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PREPARATION OF 4-NITROPHTHALIC ANHYDRIDE FROM N-METHYL-4-NITROPHTHALIMIDE

Romas J. Kazlauskas^a

^a GE Corporate Research & Development, Schenectady, N. Y.

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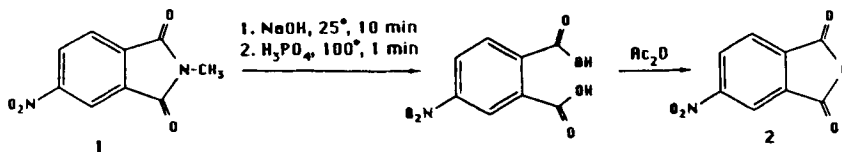
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PREPARATION OF 4-NITROPHthalIC ANHYDRIDE
FROM N-METHYL-4-NITROPHthalIMIDE

Submitted by Romas J. Kazlauskas
(09/21/87)

GE Corporate Research & Development
P. O. Box 8, Schenectady, N. Y. 12301

Although 4-nitrophthalic anhydride (2) is potentially useful for the preparation of high temperature polymers¹ such as polyimides and polyetherimides, the lack of a convenient and inexpensive synthesis² has limited its use. We now describe the preparation of 4-nitrophthalic anhydride from N-methyl-4-nitrophthalimide (1), readily obtained by nitration of N-methylphthalimide.³ The most effective method involves the basic hydrolysis of 1 to N-methyl-4-nitrophthalamic acid followed by the addition of acid to a hot solution of the amic acid. This hydrolysis reaction is clean and the unhydrolyzed light-yellow imide (1) precipitates



while the diacid remains in solution. After removal of the imide by filtration (39% was recovered), the diacid was extracted into ether and without isolation was converted to the anhydride with acetic anhydride in 55% overall yield. Instead of this two-step method, heating 1 in 85% sulfuric acid for 2 hrs. at 160° results in complete hydrolysis to the diacid; however, for synthetic purposes, this method is less convenient

(longer reaction times, more difficult workup) than the method described above.

EXPERIMENTAL SECTION

4-Nitrophthalic Anhydride.- A solution of 72 g (1.8 mol) sodium hydroxide in 1.0 L of water was added to 345 g (1.67 mol) of N-methyl-4-nitrophthalimide (Bofors Nobel, Inc., Mushegan, MI) in a 2-L, 3-necked flask. After stirring for 10 min., the phthalimide dissolved and the solution was heated rapidly to reflux. The heating was stopped and 85% phosphoric acid (300 mL, 4.4 mol) was added rapidly (CAUTION: Neutralization causes additional boiling). A precipitate formed within a minute after the addition of phosphoric acid was complete. The mixture was cooled in an ice-water bath and the precipitated N-methyl-4-nitrophthalimide (136 g, 39%), was removed by suction filtration. The filtrate was extracted twice with 1.5 L portions ethyl ether. The combined extracts were dried over $MgSO_4$, filtered and concentrated to 500 mL. Acetic anhydride (300 mL, 3.2 mol) was added and the mixture stirred for 30 min. at r.t. and concentrated *in vacuo* to 500 mL on a rotary evaporator while warming in a water bath. Upon cooling, 177 g (55%) of 2 crystallized as a pale-yellow solid, mp. 117-119° (uncorr. open capillary), lit.⁴ mp. 120-121.5°.

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