

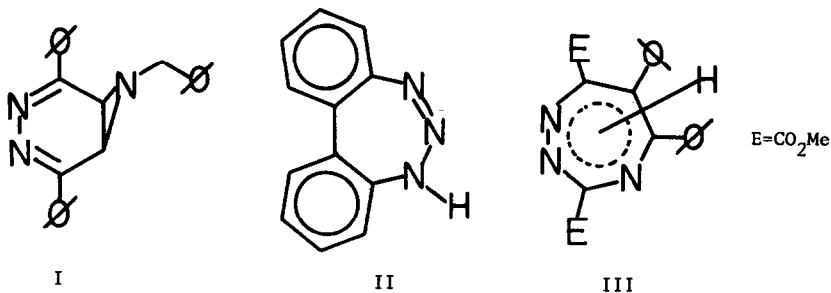
TRIAZACYCLOHEPTATRIENES: THE CYCLOADDITION OF AZIRINES
TO DICARBOMETHOXY-*s*-TETRAZINE

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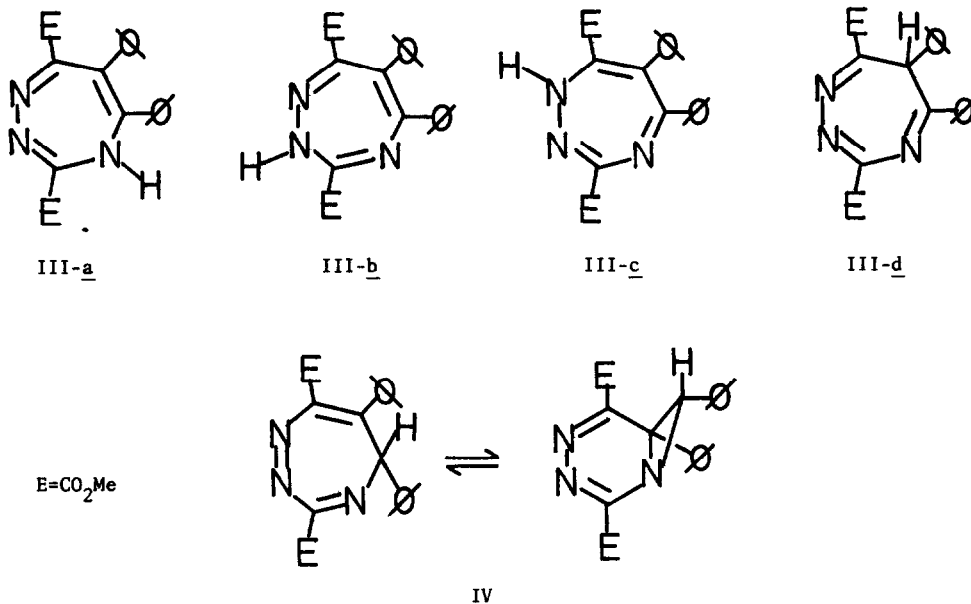
Much of the impetus for the chemical studies of azepines and oxepines,¹ as well as their more highly heterosubstituted relatives such as diazepines,² has derived from the questions of antiaromaticity and valence bond isomerization in these systems. In an effort to further probe such factors, we have elected to investigate the triazacycloheptatriene system. To date only two members of this family, the 1,4,5-triaza³ and 1,2,3-triaza⁴ isomers (I and II) have been described. We have prepared the 1,2,4-triazacycloheptatriene III in 67% yield by reacting dicarbomethoxy-*s*-tetrazine with 2,3-diphenylazirine. The reaction was



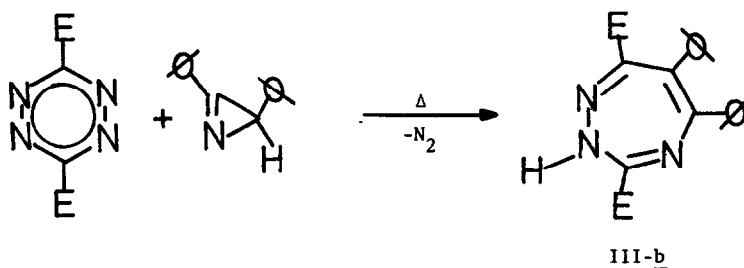
effected in a benzene solution protected from light; after two days at room temperature, the reaction was concentrated and cooled to produce III as a red-orange solid [mp. 134-136°C with decomp; ir (paraffin oil) ν_{NH} 3337 cm^{-1} , $\nu_{\text{CO}_2, \text{CN}}$ 1731, 1711 and 1678 cm^{-1} ; nmr (100 MHz, CDCl_3) 3.46 δ (s, 3.0 H), 3.90 δ (s, 3.1 H), 6.80-7.50 δ (m, 10.1 H), 8.29 δ (br s, 0.8 H); uv (hexane) 225 nm (ϵ 33400), 252 (ϵ 28000), 388 (ϵ 1360); precise mass measurement: calcd for

$C_{20}H_{17}N_3O_4$: 363.1219, found: 363.1219].

Apparently, the expected adduct IV rearranges to a structure devoid of the destabilizing effects attributable to nitrogen-nitrogen double bonds⁵ and cyclopropane rings. There are four such isomers of III (a - d); however, the presence of the N-H stretch in the infra-red

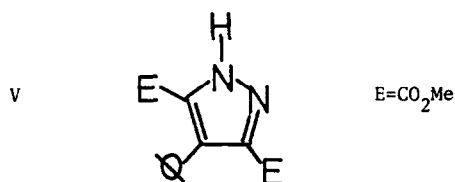


spectrum, as well as the low field chemical shift of the singular proton [8.29 δ ; compare to 7-phenylcycloheptatriene (2.676 δ)⁶] argue convincingly against III-d. As 2H-⁷ and 4H-azepines⁵ readily rearrange into the apparently more stable 3H analogues, we favored structures a and b over c. However, only b and c can be formed by a single [1,5] hydrogen shift, generation of a requiring an additional [1,5] shift. As it is known that hydrogen shifts do not occur in



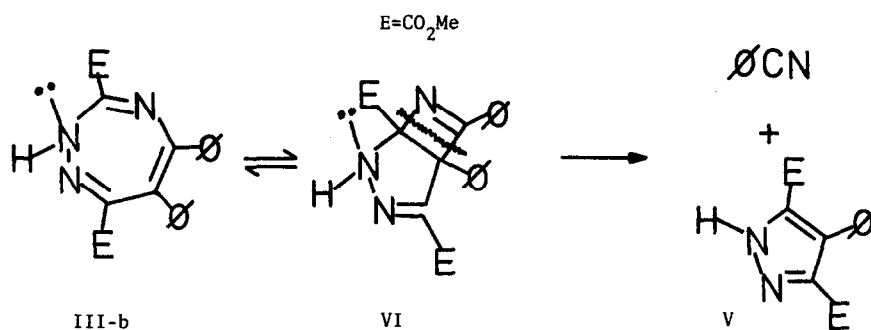
1H-azepines, ^{7b} formation of a from c appears unlikely. Hence, we prefer structure III-b on the basis of the above arguments and also because of its compatibility with the fragmentation data (*vide infra*).

The 100 MHz pmr spectrum of III remains invariant between -50°C and +70°C, no new peaks attributable to any isomers being detected. When a sample of triazepine III in benzene solution is heated at 80°C for 8 hours, it cleanly fragments to benzonitrile and pyrazole V⁸. The same cleavage occurs spontaneously if a trace of trifluoroacetic acid is added to a solution



of III. Additionally, photolysis of a cooled benzene solution of III through pyrex with a 450w high pressure mercury lamp resulted in rapid scission to the same two products. III does not yield an adduct with dimethyl acetylenedicarboxylate or tetracyanoethylene.

In III-b, π participation of the 1H nitrogen lone pair would give rise to a cycloheptatrienyl anion equivalent. Thermal disrotatory closure to bicyclic VI and subsequent fragmentation would account for the observed products, V and benzonitrile. The apparent ease with which these last two steps occur is, no doubt, a reflection upon the electronic destabilization in



III-b and the thermodynamic stability of the final products.

Further investigation of these factors as well as the preparation of new tri and tetra-azacycloheptatrienes are the subjects of continuing research.

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