position, which is contrary to the conclusion that can be drawn from simple stereochemical considerations. To obtain these compounds by the chosen method, we needed aminotriazepines XLII and XLIII. We decided to begin with the synthesis of the latter, inasmuch as the starting



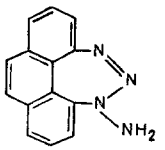
XXXIX



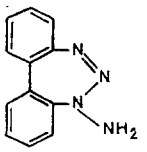
XL



XLI



XLII



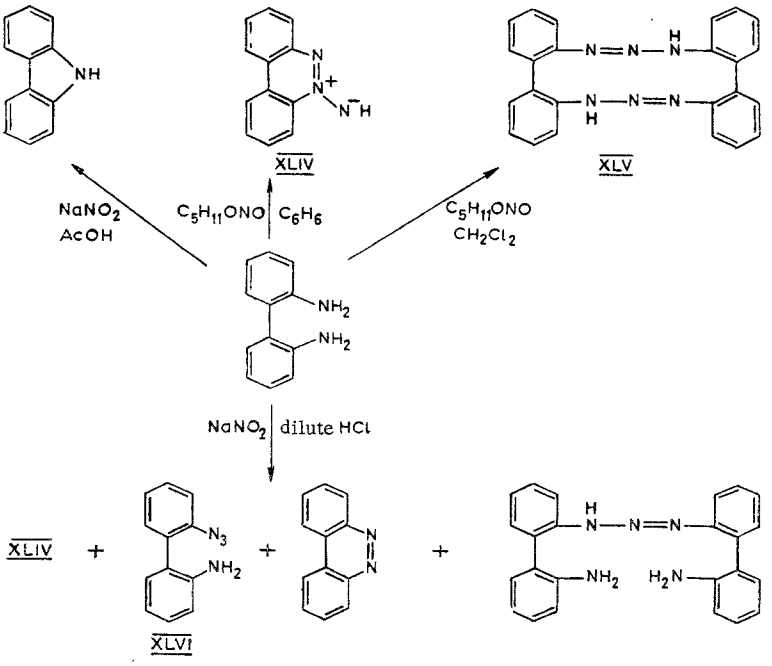
XLIII

compounds for its preparation were more accessible and, in addition, the probability of the formation of a seven-membered ring in this more flexible system was higher. Dibenzo[d,*f*]-1,2,3-triazepine (XLVII), which, like acyclic diaryltriazines, might have proved to be unstable and possibly nonplanar and nonaromatic (or even antiaromatic with an 8π-electron system), was necessary for the amination and oxidation.

The precursor of triazepine XLVII is 2,2'-diaminodiphenyl, which can be intramolecularly cyclized to a triazepine on diazotization [22, 23]. However, the diazotization proved to be extremely complex, and we were unable to isolate a triazepine, although it is possibly an intermediate. (See scheme on following page.)

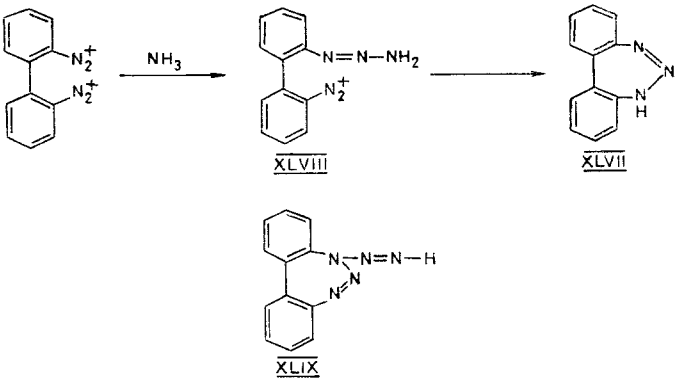
Diazotization in dilute HCl gave all of the products shown in the scheme above. Carbazole was obtained in high yield by diazotization in 5 N HCl or 50% acetic acid. Aprotic diazotization with pentyl nitrite in refluxing benzene gave iminobenzocinnolinium ylid XLIV, which is an isomer of triazepine XLVII. A 14-membered cyclic bistriazine (XLV) was obtained in refluxing methylene chloride containing catalytic amounts of hydrogen chloride.

Attempts to facilitate the formation and increase the stability of the triazepine stereochemically by means of removal of the aromatic rings from coplanarity by means of 6,6' substituents and also by means



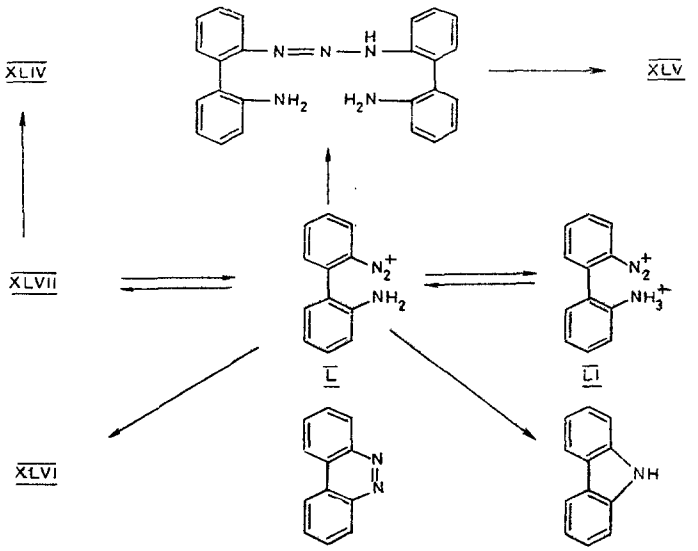
of increasing the angles between the bonds in the seven-membered ring, linking the 6 and 6' positions through the carbonyl group, and attempts to synthesize the more stable N-substituted triazepine from mono-N-substituted diaminodiphenyl were unsuccessful. We then turned to the preparation of the triazepine by formation of a C–N bond rather than an N–N bond, just as in all of the preceding reactions.

After several unsuccessful attempts, we arrive at the conclusion that this can be achieved by tetraazotization of diaminodiphenyl and subsequent treatment with ammonia. This would lead to linear triazine XLVIII in which the nucleophilic side chain may replace the diazonium group to give a triazepine ring. Of course, cyclization of the triazine to give XLIX is also possible, but the latter will readily split out nitrogen to give triazepine XLVII. This method proved to be extremely successful: triazepine XLVII (a stable light-yellow crystalline substance with mp 100°) was obtained in 75% yield by tetraazotization of diaminodiphenyl in dilute HCl at 0° with subsequent careful alkalization with ammonia at 0°. A tetrazonium boro-

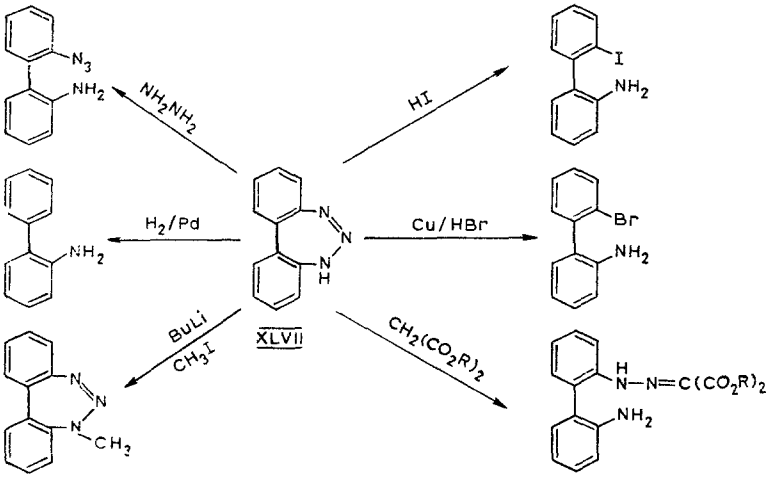


fluoride, which gave a triazepine on treatment with NH_3 [23], has also been isolated.

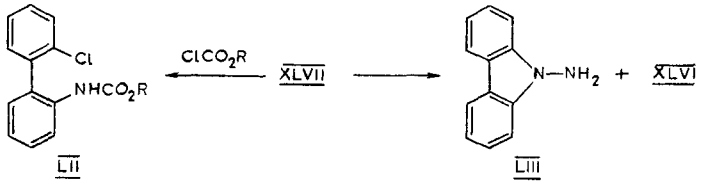
After isolation of the triazepine and investigation of its properties, it became possible to explain the complexity of the diazotization of 2,2'-diaminodiphenyl. On gentle heating in benzene, the triazepine was converted quantitatively to ylid XLIV, but in 5 N HCl or 50% acetic acid it gave a quantitative yield of carbazole. However, the triazepine can be obtained in more acidic media (concentrated HCl or 50% H_2SO_4), in which it apparently exists as a stable dication (LI). The formation of all of the products of diazotization of diaminodiphenyl can be explained by rearrangement of triazepine XLVII to ylid XLIV or by reaction of aminodiazonium salt L with the ylid to give aminoazide XLVI and benzocinnoline, and also by other reactions indicated in the scheme. (See scheme on following page.) The IR spectrum of triazepine XLVII does not contain the characteristic band of the diazonium group, although its chemical properties, as in-



dicated below in the scheme, are primarily properties of the diazo compound. It also couples with β-naphthol to give an azo dye.



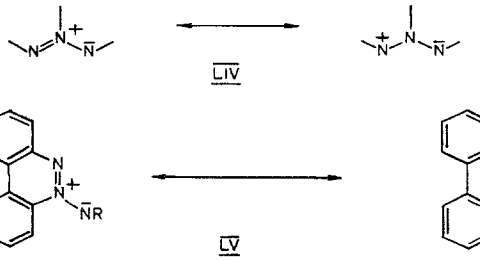
The triazepine ring was not disrupted during N-methylation of the lithium salt, but it cannot be preserved when functional groups are introduced. Thus, for example, reaction with benzoyl chloride and ethyl chloroformate gave ring-opening products of the LII type.



In particular, we were unable to isolate N-amino compound LIII, although it is also formed during amination. The triazepine does not react with chloramine or with O-(2,4-dinitrophenyl)hydroxylamine. Hydroxylamine-O-sulfonic acid gives aminoazide XLVI in high yield, while aminoazide XLVI (30%) and N-aminocarbazole LIII (40%) are formed on treatment of the lithium salt with O-(mesitylsulfonyl)hydroxylamine. Both of these products can be formed from N-aminotriazepine XLIII during ring opening to give a diazonium–hydrazine ion pair, in which replacement of the nitrogen can lead to LIII, while intramolecular nitrogen transfer can lead to XLVI (in analogy with the intermolecular reaction between diazonium ions and hydrazines).

The research on dibenzo[d,*f*]-1,2,3-triazepine (XLVII) also proved to be of value in another respect. As already pointed out, when this triazepine is heated in benzene it rearranges to give N-iminobenzocinnolinium ylid XLIV. This ylid was also obtained directly by reaction of 2,2'-diaminodiphenyl with pentyl

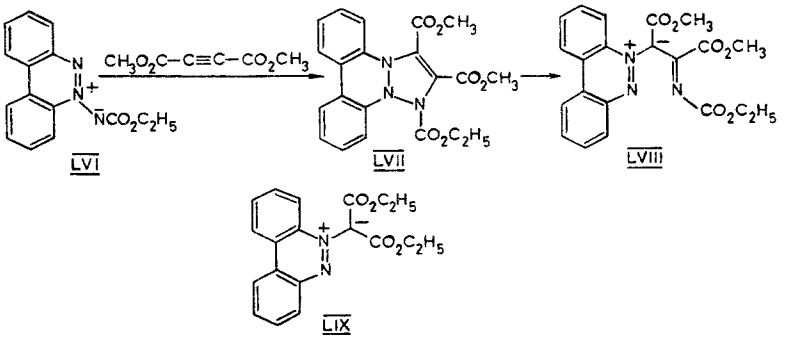
nitrite in refluxing benzene and subsequent amination. The mechanism of the XLVII–XLIV transformation was partially elucidated by means of ^{15}N. The ylid and its N-substituted derivatives (LV, R = Me, Et, MeCO, PhCO, MeO_2C, EtO_2C, and $ArSO_2$) constitute examples of the rare 4π-electron 1,3-dipolar systems with three nitrogen atoms (LIV). Huisgen [24] has proposed that they be called azimines and has predicted 1,3-dipolar cycloaddition reactions for them (see also 25]). Attempts to demonstrate this cycloaddition with azimines have as yet been unsuccessful [26, 27].



LIV

LV

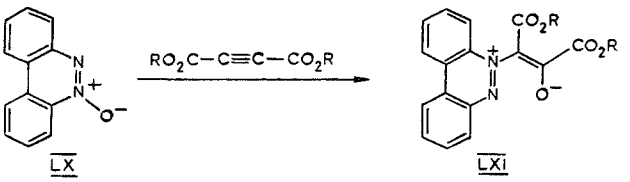
However, azimines of the LVI type react exothermally with dimethyl and diethyl acetylenedicarboxylates in benzene or dimethylformamide (DMF) at room temperature to give quantitative yields of 1:1 adducts. The green coloration of these compounds presupposes that they are not the original 1,3-dipolar adducts (LVII) but rather azomethine imines (LVIII). This structure is completely confirmed by the spectral data, which are similar for the independently synthesized [28] simpler azomethine ylid (LIX).



LVI LVII LVIII LIX

The formation of LVIII is weighty proof in favor of the initial 1,3-dipolar cycloaddition of azimine LIV with subsequent ring opening of labile triazoline LVII to give the considerably more stable azomethine (LVIII). This is a rare example of retro-1,5-dipolar cyclization.

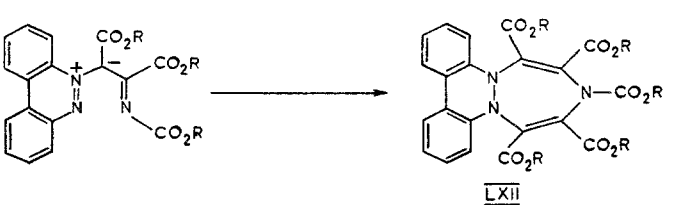
We have previously observed a similar chain of reactions with benzocinnoline N-oxide (LX), although the reaction occurred under considerably more severe conditions and gave poorer yields. The products



LX LXI

of the reaction of LXI are also obtained as a result of 1,3-dipolar cycloaddition with subsequent retro-1,5-dipolar cyclization. We feel that this reaction is the first example of the manifestation of 1,3-dipole properties by an azoxy compound.

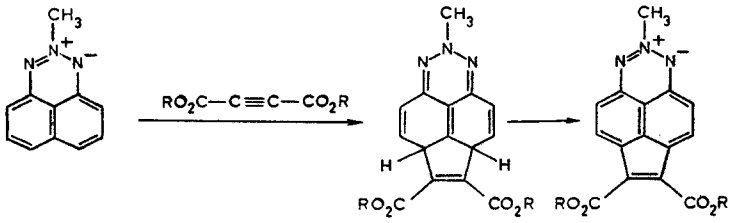
The azomethine imines (LVIII) mentioned above may act as 1,3(4π)-, 1,5(6π)-, or even 1,7(8π)-dipoles. In actuality, they react with acetylenic esters to give symmetrical 1:2 adducts (LXII) [29]. Thus the reaction proceeds primarily in the direction of ($6\pi + 2\pi$)-cycloaddition, which is not formally allowed, and the next process is possibly:



LXII

The formation of adducts LXII is an example of the extremely rare 1,5-dipolar cycloaddition reaction. Their structures were confirmed by their spectroscopic properties. The symmetry of adducts LXII follows from the identical character of the products of the reaction of the starting azimine (LXI) initially with one mole of dimethyl acetylenedicarboxylate and then with diethyl acetylenedicarboxylate and vice versa. Their structures were also confirmed by means of x-ray crystallography.*

In contrast to the widely known and diverse 1,3-dipolar cycloaddition reactions, reactions similar to the 1,5-dipolar cycloaddition reaction described above have received practically no study. The fact that these reactions may be extremely general in character is confirmed by the properties of 2-substituted naphthotriazines of the LXIII type [30]. The slow addition of acetylenic esters to LXIII in refluxing o-dichlorobenzene gave 2-methylacenaphthotriazines LXIV in 30-40% yields. 1,11-Dipolar ($12\pi+2\pi$) cycloaddition apparently occurs initially and is followed by spontaneous dehydrogenation.



LXIII LXIV

LXV LXVI

In conformity with this, the reactions proceeded better and gave higher yields in the presence of sulfur. Cyclic sulfodiimide LXV reacts similarly, although the dipolar C–S–C system (LXVI) acts only as a 1,3-dipole [31, 32]. Cycloaddition processes of this sort open up wide synthetic possibilities with the participation of vinylogs of dipolar systems containing more than four π electrons.

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