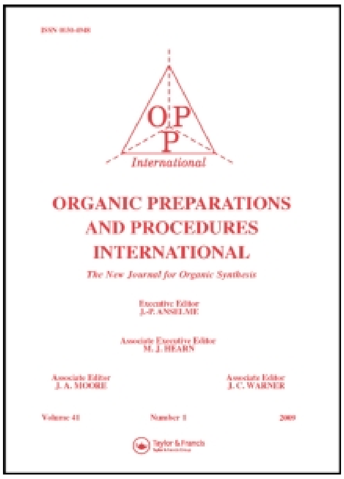

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2,6-DIMETHYL-4-(MONO- AND DI-p-NITROBENZENESULFENYLMETHYLENE)-4H-PYRAN

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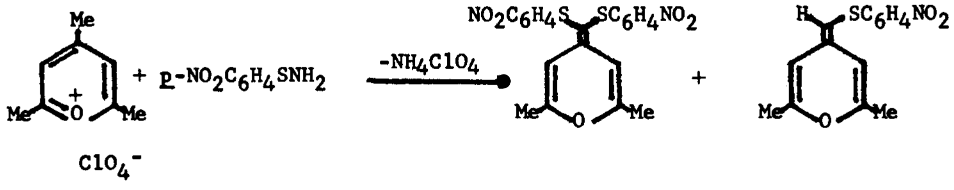
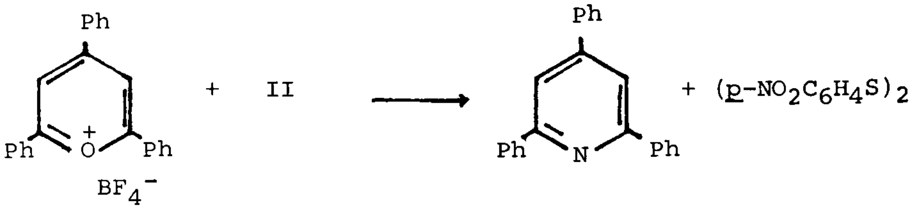
We have found that arylsulfenamides can effect the arylsulfenation of active methylene groups. In view of the recent report on the use N,N-disubstituted sulfenamides for this purpose,[1] we now report the p-nitrobenzenesulfenation of 2,4,6-trimethylpyrylium perchlorate (I).

Reaction of I with p-nitrobenzenesulfenamide (II) gave a mixture of III and IV and ammonium perchlorate. On the other hand, reaction of II with 2,4,6-triphenylpyrylium tetrafluoroborate (V) in dry ethanol gave 2,4,6-triphenylpyridine (VI) and di-p-nitrophenyldisulfide. In neither case was any N-(p-nitrophenylthio)pyridine derivative detected.



I II III IV

The structures of III and IV were confirmed by their nmr and mass spectra. III exhibited a 4H multiplet at τ 1.92 due to the protons *ortho* to the nitro-group, a 4H multiplet at τ 2.80 due to the protons *meta* to the nitro-group, a 2H singlet at τ 3.45 (pyran β protons), and a 6H singlet at τ 7.89 (CH_3). IV exhibits a 2H multiplet a τ 2.00 (H *ortho* to NO_2), a 2H multiplet a τ 2.84 (H *meta* to NO_2), two separate 1H multiplets at τ 4.02 and 4.30 corresponding to the different β-protons, a 1H singlet at τ 5.00 due to the exocyclic methylene proton, and a 6H doublet (*J* = 2Hz) at τ 8.02 due tothe methyl groups.



V

VI

EXPERIMENTAL

p-Nitrobenzenesulfenation of 2,4,6-Trimethylpyrylium Perchlorate. - A solution of *p*-nitrobenzenesulfenamide (1.15 g, 6.75 mmole) in absolute ethanol (55 ml) was added dropwise under nitrogen to a solution of 2,4,6-trimethylpyrylium perchlorate (1.50 g, 6.75 mmole) in absolute ethanol (200 ml), and the mixture stirred at room temperature for 12 hr. The mixture was then filtered to give *2,6-dimethyl-4-(di-*p-*nitrobenzenesulfenylmethylene)-*4H-*pyran* (III) (0.664 g, 46%), m.p. 206-207° (decomp.) (recrystallized from light petroleum-

2,6-DIMETHYL-4-(MONO- AND DI-p-NITROBENZENESULFENYLMETHYLENE) benzene). I.R. (KBr): 1670, 1570, 1500, 1330, 1080, 850, 840, and 745 cm^{-1}; ms (70 eV) m/e 428 (M^+).

Anal. $C_{20}H_{16}N_2O_2S_2$ requires: C, 56.12; H, 3.77. Found: C, 56.22; H, 3.82.

The filtrate was concentrated to give a yellow-red solid which was continuously extracted with boiling light petroleum (200 ml) for 3 hr and filtered to give a yellow solution and a yellow green solid. The solid was extracted with chloroform to give ammonium perchlorate (0.509 g, 74%). The light petroleum filtrate was concentrated to 40 ml and cooled in the refrigerator to give 2,6-dimethyl-4-(p-nitrobenzenesulfenylmethylene)-4H-pyran as a red solid (0.703 g, 38%), m.p. 102-103° (from light petroleum). I.R. (KBr): 1680, 1590, 1570, 1330, 1280, 1180, 900, 860, 850, and 750 cm^{-1}; ms (70 eV) m/e 275 (M^+).

Anal. $C_{14}H_{13}NO_3S$ requires C, 61.14; H, 4.77. Found: C, 61.01; H, 4.86.

Reaction of p-Nitrobenzenesulfenamide with 2,4,6-Triphenylpyrylium Tetrafluoroborate. - The pyrylium salt (0.50 g, 1.26 mmole) in absolute ethanol (40 ml) was treated with the sulfenamide (0.217 g, 1.27 mmole) in absolute ethanol (20 ml) and the solution was boiled under reflux under nitrogen for 48 hr. The cooled mixture was filtered to give di-p-nitrophenyldisulfide (0.062 g), the filtrate was concentrated to 35 ml and unreacted pyrylium salt (0.172 g, 34% was recovered. The filtrate was chromatographed on basic alumina (30 g); elution with light petroleum-benzene (6:4 v/v) (500 ml) gave 2,4,6-triphenylpyridine (0.140 g, 55%), m.p. 138.5-139.5° (lit.[2], m.p. 137.5°); ms (70 eV) m/e 307 (M^+). Elution with benzene (500 ml) gave an additional quantity of di-*p*-nitrophenyldisulfide (0.020 g; overall yield 42%).

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