3a,6a-Diazapentalenes. Synthesis and Chemistry[1]

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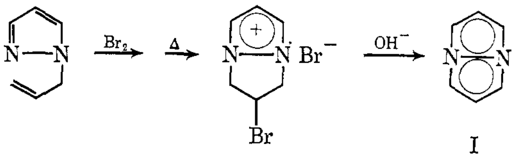
Abstract: The parent compound, 3a,6a-diazapentalene,[2] and other 3a,6a-diazapentalenes were synthesized and isolated. The synthetic route involved bromination and cycloquaternization of appropriately substituted 1-allylpyrazoles, followed by double dehydrohalogenation with base. These new heteroaromatic and mesoionic compounds are colorless, air-sensitive solids which react with electrophiles as allylic carbanions to yield mainly 1,3-disubstitution products. Substitution with electron-delocalizing groups at positions 1 and 3 stabilizes 3a,6a-diazapentalenes and introduces strong absorption in the visible. The nature of the mesoionic 3a,6a-diazapentalene ring and its chemical reactivity are discussed.

A great deal of work has been done in the past decade to demonstrate the general applicability of Hückel's $4n + 2$ rule, which states that cyclic, planar molecules containing $4n + 2$ π electrons possess relative electronic stability while those with $4n$ π electrons do not. Although strictly intended for monocyclic systems, this rule may also be applied in certain cases to the π-bonded periphery of a polycyclic molecule. Recent examples of such aromaticity are numerous, running the gamut through carbocyclic and heterocyclic compounds, which, in turn, may be not only neutral entities but anionic or cationic species as well.

A good case in point is pentalene. It is a bicyclic 8 π-electron system and as such ought to be nonaromatic. The parent pentalene has thus far eluded all synthetic efforts. On the other hand, its dianion, a 10 π-electron system, has been synthesized[3] and shown to be aromatic in the sense of, for instance, exhibiting a ring current.

Closely related to the pentalene–pentalene dianion pair are azapentalenes, the type of relationship to the pentalene counterpart being determined by the location of nitrogen atoms. Thus, polyazapentalenes with unsubstituted nitrogens at positions other than 3a,6a should be 8 π-electron systems expected to resemble pentalene and should be nonaromatic while those containing nitrogen atoms at the 3a,6a positions should have 10 π electrons and exhibit aromaticity. Indeed, the reported tetraazapentalenes,[4] triazapentalenes,[5] and diazapentalenes[6] containing annular nitrogen atoms showed remarkable stability and properties consistent with aromaticity. All of these compounds, however, contained at least two substituents on the polyazapentalene ring. Since an otherwise nonviable system might be stabilized by appropriate substitution,[7] it was of interest to examine the unsubstituted parent systems, in particular 3a,6a-diazapentalene (I), which is the simplest representative of this class, and to devise a general synthetic approach to other substituted 3a,6a-diazapentalenes.

The synthesis of 3a,6a-diazapentalene has been effected by a route[8] consisting of the following reaction sequence: allylation of pyrazole; bromination of the double bond, followed by intramolecular quaternization without isolating the dibromide; and finally double dehydrohalogenation with base. Independently, a similar approach has been adopted by others.[9] Obviously, by starting with appropriately substituted pyrazoles and substituted allyl halides, one should be able to follow this scheme and obtain diversely substituted 3a,6a-diazapentalenes.



I

Results and Discussion

The above reaction sequence was studied mainly as a function of substituents on the pyrazole ring. It was found that allylation of pyrazoles proceeds readily regardless of the nature of their substituents (Table I). The addition of bromine to the double bond was equally facile although some concurrent bromination of an open 4 position could not be avoided. It was expedient to quaternize the crude bromination product and to purify the quaternary salts, monitoring this purification by nmr. In some instances purification was facilitated by converting them to the sparingly soluble hexafluorophosphate salts. The bromides as well as the hexafluorophosphates are stable to storage and have shown no sign of deterioration on exposure to air and moisture for over 3 years.

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(1) Presented in part at the 151st National Meeting of the American Chemical Society, Pittsburgh, Pa., March 1966.

(2) Pyrazolo[1,2-*a*]pyrazole. The numbering of the pentalene nucleus conforms with accepted usage ("The Ring Index," 2nd ed, p 137), the bridgehead positions being 3a,6a.

(3) T. J. Katz, M. Rosenberger, and R. K. O'Hara, *J. Am. Chem. Soc.*, **86**, 249 (1964).

(4) (a) R. A. Carboni and J. E. Castle, *ibid.*, **84**, 2453 (1962); (b) R. Pfleger, E. Garthe, and K. Rauer, *Ber.*, **96**, 1827 (1963); (c) M. Brufani, W. Fedeli, G. Giacomello, and A. Vaciago, *ibid.*, **96**, 1840 (1963); (d) Aromatic Azapentalenes. I: R. A. Carboni, J. C. Kauer, J. E. Castle, and H. E. Simmons, to be submitted. (e) Aromatic Azapentalenes. II: R. A. Carboni, J. C. Kauer, W. R. Hatchard, and R. J. Harder, to be submitted. (f) Aromatic Azapentalenes. III: J. C. Kauer and R. A. Carboni, to be submitted.

(5) B. M. Lynch and Y.-Y. Hung, *J. Heterocyclic Chem.*, **2**, 218 (1965).

(6) T. G. W. Solomons, F. W. Fowler, and J. Calderazzo, *J. Am. Chem. Soc.*, **87**, 528 (1965).

(7) While pentalene is unknown, hexaphenylpentalene [E. LeGoff, *ibid.*, **84**, 3975 (1962)] and dibenzopentalene [C. T. Blood and R. P. Linstead, *J. Chem. Soc.*, 2255, 2263 (1952), and C. C. Chuen and S. W. Fenton, *J. Org. Chem.*, **23**, 1538 (1958)] have been prepared.

(8) S. Trofimenko, *J. Am. Chem. Soc.*, **87**, 4393 (1965).

(9) T. W. G. Solomons and C. F. Voigt, *ibid.*, **87**, 5256 (1965); **88**, 1992 (1966).

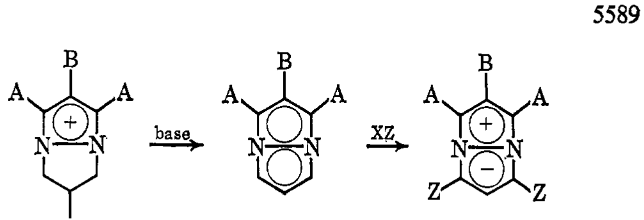
As might be expected, the ease of intramolecular quaternization is a function of electron supply at the 2-nitrogen. Thus, while the dibromides derived from alkyl-substituted 1-allylpyrazoles (and 1-allylpyrazole itself) were quaternized readily at 100°, longer heating was necessary for the dibromide from 1-allyl-4-bromopyrazole. Dibromides from 1-allyl-4-cyanopyrazole and 1-allyl-3,4,5-tribromopyrazole failed to be quaternized; dehydrobromination and decomposition occurred under forcing conditions.

The double dehydrohalogenation of these quaternary salts has been carried out in a number of ways—most simply by mixing their aqueous solutions with aqueous alkali. The 3a,6a-diazapentalenes thus produced are colorless solids soluble in, yet unaffected by, water. They are, however, very sensitive to air, especially the parent compound, and have to be handled in an inert atmosphere. Even then their lifetime is relatively short. 3a,6a-Diazapentalenes react instantaneously with tetracyanoethylene to form a brilliant red dye which constitutes a convenient qualitative test.[10]

Evidence for the structure of 3a,6a-diazapentalene rests on (a) its simple infrared spectrum with peaks at 3160 (s), 1430, 1140, 1139 (s), 1040, and 929 (s) cm^{-1}, indicating a highly symmetrical structure; (b) its nmr spectrum, which consists of a doublet at τ 2.99 and a triplet at τ 3.35 (J = 2.5 cps), with relative areas 2:1; and (c) its mass spectrum where the most abundant peak is that of the parent ion, $C_6H_6N_2$, m/e 106, along with peaks of m/e 80 (parent less C_2H_2), 53 (C_2HN_2), 52 (C_2N_2), and 39 (C_3H_3). The structure of 2-bromo-3a,6a-diazapentalene, purified by sublimation, was established in similar fashion. This colorless crystalline compound has a simple infrared spectrum with main peaks at 3170 (s), 1430, 1400, 1139 (s), 1041, and 929 (s), very similar to that of 3a,6a-diazapentalene. Its nmr spectrum has a two-peak system at τ 2.85 and 2.92 in 3:1 ratio, resulting from overlap of the 1,3-H singlet with the 4,6-H doublet, and a triplet (J = 2.5 cps) at τ 3.27. Its mass spectrum has two sharp parent peaks of m/e 184 and 186, corresponding to $C_6H_5BrN_2$ with the Br^{79} and Br^{81} isotopes. It also has peaks of m/e 146, 148 (bromopyrazole), 105 (parent less Br), 68 (pyrazole), 53 (C_3H_3N), 52 (C_3H_2N), and 51 (C_3HN).

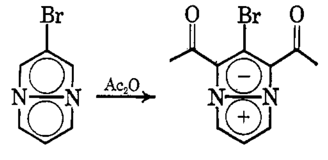
This compound, like 3a,6a-diazapentalene, turns dark green on exposure to air, although less rapidly than the parent. By contrast, 1,2,3-trimethyl-3a,6a-diazapentalene and 1,3-dimethyl-2-bromo-3a,6a-diazapentalenes react with air to give red-violet products.

Further support for the structural assignment was obtained by preparing stable acetyl-, benzoyl-, and cyano-substituted derivatives, II–VII, by treating the various 3a,6a-diazapentalenes with acetic anhydride, benzoyl chloride, and cyanogen chloride, respectively. In each case the products were those of 1,3 disubstitution. Their structures were established unequivocally by nmr.

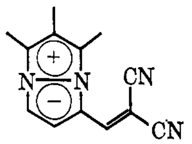


II, A = B = H; Z = CH_3CO
III, A = B = H; Z = C_6H_5CO
IV, A = B = H; Z = CN
V, A = B = CH_3; Z = CH_3CO
VI, A = B = CH_3; Z = C_6H_5CO
VII, A = CH_3; B = Br; Z = CN

Acetylation and benzoylation of 2-bromo-3a,6a-diazapentalene gave rise to the 1,3 derivatives, no 4,6-disubstitution product being detected.



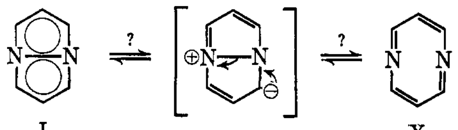
VIII



XI

Reaction of 1,2,3-trimethyl-3a,6a-diazapentalene with ethoxymethylenemalononitrile yielded the orange 4-(2,2-dicyanovinyl) derivative IX. Compounds II–IX are stable to air and have been stored for over 2 years without deterioration, although some of the diacetyl derivatives are photosensitive.

The question of 3a,6a-diazapentalene structure *vs.* the valence bond tautomer, 1,5-diazacyclooctatetraene (X), is pertinent to all polyazapentalenes with two



I Ia X

annular nitrogen atoms. It has been resolved in the case of tetraazapentalenes by X-ray work[2c] as well as by chemical studies and HMO calculations.[11] These indicate that the 10 π-electron polyazapentalene structure is more stable than the 8 π-electron polyazacyclooctatetraene and that the latter, if ever formed, should isomerize exothermally to the former. Analogous reasoning applies to 3a,6a-diazapentalene where 16 nonexcited, charge-separated resonance structures can be written.

The chemical reactivity of 3a,6a-diazapentalene is reconciled best with structure I which, while of D_{2h} symmetry, would show nucleophilic behavior of an allylic carbanion.[12] Once an electron-delocalizing substituent has been introduced, however, the charge separation within the two rings becomes "fixed" and the second substituent is directed into the 3 position. At this point the negative charge is sufficiently delocalized to change the character of the molecule to betaine-like, so that one could write structure II as XI. This point is reached at the monosubstitution stage if the substituent is a particularly good electron delocalizer, as is the dicyanovinyl group.

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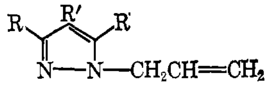
[10] We did not notice a separate π-complex stage prior to tricyanovinylation; this is in contrast to the reaction of tetracyanoethylene with N,N-dimethylaniline [B. C. McKusick, R. E. Heckert, T. L. Cairns, D. D. Coffman, and H. F. Mower, *J. Am. Chem. Soc.*, 80, 2806 (1958)] or benzotetraazapentalenes[4e,f] where the formation of a discrete blue π complex of moderate lifetime is observed before formation of the red tricyanovinyl dye.

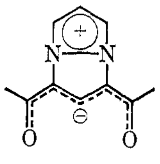
[11] Aromatic Azapentalenes. IV: Y. T. Chia and H. E. Simmons, to be submitted.

[12] Mechanistically, the products obtained could have also arisen by way of dipolarophilic addition at positions 1,6 followed by rearrangement.

Table I. Allylpyrazoles of Structure



R	R′	Bp, °C (mm)	nD	% yield	Calcd, % C	Calcd, % H	Calcd, % N	Calcd, % Br	Found, % C	Found, % H	Found, % N	Found, % Br
H	Br	43 (0.31)	1.5272	82	38.5	3.74	...	42.7	38.6	4.09	...	42.0
H	CN	80–84 (0.35)	1.5146	52	63.1	5.30	31.6	...	62.2	5.39	31.3	...
Me	H	45 (0.45)	1.4836	91	70.6	8.88	20.6	...	70.5	8.73	20.5	...
Me	Me	58 (0.4)	1.4876	91	72.0	9.39	18.6	...	72.0	9.33	18.6	...
Me	Br	80 (2.5)	1.5189	67	44.7	5.12	...	37.2	44.6	5.29	...	36.8
Br	Br	91–93 (0.32)	1.5894	65	20.9	1.45	...	69.6	21.4	1.80	...	65.8



XI

The above is borne out by the stability of II and the great similarity of its nmr spectrum (4,5,6-hydrogens) with that of the pyrazolium cation.

Indications are that a continuum exists between the two extremes, the symmetrical I and the "charge-fixed" XI, represented by various 3a,6a-diazapentalenes with substituents that polarize the molecule. This ease of polarization can be judged from the exclusive direction of, *e.g.*, acylation in 2-bromo-3a,6a-diazapentalene. Certainly, had any substituent gone to the 4 or 6 position it would have given rise to the oppositely polarized molecule with the formation of a 4,6-disubstitution product, none of which was detected.

Experimental Section

Allylation of the various pyrazoles was carried out in several ways: by preparing a sodium or potassium salt of the substituted pyrazole (*via* sodium hydride or potassium metal) and heating it with allyl bromide, or by refluxing the pyrazole in question with equimolar amounts of allyl bromide and diisopropylethylamine. The last method is the preferred one and is exemplified below.

1-Allyl-4-bromopyrazole. A solution of 195 g (1.33 moles) of 4-bromopyrazole, 172 g (1.33 moles) of diisopropylethylamine, and 170 g (1.40 moles) of allyl bromide in 850 ml of dry tetrahydrofuran was refluxed for 3 days, after which time the solution ceased to be basic. The mixture was cooled with stirring, 1 l. of ether was added, and the mixture was filtered. The hydrobromide was washed with ether and saved for later recovery of the amine. The filtrates were combined, the solvent was stripped, and the residual liquid was distilled *in vacuo*. There was obtained 204 g (82%) of a colorless liquid.

Results of other allylations are summarized in Table I.

1,2-(2-Bromotrimethylene)pyrazolium Bromide (A) and 1,2-(2-Bromotrimethylene)-4-bromopyrazolium Bromide (B). A solution of 0.5 mole of 1-allylpyrazole[13] in 500 ml of carbon tetrachloride was stirred at 0–5°. A solution of 80 g (0.5 mole) of bromine in 500 ml of carbon tetrachloride was added slowly. The solution was decanted from a gummy residue, the solvent was stripped, and the residue was heated on a steam bath until it had largely solidified. The mixture was filtered; the solid was washed with ether and recrystallized from absolute alcohol. The first product that precipitated in 2.4 g yield was predominantly B (about 9:1 ratio of B:A). B decomposes slowly at around 230°. The filtrate was mixed with a large excess of ether which precipitated compound A, mp 158–159° (by nmr a 92:8 mixture of A and B), in a 23.5-g yield. From the mother liquors another 3.0 g of crude A was obtained.

Anal. (A) Calcd for $C_6H_8Br_2N_2$: C, 26.9; H, 2.99; Br, 59.8; N, 10.4. Found: C, 26.8; H, 2.81; Br, 60.1; N, 9.63. *Anal.* (B) Calcd for $C_6H_7Br_3N_2$: C, 20.8; H, 2.08; Br, 69.2; N, 8.07 Found: C, 21.1; H, 2.23; Br, 69.1; N, 7.89.

The ultraviolet spectrum of B had λ_{max} 244 mμ (ϵ 3130); that of A had λ_{max} 224 mμ (ϵ 4450).

The nmr spectrum of B (D_2O) consists of a singlet at τ 1.16, a multiplet at τ 4.30, and a doublet at τ 4.65 (J = 3.4) with relative areas 2:1:4, respectively. The nmr spectrum of A (D_2O) consists of a doublet at τ 1.65 (J = 2.9), triplet at τ 3.02 (J = 2.9), a multiplet at τ 4.52 (J = 3.5) and doublet at τ 4.89[14] (J = 2.9).[15] In each case the low-field peak of the four-proton doublet showed additional splitting of 1.7 (A) and 1.3 cps (B).

Compound A was purified by repeated recrystallization from isopropyl alcohol (10 ml/g), the purity being determined by the peak ratio of the 3,5-hydrogens. Starting with a 95:5 mixture, the amount of B was reduced to 3.7% by two recrystallizations.

When a solution of the 95:5 salt mixture was treated with an aqueous solution of ammonium hexafluorophosphate, the sparingly soluble hexafluorophosphates derived from A and B precipitated. The pure hexafluorophosphate of A was obtained after a single recrystallization from acetone. It melts at 185–186°.

Anal. Calcd for $C_6H_8BrF_6N_2P$: C, 21.8; H, 1.52; N, 8.49; F, 34.5. Found: C, 22.1; H, 1.68; N, 8.42; F, 34.3.

1,2-(2-Bromotrimethylene)-4-bromopyrazolium Bromide. 1-Allyl-4-bromopyrazole (202 g, 1.08 moles) was dissolved in 1700 ml of carbon tetrachloride, and 180 g (1.12 moles) of bromine was added slowly without external cooling. The solution was decanted from a small amount of gummy material, and the solvent was stripped. The residual oil was heated on a steam bath for 2 days. The resulting solid was recrystallized from 1 l. of water (the color being removed with Darco) and was washed successively with water, ethanol, and ether. The first crop weighed 196 g (52.5%). By concentration of the filtrate further crops of 69.0 and 10.1 g (18.4 and 2.7%) were obtained. The final filtrate was evaporated to dryness and triturated with hot methanol, yielding another 23.0 g (6.1%) of less pure product for a total yield of 79.7%.

The product was identical in all respects (melting point, infrared and nmr spectra) with authentic material (compound B from the preceding experiment).

1,2-(2-Bromotrimethylene)-3,5-dimethyl-4-bromopyrazolium Bromide. To 136 g (1 mole) of 1-allyl-3,5-dimethylpyrazole stirred at 10–15° in 800 ml of CCl_4 was added dropwise 160 g (1 mole) of bromine. The solution was decanted from a heavy oil, and the solvent was stripped on a steam bath. The semisolid residue was triturated with chloroform and filtered. The solid was purified by recrystallization from water for a yield of 28 g (7.5%). It decomposes slowly above 220°.

Anal. Calcd for $C_8H_{11}Br_3N_2$: C, 25.6; H, 2.94; Br, 64.1. Found: C, 25.8; H, 2.94; Br, 63.7.

The nmr spectrum was confirmatory with a quintuplet at τ 4.42 (J = 3 cps), doublet at τ 3.90 (J = 3 cps), and singlet at τ 7.45 with relative areas of 1:4:6, respectively, corresponding to the 2-methylene proton, 1,3-methylenes, and 3,5-methyls.

The same material was obtained in better yield (32%) by running the bromination and quaternization on 1-allyl-3,5-dimethyl-4-bromopyrazole. The loss of product occurred in the cyclization step due to competing dehydrohalogenation.

1,2-(2-Bromotrimethylene)-3,4,5-trimethylpyrazolium Bromide. 1-Allyl-3,4,5-trimethylpyrazole was dissolved in carbon tetrachloride and treated with an equimolar amount of bromine. The solution, after decantation from some resin, was stripped of solvent

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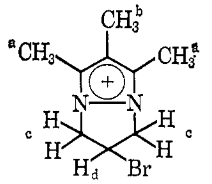
(13) L. L. Finar and K. Utting, *J. Chem. Soc.*, 5272 (1960).

(14) The value of τ 5.32 reported[8] is an error.

(15) All J values in cps.

on a steam bath. The residual oil was heated on the steam bath until it partly solidified. The solid was dissolved in ethanol, and the solution was stirred with Darco and filtered. Ether was added to the filtrate, causing the separation of some solid. The nmr of this solid was in accord with structure



having a multiplet at τ 4.50, doublet at τ 5.07, and singlets at τ 7.58 and 7.91 with relative areas 1:4:6:3, corresponding to hydrogens d, c, a, and b, respectively. The material was extremely soluble in water and alcohols and could not be conveniently recrystallized. It was used directly in all conversions to 1,2,3-trimethyl-3a,6a-diazapentalene and its derivatives.

The hexafluorophosphate was prepared readily by mixing aqueous solutions of the bromide and of ammonium hexafluorophosphate. This derivative was recrystallized from ethanol and melted at 135–136°.

Anal. Calcd for $C_9H_{14}BrF_6PN_2$: C, 28.8; H, 3.74. Found: C, 29.0; H, 3.88.

3a,6a-Diazapentalene. To 10 ml of 0.5 *M* aqueous solution of 1,2-(2-bromotrimethylene)pyrazolium bromide was added 20 ml of 25% sodium hydroxide. A solid formed, which was quickly filtered and bottled. Despite the fact that all these operations were carried out in a nitrogen tent, the product became brown. Small portions of it were sublimed in a tube at 70° (1 mm) to yield white crystals. The crystals were mulled with Nujol (under nitrogen) for taking the infrared spectrum, which was rather simple with bands at 3160 (strong), 1430, 1400, 1139 (strong), 1040, and 929 (strong) cm^{-1}. On exposure to air the crystals became black.

Because of such high air sensitivity, 3a,6a-diazapentalene was analyzed by mass spectrometry, being injected directly into the ionization chamber. The structure was confirmed by the presence of a strong parent peak at m/e 106.

The nmr spectrum consisted of a doublet at τ 2.99 and a triplet at τ 3.35 (J = 2.5 cps) with relative areas of 2:1, in accord with the 3a,6a-diazapentalene structure.

Solutions of 3a,6a-diazapentalene, even when kept under nitrogen, deposit a black solid.

2-Bromo-3a,6a-diazapentalene. An aqueous solution of 1,2-(2-bromotrimethylene)-4-bromopyrazolium bromide was poured into excess 25% sodium hydroxide, and the resulting clay-colored solid was quickly pressed dry and sublimed at 80° (1 mm). A white, crystalline sublimate was obtained. It is less air sensitive than 3a,6a-diazapentalene. It has no well-defined melting point but darkens gradually on being heated in a capillary tube.

The nmr spectrum is confirmatory with a two-peak system of four hydrogens at τ 2.85 and 2.92 in 3:1 ratio, resulting from overlap of the 1,3-proton singlet with the 4,6-proton doublet, and a triplet corresponding to the 5-proton (J = 2.5 cps) at τ 3.27.

Analysis of 2-bromo-3a,6a-diazapentalene was carried out by mass spectrometry. The 2-bromo-3a,6a-diazapentalene structure was confirmed by the presence of strong m/e 184 and m/e 186 parent isotope ions.

1,2,3-Trimethyl-3a,6a-diazapentalene. An aqueous solution of 1,2-(2-bromotrimethylene)-3,4,5-trimethylpyrazolium bromide was mixed with 25% sodium hydroxide solution, and the product was quickly extracted with chloroform-*d*. The nmr spectrum was determined immediately. It exhibited two singlets in 2:1 ratio at τ 7.55 and 7.77 assigned to the CH_3 groups. The concentration was too low for detecting the ring H atoms.

When the above reaction was repeated without extracting the product, dark oily globules formed which solidified on standing. The compound can be distilled *in vacuo* yielding a colorless oil which solidifies on cooling. Upon exposure to air it turns violet immediately, then black. 1,3-Dimethyl-2-bromo-3a,6a-diazapentalene showed similar behavior.

Tests on 3a,6a-Diazapentalenes. A simple test for the formation of 3a,6a-diazapentalenes consists of adding a few milliliters of benzene containing tetracyanoethylene to an aqueous solution of the appropriate quaternary pyrazolium salt, followed by 1 ml of 25% aqueous sodium hydroxide. The 3a,6a-diazapentalene is extracted into the benzene layer where it forms instantaneously a deep red dye. In the absence of tetracyanoethylene, the reaction with air proceeds at the surface to give the dark decomposition products derived from diazapentalene.

A convenient test for the reaction or nonreaction of a compound with 3a,6a-diazapentalene consists of replacing tetracyanoethylene in the above experiment with a second reaction component. In the case of nonreaction, the usual oxidation of 3a,6a-diazapentalene with air is observed (this happens with, *e.g.*, tolane or phenylacetylene). If on the other hand a reaction takes place, the oxidative reaction is not observed, and a clear solution of the addition product results.

3a,6a-Diazapentalene (and 2-bromo-3a,6a-diazapentalene) were found to react, by the above criterion, with dimethyl acetylenedicarboxylate, dimethyl azodicarboxylate, and acrylonitrile, presumably *via* 1,3-dipolar addition (*i.e.*, 1,6 addition by the pentalene numbering system).

3a,6a-Diazapentalene-1,3-dicarbonitrile. A 0.5 *M* solution of 1,2-(2-bromotrimethylene)pyrazolium bromide (100 ml) was added to a nitrogen-flushed separatory funnel containing 150 ml of chloroform and 150 ml of 25% sodium hydroxide solution. The 3a,6a-diazapentalene was quickly extracted with chloroform, and the extract was poured into 150 ml of chloroform containing about 5 ml of cyanogen chloride. This reaction mixture was stirred with anhydrous magnesium sulfate and with Darco and was filtered. The solid was washed thoroughly with chloroform and the filtrate stripped of solvent to yield 1.3 g (18%) of a dark reddish-brown solid. The product was purified by sublimation at 220° (1 mm). A white crystalline material was obtained which sintered at around 226° and slowly decomposed at higher temperatures.

Anal. Calcd for $C_8H_4N_4$: C, 61.5; H, 2.58; N, 35.9; mol wt, 156. Found: C, 61.7; H, 2.73; N, 36.0; mol wt, 163 (by osmometry in chloroform).

The infrared spectrum has a very strong conjugated nitrile band at 2210 cm^{-1}.

1,3-Dimethyl-2-bromo-3a,6a-diazapentalene-4,6-dicarbonitrile. 1,2-(2-Bromotrimethylene)-3,5-dimethyl-4-bromopyrazolium bromide (20 g, 0.053 mole) was dissolved in 150 ml of water. This solution was added with 250 ml of chloroform to a 1-l. separatory funnel blanketed with nitrogen. Sodium hydroxide (100 ml, 25%) was added, and the 1,3-dimethyl-2-bromo-3a,6a-diazapentalene was quickly extracted into the chloroform layer which was then promptly poured into a chloroform solution of 10 ml (large excess) of cyanogen chloride. The resulting dark mixture was filtered and the filtrate stripped of solvent. The residue was stirred with chloroform, and the mixture was filtered, yielding a total of 3.6 g (25%) of light tan needles decomposing at ~260°. The compound was purified by recrystallization from toluene and by sublimation.

Anal. Calcd for $C_{10}H_7BrN_4$: C, 45.7; H, 2.66; N, 21.3. Found: C, 45.7; H, 2.88; N, 20.6.

The nmr spectrum was confirmatory with two singlets at τ 2.58 and 7.30 (intensity ratio 1:6) corresponding to the 5-hydrogen and the 1,3-methyl hydrogens, respectively. The infrared spectrum had a very strong conjugated nitrile band at 2220 cm^{-1}.

1,3-Dibenzoyl-3a,6a-diazapentalene. A benzene solution of 3a,6a-diazapentalene was prepared by adding 20 ml of a 0.5 *M* solution of 1,2-(2-bromotrimethylene)pyrazolium bromide to a large excess of 25% sodium hydroxide covered with about 200 ml of benzene. The two-phase system was stirred and the benzene layer transferred under nitrogen into a second flask containing 3 g of benzoyl chloride. The resulting mixture was filtered, and the solid was heated at 300° (1 mm), whereupon an orange liquid distilled and solidified on cooling. The product was purified by recrystallization from ethanol, mp 188–189°.

Anal. Calcd for $C_{20}H_{14}N_2O_2$: C, 76.4; H, 4.49; N, 8.90; mol wt, 314. Found: C, 76.4; H, 4.59; N, 8.66; mol wt, 323 (by osmometry in chloroform).

The nmr spectrum has the 4,6-hydrogens as a doublet (J = 2.9) at τ 1.36; the 2-hydrogen is overlapped by the phenyl hydrogens, a multiplet in the τ 2.15–2.58 range. The 5-hydrogen appears as a triplet (J = 2.9) further split into doublets (J = 1.1) at τ 3.12.

The ultraviolet spectrum has maxima at 430 mμ (ϵ 30,200), 342 (16,100), 250 (14,900), and 228 (16,500).

A better yield (32%) of 1,3-dibenzoyl-3a,6a-diazapentalene was obtained when the diazapentalene was extracted into chloroform, and the crude product was purified by chromatography.

1,3-Diacetyl-3a,6a-diazapentalene. 3a,6a-Diazapentalene was prepared from 10 g of 1,2-(2-bromotrimethylene)pyrazolium bromide as described in the preceding experiment. The chloroform extract of 3a,6a-diazapentalene was stirred for 10 min with 30 ml (large excess) of acetic anhydride under nitrogen. The product was purified by chromatography on alumina and was obtained as a yellow solid, mp 155°, in 34% yield.

Anal. Calcd for $C_{10}H_{10}N_2O_2$: C, 63.1; H, 5.30; N, 14.7. Found: C, 62.9; H, 5.29; N, 14.7.

The nmr spectrum was in accord with the assigned structure having a doublet (J = 2.8 cps) at τ 1.66, a doublet (J = 1.1) at τ 2.60, a triplet (J = 2.8) further split into doublets (J = 1.1) at τ 3.26, and a singlet at τ 7.57 in 2:1:1:6 ratio.

The ultraviolet spectrum had maxima at 396 mμ (ϵ 31,400), 322 (20,000), sh 262 (2990), 247 (6260), with a doublet at 223 and 219 (15,900 and 15,800). This compound has a dipole moment of 2.12 D. A 76% yield was obtained by the method used in the experiment below.

1,3-Diacetyl-2-bromo-3a,6a-diazapentalene. A mixture of 17.4 g (0.05 mole) of 1,2-(2-bromotrimethylene)-4-bromopyrazolium bromide and 27.6 g (0.2 mole) of anhydrous potassium carbonate in 150 ml of acetic anhydride was stirred and refluxed (under nitrogen) for 2 hr. The mixture was filtered, and the cake was washed with chloroform. The filtrate and washings were stripped of solvent, and the residue was chromatographed on alumina, with methylene chloride as eluent. There was obtained 10.5 g (78%) of canary yellow solid which was purified by recrystallization from ethanol and melted at 146–147°.

Anal. Calcd for $C_{10}H_9BrN_2O_2$: C, 44.7; H, 3.35. Found: C, 44.9; H, 3.51.

The nmr spectrum was confirmatory with a doublet at τ 1.45, triplet at τ 3.25 (J = 2.9 cps), and singlet at τ 7.35 in a 2:1:6 ratio. The dipole moment was 1.82 D.

1,3-Dibenzoyl-2-bromo-3a,6a-diazapentalene. A solution of 14 g (0.04 mole) of 1,2-(2-bromotrimethylene)-4-bromopyrazolium bromide in 100 ml of hot (60°) water was added to a nitrogen-blanketed flask containing 300 ml of chloroform and 100 ml of 13% sodium hydroxide. The two-phase system was stirred until the aqueous layer was clear; 18 g (0.13 mole) of benzoyl chloride was then added. The reaction mixture was stirred for 70 min, and the organic layer was chromatographed on alumina. The orange eluate was concentrated to 100 ml and was rechromatographed on alumina.

The product was obtained in 4.2 g (27%) yield. It was recrystallized from ethanol and obtained as silky yellow fibers, mp 186–187° dec.

Anal. Calcd for $C_{20}H_{13}BrN_2O_2$: C, 61.1; H, 3.31; Br, 20.3. Found: 61.2; H, 3.21; Br, 19.9.

The nmr spectrum has a doublet at τ 1.35 (J = 2.8), a multiplet at τ 2.56, and a triplet at τ 3.12 in a 2:10:1 ratio.

The ultraviolet spectrum has maxima at 428 mμ (ϵ 26,800), 330 (12,300), 260 (13,800), and 230 (9500).

1,2,3-Trimethyl-4-(2,2-dicyanovinyl)-3a,6a-diazapentalene. A mixture of 15.5 g (0.005 mole) of 1,2-(2-bromotrimethylene)-3,4,5-trimethylpyrazolium bromide, 27.6 g (0.2 mole) of anhydrous potassium carbonate, and 24.4 g (0.2 mole) of ethoxymethylenemalononitrile in 250 ml of methanol was stirred and refluxed under nitrogen for 2 hr. The mixture was filtered, and the filtrate was stripped to dryness. The residue was purified by chromatography on alumina, the orange band being eluted with methylene chloride. There was obtained 4.8 g (43%) of orange solid which, after recrystallization from dimethylformamide, melted at 264–265°. It has an intense CN band at 2400 cm^{-1}. When the above reaction was run in dimethylformamide instead of methanol, the yield dropped to 22%.

Anal. Calcd for $C_{13}H_{12}N_4$: C, 69.6; H, 5.39; N, 25.0. Found: C, 69.3; H, 5.40; N, 25.1.

1,2,3-Trimethyl-4,6-diacetyl-3a,6a-diazapentalene. A mixture of 15.5 g (0.005 mole) of 1,2-(2-bromotrimethylene)-3,4,5-trimethylpyrazolium bromide and 27.6 g (0.2 mole) of anhydrous potassium carbonate in 150 ml of acetic anhydride was stirred and refluxed under nitrogen for 2 hr. The mixture was filtered hot, and the cake was washed with chloroform. The filtrate and the washings were stripped to dryness, and the residue was chromatographed on alumina, the yellow band being eluted with methylene chloride. There was obtained 8.7 g (75%) of bright yellow solid, which was purified by recrystallization from ethanol and melted at 154–155°. This compound has a dipole moment of 2.00 D.

Anal. Calcd for $C_{13}H_{16}N_2O_2$: C, 67.2; H, 6.94. Found: C, 67.0; H, 6.97.

The nmr spectrum has four singlets at τ 2.60, 7.37, 7.67, and 8.00 with relative areas 1:6:6:3

The ultraviolet spectrum has maxima at 410 mμ (ϵ 24,600), 335 (15,500), 263 (6240), and 225 (13,200).

1,2,3-Trimethyl-4,6-dibenzoyl-3a,6a-diazapentalene. A solution of 15.5 g (0.05 mole) of 1,2-(2-bromotrimethylene)-3,4,5-trimethylpyrazolium bromide in 70 ml of water was added to a nitrogen-flushed flask containing 300 ml of chloroform and 200 ml of 13% sodium hydroxide. The dark two-phase mixture was stirred for 10 min, and 25 ml (large excess) of benzoyl chloride was added. The reaction mixture was stirred for 30 min; the chloroform layer was poured directly onto a chromatography column packed with alumina and eluted with methylene chloride. The orange-red band was collected and stripped of solvent. There was obtained 7.4 g (42%) of orange solid which was purified by recrystallization from ethanol and melted at 202–204°.

Anal. Calcd for $C_{23}H_{20}N_2O_2$: C, 77.5; H, 5.62; N, 7.87. Found: C, 76.7; H, 5.65; N, 7.87.

The nmr spectrum ($CDCl_3$) has a phenyl multiplet centered at τ 2.35 and singlets at τ 2.90, 7.32, and 7.82 in a 10:1:6:3 ratio.

The ultraviolet spectrum has maxima at 440 mμ (ϵ 22,100), 360 (15,200), 248 (sh, 16,400), and 234 (17,000).