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THE FORMATION OF 2,6-DIPHENYLPYRIDAZINE AND 2,5-DIPHENYLPYRROLE FROM α-STYRYL AZIDE

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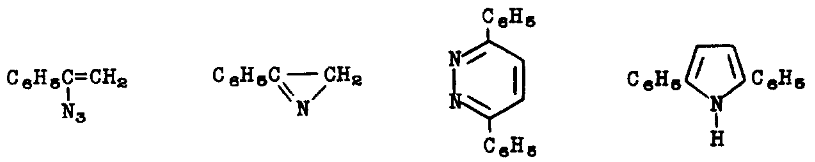
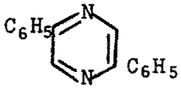
Two new thermal reactions of neat α-styryl azide have been observed. After one month at room temperature in a tightly closed screw-cap brown glass bottle, 21.0 g. (0.14 mole) of neat α-styryl azide, 1, is transformed into 2-phenylazirine (1,2), 2 (ca. 10%), 3,6-diphenylpyridazine, m.p. 221-223°C (3), 3, (0.7 g., 0.003 mole, 7%) and 2,5-diphenylpyrrole, m.p. 137.5-141.5°C (4), 4, (3.0 g., 0.013 mole, 32%). Yields are based on 40% recovered α-styryl azide (8.5 g., 0.06 mole). Each day the bottle was opened to allow accumulated gas to escape. By the end of the first week an appreciable quantity of insoluble 3 was noted; both 2 and 4 remained in solution.



1 2 3 4

Neither 2,5-diphenylpyrazine, 5, nor its 3,6-dihydroderivative, 6, the known (5) dimer of 2-phenylazirine, 2 (or its valence tautomer, α-styrylnitrene, 7), was detected. Since 2 does not dimerize to 8, an explanation for the formation of a nitrogen to nitrogen bond requires the initial formation of azo-α-styrene, 9 by an interaction between two molecules of 1. Ring-closure by valence isomerization transforms 9 into 8 and aromatization produces 3.



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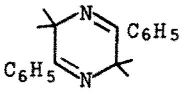

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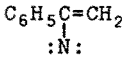

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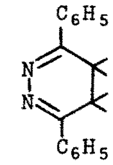

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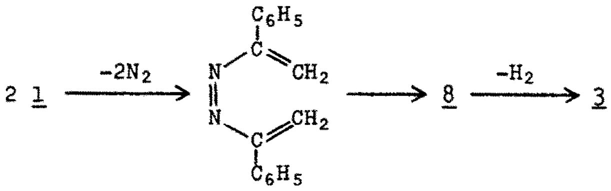

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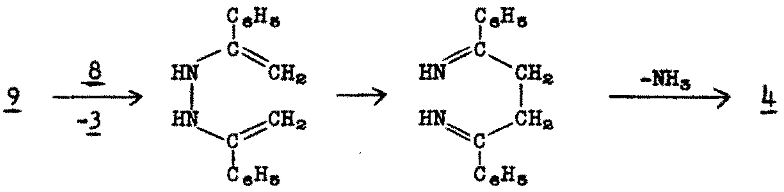
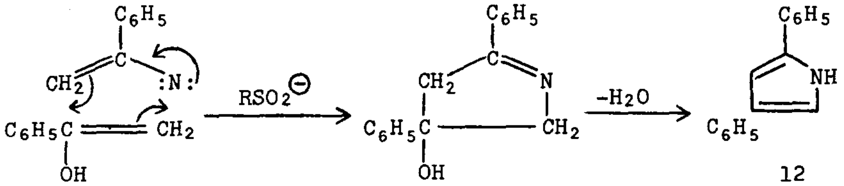
Azostyrene, 9, apparently is not formed from an interaction between 7 (or 2) and 1. From a mixture of 2.9 g. (0.02 mole) of 1 and 2.3 g. (0.02 mole) of 2 in a closed brown bottle for one month, a 67% yield of 6, a red solid, was obtained. Air oxidation during recrystallization from ethanol produces 5, m.p. 192-195° (5), a yellow compound. The presence of 2,5-diphenylpyrrole, 4, was detected by i.r. and n.m.r. but was not isolated and other products, unidentified, were obtained.

Whether or not the transformations 1 → 3 and 1 → 4 have (a) common intermediate(s) has not been determined. It is conceivable that reduction of 9 to the hydrazine 10 occurs as 8 is dehydrogenated to 3. Following a Cope rearrangement, 10 → 11, cyclization with the elimination of ammonia affords the pyrrole 4.



10 11

On the other hand, the formation of 3 may be independent of the formation of 4. The formation of 2,4-diphenylpyrrole, 12, from 2 and acetophenone, in the presence of sulfinate anion was recently reported (6). Apparently either the enol or the enolate anion attacks the electron deficient nitrogen of 7, the valence tautomer of 2. As shown below, a comparable reaction between two



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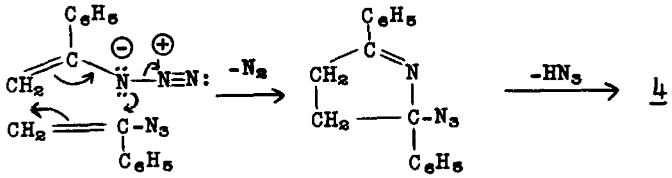
molecules of α-styryl azide may be initiated in a nucleophilic attack by a terminal azido nitrogen upon the α-carbon of α-styryl azide. Nitrogen elimination may be concerted with new bond formations. Subsequent elimination of hydrogen azide would produce 4.



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References

1. G. Smolinsky, J. Org. Chem. 27, 3557 (1962) obtained 2 on vapor phase pyrolysis of 1 at 350-360° (0.1-0.3 mm.) in 80% yield. About 5% of an unstable substance assumed to be $C_6H_5N{=}C{=}CH_2$ was also obtained but has not been detected in the present work.

2. Compound 2 was obtained together with recovered 1 on elution with hexane from an alumina column to which the liquid portion of the reaction mixture had been applied. The mixture was shown by nmr to consist of ca. 10% 2 (singlet 1.58 ppm (1)) and ca. 90% 1.

3. H. Keller, R. Pasternak and H. V. Halban, Helv. Chim. Acta 29, 512 (1946). A mixture m.p. of 3 with authentic material showed no depression.

4. Obtained on further elution with ether of the liquid portion of the reaction mixture on alumina. G. A. Kreutzberger and P. A. Kalter, J. Org. Chem. 25, 554 (1960) report m.p. 143-144°C. Infrared absorption for 4 agreed with that reported by G. A. Kreutzberger and P. A. Kalter, J. Phys. Chem. 65, 624 (1961). The nmr spectrum of 4 in deuterochloroform consisted of a pair of spikes at 6.52 ppm (2H, spacing of 3 cps), a multiplet centered at 7.40 ppm (10H) and a broad flat peak at ca. 8.43 ppm (1H exchangeable with D_2O). Elemental analysis for 4: Calc'd. for $C_{16}H_{13}N$: C, 87.63; H. 5.98; N, 6.39; m.w. 219.3. Found: C, 87.56; H, 6.06; N, 6.35; m.w. 219 (m/e).

5. L. Horner, A. Christman and A. Gross, Chem. Ber. 96, 399 (1963).

6. S. Sato, H. Kato and M. Ohta, Bull. Chem. Soc. Japan 40, 1014 (1967).