

AN UNUSUAL CONVERSION OF A PYRIDAZINE DERIVATIVE  
INTO A PYRROLE DERIVATIVE

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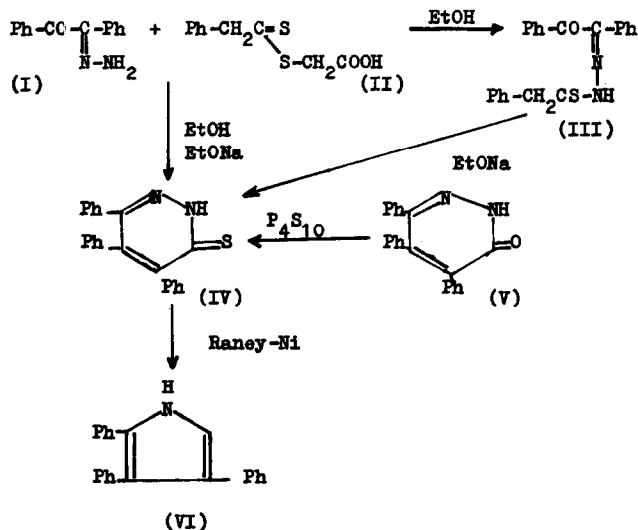
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IN an attempt to prepare 3,4,5-triphenylpyridazine through desulfurization of 4,5,6-triphenyl-3(2H)-pyridazinethione an unusual transformation of the latter compound in 2,3,4-triphenylpyrrole was observed. A transformation of a pyridazine derivative into the corresponding pyrrole has not been noted until recently,<sup>1</sup> when an acid catalyzed reaction of some partially hydrogenated 1-tosylpyridazines converted them into N-tosylamidopyrrole, or when 1-phenyl-3,5-dichloro-6(1H)-pyridazinone was converted into 1-phenyl-3-hydroxy-pyrrole carboxylic acid by treatment with alkali hydroxide solution.<sup>2</sup> On the other hand there are no known examples of changes in the ring size as a result of the action of Raney nickel on organic compounds with exocyclic sulfur<sup>3</sup> and 3-mercaptopyridazine has been reported to give with Raney nickel the expected sulfur-free product on desulfurization.<sup>4</sup>

We have prepared 4,5,6-triphenyl-3(2H)-pyridazinethione on two different ways. A mixture of equimolar quantities of benzil monohydrazone (I) and carboxymethyl dithiophenylacetate<sup>5</sup> (II) was condensed in ethanolic solution for 3 hr. The intermediate N-phenylthioacetyl benzilmonohydrazone (III, yellow needles, m.p. 205-206°, <sup>6</sup> yield 23%) was cyclized in ethanolic solution in the presence of sodium ethoxide to afford 4,5,6-triphenyl-3(2H)-pyridazinethione (IV, yield 28%) as yellow needles, m.p. 303-4° (in etha-

mol  $\lambda_{\max}$ : 308  $m\mu$ ,  $\epsilon = 23,800$ ; the infrared spectrum exhibits inter alia an absorption at 3145  $cm^{-1}$  indicating the presence of a NH group). The pyridazine derivative (IV) can be obtained preferentially in one-step reaction without isolating the intermediate (III) when using 3 moles of sodium ethoxide and refluxing the ethanolic solution for 3 hr (yield 29%). On the other hand the pyridazine derivative (IV) was prepared from the corresponding 4,5,6-triphenyl-3(2H)-pyridazinone (V) (m.p. 294-5°, lit. <sup>7</sup> gives m.p. 275-6°) with  $P_4S_{10}$  in toluene (yield 17%). The infrared spectrum was identical with that of (IV) prepared through cyclization.



When submitting the pyridazine derivative (IV) to desulfurization with Raney nickel W6<sup>8</sup> in boiling ethanolic ammonia, 2,3,4-triphenylpyrrole (VI) as colourless needles, m.p. 168° (yield 21%) was obtained (in ethanol:  $\lambda_{\max}$ : 249 and 300  $m\mu$ ,  $\epsilon = 22,420$  and 16,750 respectively). Besides the analytical data, the structure of this pyrrole derivative is supported by the following observations. The infra-red spectrum revealed only a strong absorption

maximum characteristic for a secondary NH group at  $3460\text{ cm}^{-1}$  region and no peaks in the  $1565\text{ cm}^{-1}$  region characteristic for a pyridazine ring system.<sup>9</sup> Furthermore, the compound gave a positive colour reaction with p-dimethylaminobenzaldehyde, characteristic for pyrrole derivatives with at least one unsubstituted  $\alpha$ -position in the pyrrole ring.<sup>10</sup> This colour reaction was positive already with few  $\mu$  of the compound when a deep red-violet colour developed which turned blue after making the solution alkaline.

Satisfactory elemental analyses have been obtained on every recrystallized product. Full details of this research and other reactions will be reported elsewhere.

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