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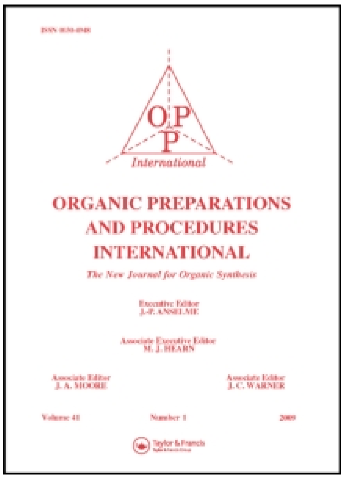

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FLUORENONE IMINE

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FLUORENONE IMINE

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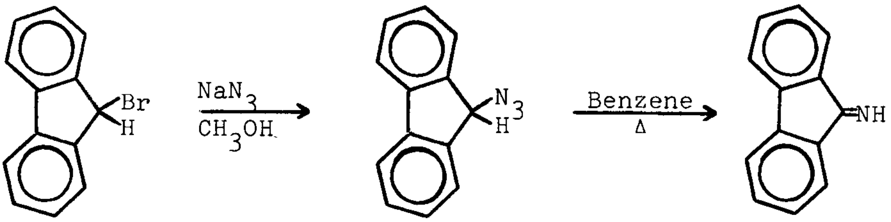
The standard preparation of aryl and of mixed aralkyl ketimines from the reaction of the aromatic nitriles and organometallic compounds[1] cannot be utilized to synthesize fluorenone imines. While many reactions result in the formation of fluorenone imine in varying amounts,[2] only the action of gaseous ammonia on fluorenone is of practical use. Over a period of several weeks, at room temperature, a quantitative yield is obtained;[3] at 160°, a 66% conversion is achieved after separation from unreacted fluorenone.[4]

The following sequence of reactions[5] obviates the long period of time necessary in the first procedure and the experimental difficulties involved in separating the product from unreacted fluorenone. It provides a simple and efficient method for the preparation of either small or large quantities[10] of fluorenone imine in about 50% yield from 9-bromofluorene.



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*Fellow of the Alfred P. Sloan Foundation.

Experimental

9-Azidofluorene. A mixture of 7.12 g. (0.025 mole) of 9-bromofluorene[6] and 2.37 g. (0.038 mole) of sodium azide in 30 ml. of methanol is heated under reflux for 6 hrs.[7] The reaction mixture is allowed to cool to room temperature and poured into 100 ml. of cold water and the whole extracted with two 75-ml. portions of ether. The combined ethereal extract is washed successively with three 50-ml. portions of water, two 50-ml. portions of 0.1 N sodium hydroxide and finally with water until the washings are neutral. After being dried over anhydrous sodium sulfate for 2 hrs., the solution is evaporated on a rotary evaporator; the white solid obtained, m.p. 35-37°, is recrystallized from aqueous methanol to give 3.86 g. (75%) of tiny white needles, m.p. 43-44°.[8]

Fluorenone imine. A 100-ml. flask containing 3.10 g. (0.015 mole) of 9-azidofluorene in 30 ml. of dry benzene is fitted with a condenser to which is attached a gas bubbler. Agitation is conveniently provided by a magnetic stirring bar. The solution is gently heated under reflux until the evolution of nitrogen is complete.[9] The solvent is removed on a rotary evaporator and the yellow residue is recrystallized from hexane to give 1.10 g. (65%) of fluorenone imine as yellow rods, m.p. 123-124°.[10]

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3. L. A. Pink and G. E. Hilbert, J. Am. Chem. Soc., 56, 490 (1934).

4. G. H. Harris, B. R. Harrison and K. W. Wheeler, ibid., 68, 846 (1946).

5. The procedures are adapted from the work of Arcus and Mesley, J. Chem. Soc., 178 (1953).

6. 9-Bromofluorene can easily be prepared by the reaction of fluorene with N-bromosuccinimide according to the procedure of Wittig and Felletschin, Ann., 555, 133 (1944). It is also commercially available from Aldrich Chemical Co.

7. All the reactions and subsequent operations should be carried out in a hood and behind a protective shield, although, to date, no explosion has occurred.

8. The crude azide may be decomposed without appreciable loss in the yield or the purity of the final product.

9. The reaction time for the decomposition may be shortened by using a higher boiling solvent such as toluene.

10. A large scale preparation (0.75 mole of 9-bromofluorene) has given comparable yields of the imine. The sequence starting from fluorene has been carried out without purification of the intermediates with no appreciable effects on the overall yield of the final product.

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