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HETEROCYCLIC ANALOGS OF PLEIADIENE

XXIX.* CONVENIENT METHOD FOR THE DEHYDROGENATION OF 2-R-2,3-DIHYDROPERIMIDINES

N. M. Starshikov, A. F. Pozharskii, and F. T. Pozharskii†

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In most cases 2-R-2,3-dihydroperimidines are smoothly dehydrogenated by sulfur in refluxing xylene to give 2-substituted perimidines in high yields. 2-(5-Halo-2-furyl)-2,3-dihydroperimidines, which form IV and 2-(5-halo-2-furyl)perimidines when they are heated with sulfur, constitute an exception.

The reaction of 1,8-naphthalenediamine (I) with carboxylic acids and their derivatives as a method for the preparation of 2-substituted perimidines is frequently complicated by side processes [2]. Diamine I reacts much more smoothly with aromatic aldehydes [1, 2], but the products of this reaction are extremely stable 2-R-2,3-dihydroperimidines (II). Palladium on carbon [2], chloranil, and manganese dioxide [3] have been proposed for their aromatization to 2-R-perimidines (III). Each of these reagents has disadvantages: high cost, difficulties involved in the isolation of the reaction products, yields that are not always good, etc. We have found a considerably simpler and cheaper method for the dehydrogenation of II, which con-

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* See [1] for communication XXVIII.

† Deceased.

Shakhty Technological Institute of Everyday Repairs and Other Services, Shakhty 346500. Rostov State University, Rostov-on-Don 344006. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 7, pp. 986-988, July, 1977. Original article submitted July 27, 1876.

TABLE 1. 2-R-Perimidines (III)

Compounds III	R*	mp of III, °C (solvent)†	IR spectra, ν_{NH}, cm^{-1}	Yield of III, %
a	Phenyl	183—184^{2}‡	3310	97
b	p-Bromophenyl	169—170^{1}	3300	95
c	2,4-Dichlorophenyl	193—194 (dec.)^{1}	3240	95
d	2-Pyrrolyl	106—107^{1}	3320	70
e	3-Indolyl	148—149^{1}	3420	50
f	2-Thienyl	165—166^{1}	3320	95
g	2-Quinolyl	290—300 (dec.)^{5}	3350	95
h	2-Furyl	178—179^{2}	3320	95
i	5-Methyl-2-furyl	230 (dec.)^{1}	3320	95
j	5-Chloro-2-furyl	224—225^{1}	3200	40
k	5-Bromo-2-furyl	210 (dec.)^{7}	3210	40
l	5-Iodo-2-furyl	217—218^{1}	3200	40

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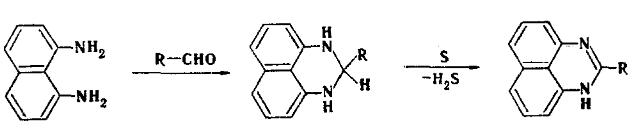
* The type of group in III corresponds to that in the analogous II.

† The compounds were crystallized: IIIa,d,f,i-l from aqueous alcohol, IIIb,c from toluene, IIIe from benzene–cyclohexane, IIIg from alcohol, and IIIh from ethyl acetate.

† According to the data in [6], this compound has mp 187-188°C.

sists in heating them with powdered sulfur in refluxing xylene. Dehydrogenation does not occur in solvents with lower boiling points (benzene, toluene, and alcohol).



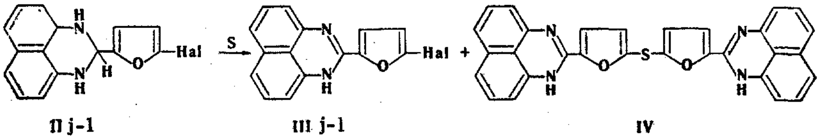
I

IIa-i

IIIa-i

In most cases the 2-substituted perimidines are formed in close-to-quantitative yields, but there are exceptions (Table 1). A reduced yield of III is observed in the dehydrogenation of 2-pyrrolyl- (IId) and 2-(3-indolyl)-2,3-dihydroperimidine (IIe). There is no doubt that the reason for this consists in the ability of these compounds to undergo aromatization at high temperatures with splitting out of a molecule of pyrrole or indole to give the perimidine [1]. Another exception is found in the case of 2-(5-halo-2-furyl)-2,3-dihydroperimidines (IIj-l), which, when they are heated with sulfur, form 2-(5-halo-2-furyl)perimidines (IIIj-l, in 40% yields) and a brown compound of the composition $C_{30}H_{18}N_4O_2S$, which does not contain halogen and is only slightly soluble in most solvents. We assigned sulfide structure IV to this substance. It might be assumed that this sort of process is associated with replacement of the halogen in IIj-l by a mercapto group and subsequent reaction of the mercaptan with a molecule of the starting IIj-l and dehydrogenation. Replacement of halogen evidently precedes dehydrogenation of IIj-l, since 2-(5-halo-2-furyl)perimidines (IIIj-l) remain unchanged when they are heated with sulfur in xylene. It is also interesting that 2-(halophenyl)-2,3-dihydro-perimidines (IIb,c) are oxidized by sulfur to IIIb,c without any side reactions. The high activity of halogen in 2-(5-halofuryl)azoles with respect to nucleophiles is well known [4].

The use of sulfur as the dehydrogenating agent makes the reaction of I with aldehydes the simplest method for the preparation of 2-substituted perimidines.



IIj-l

IIIj-l

IV

EXPERIMENTAL

The preparation and properties of the corresponding 2-R-2,3-dihydroperimidines (II) were described in [1]. The structures of the 2-R-perimidines were established from the fact that their melting points and IR spectra were identical to those of authentic samples.

2-R-Perimidines (IIIa-d,f-i). A mixture of 0.01 mole of 2-R-2,3-dihydroperimidine (IIa-d,f-i), 30 ml of xylene, and 0.32 g (0.01 g-atom) of sulfur was refluxed for 2-3 h, after which it was cooled, and hydrogen chloride was bubbled into it. The precipitated crystals of the hydrochloride were removed by filtration, washed with acetone, and dried. A suspension of the hydrochloride in water was treated with ammonium hydroxide until the mixture was weakly alkaline. The crystals of the base were removed by filtration, washed with water, dried, and crystallized.

2-(5-Halo-2-furyl)perimidines (IIIj-l). A mixture of 0.01 mole of 2-(5-halo-2-furyl)-2,3-dihydroperimidine (IIj-l), 50 ml of xylene, and 0.32 g (0.01 g-atom) of sulfur was refluxed for 3 h, after which the mixture was cooled, and hydrogen chloride was bubbled into it. The precipitated crystals of the hydrochloride of IV were removed by filtration, washed with chloroform, dried, and dissolved in the minimum amount of DMF. The solution was diluted to twice its volume with water to hydrolyze the hydrochloride. The precipitated crystals of base IV were removed by filtration, washed with water, and dried to give a product with mp > 350° in 50% yield. Found: C 72.2; H 3.7; N 11.1; S 6.6%. $C_{30}H_{18}N_4O_2S$. Calculated: C 72.3; H 3.6; N 11.2; S 6.4%.

The mother liquor from the separation of the hydrochloride was evaporated, and the residue was dissolved in 30 ml of chloroform. The chloroform solution was passed through a column filled with aluminum oxide (elution with chloroform). Workup of the first fraction gave IIj-l in 40% yields.

2-(3-Indolyl)perimidine (IIIe). A mixture of 5.7 g (0.02 mole) of 2-(3-indolyl)-2,3-dihydroperimidine (IIe), 150 ml of toluene, and 0.64 g (0.02 g-atom) of sulfur was refluxed for 10 h, after which the hot mixture was filtered, and the toluene was removed from the filtrate under reduced pressure. The residue was dissolved in chloroform, and the solution was passed through a column filled with aluminum oxide. The yellow-green portion of the aluminum oxide column was cut out, and the 2-(3-indolyl)perimidine (IIIe) was extracted with acetone. The acetone was removed by distillation, and the residue was crystallized from benzene–cyclohexane.

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