CHEMISTRY LETTERS, pp. 1379-1380, 1976. Published by the Chemical Society of Japan

REACTION OF KETENIMINE AND SULFUR DIIMIDE

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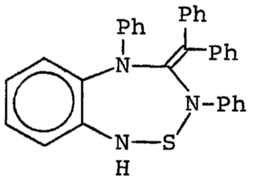
The reaction of diphenylketene-N-phenylimine (1) and diphenylsulfur diimide (2) gave the 2-aminoindole 4 as a major product together with the benzothiatriazepine 3 and the amidine 5.

As a part of our studies on chemistry of ketenimines,[1] we now wish to report the reaction of a ketenimine with a sulfur diimide in comparison with that of ketenes which gave various heterocycles containing one sulfur atom.[2]

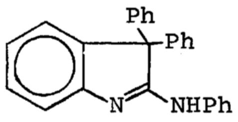
The reaction of diphenylketene-N-phenylimine (1) with diphenylsulfur diimide (2) was carried out in toluene at 110-120°C for 20 hr under nitrogen atmosphere. After removal of the solvent, the reaction mixture was chromatographed on a silica gel column using hexane-benzene as an eluent to give 5,6-benzo-2,4-diphenyl-3-diphenylmethylenetetrahydro-1,2,4,7-thiatriazepine (3, 8%), 2-anilino-3,3-diphenyl-3H-indole (4, 25%), N^1,N^2-diphenyl-α-anilinodiphenylacetamidine (5, 4%), azobenzene (18%), and sulfur (70%). Besides these products, a compound which consists of two molecules of the ketenimine and a moiety of PhN was isolated in 6% yield, but the structure is not yet established.[3]

$$\underset{\underline{1}}{Ph_2C{=}C{=}N\text{-}Ph} + \underset{\underline{2}}{Ph\text{-}N{=}S{=}N\text{-}Ph} \xrightarrow[\text{toluene}]{110\text{-}120°C,\ 20\ hr} Ph\text{-}N{=}N\text{-}Ph + S_x +$$



3

+



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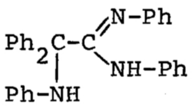

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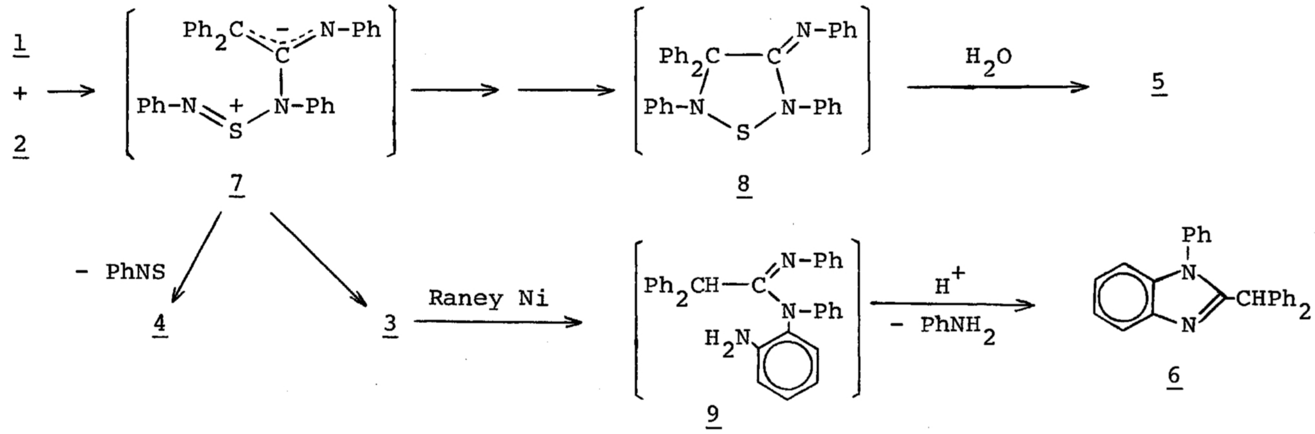
	3	4	5
Mp (°C)	159-160	211-212	206-207
Ir (nujol, cm^{-1})	3440(NH),1620(C=C)	3430(NH),1560(C=N)	3410,3310(NH),1640(C=N)
Nmr ($CDCl_3$, δ)	6.01(s,1H,NH) 6.7-7.5(m,24H)	ca.6.4(br,1H,NH) 6.8-7.8(m,19H)	ca.5.8(br,1H,NH) 6.4-7.8(m,26H,NH,5Ph)
Mass (m/e)	483(M^+), 451 269, 214	360(M^+), 267 241, 180	453(M^+), 360 258, 195

(Elemental analyses for all compounds were satisfactory.)

The structures of 3 and 4 were supported by ^{13}C nmr. The thiatriazepine 3 shows no signal in the field higher than 120 ppm. The aminoindole 4 has signals at 69.2 (sp^3 carbon), 118-155, and 170.7 ppm (C=N). Reduction of the thiatriazepine 3 with Raney Ni gave crude oily material 9 which had ir absorptions at 3430,3380 (NH), and 1640 cm^{-1} (C=N). After the treatment of the oil 9 with picric acid in ethanol, 1-phenyl-2-diphenylmethylbenzimidazole (6) was isolated in 22% overall yield instead of a picrate, suggesting that 9 is N^1-phenyl-N^1-2-aminophenyl-N^2-phenyldiphenylacetamidine.[4] The benzimidazole 6 was colorless needles (mp 198-199°C) and has ir absorptions at 1590 and 1500 cm^{-1}. In the nmr spectrum of the benzimidazole 6, the methine proton (s, 1H) and the aromatic protons (m, 19H) appeared at δ 5.52 and 7.0-8.0, respectively.

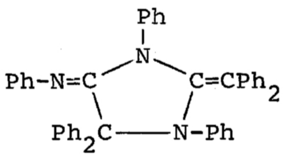


The reaction of the ketenimine 1 and the sulfur diimide 2 would be accounted for by the intermediacy of 7, which eliminates thionitrosobenzene to form 4 or cyclizes to 3 and 8. The amidine 5 was probably formed by hydrolysis of 8, whose formation via 7 is analogous to that of the thiadiazolidine derivative from diphenylketene and the sulfur diimide 2.[2]

Study on the effect of substituents is now in progress.

References and Note

1) M. Komatsu, Y. Ohshiro, H. Hotta, and T. Agawa, J. Org. Chem., 39, 948 (1974); N. Murai, M. Komatsu, Y. Ohshiro, and T. Agawa, ibid., in press.
2) T. Minami, K. Yamataka, Y. Ohshiro, T. Agawa, N. Yasuoka, and N. Kasai, ibid., 37, 3810 (1972).
3) The molecular formula was determined as $C_{46}H_{35}N_3$ by elemental analysis and mass spectrum, and the spectral data suggest the following plausible structure.



Mp 222-223°C;
ir (nujol) 1705, 1690, 1600, and 1590 cm^{-1};
nmr ($CDCl_3$) δ 6.0-7.6 (all protons);
mass m/e 629 (M^+),358,269,180, and 165.

4) F. E. King and R. M. Acheson, J. Chem. Soc., 1949, 1396.

(Received October 15, 1976)