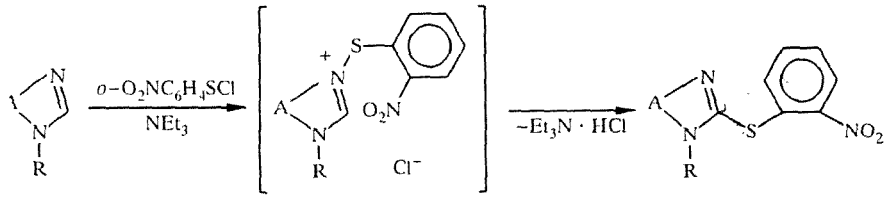
-ARENESULFENYLATION OF 1,3-AZOLES WITH RENESULFENYL CHLORIDES

A. A. Tolmachev, A. A. Yurchenko, V. A. Man'ko, A. S. Merkulov, and A. M. Pinchuk

The traditional methods of arenesulfenylating 1,3-azoles are based on the reactions of their halogen derivatives with iophenolates or aromatic compounds containing a labile halogen atom with the sodium salts of azole thio derivatives [1, 2]. e have found that it is possible to 2-arenesulfenylate 1,3-azoles readily with arenesulfenyl chlorides in basic media. As amples results are given on the reaction of 2-nitrophenylsulfenyl chloride with 1-ethylimidazole (I), 1-ethylbenzimidazole I), a 1-p-tolyl-1,3,4-triazole (III) in the presence of triethylamine.



I–III IV V–VII

I, V A = —CH=CH—, R = Et; II, VI A = *o*-phenylene, R = Et; III, VII A = —N=CH—, R = *p*-Me—C_6H_4

We consider that the arenesulphenylation, like the 2-acylation and 2-phosphorylation of 1,3-azoles, occurs through ıtermediate abducts of type (IV). The structures of compounds (V)-(VII) were confirmed by data of ^1H and ^{13}C NMR pectra.

A solution of 2-nitrophenylsulfenyl chloride (0.01 mole) [0.02 mole for compound (III)] in dry benzene (50 ml) was ıdded to a mixture of the initial heterocycle (0.01 mole), triethylamine (0.01 mole) [0.02 mole in the case of compound III)], and dry benzene (50 ml). The reaction mixture was left for 20 h at room temperature, and the precipitate of triethylımine hydrochloride then removed. The filtrate was evaporated to dryness and the residue crystallized. Yields were 70-80%.

1-Ethyl-2-(2-nitrophenylthio)imidazole (V) $C_{11}H_{11}N_3O_2S$. Yellow crystals of mp 82°C (from ethanol). PMR spectrum (CD_3OD): 1.31 (3H, t, $^3J_{HH}$ = 7.0 Hz, $NCH_2\underline{CH_3}$); 4.10 (2H, q, $^3J_{HH}$ = 7.0 Hz, $N\underline{CH_2}CH_3$); 6.54 (d.d, $^3J_{HH}$ = 8.1 Hz, $^4J_{HH}$ = 1.4 Hz, o-SAr); 7.30 (1H, d, $^3J_{HH}$ = 1.2 Hz, 5-H); 7.39 (1H, t, $^3J_{HH}$ = 7.8 Hz, p-SAr); 7.52 (t, $^3J_{HH}$ = 7.8 Hz, p-O_2NAr); 7.55 (1H, d, $^3J_{HH}$ = 1.2 Hz, 4-H); 8.29 ppm (1H, d.d, $^3J_{HH}$ = 8.1 Hz, $^4J_{HH}$ = 1.2 Hz, o-O_2NAR). ^{13}C NMR spectrum ($CDCl_3$): 16.43 (CH_3), 42.19 (CH_2), 122.72 (o-SAr); 125.94 ($C_{(5)}$); 125.98 (p-SAr); 127.95 (p-O_2NAr); 131.0 ($C_{(4)}$); 134.01 (o-O_2NAr); 135.49 (i-SAr); 137.17 (i-O_2NAr); 145.03 ($C_{(2)}$).

1-Ethyl-2-(2-nitrophenylthio)benzimidazole (VI) $C_{15}H_{13}N_3O_2S$. Yellow crystals of mp 114°C (from heptane). PMR spectrum ($CDCl_3$): 1.34 (3H, t, $^3J_{HH}$ = 7.0 Hz, $NCH_2\underline{CH_3}$); 4.33 (2H, q, $^3J_{HH}$ = 7.0 Hz, $N\underline{CH_2}CH_3$); 6.85 (1H, d.d, $^3J_{HH}$ = 7.5 Hz, $^4J_{HH}$ = 2.0 Hz, o-SAr); 7.29-7.41 (5H, m, arom); 7.88 (1H, m, p-O_2NAr); 8.28 ppm (1H, d.d, $^3J_{HH}$ = 7.5 Hz, $^4J_{HH}$ = 2.0 Hz, o-O_2NAr).

2,5-Di-(2-nitrophenyl)-1-p-tolyl-1,3-4-triazole (VII) ($C_{21}H_{15}N_5O_4S_2$) is precipitated from the reaction mixture with the triethylamine hydrochloride. The solid was washed with water and with alcohol. Yellow crystals of mp 243°C (from acetonitrile). PMR spectrum (CF_3COOD): 2.40 (3H, s, CH_3); 7.14 (2H, d, $^3J_{HH}$ = 8.5 Hz, o-$CH_3\underline{Ar}$); 7.28 (2H, d, $^3J_{HH}$ = 8.5 Hz, m-$CH_3\underline{Ar}$); 7.62-7.81 (3H, m, Ar); 8.16 ppm (1H, d, $^3J_{HH}$ = 7.1 Hz, o-O_2NAr).

Institute of Organic Chemistry, Ukrainian Academy of Sciences, Kiev 252094. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 9, pp. 1292-1293, September, 1994. Original article submitted August 5, 1994.

0009-3122/94/3009-1123$12.50

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