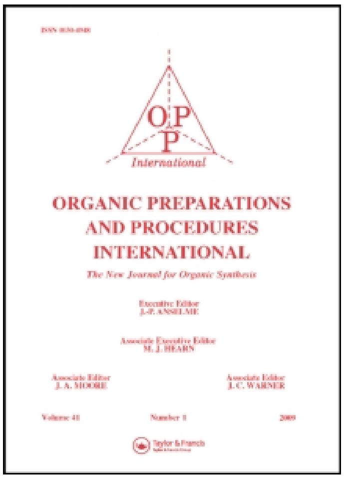

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# ELECTROLYTIC PREPARATION OF bis-DIMETHYL-2-HYDROXYPROPYLAMINEAZOBENZIMIDES

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# ELECTROLYTIC PREPARATION OF
# bis-DIMETHYL-2-HYDROXYPROPYLAMINEAZOBENZIMIDES

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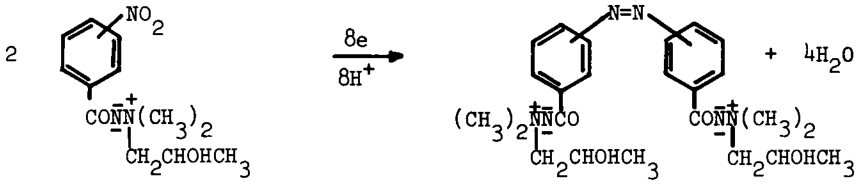
bis-Dimethyl-2-hydroxypropylamine-p-azobenzimide and bis-dimethyl-2-hydroxypropylamine-m-azobenzimide have been prepared by the electrochemical reduction of dimethyl-2-hydroxypropylamine-p-nitrobenzimide and dimethyl-2-hydroxypropylamine-m-nitrobenzimide respectively. The products are of interest since they are bifunctional aminimides and can serve as precursors of diisocyanates containing a chromophoric group.



The electrochemical method is superior to the chemical method using zinc and sodium hydroxide since the purification necessary is minimal. Evidence for the structures was based on the infrared spectra and the elemental analyses. The starting materials were prepared from the methyl esters, 1,1-dimethylhydrazine and propylene oxide using conventional methods.[1]

## EXPERIMENTAL

Melting points are uncorrected. Infrared spectra were determined using a Perkin-Elmer Model 137B spectrophotometer.

Dimethyl-2-hydroxypropylamine-m-nitrobenzimide.- The reaction of methyl m-nitrobenzoate, 1,1-dimethylhydrazine and propylene oxide was carried out in isopropyl alcohol at reflux for 3.5 hr. and gave a 94% yield of the aminimide. Recrystallization from isopropyl alcohol gave a sample melting at 150° (dec. at 200°); ir(Nujol) 3.01μ(OH), 6.25(CO), 6.56, 7.50($NO_2$).

Anal. Calcd for $C_{12}H_{17}N_3O_4$: C, 53.92; H, 6.42; N, 15.72. Found: C, 53.78; H, 6.43; N, 15.60.

Dimethyl-2-hydroxypropylamine-p-nitrobenzimide.- The reaction of methyl p-nitrobenzoate, 1,1-dimethylhydrazine and propylene oxide was carried out in isopropyl alcohol at reflux for 6 hr. and gave a theoretical yield of the aminimide. Crystallization from acetonitrile gave a sample melting at 155-156° (dec. at 183°); ir(Nujol) 3.1μ(OH), 6.15(CO), 6.61, 7.44($NO_2$).

Anal. Calcd for $C_{12}H_{17}N_3O_4$: C, 53.92; H, 6.42; N, 15.72. Found: C, 53.90; H, 6.27; N, 15.50.

Bis-Dimethyl-2-hydroxypropylamine-p-azobenzimide.- Dimethyl-2-hydroxypropylamine-p-nitrobenzimide (25g) was electrolyzed at a nickel screen cathode in a solution of 70% ethanol (200 ml) containing sodium acetate (5g). The nickel screen cathode was wrapped around a porous cup (5.3 cm. diameter x 10 cm.) which served as the anode compartment. The anode was a lead sheet and the anolyte was a saturated sodium carbonate solution.[2] The electrolysis was carried out at 7 volts and 2.1-2.2 amperes for 5 hrs. at which point hydrogen was discharged at the cathode. Removal of the alcohol followed by the addition of water gave 16.0g of the azo compound which after one recrystallization from ethanol melted at 243.5° (dec.); ir(nujol) 3.05μ(OH); 6.37($\mathrm{CO\bar{N}\overset{+}{N}}$).

Anal. Calcd for $C_{24}H_{34}N_6O_4$: C, 61.28; H, 7.23; N, 17.87. Found: C, 61.51; H, 7.5; N, 17.99.

Bis-Dimethyl-2-hydroxypropylamine-*m*-azobenzimide.- Dimethyl-2-hydroxypropylamine-*m*-nitrobenzimide was reduced as described above and gave a 97% yield of the azo compound which upon recrystallization from ethanol melted at 232°(dec.); ir(Nujol) 3.09μ(OH); 6.41($\mathrm{CO\bar{N}\overset{+}{N}}$).

Anal. Calcd for $C_{24}H_{34}N_6O_4$: C, 61.28; H, 7.23; N, 17.87. Found: C, 61.20; H, 7.18; N, 17.52.

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2. C. Weygand, Organic Preparations, p. 249, Interscience Publishers, Inc., New York, N.Y. 1945.

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