SYNTHESIS OF PHENYLSULFONYL-SUBSTITUTED PHENOXAZINES

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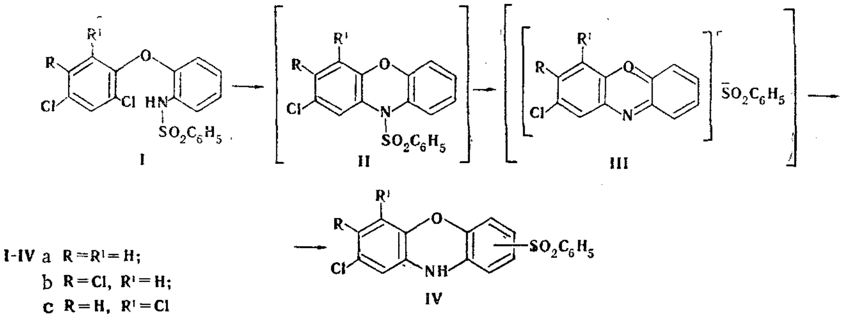
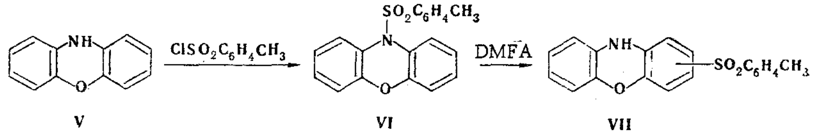
In an attempt to cyclize 2-chloro-2^1-benzenesulfonamidodiphenyl ethers (I) to 10-phenylsulfonylphenoxazines (II) we obtained compounds containing an NH group in the phenoxazine ring and a phenylsulfonyl residue. The presence of this phenoxazine skeleton was proved by the identical character of the IR spectra (KBr pellets) of unsubstituted phenoxazines (V) (3410 m, 3070 w, 1630 w, 1590 m, 1510 s, 1415 m, 1300 s, 1240 w, 1210 m, 1120 s, 1035 w, 920 m, 830 m, and 740 s cm^{-1}) and of the compounds obtained, except for the absorption bands of SO_2 and Cl groups.

It is assumed that the cyclization of I in a strongly polar solvent and the subsequent migration of the phenylsulfonyl group from the nitrogen atom to the condensed ring of the phenoxazine molecule proceeds via the following scheme:



I-IV a R=R¹=H;
b R=Cl, R¹=H;
c R=H, R¹=Cl

The scheme is confirmed by the isolation of IIc and by its isomerization to IVc on heating in dimethylformamide (DMFA). In addition, the rearrangement of N-tolylsulfonylphenoxazine VI proceeds similarly in the absence of catalysts and of any substituents in the ring:



EXPERIMENTAL

2-Chloro-x-phenylsulfonylphenoxazine. A solution of 0.005 mole of sodium methoxide and 0.005 mole of Ia in methanol was vacuum evaporated to dryness, DMFA was added to the residue, and the mixture was refluxed for 7 h. It was then cooled and poured into water, and the resulting precipitate was removed by filtration, dried, washed with benzene, and crystallized from nitromethane to give a product with mp 242-244° in 38% yield. IR spectrum, cm^{-1}: 3350 m, 3080 w, 1630 w, 1580 m, 1510 s, 1400 m, 1310 s, 1240 w, 1210 m, 1150 s, 1110 s, 1010 w, 940 w, 820 m, and 740 s.

Similar cyclization of Ib gave 2,3-dichloro-x-phenylsulfonylphenoxazine (IVb) with mp 272-273° in 47% yield. IR spectrum, cm^{-1}: 3310 s, 3080 w, 1635 w, 1580 s, 1520 s, 1430 m, 1300 s, 1260 w, 1210 m, 1160 m, 1120 s, 1080 w, 980 m, 880 m, and 770 m.

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Under these conditions, Ic gave 2,4-dichloro-x-phenylsulfonylphenoxazine (IVc) with mp 251-253° in 38% yield. IR spectrum, cm^{-1}: 3330 m, 3070 w, 1610 w, 1570 m, 1510 s, 1390 m, 1300 s, 1240 w, 1210 m, 1160 s, 1140 m, 1090 s, 1070 w, 970 w, 920 w, and 810 m.

N-Tolylsulfonylphenoxazine. A solution of 0.01 mole of V and 0.015 mole of toluenesulfonyl chloride in 2 ml of pyridine was allowed to stand for 2 h, after which the resulting precipitate was washed with isopropyl alcohol, removed by filtration, and crystallized from isopropyl alcohol to give a product with mp 174-176° in 82% yield. IR spectrum, cm^{-1}: 3040 w, 1565 w, 1470 s, 1350 s, 1290 m, 1260 s, 1200 m, 1170 s, 1120 m, 1090 w, 1030 w, 910 w, 910 m, 860 m, and 780 s.

X-Tolylsulfonylphenoxazine. A solution of VI in DMFA was refluxed for 20 h, after which it was cooled and poured into water. The resulting precipitate was removed by filtration, dried, washed with benzene, and crystallized from nitromethane to give a product with mp 176-178° in 40% yield. IR spectrum, cm^{-1}: 3400 m, 3060 w, 1620 w, 1580 s, 1510 s, 1410 m, 1310 s, 1240 w, 1210 m, 1150 s, 1110 m, 1010 w, 1090 s, 930 w, 820 m, and 740 s.

The results of elementary analysis of the synthesized compounds were in agreement with the calculated values.