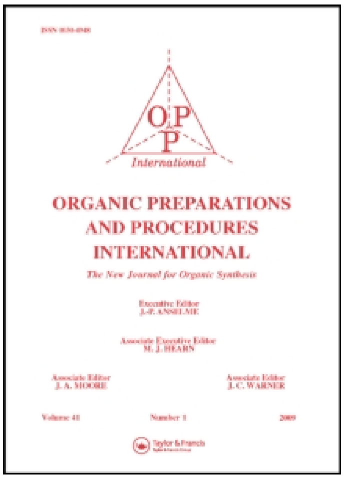

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PREPARATION OF 4-NITROPHTHALIC ANHYDRIDE FROM N-METHYL-4-NITROPHTHALIMIDE

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

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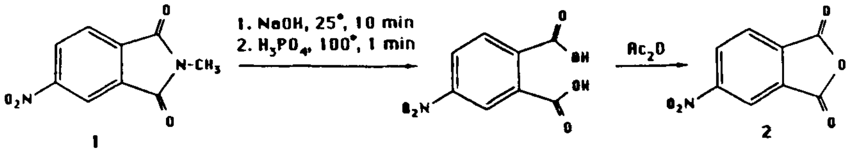
Although 4-nitrophthalic anhydride (2) is potentially useful for the preparation of high temperature polymers[1] such as polyimides and polyetherimides, the lack of a convenient and inexpensive synthesis[2] has limited its use. We now describe the preparation of 4-nitrophthalic anhydride from N-methyl-4-nitrophthalimide (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 methods 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°.

REFERENCES

1. E. g., B. K. Mandal and S. Maiti, J. Polym. Mater., 2, 115 (1985); L. S. Tan and F. E. Arnold, Polym. Prepr., 26, 178 (1985); C. G. Overberger and M. D. Shalati, J. Polym. Sci. Polym. Chem. Ed., 21, 3403 (1983); D. M. White, T. Takekoshi, F. J. Williams, H. M. Relles, P. E. Donahue, H. J. Klopfer, G. R. Loucks, J. S. Manello, R. O. Matthews and R. W. Schluenz, ibid., 19, 1635 (1981); T. Takekoshi, J. G. Wirth, D. R. Heath, J. E. Kochanowski, J. S. Manello and M. J.

Webber, ibid., 18, 3069 (1980); N. C. Fawcett, R. A. Lohr and P. E. Cassidy, ibid., 17, 3009 (1979).

2. Other methods include the nitration of indene [J. D. Bacha, J. G. D. Schulz and A. Onopchenko, J. Org. Chem., 44, 648 (1979)], of phthalic acid and phthalic anhydride [W. A. Lawrence, J. Am. Chem. Soc., 42, 1871 (1920); P. J. Culhane and G. E. Woodward, Org. Syn. Coll., 1, 408 (1941)] and of phthalimide followed by hydrolysis [E. H. Huntress, E. L. Schloss, Jr. and P. Ehrlick, Org. Syn. Coll., 2, 457 (1943)].

3. The nitration of N-methylphthalimide proceeds more selectively for the 4-isomer and in higher yield than the starting materials listed in ref. 2. F. J. Williams and P. E. Donahue, J. Org. Chem., 43, 1608 (1978); N. C. Cook and G. C. Davis, U. S. Patent 4,005,102 (1977); Chem. Abstr., 86, 189467 (1977).

4. T. W. Campbell, R. Ginsig and H. Schmid, Helv. Chim. Acta, 36, 1489 (1953).