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New Heterocyclic Conjugated π -Electron Systems.
Syntheses and Properties

Klaus Hafner

Institut für Organische Chemie der Technischen Hochschule Darmstadt,
D-61 Darmstadt, Germany

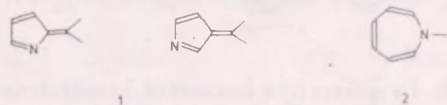
New Heterocyclic Conjugated π -Electron Systems. Syntheses and Properties

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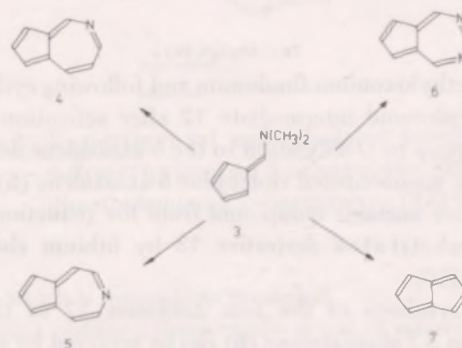
In search of the causes and the nature of "aromaticity" numerous non-benzenoid carbocyclic conjugated π -electron systems proved to be valuable touchstones for quantum chemical calculations. In this respect heterocyclic analogues were taken into consideration only occasionally, one reason being the fear of the obvious complications of introducing a heteroatom into the perimeter, when the reactivity and bonding structure of the corresponding carbocyclic compounds is not yet completely understood. As frequently used in chemistry even here a concept of limited applicability should be of heuristic value, as long as the complexity of the problem does not require recourse to first principles. To such concepts belongs, resulting from the study of 5- and 6-membered heterocycles, a rule of thumb, that the cyclic conjugation of π -electron systems will be disturbed but not cancelled by substitution of a methine group by nitrogen or a vinylene group by oxygen, sulfur or a nitrogen group. Corresponding results with hetero analogues of non-benzenoid mono- or polycarbocyclic π -electron systems are rather limited (1), e.g. the studies on oxepine and azepine (2) or on oxonine and azonine (3) as well as those on heteroannulenes (4) and pseudoazulenes, e.g. azalenes, thialenes and oxalenes (5).

However, detailed information about the influence of the heteroatoms in the perimeter on bonding character and reactivity of nonbenzenoid π -electron systems are desirable for an experimental support of quantum chemical predictions as well as for the synthesis of new heterocycles. Part of our recent work, concerned with the synthesis and chemistry of azapentalenes 1 and azepines 2 (6), grew out of attempts to synthesize bicyclic systems derived from



these, namely azaazulenes as well as related heterocycles. While azaazulenes with one or more nitrogens in the five-membered ring have been known for several years (7) bicyclic heteroazulenes with nitrogen in the seven-membered ring are almost unknown (8). Assuming that a study of the latter would be of considerable theoretical and synthetic value, we decided to start an investigation of these

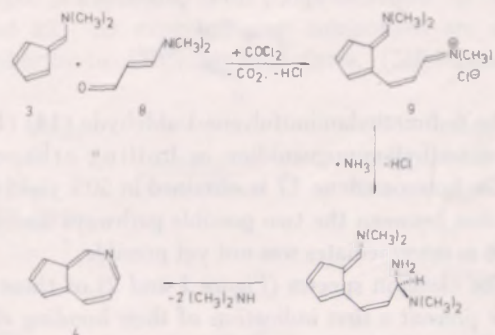
compounds and extended these studies to azapentalenes. 6-Dimethylaminofulvene (3) and its derivatives proved to



be useful starting materials for the synthesis of 5-aza- (4), 6-aza- (5) and 5,7-diazaazulenes (6) as well as of derivatives of 2-azapentalene (7).

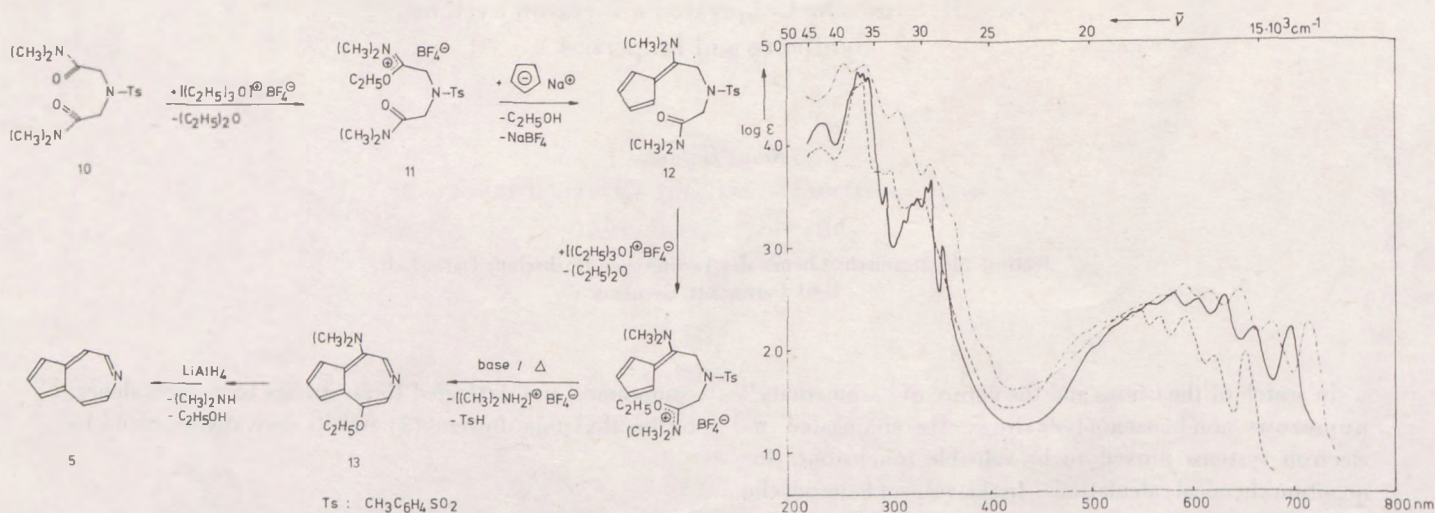
Azaazulenes

As already reported (9) 5-azaazulene (4) and numerous of its derivatives are easily prepared by cyclization of the fulvenoid iminiumsalt 9, readily obtained by reaction of 3 or its derivatives with 3-dimethylaminopropenal (8) or



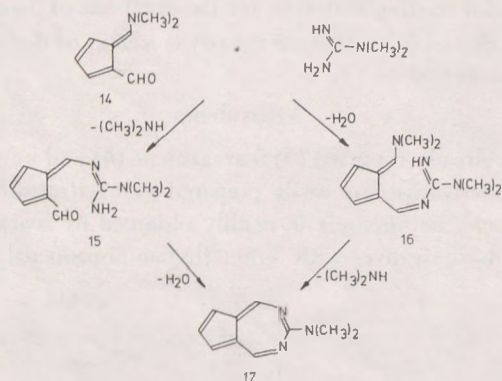
analogous α,β -unsaturated aldehydes and ketones in the presence of phosphine. The violet parent compound 4 combines pronounced thermal stability with a high sensitivity to oxygen. Alkyl or aryl groups in position 4 and/or 6 however considerably stabilize the 5-azaazulene system.

The hitherto unknown 6-azaazulene (5) can be synthesized by condensation of sodium cyclopentadienide with the fluoborate 11 obtained by *O*-alkylation of 2,2'-(*p*-toluenesulfonylimino)bis(*N,N*-dimethylacetamide) (10)



with triethylxonium fluoborate and following cyclization of the fulvenoid intermediate **12** after activation of the amide group by *O*-alkylation to the 6-azaazulene derivative **13**. The unsubstituted violet-blue 6-azaazulene (**5**) results as a rather unstable compound from the reduction of the 4,8-disubstituted derivative **13** by lithium aluminum hydride (**10**).

The synthesis of the first derivative **17** of the still unknown 5,7-diazaazulene (**6**) can be achieved by reaction



of the 6-dimethylaminofulvene-1-aldehyde (**14**) (**11**) with *N,N*-dimethylaminoguanidine in boiling ethanol. The yellow heteroazulene **17** is obtained in 50% yield (**12**). A decision between the two possible pathways leading to **15** or **16** as intermediates was not yet possible.

The electron spectra (Figure 1 and 2) of these azaazulenes present a first indication of their bonding structure and agree with quantum chemical calculations (**12**). The shape of the spectra of the 5-azaazulene (**4**) and 6-azaazulene (**5**) resembles perfectly that of azulene. The nitrogen in **4** causes a predicted hypsochromic shift of the absorption maxima in the visible region of 35 nm, while in the uv region nearly no shifts are observed. Contrary to this influence of nitrogen in a position of comparatively high electron density, in 6-azaazulene (**5**) the heteroatom in a position of low electron density effects a bathochromic shift of the longest wave length absorption of about 12 nm

Figure 1: Uv spectra (in *n*-hexane) of azulene ———; 5-azaazulene (**4**) - - - - -; 6-azaazulene (**5**) ······

similar to electronegative substituents in this position. In the case of 5,7-diazaazulene (**6**) the influence of both nitrogens is additive and results therefore in a stronger hypsochromic shift of the absorption at longest wave length than by introduction of one nitrogen into the 5-position of azulene. In the region below 400 nm the spectrum of **17** (Figure 2) resembles that of the 6-dimethylamino-5-

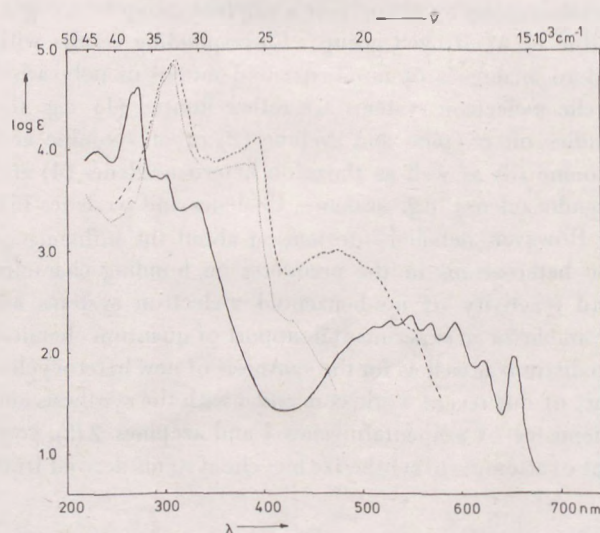
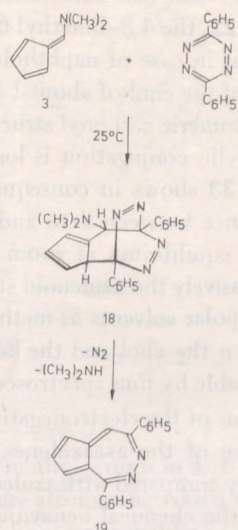


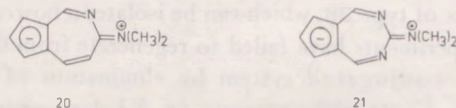
Figure 2: Uv spectra (in *n*-hexane) of 5-azaazulene (**4**) ———; 6-dimethyl-5-azaazulene (**20**) - - - - -; 6-dimethyl-5,7-diazaazulene (**17**) ······

azaazulene (**20**) (**12**) as well as that of the unsubstituted 5-azaazulene (**4**). The fine structure, characteristic for azulene in the visible region (**13**), is however reduced to two shoulders. This agrees with the results, obtained by



T. Sasaki, *et al.*, who synthesized very recently the 4,7-diphenyl-5,6-diazaazulene (**19**) by a 6+4-cycloaddition of **3** with 3,6-diphenyltetrazine followed by elimination of nitrogen and dimethylamine from the first formed adduct **18** (14). According to the assumption that the heteroatoms exerts chiefly an inductive effect on the azulenoid system, the substitution of a methine group in 5- and/or 7- as well as 6-position of azulene by nitrogen seems to cause only a slight disturbance of the π -electron delocalization of the azulene system. The almost similar influence of substituents on the longest wave length absorption by carbocyclic azulenes and its 5-azaanalogues confirm this presumption (15). On the other hand the different stability of **4** and **5** shows, in agreement with quantum chemical results (16), that the position of nitrogen in the azaazulene system affects the reactivity of the bicyclic system.

The dipole moment of 2.19 D for 6-dimethylamino-5,7-diazaazulene (**17**) is smaller than the value of 3.70 D for the 6-dimethylamino-5-azaazulene (**20**) and shows that the introduction of electronegative heteroatoms into the 7-membered ring, counteracting the electronwithdrawing 5-membered ring moiety, results in a decrease of polarization (12). On the other hand we may expect that dimethylamino groups in 6-position of the mono- and diazaazulenes **4** and **6** cause a polarization of the ring system in the sense of the resonance structures **20** and **21**, which also may



contribute to the stabilization of these heteroazulenes. Although in accord with SCF-calculations (12), the results of an X-ray analysis (Figure 3) stress that these effects should not be overemphasized (17). A comparison of the calculated and measured bond length generally shows good agreement, but with the exception of the exocyclic C-N-

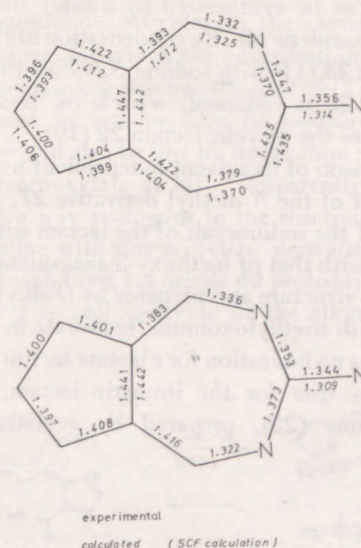
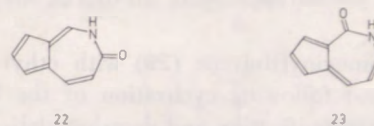


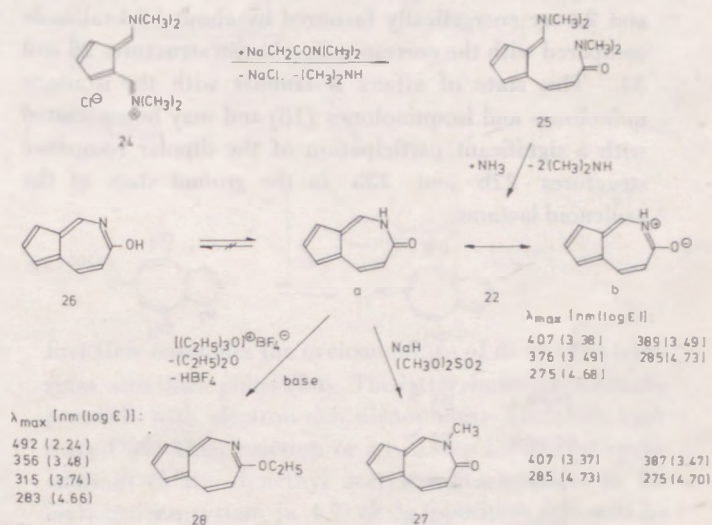
Figure 3: Experimental and calculated bondlength of 6-dimethylamino-5-azaazulene (**20**) and 6-dimethylamino-5,7-diazaazulene (**17**) (17).

bond, which is longer than predicted.

Having obtained these results it was of interest to learn more about the π -electron delocalization of the 5-azaazulene system by studying equilibria between tautomeric structures, familiar in the chemistry of the corresponding 6-membered ring systems (18). Accordingly we have been

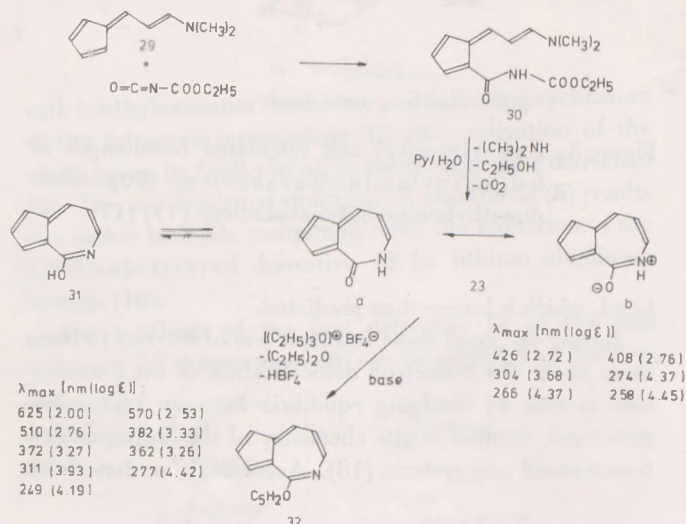


interested in a synthesis of the (5H)5-azaazulene systems **22** and **23**. As expected such compounds are readily accessible by two different procedures. (5H)5-azaazulene-



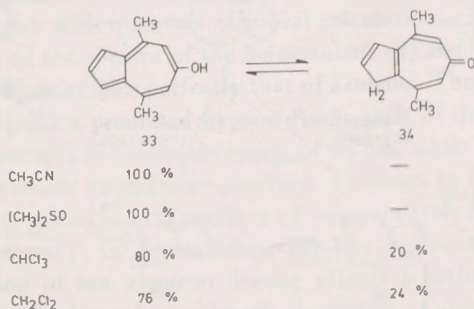
6-one (22) can be synthesized by a route similar to that used for 5-azaazulene (4). By condensation of the fulvenoid iminium salt 24 (11) with sodium *N,N*-dimethylacetamide the fulvene 25 is obtained, which on treatment with ammonia gives the bicyclic lactam 22 (19).

A comparison of its solvent independent uv and ir spectra with that of the *N*-methyl derivative 27, obtained by alkylation of the sodium salt of the lactam with dimethyl sulfate, and with that of 6-ethoxy-5-azaazulene (28), fixed in the lactim structure and prepared by *O*-alkylation of the lactam 22 with triethylxonium fluoborate in the presence of base, shows no indication for a lactam-lactim equilibrium. The same is true for the isomeric lactam, the (5*H*)-5-azaazulene-4-one (23), prepared by acylation of 6-(2'-



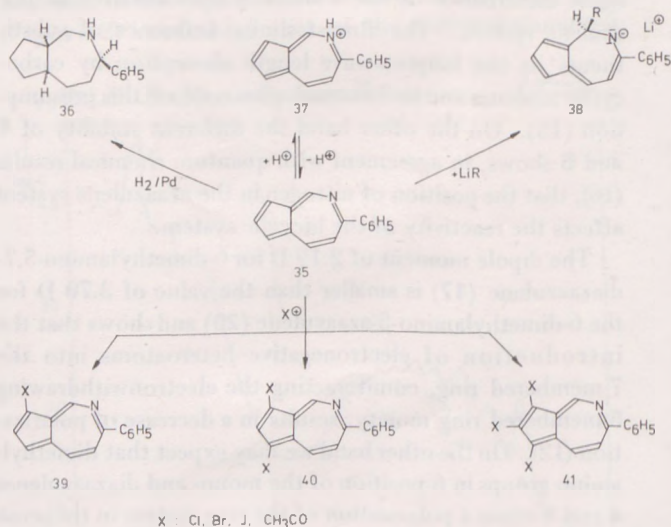
dimethylaminovinyl)fulvene (29) with ethyl isocyanatoformate and following cyclization of the bifunctional fulvene 30, saponification and decarboxylation in boiling pyridine/water. The uv spectrum of 23 shows no similarity with that of the 4-ethoxy-5-azaazulene (32) (20).

These results are in good agreement with SCF-calculations (21), which suggest, that the lactam structures 22 and 23 are energetically favoured by about 10 kcal/mole compared with the corresponding lactim structures 26 and 31. This state of affairs is familiar with the isomeric quinolones and isoquinolones (18) and may be associated with a significant participation of the dipolar resonance structures 22b and 23b in the ground state of the azulenoid lactams.

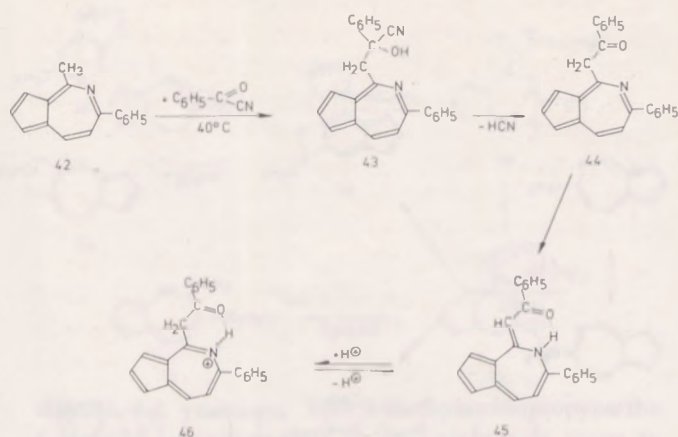


Contrary to this result SCF-calculations for the carbocyclic analogue of 22, the 4,8-dimethyl-6-hydroxyazulene (33) (22) shows - as in case of naphtholes - a slight energetical superiority of the enol of about 1.5 kcal/mole compared with the tautomeric carbonyl structure 34, in which the azulenoid bicyclic conjugation is lost. However, the 6-hydroxyazulene 33 shows in consequence of the very low energy difference between keto and enol structure a solvent dependent equilibrium at room temperature. In polar solvents exclusively the azulenoid structure is observable, while in less polar solvents as methylene chloride an equilibrium between the enol and the ketone in a ratio of about 3:1 is detectable by nmr spectroscopy (21).

The participation of the electronegative nitrogen in the bicyclic conjugation of the azaazulenes should reflect in a different reactivity compared with azulene as it is obvious by comparison of the chemical behaviour of naphthalene and quinoline or isoquinoline. A detailed study of the reactions of 5-azaazulene (4) confirmed this expectation. Thus, e.g., the 6-phenyl derivative 35 resembles azulene in respect to its easy hydrogenation yielding the saturated system 36. Compared with azulene, 35 shows a stronger basicity. The latter is shown by reversible protonation already in weak acetic acid to 37. In their pronounced tendency to nucleophilic substitution in 4-, 6- and 8-position, the 5-azaazulenes behave like quinoline and iso-

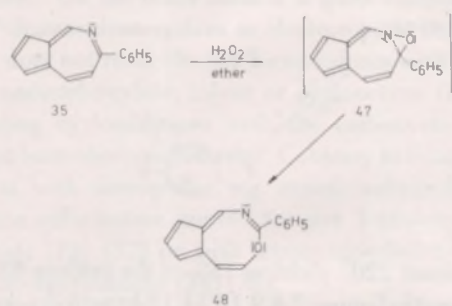


quinoline (23). With alkyl lithium 35 gives addition products of type 38, which can be isolated; however until now experiments have failed to regenerate from these the bicyclic conjugated system by elimination of lithium hydride. Electrophilic reagents, i.e. *N*-halosuccinimides or acylating agents, attack the 5-azaazulene system in the presence of protic acids under rather mild conditions compared with quinoline or isoquinoline. Like azulene the heteroanalogue 35 is substituted in the 1- and 3-position, and contrary to the first one, also in the 2-position, affording the products 39, 40 or 41 (15).



Furthermore methyl groups in 4-, 6- or 8-position of the bicyclic system are stronger activated than in azulene (24). Similarly to picolines or quinaldine (23) such methylated 5-azaazulenes are subject to substitution and condensation reactions with electrophilic reagents. The reaction of 4-methyl-6-phenyl-5-azaazulene (42) with benzoyl cyanide illustrates that the 10 π -electron system in such heteroazulenes is lost quite easily. The primary reaction product 43 loses hydrocyanic acid. However, instead of the expected 4-phenacyl-5-azaazulene (44) the tautomer 45 is obtained in 57% yield. As in the lactam-lactim equilibrium of 23 the tautomeric merocyanine 45 evidently possesses lower energy than the azulenoid structure (15). In cyanines the charge distribution across the polyene chain is hindered by protonation of one of the terminal heteroatoms. Accordingly the uv spectrum of the protonated species 46 shows again the characteristic absorption of the 5-azaazulene system. Opposite to these similar reactions of 2-methylpyridine proceed by conservation of the pyridine system (25).

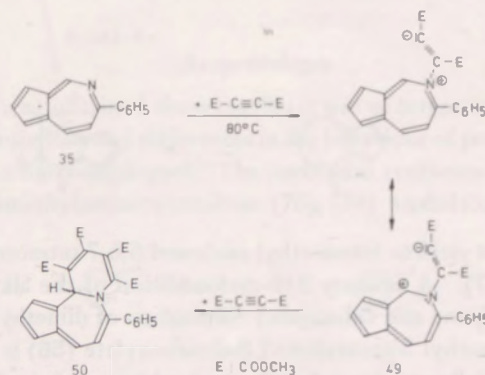
On the other hand all attempts to prepare *N*-oxides of 5-azaazulenes have failed so far. Unlike quinoline or isoquinoline (23) the 5-azaazulene derivative 35 reacts with hydrogen peroxide by ring enlargement yielding 3-phenylcyclopent[*e*] [1,3]oxazocine (48) (26). Presumably the C-N-bond of the heterocyclic system is oxidized first by



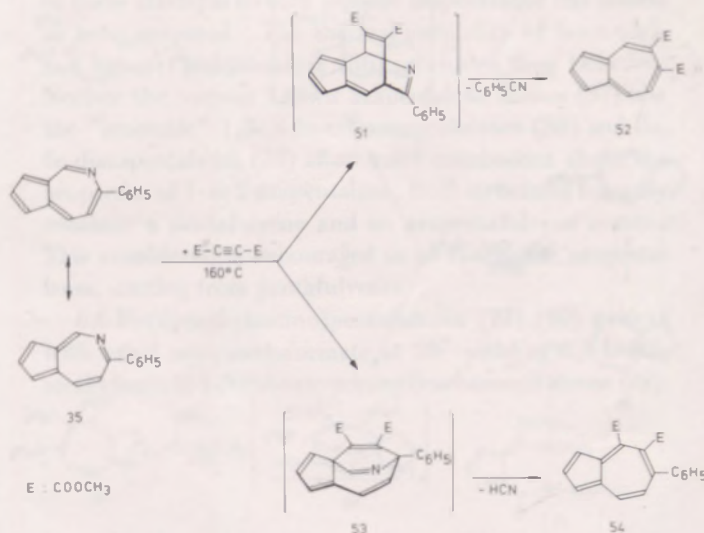
formation of the oxaziridine 47, which rearranges to the interesting 12 π -electron system 48. For this reaction a similar pathway is assumed as for the photolysis of quino-

line or isoquinoline *N*-oxides to the corresponding 1,3-benzoxazepines, for which the contribution of an oxaziridine intermediate has also been suggested (27).

In contrast to azulene, the 10 π -electron system of 5-azaazulene will also be lost by its reaction with dimethyl acetylenedicarboxylate at 80° . Apparently this reaction proceeds in a way analogous to the reaction of quinoline or isoquinoline with this acetylene derivative (28). Thus a resonance stabilized 1,4-dipole 49 probably first formed, reacts with a second molecule of the alkyne in a cyclo-

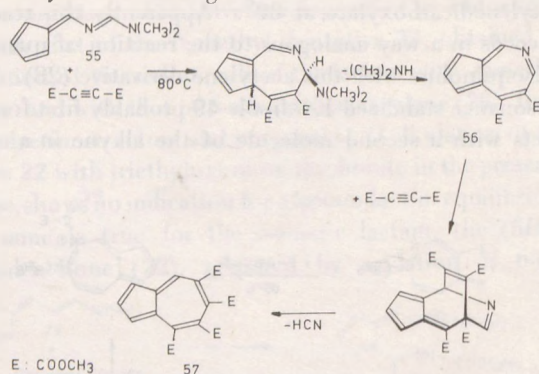


addition to give the yellow tricyclic adduct 50, the structure of which could be confirmed by nmr spectroscopy (29). On the other hand the reaction of the same compounds at 160° leads besides benzonitril and hydrocyanic acid to 20% of the two blue isomeric dimethyl azulenedicarboxylates 52 and 54. This unexpected transformation of the heteroazulene 35 into the azulene derivatives 52 and 54 to



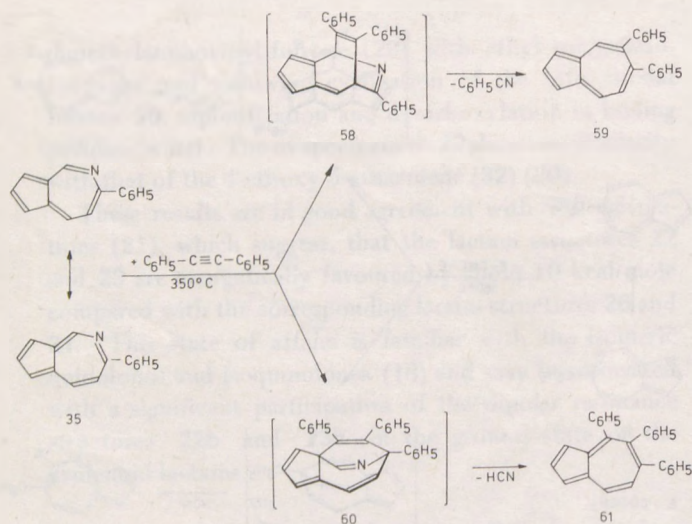
first view resembles the cycloadditions of di- tri- and tetrazines with dienophiles (30). The latter, however, normally proceeds with electron-rich dienophiles. Therefore a primary Diels-Alder reaction or a two step 1,4-dipolar cycloaddition of the dimethyl acetylenedicarboxylate to the 5-azaazulene system in 4,7- or 3a,6-position followed by

an Alder-Rickert cleavage of the primary formed adducts **51** and **53** seems likely. A similar cycloaddition of a 5-azaazulene and following cycloelimination of hydrocyanic acid obviously takes place in the reaction of 6-(1'-aza-2'-dimethylaminovinyl)fulvene (**55**) with dimethyl acetylenedicarboxylate in boiling benzene. This reaction leads in

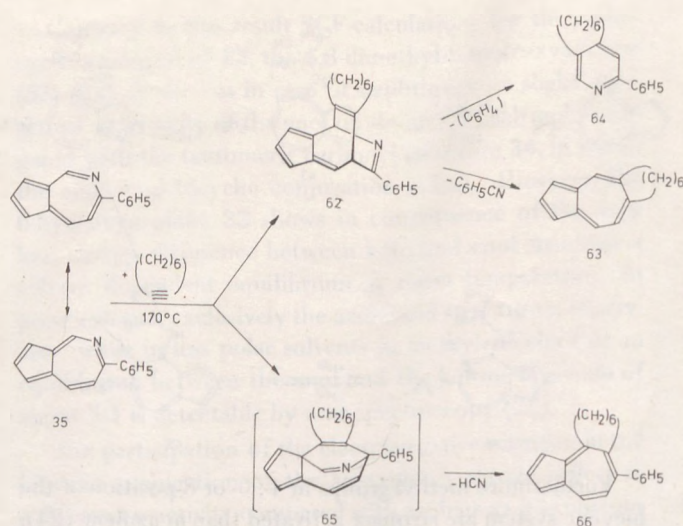


modest yield to tetramethyl azulene-4,5,6,7-tetracarboxylate (**57**). A primary 2+8-cycloaddition of the alkyne to the fulvene and subsequent elimination of dimethylamine to dimethyl 5-azaazulene-7,8-dicarboxylate (**56**) is apparently followed by a further cycloaddition of the heteroazulene with the alkyne.

To clarify the mechanistic approach for these reactions, 6-phenyl-5-azaazulene (**35**) was reacted with different acetylene derivatives with the aim to isolate intermediate cycloadducts. As expected the thermolysis of the heteroazulene with tolane at about 350° gives 30% 5,6-diphenylazulene (**59**) and 5% of 4,5,6-triphenylazulene (**61**) besides

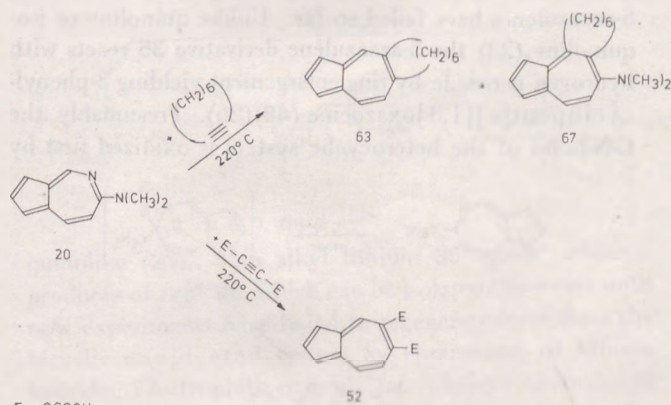


benzonitrile and hydrocyanic acid. Although this result suggests the intermediate formation of the two 1,4-adducts **58** and **60**, none of these could be detected (**31**). However, one of the expected 1,4-adducts of these cycloadditions could be isolated by reacting the 5-azaazulene derivative **35** with cyclooctyne - a highly reactive dienophile - at 170° . In this case 25% of the addition product **62** of the cyclo-



alkyne at the α,β -unsaturated azomethine moiety of the 7-membered ring was obtained. At 250° this adduct decomposes to 60%, 5,6,7,8,9,10-hexahydrocycloocta[*f*]azulene (**63**) by loss of benzonitrile and a trace of 3-phenyl-5,6,7,8,9,10-hexahydrocycloocta[*e*]pyridine (**64**) by loss of the fulvenoid moiety of the adduct. In both cases the cleavage energetically profits from the formation of a cyclic conjugated π -electron system. Besides the 1,4-adduct 30% of the 6-phenyl-7,8,9,10,11,12-hexahydrocycloocta[*e*]azulene (**66**) were isolated, apparently by cleavage of the primary formed strained spiroadduct **65** (**31**), which is unstable under the reaction conditions. If the 4- and 6-position of the 5-azaazulene are substituted by phenyl groups, the cycloaddition with cyclooctyne as well as the following cycloelimination of benzonitrile proceeds nearly quantitatively, yielding 48% of **66** and 49% of 4-phenyl-5,6,7,8,9,10-hexahydrocycloocta[*f*]azulene (**29**).

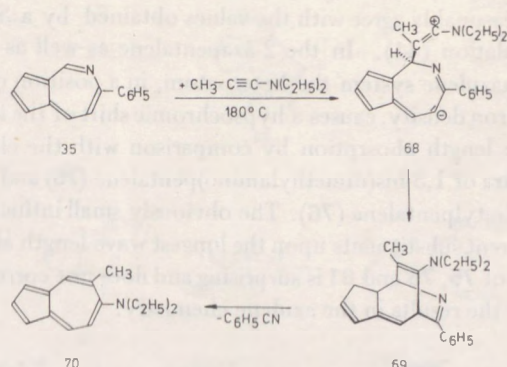
In a similar fashion 6-dimethylamino-5-azaazulene (**20**) reacts with cyclooctyne or dimethyl acetylenedicarboxylate



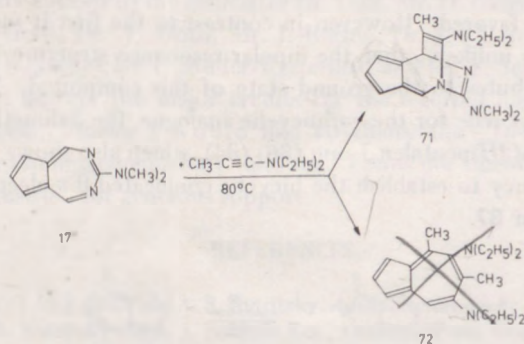
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late at about 220° yielding 13% of the azulene **63** besides 9% 6-dimethylamino-7,8,9,10,11,12-hexahydrocycloocta[*e*]azulene (**67**) or 13% of **52**, respectively.

Moreover it is of interest for mechanistic reasons, that a similar 1,4-cycloaddition takes place even with electron-rich

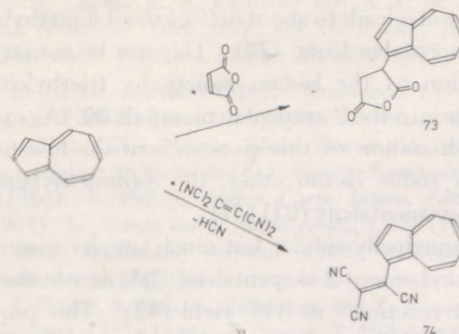


alkynes, e.g. ynamines. With 1-diethylaminopropyne the 6-phenyl-5-azaazulene (**35**) at 180° exclusively reacts to 6-diethylamino-5-methylazulene (**70**). The orientation of this cycloaddition, deducible from the structure of the product, leads to the assumption that the reactions of the 5-azaazulene system with alkynes do not proceed via a synchronous cycloaddition, e.g. a Diels-Alder reaction with inverse electron demand, but by a two step 1,4-addition with resonance stabilized dipolar intermediates like **68**, which presumably cyclize to adducts of type **69**. The formation of the cycloaddition product **69** is confirmed by the reaction of 6-dimethylamino-5,7-diazaazulene (**17**) with the same ynamine. Already in boiling benzene this leads to 25% of the adduct **71** which is remarkably stable even at



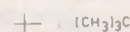
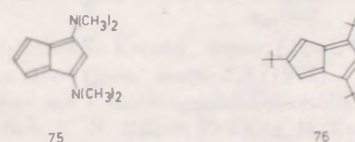
300°. To our surprise, we obtained from this reaction, besides **71**, also 13% of the azulene derivative **72**. So far we have no conclusive explanation for the formation of the latter. On the other hand it is quite reasonable that the 5,7-diazaazulene system as electron-poor heterocyclic system does not react like the 5-azaazulenes with dimethyl acetylenedicarboxylate, tolane or cyclooctyne (**29**). Corresponding cycloadditions with the carbocyclic azulene have not been observed hitherto. Contrary to 5-azaazulenes it reacts with dienophiles, e.g. maleic anhydride, via an "addition-substitution route" to give 1-azulenylsuccinic anhydride (**73**) (**32**) or with tetracyanoethylene to yield 1-tricyanovinylazulene (**74**) (**33**).

These results indicate a strong influence of the heteroatom in the 7-membered ring of the 5-azaazulene system on the reactivity which differs in several respects from that of the carbocyclic azulene system.



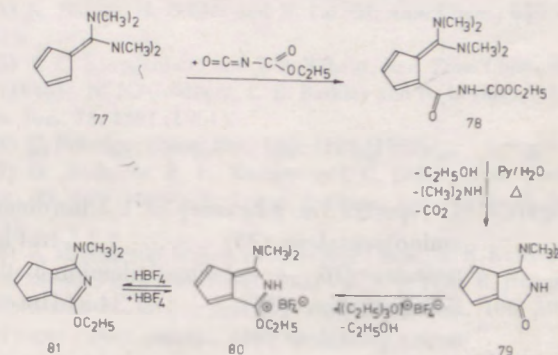
Azapentalenes

Having obtained these results, it was of interest to look for similarities and differences in the behaviour of pentalene and its heteroanalogues. The successful syntheses of 1,3-bis(dimethylamino)pentalene (**75**) (**34**) and 1,3,5-tri-



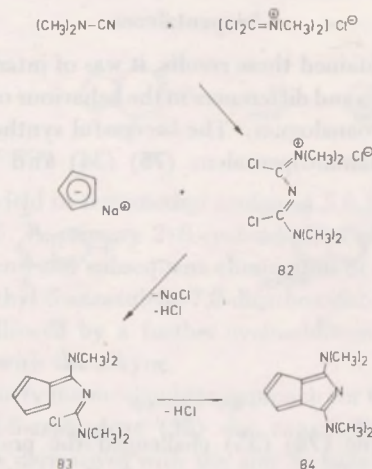
butylpentalene (**76**) (**35**) challenged the preparation of the corresponding azaanalogues. As 8 π -electron systems 1- and 2-azapentalene as well as polyazapentalenes with C-fusion of the two 5-membered rings should be "anti-aromatic", just as the carbocyclic analogues (**16**). In spite of many attempts no such bicyclic azapentalene has hitherto been prepared. The thermal instability of benzo[*b*] and benzo[*f*]azapentalene (**36**) precluded their isolation. Neither the various known azapentalene anions (**37**) nor the "aromatic" 1,3a,4,6a-tetraazapentalenes (**38**) and 3a,6a-diazapentalenes (**39**) allow valid conclusions about the properties of 1- or 2-azapentalene. Both structures formally combine a pentafulvene and an azapentafulvene system. This consideration encouraged us to synthesize azapentalenes, starting from pentafulvenes.

6,6-Bis(dimethylamino)pentafulvene (**77**) (**40**) reacts with ethyl isocyanatoformate at 20° yielding 6,6-bis(dimethylamino)-1-*N*-(ethoxycarbonyl)carbamoylfulvene (**78**).



The thermolysis of this bifunctional fulvene in boiling pyridine/water leads to about 50% of the 3-dimethylamino-(2*H*)2-azapentalen-1-one (**79**). This can be converted by *O*-alkylation of the lactam moiety by triethyloxonium fluoborate into the 2-azapentalenium salt **80**. As expected the deprotonation of this gives 37% of the bluish-violet, thermally stable lactim ether, the 3-(dimethylamino)-1-ethoxy-2-azapentalene (**81**) (41).

In a principally similar but much simpler manner 1,3-bis(dimethylamino)-2-azapentalene (**84**) is obtained in a "one pot reaction" in 84% yield (42). This procedure consists in the reaction of sodium cyclopentadienide with



N,N,N',N'-tetramethyl-1,3-dichloro-2-azatrimethincyanine chloride (**82**), which is easily available from dimethylcyanamide and *N*-dichloromethylene-*N,N*-dimethylammonium chloride (43). Even at -20° it is impossible to isolate the azafulvene **83**, which is expected as intermediate. The red 1,3-bis(dimethylamino)-2-azapentalene (**84**) is formed immediately and can be purified by sublimation at 150° .

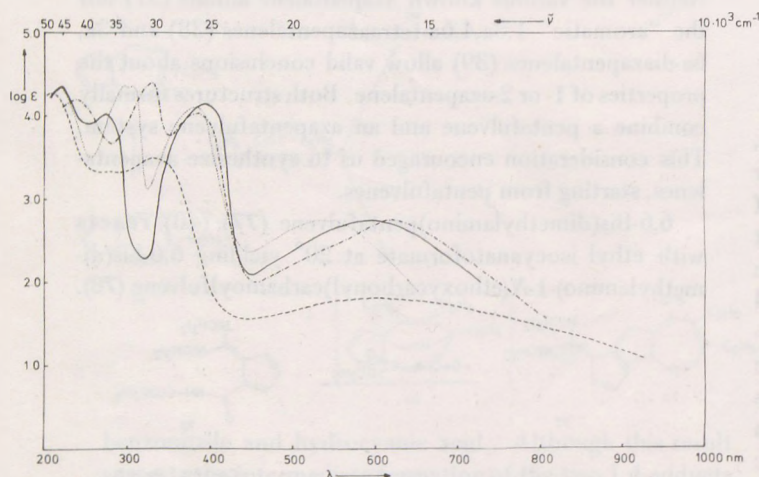
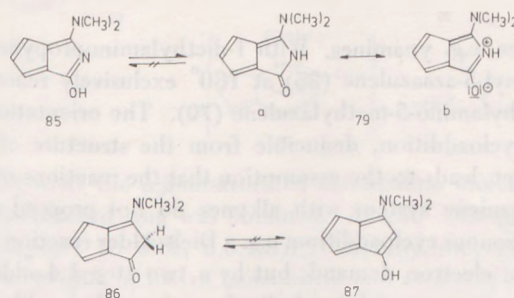
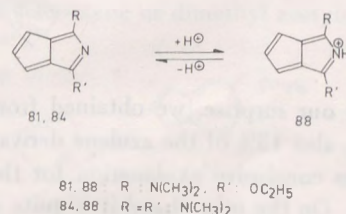


Figure 4: Uv spectra (in *n*-hexane) of 1,3-bis(dimethylamino)pentalene (**75**) - - - -; 1,3,5-tri-*t*-butylpentalene (**76**) ·····; 1-dimethylamino-3-ethoxy-2-azapentalene (**81**) ———; 1,3-bis(dimethylamino)-2-azapentalene (**84**) - · - · - ·

The uv spectra (Figure 4) of the 2-azapentalenes **81** and **84** reasonably agree with the values obtained by a SCF-CI calculation (44). In the 2-azapentalene as well as in the 5-azaazulene system the heteroatom, in a position of high electron density, causes a hypsochromic shift of the longest wave length absorption by comparison with the electron spectra of 1,3-bis(dimethylamino)pentalene (**75**) and 1,3,5-tri-*t*-butylpentalene (**76**). The obviously small influence of different substituents upon the longest wave length absorption of **75**, **76** and **81** is surprising and does not correspond with the results in the azulene chemistry.

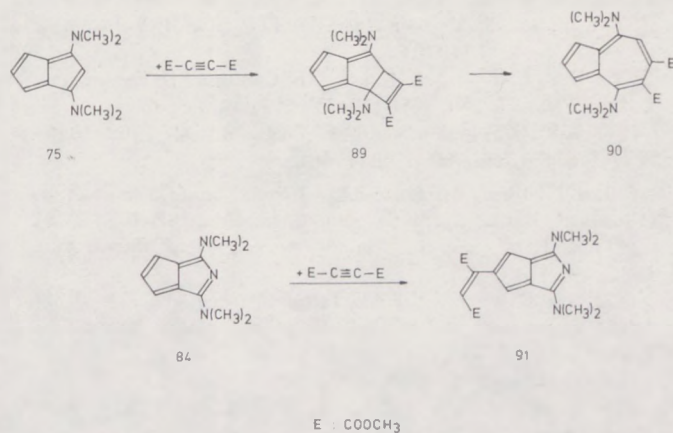


On the other hand, as expected, the uv and ir spectra of the 3-dimethylamino-(2*H*)2-azapentalen-1-one (**79**) do not allow detection of an equilibrium with the tautomeric lactim structure **85** with an 8 π -electron perimeter. As in case of the (5*H*)5-azaazulenes **22** and **23** the fulvenoid lactam structure of the 2-azapentalene-1-one **79a** is energetically favored. However, in contrast to the first it seems rather unlikely, that the dipolar resonance structure **79b** contributes to the ground state of this compound. The same is true for the carbocyclic analogue, the 3-dimethylamino(2*H*)pentalen-1-one (**86**) (34), which also shows no tendency to establish the bicyclic conjugated 8 π -electron system **87**.



Both 2-azapentalene derivatives **81** and **84** show a marked basicity and are converted already by very dilute acetic acid (10^{-3} *N*) in a reversible reaction into the conjugated acids **88**.

Contrary to 1,3-bis(dimethylamino)pentalene (**75**), which reacts with dimethyl acetylenedicarboxylate in a 2+2- or 2+8-cycloaddition to the cyclobutene derivative **89** which undergoes a valence isomerization to the azulene derivative **90** (45), the aza analogue **84** combines with this alkyne by a Michael addition to 72% of the dimethyl 1,3-bis(dimethylamino)-2-azapentalen-5-yl-fumarate (**91**).



To conclude, the heterocyclic systems discussed in this paper show in comparison to their carbocyclic analogues a detectable influence of nitrogen on the bonding structure and a strong effect on the reactivity, which obviously depends on the position of the heteroatom in the perimeter. From further studies in this field similar reactions and differences between nonbenzenoid carbocyclic conjugated π -electron systems and their hetero analogues as well as further information about the validity of theoretical concepts, well proved in the carbocyclic series, for their heterocyclic counterparts will be expected.

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