Tetrahedron Letters No. 15, pp 1291 - 1294, 1978. Pergamon Press. Printed in Great Britain.

MESOIONIC 1,3a,6a-TRIAZAPENTALENES[1)]

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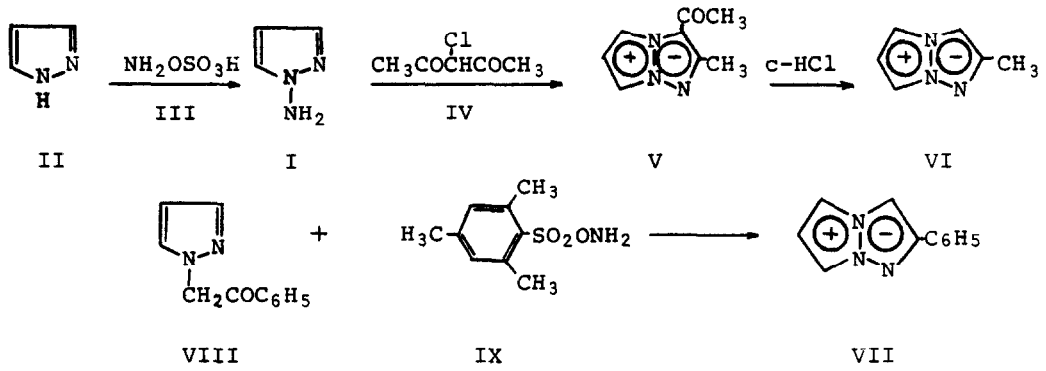
(Received in Japan 12 January 1978; received in UK for publication 27 February 1978)

Since the early 1960's, aromatic amine N-imines have been studied extensively and have been found to have a theoretical importance and wide application in synthetic work. In connection with our synthetic investigations on nitrogen-bridged heteroaromatics using aromatic amine N-imines [2,3)] syntheses and reactions of pyrazoloazoles and pyrazoloisoazoles have been recently reported.[4)] We wish to report in this paper the synthesis of 1,3a,6a-triazapentalenes via pyrazole-N-imines and their chemical properties. Benzo-1,3a,6a-triazapentalenes were already synthesized via nitrene intermediates,[5)] but simple 1,3a,6a-triazapentalenes have not been prepared.

1-Aminopyrazole (I, colorless oil), prepared by the reaction of pyrazole (II) with hydroxylamine O-sulfonic acid (III) in 51.6% yield, was heated with 3-chloropentane-2,4-dione (IV) in benzene for 1 hr, to give 3-acetyl-2-methyl-1,3a,6a-triazapentalene (V) in 57.8% yield. On the other hand, when I was allowed to react with chloroacetaldehyde or phenacyl bromide, an intractable black powdery product, probably produced by rapid air oxidation of the initial product, 1,3a,6a-triazapentalene derivative, was obtained. In the hope of obtaining the parent substance, V was subjected to acid hydrolysis. V was deacetylated on being refluxed with conc. HCl, followed by careful basification with K_2CO_3, to afford the desired 2-methyl-1,3a,6a-triazapentalene (VI) as colorless oil in 95.0% yield. While V is quite stable to air and light, VI is very sensitive to air. With removal of electron withdrawing group as in VI, the molecule becomes highly susceptible to air oxidation. This is analogous to the behavior of the simple 3a,6a-diazapentalenes,[6)] although VI appears to be somewhat more stable and easier to handle. The structure of VI was established by the following data. NMR($CDCl_3$) δ: 2.28 (3H, s, 2-CH_3), 6.50 (1H, t, J=3 Hz, 5-H), 6.86 (1H, s, 3-H), 6.96 (1H, d, J=3 Hz, 4-H), 7.27 (1H, d, J=3 Hz, 6-H). Mass spectrum (MS) m/e: 121 ($C_6H_7N_3$, M^+), 80 ($M^+ - CH_3CN$), 53, 52, 39. UV $\lambda_{max}^{95\%EtOH}$ nm(ε): 285 (10520).

2-Phenyl-1,3a,6a-triazapentalene (VII) was synthesized by N-amination of 1-phenacylpyrazole (VIII) with O-mesitylenesulfonylhydroxylamine (IX). Treatment of VIII with IX in methylene chloride at room temperature for 2 hr, followed by basification with aqueous K_2CO_3, gave VII (mp 86-87°) as colorless crystals in 65.6% yield. Although VII is readily oxidized by air, it seems to be more

stable than VI. VII: NMR ($CDCl_3$)δ: 6.55 (1H, t, J=3Hz, 5-H), 7.04 (1H, d, J=3Hz, 4-H), 7.20-7.50 (5H, m), 7.65-7.90 (2H, m). MS m/e: 183 ($C_{11}H_9N_3$, M^+) 103 (C_6H_5CN), 80 ($M^+ - C_6H_5CN$), 53, 52, 39. UV$\lambda_{max}^{95\%EtOH}$ nm(ε): 249 (25200), 278 (20800), 329 (5680).



VI and VII easily underwent electrophilic substitution at the 3-position, 3-Acetyl derivatives, V (mp 161-163°, colorless needles) and X (mp 176-178°, colorless powder) were obtained in a quantitative yield by the reaction of VI and VII with acetic anhydride at 60-70° for 2 hr under nitrogen atmosphere. Nitrosation of VI and VII with $NaNO_2$ in 15% HCl at room temperature for 1.5 hr afforded 3-nitroso derivatives, XI [mp 163-164° (decomp.), red needles] and XII [mp 204° (decomp.), green crystals] in a nearly quantitative yield. The carbonyl bands at 1577 and 1585 cm^{-1} in V and X appear, respectively, indicating the strong electron-donating character of the 1,3a,6a-triazapentalene ring.

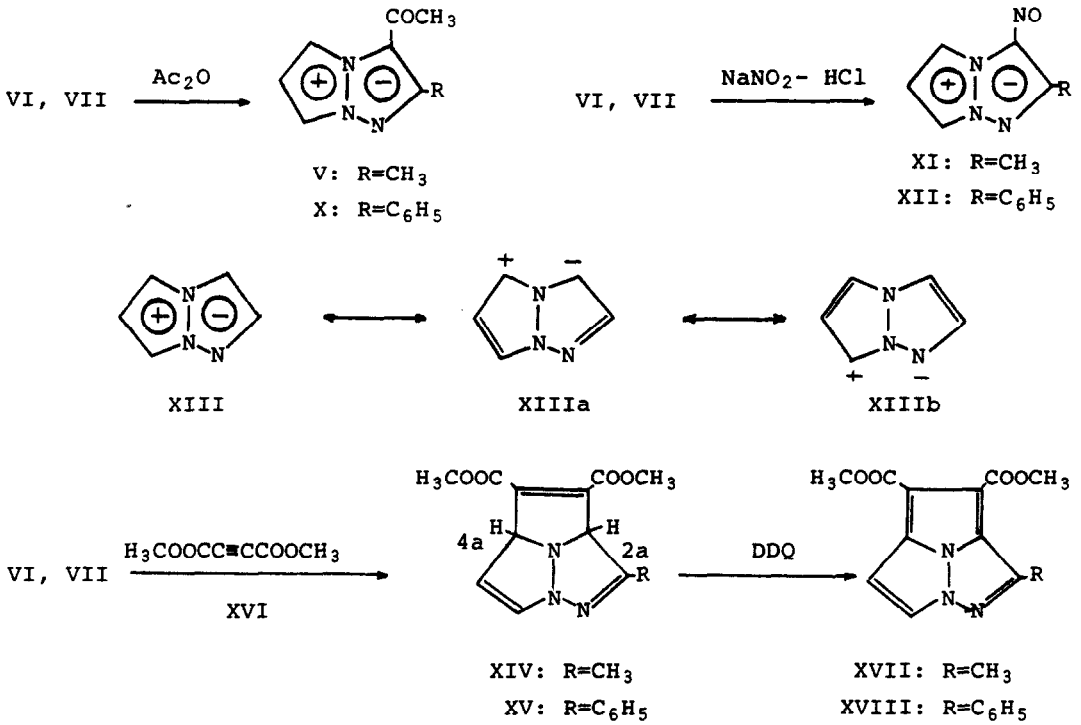
The possibility of a cycloaddition reaction of mesoionic azapentalenes was shown initially by Boekelheide and Fedoruk.[7] Recently, Tsuge and Samura[8] showed that dibenzo-1,3a,6a-triazapentalenes with dimethyl acetylenedicarboxylate underwent dipolar cycloaddition across the azomethine-imine-ylide.

Mesoionic 1,3a,6a-triazapentalene (XIII) can be regarded as a resonance hybrid of dipolar contributors and its behavior as both azomethine-ylide (XIIIa) and azomethine-imine-ylide (XIIIb) might be anticipated in a cycloaddition reaction.

Treatment of VI and VII with an equimolar amount of dimethyl acetylenedicarboxylate (XVI) at room temperature for 30 min respectively afforded a 1 : 1 adducts; XIV yellow oil, m/e: 263 (M^+), NMR($CDCl_3$)δ: 2.00 (3H, s, 2-CH_3), 3.79, 3.82 (each 3H, s, OCH_3), 5.05-5.23 (2H, m, 2a, 4a-H), 5.42 (1H, dd, J=4.1, 2.6 Hz, 5-H), 6.51 (1H, dd, J=4.1, 2.0Hz, 6-H) and XV yellow oil, m/e: 325 (M^+), NMR ($CDCl_3$) : 3.37, 3.70 (each 3H, s, OCH_3), 5.20 (1H, m, 4a-H), 5.51 (1H, dd, J=4.1, 2.6Hz, 5-H), 5.78 (1H, d, J=1.9Hz, 2a-H), 6.62 (1H, dd, J=4.1, 2.0Hz,6-H),

7.25-7.70(5H, m) in 90.5 and 70.0% yield. These adducts have been definitely assigned to the dihydrodiazacycl[2,2,2]azine structure on the basis of their spectral data. An unusual feature of the NMR spectra of XV in the magnitude (1.9 Hz) of the long-range coupling constant $J_{2a,4a}$ indicates that the hydrogen atom (2a-H) would be located cis to 4a-H.[9]

In order to obtain further support for the structure of the [π8 + π2] type cycloadducts (XIV and XV), these adducts were oxidized with 2,3-dichloro-5,6-dicyano-1, 4-benzoquinone (DDQ) in benzene at room temperature to give diazacycl [2,2,2]azines : XVII mp 90-92°, colorless needles, m/e: 261(M^+), NMR($CDCl_3$)δ: 2.81(3H, s, 2-CH_3), 3.99 (6H, s, 2 x OCH_3), 7.08 (1H, d, J=3 Hz, 5-H), 8.02, (1H, d, J=3 Hz, 6-H) and XVIII mp 125°, colorless powder, m/e: 323(M^+), NMR ($CDCl_3$)δ: 3.95 (6H, s, 2 x OCH_3), 7.13 (1H, d, J=3 Hz, 5-H), 7.45-7.73 (3H, m),



.8.00-8.20 (3H, m) in 30.8 and 46.2% yield, respectively. The ring protons at C-5 and C-6 of XVII and XVIII absorb in the aromatic region at δ7.08-8.20, deshielded relative to the resonances in their 2a,4a-dihydro analogs (XIV and XV), indicating that XVII and XVIII are aromatic.

These results show that, in this ring system, the azomethine-ylide function was more reactive than the azomethine-imine-ylide system under our condition.

1,3a,6a-Triazapentalenes seem to owe their great reactivity principally to a highlying HOMO and the consequently narrow gap between frontier molecular orbitals.[10]

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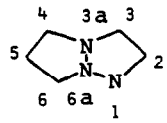
1) The following numbering system has been adopted in this paper.



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10) By using the Hückel parameters, $\alpha_N^{\cdot\cdot} = \alpha + 1.5\beta$ (pyrrole-like N), $\alpha_N^{\cdot} = \alpha + 0.5\beta$ (pyridinelike N), all $\beta = \beta_{CC}$, and auxiliary inductive parameter $\alpha_{C(N)} = \alpha + 0.1h_N\beta$, the HOMO is found at $\alpha + 0.24\beta$ for 1,3a,6a-triazapentalene itself.