esr spectrum in the same manner as for the photolysis product resulted in no detectable signal.

**Determination of Isotopic Composition.** Mass spectra were determined on an Atlas CH-4 instrument at an ionizing voltage of 70 eV. The background was scanned before each run. The $m/e$ 28 peak in the background was usually 2-4% that in the sample. Background was subtracted from the $m/e$ 28 and 29 peaks before computing the per cent $^{29}N_2$. This percentage was then corrected for the natural abundance of $^{29}N_2$ ( $2 \times 0.36\%$) and for 98.0% $^{15}N$ in the terminal nitrogen of the reactant triphenylphenyl azide in order to calculate the per cent retention of label. The results are recorded in Table I. The peak at $m/e$ 30 was scanned for the nitrogen from two of the photolyses and found to be 0.41 ± 0.01% of the peak at $m/e$ 29. Assuming natural abundance of $^{15}N$ in the next-to-terminal nitrogen of the triphenylmethyl azide and neglecting isotope effects, this figure should be approximately 0.36%. Similiarly, nitrogen from three of the pyrolyses gave a peak at $m/e$ 30 which was 0.35 ± 0.02% of the peak at $m/e$ 29.

# Syntheses of Fused Aromatic Heterocycles by 1,3-Dipolar Addition Reactions. 1,3a-Diazapentalenes[1]

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**Abstract:** The reaction of acetylenic esters with ylides derived from imidazole yields derivatives of 1,3a-diazapentalene (IV). The properties of this new class of compounds indicate the presence of aromatic character and are analogous to those of the known 3a,6a-diazapentalenes (III). Unexpectedly, the dicyanomethyl ylides of imidazole and thiazole underwent addition with dimethyl acetylenedicarboxylate to give derivatives of pyrrocoline rather than pentalene.

The reaction of pyrrocoline with dimethyl acetylenedicarboxylate to form cycl[3.2.2]azine derivatives was first observed in 1959.[3] Subsequently, it was shown that this type of 1,3-dipolar addition reaction to give fused aromatic heterocycles is general in nature and can be employed with various heterocyclic zwitterions.[4-7] However, thus far, all of the examples studied have involved the reaction of six-membered heterocyclic zwitterions such as I, yielding substituted pyrrocolines such as II.
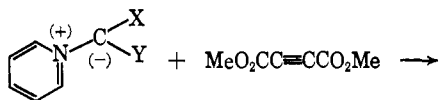


Ia, X = H; Y = C(=O)C₆H₅
b, X = Y = CN
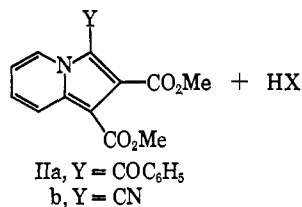
IIa, Y = COC₆H₅
b, Y = CN

In view of the current interest in azapentalenes as examples of Hückel aromatic systems,[8,9] it seemed desirable to investigate whether this type of 1,3-dipolar addition reaction might be applied to five-membered heterocycles to give appropriately substituted azapentalenes. This goal has now been realized and the present report describes the synthesis of certain 1,3a-diazapentalene derivatives.

The dianion of pentalene has been prepared by Katz, Rosenberger, and O'Hara, and its properties[10] are in accord with the Hückel molecular orbital picture, as summarized in Figure 1, in which the highest occupied orbital is nonbonding. Intuitively, it would be expected that, if two of the carbons in the pentalene dianion were replaced by pyrrole-type nitrogen atoms, the resulting molecule, aside from being neutral rather than ionic, would have rather similar properties. As shown in Figure 1, placing the two nitrogen atoms at bridgehead positions as in 3a,6a-diazapentalene (III)[11] leads to the HMO prediction that, although there is some displacement of bonding levels to lower energies, the highest occupied orbital is still essentially a nonbonding orbital.[12] Again, the properties of 3a,6a-diazapentalene (III), as described by Solomons and Trofimenko,[8] are in accord with the molecular orbital

(1) Supported in part by the National Heart Institute of the National Institutes of Health, Grant HE-09813.

(2) Roche Anniversary Fund Fellow. We thank the Roche Fund for partial support of this investigation.

(3) (a) A. Galbraitht, T. Small, and V. Boekelheide, *J. Org. Chem.*, **24**, 582 (1959); (b) A. Gailbraith, T. Small, R. A. Barnes, and V. Boekelheide, *J. Am. Chem. Soc.*, **83**, 453 (1961).

(4) V. Boekelheide and K. Fahrenholtz, *ibid.*, **83**, 458 (1961).

(5) W. J. Linn, O. W. Webster, and R. E. Benson, *ibid.*, **87**, 3651 (1965).

(6) R. Huisgen, R. Grashey, and E. Steingruber, *Tetrahedron Letters*, 1441 (1963).

(7) V. Boekelheide and N. A. Fedoruk, *J. Org. Chem.*, **32**, 2062 (1967).

(8) With regard to 3a,6a-diazapentalene, see (a) T. W. G. Solomons and C. F. Voight, *J. Am. Chem. Soc.*, **88**, 1992 (1966), and (b) S. Trofimenko, *ibid.*, **88**, 5588 (1966).

(9) For a discussion of the dibenzotetraazapentalenes and related compounds, see R. A. Carboni, J. C. Kauer, J. E. Castle, and H. E. Simmons, *ibid.*, **89**, 2618 (1967), and the accompanying papers in their series on aromatic azapentalenes.

(10) T. J. Katz, M. Rosenberger, and R. K. O'Hara, *ibid.*, **86**, 249 (1964).

(11) The numbering system which we are employing follows that recommended by Carboni, *et al.*[9]
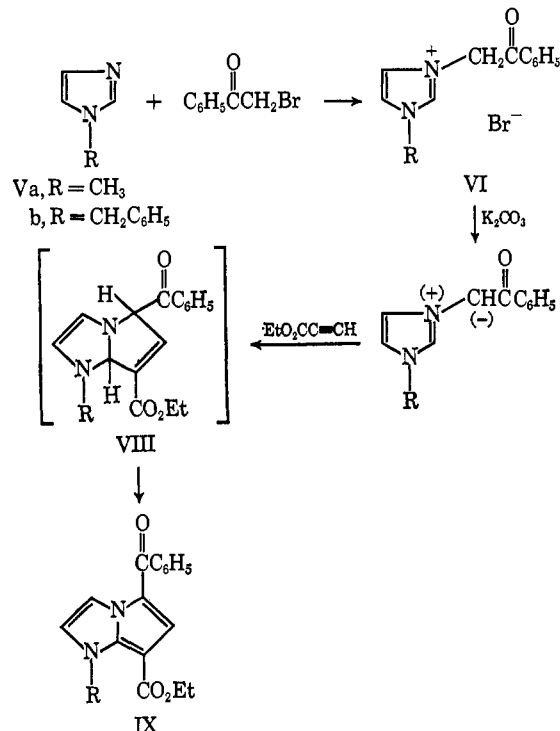
(12) We are very much indebted to Dr. C. E. Klopfenstein for the use of his computer program and his assistance in making these calculations.

picture, particularly the very rapid air oxidation of III.



III

IVa, R = CH₃.
b, R = CH₂C₆H₅
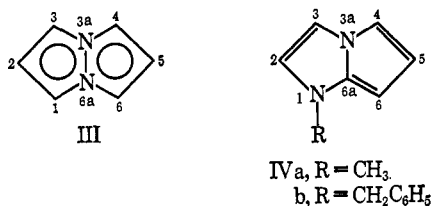
On the other hand, when one of the pyrrole-type nitrogens is placed elsewhere than at a bridgehead position, as is true for 1,3a-diazapentalenes (IV), HMO calculations predict that the highest occupied orbital should now be bonding, as is shown in Figure 1. Introduction of additional nitrogen atoms, as in the case of the tetraazapentalenes,[13] lowers the energy of the highest occupied orbital even more. Qualitatively, it would be predicted, then, that simple 1,3a-diazapentalene derivatives should exhibit properties intermediate between those of the 3a,6a-diazapentalenes and the stable tetraazapentalenes.

The synthesis of 1-methyl-1,3a-diazapentalene (IVa) was undertaken starting with 1-methylimidazole (Va) which on treatment with phenacyl bromide led smoothly to the desired 1-methyl-3-phenacylimidazolium bromide (VIa). This was then converted to the corresponding ylide VIIa and subjected to the conditions of the type of 1,3-dipolar addition discussed earlier. With ethyl propiolate the ylide underwent addition to give 1-methyl-4-benzoyl-6-carbethoxy-1,3a-diazapentalene (IXa) in 14% yield. Actually, the reaction was carried out by treating a solution of the imidazolium bromide VIa in dimethylformamide with anhydrous potassium carbonate and then adding excess ethyl propiolate to the orange mixture causing a rapid exothermic reaction. Presumably, the excess ethyl propiolate serves as a
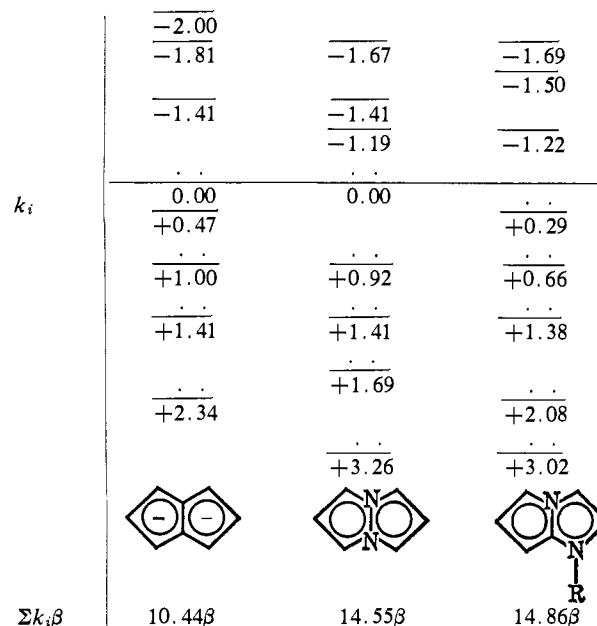


Va, R = CH₃
b, R = CH₂C₆H₅





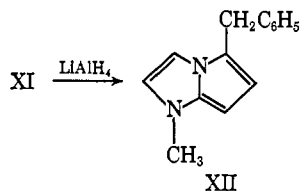Figure 1. Energy level diagrams, $E_i = \alpha + k_i\beta$.

dehydrogenating agent to effect aromatization of the initial product VIIIa.

Although it is conceivable that the addition of ethyl propiolate to VIIa could lead to two different isomers, involving attack at either the 2 or 4 positions of the imidazole ring, the assignment of the product IX as a 1,3a-diazapentalene rather than a 2,3a-diazapentalene is consistent with the known greater reactivity of the 2 position in imidazolium ions. Further, the nmr spectrum of IX, as well as those of the related derivatives to be discussed, shows aromatic doublets ($J = 2$ cps) as would be expected for the 2 and 3 protons of the 1,3a-diazapentalene nucleus but would not be explicable for the isomeric 2,3a-diazapentalene structure.

The pale yellow crystals of 1-methyl-4-benzoyl-6-carbethoxy-1,3a-diazapentalene (IXa), mp 126–127°, are quite stable to light and air. Alkaline hydrolysis of IXa gave the corresponding crystalline acid Xa which on sublimation underwent decarboxylation to give 1-methyl-4-benzoyl-1,3a-diazapentalene (XIa).



IX
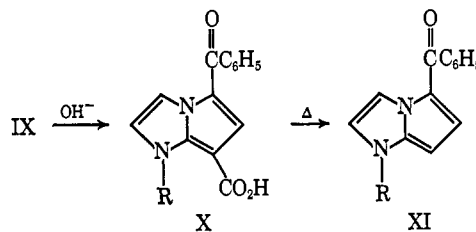
The carbonyl band of XIa appears at 6.24 mμ, exhibiting a marked shift to longer wavelengths from the normal aromatic carbonyl region and indicating the strong electron-donating character of the 1,3a-diazapentalene nucleus. Further evidence of the electron-donating character of the diazapentalene ring was provided by the lithium aluminum hydride reduction of XIa. In this case, just as is true for indole and other strongly electron-donating aromatic nuclei, the reduction resulted in loss of oxygen and gave the corresponding benzyl derivative XII.

(13) Y. T. Chia and H. E. Simmons, J. Am. Chem. Soc., **89**, 2638 (1967).

XI $\xrightarrow{\text{LiAlH}_4}$

[Structure XII: bicyclic diazapentalene with $CH_2C_6H_5$ and $CH_3$ groups]

XII

With the removal of all electron-withdrawing groups as in XII, the molecule becomes susceptible to very easy air oxidation. This is analogous to the behavior encountered with the simple 3a,6a-diazapentalenes,[8] although XII appears to be somewhat more stable and easier to handle so that it was possible to prepare analytically pure samples of XII. In the hope of obtaining the parent substance, a sample of the 1-methyl-4-benzoyl-1,3a-diazapentalene (XIa) was subjected to acid hydrolysis, a method used by Solomons, Fowler, and Calderazzo for removing the benzoyl group in the 3a,6a-diazapentalene series.[14] That hydrolysis occurred was readily evident from the presence of benzoic acid, which was isolated in good yield. However, when the parent substance IVa was liberated from the acid solution, it immediately reacted with air and was too unstable to be handled in any easy fashion.

XI $\xrightarrow[\text{H}_2\text{O}]{\text{HCl}}$ [Structure IV] $+ \ C_6H_5CO_2H$

IV
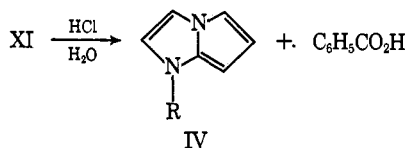
The difference in stability between 1-methyl-1,3a-diazapentalene and its corresponding 4-benzyl derivative was rather surprising and suggested that by some unknown mechanism the benzyl group might be exerting a stabilizing effect. For this reason it seemed desirable to repeat the sequence of reactions having a benzyl group at the 1 position rather than methyl. Starting with 1-benzylimidazole we were able to carry through the sequence. The properties of the products at each stage and the yields in each step were closely analogous to those in the 1-methyl series. When hydrolysis of 1-benzyl-4-benzoyl-1,3a-diazapentalene (XIb) was attempted, it was possible to isolate and measure the properties of 1-benzyl-1,3a-diazapentalene, even though it still was an unstable compound readily susceptible to air oxidation.

In our interpretation of the nmr spectrum of 1-benzyl-1,3a-diazapentalene we have assigned the doublet at $\tau$ 3.17 ($J = 2$ cps, 1 H) to the C-2 proton, the multiplet at $\tau$ 3.55 (interpreted as two overlapping doublets) to the C-3 and C-4 protons, the triplet at $\tau$ 3.78 ($J = 3.5$ cps, 1 H) to the C-5 proton, and the doublet at $\tau$ 4.92 ($J = 3.5$ cps, 1 H) to the C-6 proton. In addition the five phenyl protons appear as a singlet at $\tau$ 2.78 and the two benzyl protons as a singlet at $\tau$ 5.15. It is of interest that the signal for the C-6 proton occurs at such high field, being very close to its counterpart in the pentalene dianion which is at $\tau$ 5.02.[10]
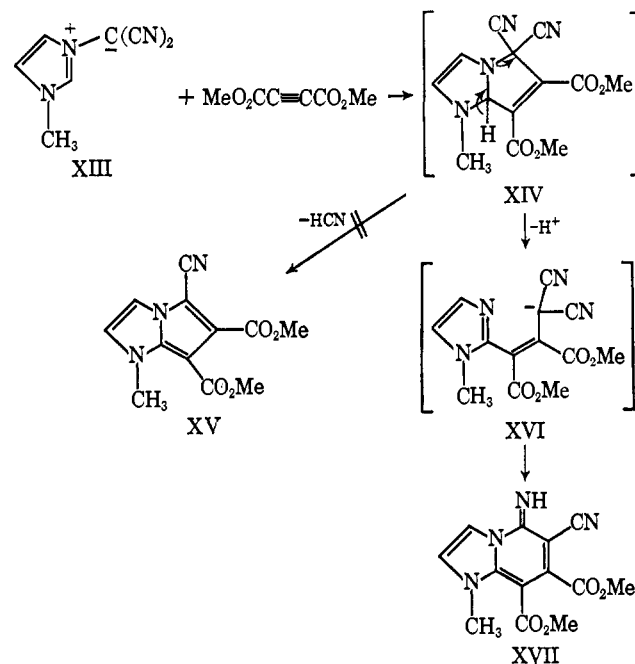
In summary, the behavior of the 1,3a-diazapentalenes parallels very closely that of the 3a,6a-diazapentalenes.[8] Thus, when electron-withdrawing groups are attached to the 1,3a-diazapentalene nucleus, the molecule is quite stable to light and air and is easy to handle. In

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

the absence of such electron-withdrawing groups, the 1,3a-diazapentalene derivatives are readily susceptible to air oxidation, giving highly colored, intractable tars.

Also, electron-withdrawing groups have a marked effect on the ultraviolet absorption spectra of the 1,3a-diazapentalenes. The presence of electron-withdrawing groups results in spectra with a long-wavelength absorption band around 360 m$\mu$ plus several bands at shorter wavelengths, whereas 1-benzyl-1,3a-diazapentalene and 1-methyl-4-benzyl-1,3a-diazapentalene, which lack electron-withdrawing groups, show a single absorption band at about 285 m$\mu$. The ultraviolet absorption spectra of the simple 1,3a-diazapentalenes are remarkably similar to those reported for 3a,6a-diazapentalene (284 m$\mu$[8a]) and the pentalene dianion (295 m$\mu$[10]), even though the calculations in Figure 1 give an indication that the 3a,6a-diazapentalene would differ from the other two.

Linn, Webster, and Benson have shown that pyridine and certain other aromatic heterocycles react with tetracyanoethylene oxide to give nicely stable ylides such as Ib and that these undergo 1,3-dipolar addition reactions with loss of hydrogen cyanide to give new aromatic molecules such as IIb.[5] It was of interest, therefore, to see whether their method could be applied in the case of five-membered heterocycles. When a solution of 1-methylimidazole in ethyl acetate was allowed to stand in the cold in the presence of tetracyanoethylene oxide, a smooth reaction occurred to give the nicely crystalline ylide XIII. Treatment of the ylide with dimethyl acetylenedicarboxylate at 0° led in 70% yield to a yellow crystalline solid. However, it was immediately apparent from its elementary analysis that the product was a simple 1:1 adduct and not the desired structure XV which requires the elimination of hydrogen cyanide. Examination of the chemical and spectral properties of the adduct suggested that the structure of the adduct was probably that of the iminopyrrocoline XVII. Its formation can be accounted for by assuming that the initial adduct XIV opens to the anion XVI, rather than eliminating hydrogen cyanide to give the expected 1,3a-diazapentalene

[Reaction scheme: XIII $\underset{CH_3}{\text{[imidazolium ylide with } \bar{C}(CN)_2]}$ $+ \ MeO_2CC{\equiv}CCO_2Me \rightarrow$ XIV → (with $-HCN$) XV; XIV → ($-H^+$) XVI → XVII]

XIII

XIV

XV

XVI

XVII

XV. A subsequent six-membered ring closure of the anion XVI would then yield the observed iminopyrrocoline XVII.

In support of the assigned structure it was observed that XVII readily underwent alkylation with methyl iodide as would be expected of an iminopyrrocoline. Also, treatment of the resulting hydriodide salt XVIII with potassium carbonate easily regenerated the N-methyliminopyrrocoline XIX.



XVII $\xrightarrow{\text{MeI}}$ XVIII $\xrightarrow{\text{K}_2\text{CO}_3}$ XIX
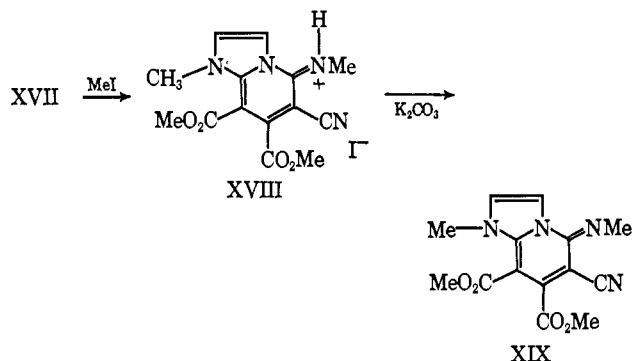
It is not obvious why the Linn procedure[5] should follow a different path with 1-methylimidazole than with pyridine. For this reason it was decided to investigate the Linn procedure with a different five-membered heterocycle, namely thiazole. The reaction of thiazole with tetracyanoethylene oxide readily afforded the corresponding ylide XX, but again, the reaction of this ylide with dimethyl acetylenedicarboxylate led to the corresponding iminopyrrocoline XXI and none of the desired 1-thia-3a-azapentalene. At present it does not seem possible to make any generalizations as to when this procedure will lead to fusion of a five- or six-membered ring, especially in view of the results obtained with isoquinoline.[5]



XX + $\text{MeO}_2\text{CC}\equiv\text{CCO}_2\text{Me}$ ⟶



XXI
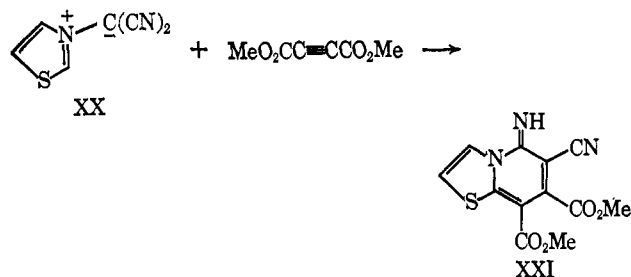
## Experimental Section[15]

**1-Methyl-3-phenacylimidazolium Bromide (VIa).** A solution of 8.2 g (0.1 mol) of 1-methylimidazole and 20.0 g (0.1 mol) of phenacyl bromide in 300 ml of ether was allowed to stand at room temperature for 16 hr. The solid, which separated, was collected and then recrystallized from acetonitrile to give 27.0 g (96%) of white crystals, mp 153–155°; $\lambda_{max}^{EtOH}$ 246 ($\epsilon$ 14,500) and 281 m$\mu$ ($\epsilon$ 1360); nmr (acetonitrile), doublets at $\tau$ 1.91 and 1.93 ($J$ = 7 cps, 2 H), multiplet at 2.35 (5 H), singlet at 3.73 (2 H), and singlet at 6.08 (3 H).

*Anal.* Calcd for $C_{12}H_{13}N_2OBr$: C, 51.28; H, 4.63; N, 9.97; Br, 28.43. Found: C, 51.11; H, 4.58; N, 10.02; Br, 28.20.

**1-Methyl-4-benzoyl-6-carbethoxy-1,3a-diazapentalene (IXa).** To a solution of 20.0 g (0.071 mol) of 1-methyl-3-phenacylimidazolium

bromide (VIa) in 250 ml of dimethylformamide there was added 10.0 g of finely powdered, anhydrous potassium carbonate, and the resulting bright orange mixture was allowed to stand at room temperature for 20 min. Then, 14.0 g (1.42 mol) of ethyl propiolate was added, causing the solution to turn red with immediate evolution of heat. After the solution had been stirred at room temperature for 2 hr, the solid potassium carbonate was removed by filtration, and the solution was concentrated under reduced pressure. After addition of water to the residual syrup, the mixture was extracted with ether. The ethereal solution was washed with water, dried, concentrated, and introduced onto a column of 300 g of alumina (Woelm, activity 3). Elution of the column with a 2:3 mixture of benzene–Skellysolve B gave first a brown band containing 2.85 g of a brown oil and then an eluate fraction containing 4.1 g of an orange crystalline solid. Recrystallization of the orange solid from ethanol, including work-up of the mother liquor, gave 3.01 g (14%) of pale yellow crystals, mp 126–127°; $\lambda_{max}^{EtOH}$ 357 (23,680), 267 (16,200), and 251 m$\mu$ ($\epsilon$ 12,600, shoulder); $\lambda_{max}^{Nujol}$ 5.92 (ester C=O), 6.25 (aryl C=O), and 6.3 $\mu$ (phenyl C=C); nmr (CCl$_4$), doublet at $\tau$ 2.00 ($J$ = 2 cps, 1 H), multiplet at 2.24 (2 H), multiplet at 2.66 (4 H), broad singlet at 3.30 (1 H), quartet at 5.96 ($J$ = 7 cps, 2 H), singlet at 5.96 (3 H), and triplet at 8.71 ($J$ = 7 cps, 3 H).

*Anal.* Calcd for $C_{17}H_{16}N_2O_3$: C, 67.59; H, 5.67; N, 9.85. Found: C, 67.67; H, 5.49; N, 9.52.

**1-Methyl-4-benzoyl-6-carboxy-1,3a-diazapentalene (Xa).** A solution of 2.1 g of 1-methyl-4-benzoyl-6-carbethoxy-1,3a-diazapentalene (IXa) in 250 ml of methanol and 50 ml of a 10% aqueous potassium hydroxide solution was boiled under reflux for 18 hr. After removal of the methanol under reduced pressure, the aqueous residue was extracted with ether and then acidified with 10% hydrochloric acid to a pH of 2.0. The solid which precipitated was collected, dried, and crystallized from acetone to give 1.6 g (85%) of essentially white crystals, mp 206–207°; $\lambda_{max}^{EtOH}$ 362 (22,530), 260 (14,740), and 249 m$\mu$ ($\epsilon$ 16,080).

*Anal.* Calcd for $C_{15}H_{12}N_2O_3$: C, 67.16; H, 4.51; N, 10.44. Found: C, 67.57; H, 4.67; N, 10.37.

**1-Methyl-4-benzoyl-1,3a-diazapentalene (XIa).** Sublimation of 800 mg of 1-methyl-4-benzoyl-6-carboxy-1,3a-diazapentalene (Xa) was carried out at 200° under 10-mm pressure. The sublimate was collected and then recrystallized from an ether–Skellysolve B mixture to give 568 mg (67%) of yellow crystals, mp 113–115°; $\lambda_{max}^{EtOH}$ 363 (23,555) and 241 m$\mu$ ($\epsilon$ 8615); $\lambda_{max}^{Nujol}$ 6.24 (aryl C=O) and 6.3 $\mu$ (phenyl C=C); nmr, doublet at $\tau$ 2.07 ($J$ = 2 cps, 1 H), multiplet at 2.30 (2 H), multiplet at 2.70 (3 H), doublet at 3.12 ($J$ = 4 cps, 1 H), doublet at 3.41 ($J$ = 2 cps, 1 H), doublet at 4.58 ($J$ = 4 cps, 1 H), and singlet at 6.51 (3 H).

*Anal.* Calcd for $C_{14}H_{12}N_2O$: C, 74.98; H, 5.39; N, 12.49. Found: C, 75.19; H, 5.17; N, 12.74.

**1-Methyl-4-benzyl-1,3a-diazapentalene (XII).** To a solution of 130 mg of 1-methyl-4-benzoyl-1,3a-diazapentalene (XIa) in 50 ml of anhydrous ether there was added an excess of lithium aluminum hydride, and the resulting mixture was stirred at room temperature overnight. The excess lithium aluminum hydride was destroyed by addition of ethyl acetate; then 10 ml of water was added, and the ether layer was separated. Concentration of the ether layer gave 60 mg of a pale yellow solid which after recrystallization from ether gave crystals, mp 116–118°. The infrared spectrum of these crystals showed the absence of carbonyl and hydroxyl absorption while in the ultraviolet in ethanol there was one maximum at 283 m$\mu$ (log $\epsilon \cong 3.5$; the extinction coefficient could not be determined exactly because air oxidation caused a continual decrease in the absorption at 283 m$\mu$ with a concurrent rise of a new absorption band at 360 m$\mu$). The nmr spectrum in carbon tetrachloride showed a sharp singlet at $\tau$ 2.92 (5 H), doublets at 3.69 and 3.71 ($J$ = 5 cps, 1 H each), doublets at 3.98 and 4.98 ($J$ = 4 cps, 1 H each), singlet at 5.95 (2 H), and singlet at 6.62 (3 H).

*Anal.* Calcd for $C_{14}H_{14}N_2$: C, 79.97; H, 6.71; N, 13.32. Found: C, 79.87; H, 6.53; N, 13.16.

**Attempted Removal of the Benzoyl Group to Give 1-Methyl-1,3a-diazapentalene (IVa).** A solution of 108 mg of 1-methyl-4-benzoyl-1,3a-diazapentalene in 20 ml of concentrated hydrochloric acid was boiled under reflux in a nitrogen atmosphere for 18 hr. Extraction of the acidic solution with ether gave 28 mg of benzoic acid. When the yellow aqueous solution was made basic, it turned red immediately and nothing useful could be removed from the aqueous solution by extraction with organic solvents.

An attempt to effect cleavage of the benzoyl group by ethanolic potassium hydroxide, a procedure used quite successfully in a similar case,[16] led only to recovery of starting material.

**1-Benzyl-4-benzoyl-6-carbethoxy-1,3a-diazapentalene (IXb).** The preparation of 1-benzylimidazole was carried out as described by Wallach[17] and then 8.85 g of 1-benzylimidazole was treated with 10.0 g of phenacyl bromide in ether as described for the preparation of VIa. However, the 18.75 g of 1-benzyl-3-phenacylimidazolium bromide (VIb) which separated proved to be extremely hygroscopic and so was used directly without further purification. A solution of 16.0 g (0.045 mol) of VIb was dissolved in 120 ml of dimethylformamide and treated with 7.0 g of anhydrous potassium carbonate. The deep orange mixture was stirred at room temperature for 15 min before 5.0 g of ethyl propiolate was added. The color of the mixture slowly changed to a dark brown, and stirring at room temperature was continued for 4 hr. After the mixture had been concentrated under reduced pressure, 20 ml of benzene was added, and the insoluble solids were collected by filtration. An additional 10 ml of benzene and 10 ml of Skellysolve B were added to the filtrate before passing it onto a column of 320 g of alumina (activity 1). The second eluate fraction was bright yellow and contained 1.45 g of a yellow solid which, after recrystallization from an ether–Skellysolve B mixture, gave pale yellow crystals, mp 103–104°; $\lambda_{max}^{EtOH}$ 356 (26,310), 267 (17,000), and 254 m$\mu$ ($\epsilon$ 14,000, shoulder); $\lambda_{max}^{CHCl_3}$ 5.93 (ester C=O) and 6.23 $\mu$ (aryl C=O); nmr, doublet at $\tau$ 1.90 ($J$ = 2 cps, 1 H), multiplets at 2.20 (2 H) and 2.59 (4 H), singlet at 2.78 (5 H), multiplet at 3.75 (1 H), singlet at 4.20 (2 H), quartet at 5.79 ($J$ = 7 cps, 2 H), and triplet at 8.69 ($J$ = 7 cps, 3 H).

*Anal.* Calcd for $C_{23}H_{20}N_2O_3$: C, 74.18; H, 5.41; N, 7.52. Found: C, 74.35; H, 5.46; N, 7.75.

**1-Benzyl-4-benzoyl-6-carboxy-1,3a-diazapentalene (Xb).** A solution of 600 mg of 1-benzyl-4-benzoyl-6-carbethoxy-1,3a-diazapentalene (IXb) in a mixture of 50 ml of methanol and 15 ml of a 10% aqueous potassium hydroxide solution was boiled under reflux for 6 hr. After removal of the methanol under reduced pressure, 20 ml of water was added to the aqueous residue, and then it was acidified with 10% hydrochloric acid. The solid, which precipitated, was collected, dried, and recrystallized from acetone to give 452 mg (82%) of pale yellow crystals, mp 181–182°.

*Anal.* Calcd for $C_{21}H_{16}N_2O_3$: C, 73.24; H, 4.68; N, 8.13. Found: C, 73.09; H, 4.98; N, 7.95.

**1-Benzyl-4-benzoyl-1,3a-diazapentalene (XIb).** A 400-mg sample of 1-benzyl-4-benzoyl-6-carboxy-1,3a-diazapentalene (Xb) was heated at 220° until gas evolution from the melt ceased (20 min). The cold melt was then taken up in benzene and chromatographed over alumina (Woelm, activity 3). From the eluate there was isolated 302 mg of a solid which after recrystallization from an ether–Skellysolve B mixture gave 215 mg of pale yellow crystals, mp 101–103°; $\lambda_{max}^{EtOH}$ 363 (27,500) and 242 m$\mu$ ($\epsilon$ 9500); $\lambda_{max}^{CHCl_3}$ 6.23 (aryl C=O) and 6.30 $\mu$ (phenyl C=C); nmr, doublet at $\tau$ 1.85 ($J$ = 2 cps, 1 H), multiplet at 2.17 (2 H), multiplet at 2.60 (8 H), doublet at 2.97 ($J$ = 4.5 cps, 1 H), doublet at 3.2 ($J$ = 2 cps, 1 H), doublet at 4.44 ($J$ = 4.5 cps, 1 H), and singlet at 4.98 (2 H).

*Anal.* Calcd for $C_{20}H_{16}N_2O$: C, 79.97; H, 5.37; N, 9.33. Found: C, 79.94; H, 5.48; N, 9.49.

**1-Benzyl-1,3a-diazapentalene (IVb).** A solution of 113 mg of 1-benzyl-4-benzoyl-1,3a-diazapentalene (XIb) in 6 ml of concentrated hydrochloric acid was boiled under reflux for 20 hr. After the solution had cooled, it was extracted with ether. From the ether solution there was isolated 45 mg (96%) of benzoic acid, mp 121–122°. The aqueous acidic solution was concentrated under reduced pressure and then made basic by addition of aqueous potassium carbonate solution. Extraction of the aqueous solution with benzene followed by concentration and chromatography over alumina (Woelm, activity 5) gave 28 mg of a white solid. On exposure to air this white solid immediately began to turn red, and it was not possible to obtain satisfactory analytical data. However, its nmr spectrum (CCl$_4$) showed a singlet at $\tau$ 2.78 (5 H), a doublet at 3.17 ($J$ = 2 cps, 1 H), a multiplet at 3.55 (2 H), a triplet at 3.78 ($J$ = 3.5 cps, 1 H), a doublet at 4.92 ($J$ = 3.5 cps, 1 H), and a singlet at 5.15 (2 H), in accord with the assigned structure. Its ultraviolet absorption spectrum showed a maximum at 285 m$\mu$, but again it was not possible to obtain an accurate extinction coefficient for the compound because of its sensitivity to air.

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**1-Methyl-3-imidazolium Dicyanomethylide (XIII).** To a solution of 7.2 g (0.05 mol) of tetracyanoethylene oxide[5] in 50 ml of ethyl acetate held at 0° there was added dropwise with stirring 4.1 g (0.05 mol) of 1-methylimidazole. When addition was complete, a brown solid began to separate from solution. This was collected by filtration, washed with cold ethyl acetate, and recrystallized from ethanol using Norit to give 2.86 g (39%) of white crystals, mp 143–144°; $\lambda_{max}^{EtOH}$ 299 m$\mu$ ($\epsilon$ 2880); $\lambda_{max}^{Nujol}$ 4.60 and 4.72 $\mu$; nmr (acetonitrile), singlet at $\tau$ 1.57 (1 H), singlet at 2.65 (1 H), singlet at 2.68 (1 H), and singlet at 6.16 (3 H).

*Anal.* Calcd for $C_7H_6N_4$: C, 57.53; H, 4.14; N, 38.33. Found: C, 57.41; H, 4.42; N, 38.37.

**1-Methyl-5-imino-6-cyano-7,8-dicarbomethoxy-1-azapyrrocoline (XVII).** A solution of 600 mg of 1-methyl-3-imidazolium dicyanomethylide in 25 ml of dimethyl formamide was cooled to 0°, 620 mg of dimethyl acetylenedicarboxylate was added, and the mixture was stirred at 0° for 4 hr. After removal of the dimethylformamide under reduced pressure, the residue was taken up in ethyl acetate and chromatographed over alumina (Woelm, activity 3). From the eluate there was isolated a yellow crystalline solid which after recrystallization from acetonitrile gave 808 mg (70%) of yellow crystals, mp 190–191°; $\lambda_{max}^{EtOH}$ 381 (14,400), 310 (23,458), 300 (16,260), and 242 m$\mu$ ($\epsilon$ 12,542); $\lambda_{max}^{Nujol}$ 4.50, 5.83, and 6.12 $\mu$; nmr, doublet at $\tau$ 2.00 ($J$ = 2 cps, 1 H), doublet at 2.90 ($J$ = 2 cps, 1 H), and singlets at 6.04 (3 H), 6.18 (3 H), and 6.80 (3 H).

*Anal.* Calcd for $C_{13}H_{12}N_4O_4$: C, 54.16; H, 4.20; N, 19.44. Found: C, 54.13; H, 4.24; N, 19.55.

**1-Methyl-5-methylamino-6-cyano-7,8-dicarbomethoxy-1-azapyrrocolinium Iodide (XVIII).** A mixture of 300 mg of 1-methyl-5-imino-6-cyano-7,8-dicarbomethoxy-1-azapyrrocoline (XVII) and 1 ml of methyl iodide in 2 ml of dimethylformamide was allowed to stand at room temperature for 3 days. Ethyl acetate was then added, and the white solid, which precipitated, was collected, washed with cold ethyl acetate, and recrystallized from methanol to give 302 mg (70%) of white crystals, mp >200° dec; $\lambda_{max}^{EtOH}$ 353 (11,200), 304 (11,600), and 250 m$\mu$ ($\epsilon$ 15,600); $\lambda_{max}^{Nujol}$ 4.45, 5.78, 6.12, and 6.24 $\mu$.

*Anal.* Calcd for $C_{14}H_{15}N_4O_4I$: C, 39.09; H, 3.51; N, 13.02; I, 29.50. Found: C, 38.98; H, 3.75; N, 12.92; I, 29.74.

**1-Methyl-5-methylimino-6-cyano-7,8-dicarbomethoxy-1-azapyrrocoline (XIX).** To a solution of 400 mg of potassium carbonate in 2 ml of water there was added 130 mg of 1-methyl-5-methylamino-6-cyano-7,8-dicarbomethoxy-1-azapyrrocoline (XVIII), and the mixture was stirred at room temperature for 10 min. The yellow solid, which separated, was collected, dried, and recrystallized from methanol to give 72 mg (80%) of yellow needles, mp 186–187°; $\lambda_{max}^{EtOH}$ 388 (17,100), 313 (27,180), 304 (20,640), and 224 m$\mu$ ($\epsilon$ 13,140); $\lambda_{max}^{CHCl_3}$ 4.50, 5.72, 5.87, and 6.10 $\mu$; nmr, doublets at $\tau$ 2.08 ($J$ = 2 cps, 1 H) and 2.98 ($J$ = 2 cps, 1 H) and singlets at 6.04 (3 H), 6.10 (3 H), 6.21 (3 H), and 6.48 (3 H).

*Anal.* Calcd for $C_{14}H_{14}N_4O_4$: C, 55.62; H, 4.67; N, 18.54. Found: C, 55.57; H, 4.74; N, 18.94.

**3-Thiazolium Dicyanomethylide (XX).** To a solution of 860 mg of tetracyanoethylene oxide[5] in 10 ml of ethyl acetate held at 0° there was added 500 mg of thiazole, and the resulting solution was allowed to stand for 12 hr. The reaction mixture was then allowed to warm to room temperature, and the solid, which had precipitated, was collected. Recrystallization from ethanol gave 230 mg (26%) of light brown crystals, mp 202–203°; $\lambda_{max}^{EtOH}$ 370 (9900), 281 (2840), and 230 m$\mu$ ($\epsilon$ 6240); $\lambda_{max}^{Nujol}$ 4.58 and 4.70 $\mu$.

*Anal.* Calcd for $C_6H_3N_3S$: C, 48.33; H, 2.03; N, 28.18. Found: C, 48.31; H, 2.17; N, 28.19.

**5-Imino-6-cyano-7,8-dicarbomethoxy-1-thiapyrrocoline (XXI).** A mixture of 110 mg of 3-thiazolium dicyanomethylide (XX) and 115 mg of dimethyl acetylenedicarboxylate in 10 ml of dimethylformamide was allowed to stand at room temperature for 2 days. After concentration under reduced pressure, the residual oil was taken up in ethyl acetate and chromatographed over alumina (Woelm, activity 3). From the eluate there was isolated a bright yellow solid which, after recrystallization from methanol, gave 96 mg (48%) of yellow crystals, mp 208–210°; $\lambda_{max}^{EtOH}$ 413 (11,950), 317 (30,000), 305 (17,670), and 259 m$\mu$ ($\epsilon$ 7800); $\lambda_{max}^{Nujol}$ 4.50, 5.70, 5.90, and 6.22 $\mu$; nmr (acetonitrile), doublets at $\tau$ 2.52 ($J$ = 5 cps, 1 H) and 3.46 ($J$ = 5 cps, 1 H) and singlets at 7.03 (3 H) and 7.14 (3 H).

*Anal.* Calcd for $C_{12}H_9N_3O_4S$: C, 49.47; H, 3.12; N, 14.43; S, 10.99. Found: C, 49.94; H, 3.32; N, 14.49; S, 10.66.