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REACTION OF 2,3-DIMETHYLINDOLE WITH 2,4-DINITROPHENYLSULFENYL CHLORIDE: AN UNEXPECTED PRODUCT (1)

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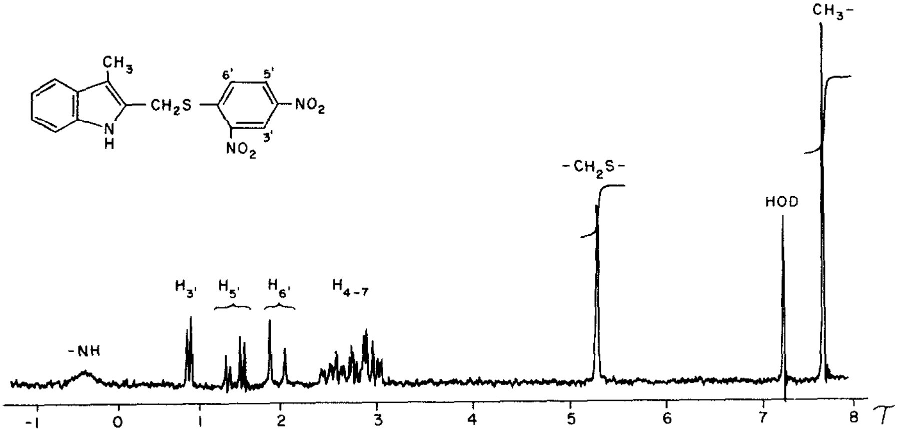
Evidence was produced recently that electrophilic substitution in the 2-position of indole occurs in certain cases by attack of the electrophilic reagent at position 3 and subsequent rearrangement (3). With 2,3-disubstituted indoles the rearrangement should not occur and the "intermediate" indolenine derivative would be expected as the final product (e.g. 4).

Nitrophenylsulfenyl chlorides react with 3-substituted indoles, under conditions of electrophilic substitution, to give 2-arylthioindole derivatives (5). When 2,4-dinitrophenylsulfenyl chloride (DNPSCl) was allowed to react with 2,3-dimethylindole, an unexpected compound, 3-methylindole-2-methylene-2',4'-dinitrophenyl sulfide (I), was formed as the major product.

DNPSCl (1.17 g) in CH_2Cl_2 (80 ml) was added, at 0° to 2,3-dimethylindole (0.72 g) in CH_2Cl_2 (40 ml) and formic acid (99-100%; 20 ml). After 10 min at 25°, the reaction mixture was washed with water and evaporated to dryness. Crude I (1.58 g) was purified by recrystallization from ethanol-water and benzene-hexane or preparative TLC (support: silica; solvent: chloroform; $\underline{R}_f$ 0.46). Properties: yellow-orange crystals, m.p. 194-5°. Calc. for $C_{16}H_{13}N_3O_4S$: C, 55.98; H, 3.82; N, 12.24; S, 9.32%. Found: C, 56.18; H, 3.78; N, 12.01; S, 9.58%. IR spectrum (KBr) 3350 cm^{-1} (N-H). Mass spectrum $\underline{m}/\underline{e}$ 343.0637 (M^+, 5%; calc.: 343.0619); 144 (100%).

The NMR spectrum of I in acetone-d_6 with assignments is shown in the figure.



That the Ar-S- group attacked the 2-methyl group was proven by two methods: (i) I in dioxane was desulfurized with Raney nickel equilibrated with D_2O. 2,3-Dimethylindole with one -CH_2D group was obtained and position 2 was assigned because of the solvent dependence of its NMR signal (CCl_4, 7.97τ; DMSO-d_6, 7.68τ; ref. 6); (ii) 2,3-dimethylindole [3-CHD_2], synthesized from 2-methyl-3-indolecarboxaldehyde by reduction with $LiAlD_4$ (cf. 7), was allowed to react with DNPSCl. The NMR spectrum of the compound obtained was compatible with structure I only, since the 3-CHD_2 group is retained undisturbed at the 3-position.

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FOOTNOTES AND REFERENCES

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