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NOVEL REARRANGEMENTS RESULTING FROM THE ACTION OF HYDRAZINES ON CIS-DIBENZOYLSTILBENE OXIDE

Albert Padwa and Martin Rostoker

Department of Chemistry
State University Of New York at Buffalo
Buffalo, New York, 14214

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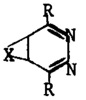
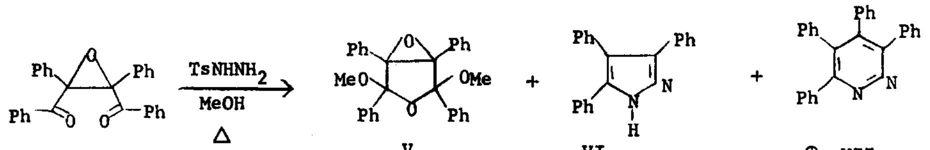
The incorporation of nitrogen atoms into the 3 and 4 positions of the norcaradiene ring has been reported to stabilize the bicyclic valence tautomer relative to its monocyclic form.(1) In fact, 2,5-diphenyl-3,4-diazanorcaradiene(I) and its substitution products are stable at room temperature.(2,3) Similarly, the 3,4,7-triazanorcaradiene(II) is also a relatively stable substance, which can again be detected only in the bicyclic form.(4) The formation of a derivative of pyridazine oxide(III) had been described by Schonberg and Rosenthal in 1921(5), but a reinvestigation of the structural assignment by Hughes and Prankprakma(6) has shown that the assignment is in fact incorrect. In an attempt to find a more convenient route to the unknown pyridazine oxide system, we investigated the reaction of <u>cis</u>-dibenzoylstilbene oxide with substitute hydrazines.



X = CH_2 (I)
X = N-R (II)
X = 0 (III)

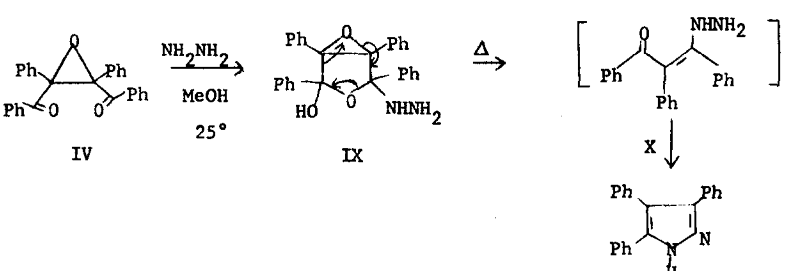
Treatment of cis-dibenzoylstilbene oxide(7) (IV) with p-tosylhydrazine in refluxing methanol resulted in the formation of five products that were subsequently identified as 2,5-dimethoxy-2,3,4,5-tetraphenyl-3,4-epoxytetrahydrofuran(V) (36%), triphenylpyrazole(VI) (26%), tetraphenylpyridazine (VII) (6%), benzoic acid (26%) and toluene-p-sulphonhydrazidium toluene-p-sulphonate(VIII) (24%). The structure of the cyclic dimethyl ketal V(8) m.p. 198-199°, was supported by spectroscopic data, hydrolysis to IV, and by comparison with an authentic sample prepared from IV and methanol. The remaining products were identified by comparison of infrared and mixture melting point with those of authentic samples.



IV V VI VII

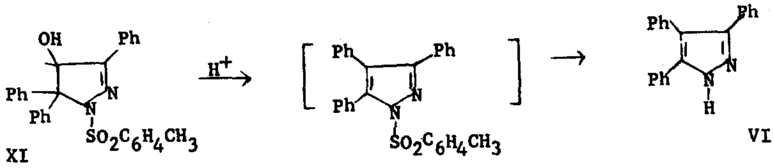
+ $PhCO_2H$ + $Ts\overset{\oplus}{NHNH_3}\ \overset{\ominus}{SO_3}C_6H_4CH_3$ (VIII)

The formation of triphenylpyrazole(VI), not being easily explicable, prompted us to a further study of the reaction mechanism. Treatment of IV with hydrazine in refluxing methanol gave VI (95%) and benzoic acid. However, when IV was allowed to react with an equimolar amount of hydrazine at 25° a new compound was isolated in 85% yield. This material is assigned structure IX, m.p. 225-227°, on the basis of its molecular formula ($C_{28}H_{24}N_2O_3$), spectroscopic data and the known "cis-group effect" of related 1,4-diketones.$^{(9,10)}$

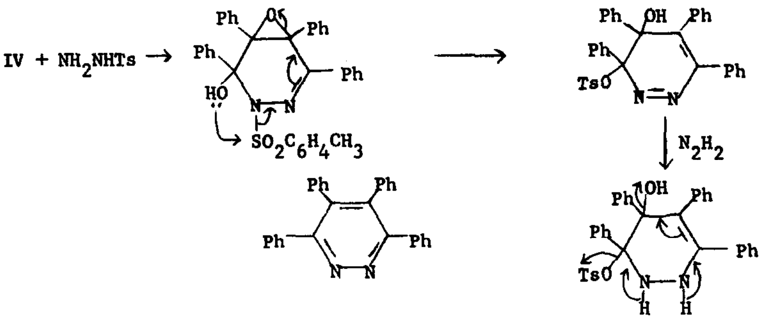


IV IX VI

Compound IX when refluxed in chloroform (or methanol) for 12 hours was converted quantitatively to triphenylpyrazole(VI) and benzoic acid. The rearrangement of IX to VI suggests that the reaction proceeds by fragmentation to X followed by intramolecular cyclization. It seems reasonable that the formation of triphenyl pyrazole in the reaction between IV and p-tosylhydrazine proceeds via comparable intermediates. Apparently the N-tosyltriphenylpyrazole initially formed loses the p-toluenesulfonyl group on aqueous workup. This interpretation is consistent with the known lability of this group in the related 2,4-diphenylpyrazole system(11) and is also in accord with the observation that the 4-hydroxypyrazoline XI(12) undergoes rapid rearrangement to VI when subjected to mild acid conditions.



It is premature to propose a precise mechanism to explain the formation of tetraphenylpyridazine(VII) from the reaction of IV and p-tosylhydrazine. As a working hypothesis, however, one could envision an intramolecular migration of the p-toluenesulfonyl group from nitrogen to oxygen followed by opening of the epoxide ring. Subsequent reduction by diimide and rearomatization readily accounts for the observed product.



The formation of diimide by the thermal decomposition of p-tosylhydrazine has been reported in the literature(13) and its presence in the above sequence provides an explanation for the formal reduction that occurred.

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