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Synthesis of *N*-Butoxyphenylmaleimides

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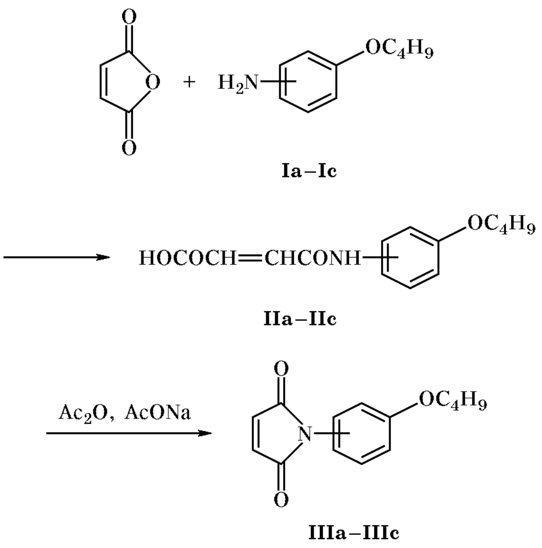
Abstract—Reactions of equimolar amounts of *o*-, *m*-, and *p*-butoxyanilines with maleic anhydride give the corresponding *N*-butoxyphenylmaleamic acids which undergo cyclization into *N*-butoxyphenylmaleimides by the action of acetic anhydride in dimethylformamide in the presence of sodium acetate.

Maleimide derivatives are promising as monomers for preparation of heat-resistant polymeric materials [1] and also as biologically active substances [2, 3]. However, known compounds of this series are relatively few in number. Therefore, we have synthesized new *N*-butoxyphenylmaleimides and studied their properties. *N*-Substituted maleimides **IIIa**–**IIIc** were prepared by cyclization of maleamic acids **IIa**–**IIc** formed by reaction of equimolar amounts of butoxyanilines **Ia**–**Ic** with maleic anhydride. The cyclization of **IIa**–**IIc** was effected by the action of acetic anhydride in the presence of anhydrous sodium acetate in dimethylformamide as solvent.



I–**III**, *ortho* (**a**), *meta* (**b**), *para* (**c**).

Maleimides **IIIa** and **IIIc** are slightly yellowish crystalline substances, and compound **IIIb** is a viscous liquid. Their structure was confirmed by the IR spectra; maleimides **IIIa** and **IIIc** were also examined by ^{1}H NMR spectroscopy. In the IR spectra of **IIIa**–**IIIc**, C–H stretching vibrations of the maleimide CH=CH moiety appeared at 3080–3085 cm^{-1}, and carbonyl absorption bands were located at 1650–1690 cm^{-1}. The ^{1}H NMR spectra of **IIIa** and **IIIc** contained a singlet at δ 7.10 ppm from protons of the five-membered ring; the aromatic protons of compound **IIIa** gave a complex multiplet in the region δ 7.00–7.40 ppm, and those of **IIIc** appeared as two doublets in the region δ 6.93–7.57 ppm.

***N*-(*o*-Butoxyphenyl)maleamic acid (IIa).** To a solution of 13.7 g (0.08 mol) of *o*-butoxyaniline in 12 ml of diethyl ether we slowly added with stirring a solution of 8.14 g (0.08 mol) of maleic anhydride in 20 ml of diethyl ether. After 2 h, the precipitate was filtered off, washed with diethyl ether (5 × 5 ml), and dried in air. Yield 17.7 g (84%), mp 101–103°C. IR spectrum, ν, cm^{-1}: 3290 (NH); 3095 (CH=CH); 1670 (CO); 1590, 810 (C_6H_4).

Compounds **IIb** and **IIc** were synthesized in a similar way using benzene as solvent.

***N*-(*m*-Butoxyphenyl)maleamic acid (IIb).** Yield 90%, mp 145–147°C. IR spectrum, ν, cm^{-1}: 3270, 3195 (NH); 3075 (CH=CH); 1670 (CO); 1215 (COC); 1595, 825, 750 (C_6H_4).

***N*-(*p*-Butoxyphenyl)maleamic acid (IIc).** Yield 52%, mp 169–172°C. IR spectrum, ν, cm^{-1}: 3250 (NH); 3075 (CH=CH); 1670 (CO); 1200 (COC); 1680, 1580, 810 (C_6H_4).

***N*-(*o*-Butoxyphenyl)maleimide (IIIa).** A mixture of 17.6 g (0.067 mol) of maleamic acid **IIa**, 10.2 g (0.1 mol) of acetic anhydride, 5.5 g (0.067 mol) of sodium acetate, and 50 ml of DMF was stirred for 4 h at 50–60°C. The mixture was cooled to 20°C and

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poured into 300 ml of water, and the precipitate was ground, filtered off, washed with water (5 × 5 ml), and dried in air. Yield 14.8 g (90%), mp 71–73°C. Double recrystallization from isopropyl alcohol gave fine yellow needles with mp 78–79°C. IR spectrum, ν, cm^{-1}: 3085 (CH=CH); 1660, 1650 (CO); 1210 (COC); 3060, 1600, 800 (C_6H_4). ^{1}H NMR spectrum, δ, ppm: 0.9 t (3H, CH_3), 1.35 sext (2H, CH_2), 1.60 q (2H, CH_2), 3.98 t (2H, CH_2O), 7.10 s (2H, 2CH=), 7.00–7.40 m (4H, H_{arom}).

Compounds **IIIb** and **IIIc** were synthesized in a similar way.

***N*-(*m*-Butoxyphenyl)maleimide (IIIb).** After pouring the reaction mixture into water, an oily material separated and was extracted into benzene. The extract was dried over anhydrous magnesium sulfate and evaporated to obtain 65% of product **IIIb** as a red viscous oil. IR spectrum, ν, cm^{-1}: 3085 (CH=CH); 1690 (CO); 1200 (COC); 3050, 1570, 800, 750 (C_6H_4).

***N*-(*p*-Butoxyphenyl)maleimide (IIIc).** Yield 92%, mp 85–88°C. IR spectrum, ν, cm^{-1}: 3080 (CH=CH); 1670 (CO); 1220 (COC); 3050, 1585, 1490, 805 (C_6H_4). ^{1}H NMR spectrum, δ, ppm: 0.85 t (3H, CH_3), 1.38 sext (2H, CH_2), 1.70 quint (2H, CH_2), 3.98 t (2H, CH_2O), 7.10 s (2H, 2CH=), 6.93 d (2H, H_{arom}), 7.57 d (2H, H_{arom}).

The IR spectra were recorded on a Specord 75IR spectrophotometer from thin films. The ^{1}H NMR spectra were obtained on a Bruker AM-300 instrument (300.13 MHz) from solutions in DMSO-d_6.

REFERENCES

1. Arkhipova, I.A., Zhubanov, B.A., and Rafikov, S.R., *Usp. Khim.*, 1978, vol. 47, no. 4, pp. 705–738.
2. JPN Patent no. 938, 1973; *Ref. Zh., Khim.*, 1973, no. 22 N 528 P.
3. US Patent no. 5 066 490, 1991; *Ref. Zh., Khim.*, 1993, no. 60 N 39 P.