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AN UNUSUAL TRANSFORMATION OF 5-AMINO-6-METHYL-3-PHENYL-4(3*H*)-PYRIMIDONE WITH SELENIUM DIOXIDE: X-RAY CRYSTAL STRUCTURE OF 3-PHENYLCARBAMOYL-4-METHYL-1,2,5-SELENADIAZOLE

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The reaction of 5-amino-6-methyl-3-phenyl-4(3*H*)-pyrimidone (1) with selenium dioxide in dioxane gave the unusual products: 6-phenyl-7(6*H*)-isoselenazolo[4,3-*d*]pyrimidone (2) and 3-phenylcarbamoyl-4-methyl-1,2,5-selenadiazole (3) in the ratio 1:2.

KEYWORDS——pyrimidine; pyrimidone; selenium dioxide; selenadiazole; isoselenazole; X-ray crystal structure; pyrazine

Selenium dioxide attacks a methyl group in the neighborhood of a ring nitrogen atom to give either an aldehyde or a carboxyl group. For instance, 2-methylpyridine gives a mixture of pyridine-2-carbaldehyde and pyridine-2-carboxylic acid.1) Recently, Yamanaka, *et al.*2) reported the selective oxidations of 2,4-dimethyl-6-phenylpyrimidine, 4,6-dimethyl-2-phenylpyrimidine or 2,4-dimethylquinoline with selenium dioxide in dioxane to give 2-methyl-6-phenylpyrimidine-4-carbaldehyde, 6-methyl-2-phenylpyrimidine-4-carbaldehyde, or 4-methylquinoline-2-carbaldehyde. We now present an example of an unusual transformation of a pyrimidone by reaction with selenium dioxide. The reactions of some pyrimidones such as 6-methyl-3-phenyl-4(3*H*)-pyrimidone3), 5-bromo-6-methyl-3-phenyl-4(3*H*)-pyrimidone3), or 5-dimethylamino-6-methyl-3-phenyl-4(3*H*)-pyrimidone4) with selenium dioxide in dioxane or xylene did not proceed, while the reaction of 5-amino-6-methyl-3-phenyl-4(3*H*)-pyrimidone5) (1) with selenium dioxide gave two unusual products: 6-phenyl-7(6*H*)-isoselenazolo[4,3-*d*]pyrimidone (2) (mp 195-6°C) and 3-phenylcarbamoyl-4-methyl-1,2,5-selenazole (3) (mp 154-5°C). The structure of 2 was determined by ^{1}H-NMR and mass spectra. In the ^{1}H-NMR spectrum signals of C_6-methyl protons and C_5-NH_2 protons disappeared, and a new signal (δ 9.85) derived from =CH-Se- function was observed. The mass spectrum also indicated the presence of a selenium element in its molecule. Treatment of 2 with sodium borohydride in methanol gave 1. On the other hand, mass spectrum and elemental analyses of 3 led to the empirical formula $C_{10}H_9N_3OSe$. ^{13}C-NMR and ^{1}H-NMR analyses of 3 suggested the elimination of C_2-carbon atom from 1. The reduction of 3 with sodium borohydride in methanol led to a compound of $C_{20}H_{18}N_4O_2$ whose structure was identified as 2,5-dimethyl-3,6-dianilidopyrazine(4). The structure of 3 was unambigously determined by singlecrystal X-ray analysis as shown in Fig. 1, which also made possible a rationalization of its ^{1}H-NMR spectrum. The formation of 3 probably is explained as depicted in Chart 1. The selenium dioxide initially attacks the C$_2$-methylene function of the resonant form of 1 to give labile aldehyde, then the elimination of the aldehyde group and the reaction of the resulting diimine with selenium dioxide occurs to give 3. This is the first known example of the transformation of a pyrimidone to a selenadiazole by reaction with selenium dioxide.

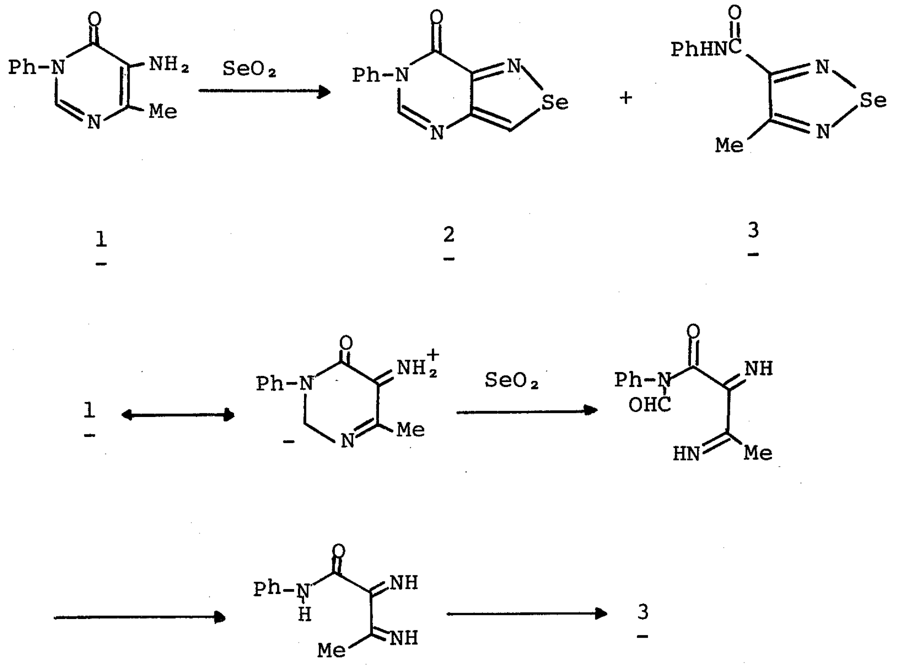

Chart 1

Table I. Yields (%) of 2 and 3 by the Reaction of 1 with Selenium Dioxide

Solvents	Reaction Temp. (°C)	SeO₂ (mole)	Reaction Time (h)	2	3
Dioxane	60-65	1.5	1	31	60
Xylene	120-140	1.5	1	26	25
Ac₂O	120-140	1.5	1	0	0
Pyridine	110-116	1.5	1	3	5

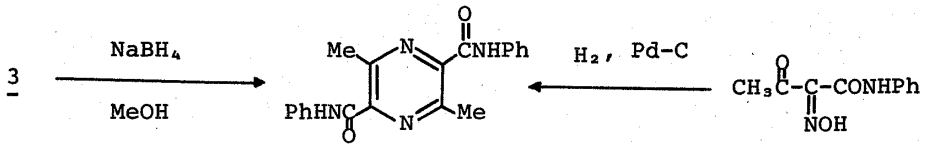

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Chart 2

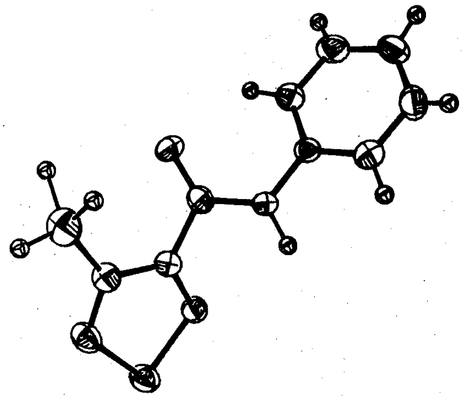

Fig. 1. Perspective Drawing of 3

Crystal data: $C_{10}H_9N_3OSe$, M=266.16, orthorhombic, space group *Pbca*, a=8.15(1), b=9.402(1), c=27.365(4) Å, U=2099.0(5) Å³, D_m=1.680(1), D_c=1.684(1) g cm^{-3}, Z=8. The structure was solved by direct methods (MULTAN 78[6]) and refined by least-squares to R=0.088 using 1787 independent reflections ($2\theta_{max} \leqq 130°$).

REFERENCES AND NOTES

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