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THE ISOLATION AND CHARACTERIZATION OF 1,4-DIBENZYL-5,6-DIPHENYL-1,2,3,4-TETRAAZA-2-CYCLOHEXENE

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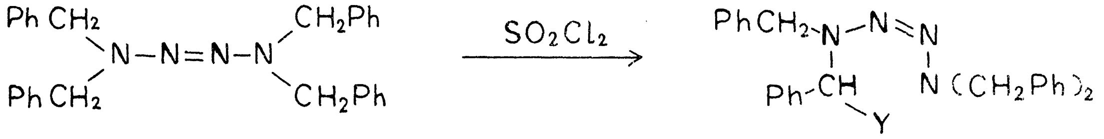
The reaction of 1,1,4,4-tetrabenzyl-2-tetrazene with sulfuryl chloride in benzene at room temperature gave benzyl azide, dibenzylamine and benzaldehyde. In addition, another compound was isolated as a very minor product. On the basis of its elemental analysis and spectral data, this compound was assigned the structure of 5,6-diphenyl-1,4-dibenzyl-1,2,3,4-tetraaza-2-cyclohexene, the first cyclic 2-tetrazene ever reported.

Although 2-tetrazenes have been known for almost 100 years, very little of their chemical properties has been studied.[1] Recently, scattered investigations[2-5] have suggested that 2-tetrazenes may possess a rich chemistry despite the fact that they are thermally labile above 100°C and very sensitive to moderately strong acids. As a continuation of our work on the oxidative fragmentation of 2-tetrazenes,[3] we have studied the reaction of 1,1,4,4-tetrabenzyl-2-tetrazene with sulfuryl chloride.[6] As in the oxidation of I with lead tetraacetate, benzyl azide (III), dibenzylamine (IV) and benzaldehyde (V) were formed;[3] presumably, α-chlorination to II followed by hydrolysis would lead to the same intermediate α-hydroxy derivative II (Y = OH), thence to the fragmentation products (III-V).[3]



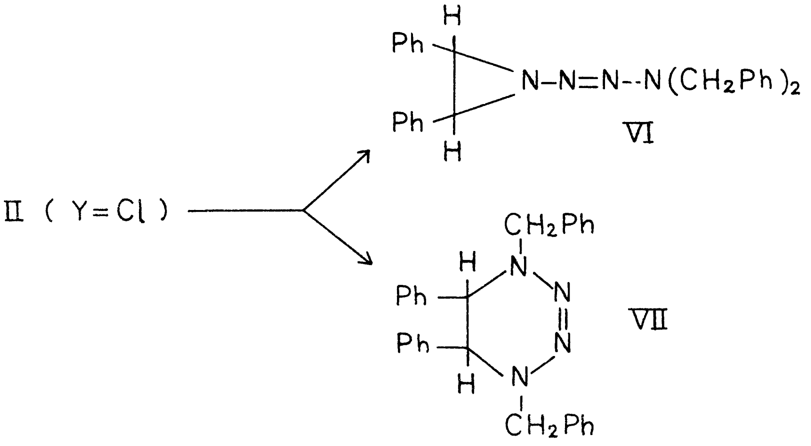
I

II, Y = Cl

During the course of this investigation, we have isolated in addition a new compound which we believe to be the first cyclic 2-tetrazene ever reported.[7]

The reaction of I with sulfuryl chloride in benzene at room temperature gave III, IV, and V as the major products. In addition, a 2.4% yield of a colorless crystalline solid, mp 161-163°C (dec.) was obtained. Its infrared spectrum though similar to that of I was clearly different. A Beilstein test was negative and the result of the elemental analysis was compatible with that calculated for I or for a "dehydro" derivative of I: Anal. Found: C, 80.23; H, 6.43; N, 13.26%. Calc'd for $C_{28}H_{28}N_4$: C, 79.96; H, 6.71; N, 13.32%; calc'd for $C_{28}H_{26}N_4$: C, 80.36; H, 6.26/ N, 13.39%. The possibility that it was the cis-isomer of I would seem unlikely since it could be recrystallized from methanol without change. The UV spectrum ($CHCl_3$) exhibited a band at 251 mμ (ε = 6900), a shoulder at 270 mμ (ε = 6870) and a maximum at 295 mμ (ε = 10,300); this spectrum was consistent with a 2-tetrazene structure.[8,9]

Thus, only two structures VI and VII are possible for this compound, both of which could conceivably arise by the cyclization of II as shown below.



The nmr spectrum in acetone-d_6 though a poor one because of the sparing solubility of the compound, is not inconsistent with structure VII. The aliphatic protons appeared as a singlet [with a shoulder at τ 5.80 (6H)] and the aromatic hydrogens as a broad peak centered at τ 2.90 (20H). The nmr spectrum of I exhibited a sharp singlet at τ 5.66 (8H) and an aromatic band centered at τ 2.80 (20H) while 1,1-dibenzylhydrazine showed the methylene protons at τ 6.28 and the aromatic hydrogens at τ 2.68. It may be reasonably assumed that the incorporation of the N-amino-2,3-diphenylaziridine moiety into a tetrazene structure such as VI, should result in a downward shift of comparable magnitude ($\Delta\tau$ = 0.6) as that observed in going from 1,1-dibenzylhydrazine to I. Since the α-protons of cis- and trans-N-amino-2,3-diphenylaziridines are reported[10] to absorb at τ 6.86 and at τ 6.67, 6.80 respectively, then the aziridinyl protons of VI might be expected to appear in the range of τ 6.02-6.24 which is not the case for our compound.

The assignment of the structure of 1,4-dibenzyl-5,6-diphenyl-1,2,3,4-tetraaza-2-cyclohexene (VII) to our compound was amply confirmed by the mass spectrum, determined on a Hitachi RMU-7L spectrometer at 70 eV. Though very weak as expected, the parent peak (m/e 418) could be observed; the fragmentation pattern was, however, the most telling argument in favor of the assigned structure. Indeed no major peak appeared until m/e 195 ($PhCH=NCH_2Ph$), the base peak; other main peaks were m/e 106 and 91. This fragmentation pattern may be rationalized by the initial and facile loss of nitrogen from VII with concurrent rupture of the 5-6 carbon-carbon single bond to give benzalbenzylamine (m/e 195).[11] Since 2-tetrazenes can be considered as bis aza analogues of azoalkanes, this type of behavior is entirely consistent with the results of the decomposition of the corresponding cyclic azo compound[12] and of the isomeric N-nitrenes.[13]

We are presently isolating additional quantities of VII for further investigation of the chemistry of this new type of 2-tetrazenes.

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9. For comparison, the cyclic bis tetrazene reported by Nelsen *et al*. (ref. 7), has the following bands (heptane): 241 (ε = 4400), 258 (ε = 6000), 267 (ε = 9000), 276 (ε = 9300), and 300 (sh,ε = 1600) mμ; the UV spectrum of I exhibits absorptions ($CHCl_3$) at 253 (ε = 7800), 269 (sh,ε = 8800) and 290 (ε = 10700).

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11. The mass spectrum of I was determined and further supported the assigned structure of VII. Not only was the fragmentation pattern *substantially* different from that of VII but m/e 195 appeared only as a very minor peak in the spectrum of I while m/e 91 was the base peak. It is also of interest to observe that the parent peak of I did not appear; this suggests that cyclic 2-tetrazenes are thermally more stable than the linear ones, a fact already noted by Nelsen *et al*. (ref. 7).

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