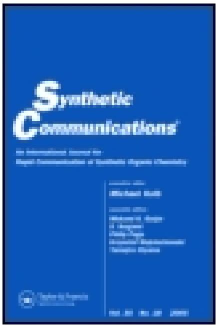

Synthetic Communications: An International Journal for Rapid Communication of Synthetic Organic Chemistry

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/lsyc20

A New Technique to Prepare 9-Oxofluorene-2-Carboxylic Acid

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To cite this article: A. Salmerón-Valverde , J. G. Robles-Martinez , A. A. Campos-Medina & A. Zehe (2000) A New Technique to Prepare 9-Oxofluorene-2-Carboxylic Acid, Synthetic Communications: An International Journal for Rapid Communication of Synthetic Organic Chemistry, 30:21, 3997-4000

To link to this article: http://dx.doi.org/10.1080/00397910008086959

SYNTHETIC COMMUNICATIONS, 30(21), 3997- 4000 (2000)

A NEW TECHNIQUE TO PREPARE 9-OXOFLUORENE-2-CARBOXYLIC ACID

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Abstract
9-Oxofluorene-2-carboxylic acid has been obtained with a yield as high as 98.5%, following a new procedure with easy product extraction, based on the reaction of 2-acetylfluorene with sodium dichromate in acetic acid.

For various decades electron acceptor properties of certain fluorene derivatives are known and have stimulated ever since the interest of researchers[1-3]. Studies of these compounds have been carried out with the formation of polymers[4,5], and applications are known in the manufacture of electrophotographic photoreceptors[6,7] and liquid crystalline polyesters[8].

The 9-oxofluorene-2-carboxylic acid (II), (FIG.1), is used as a precursor of these materials in the fabrication process. It is generally obtained after oxidation of 2-acetylfluorene (I) by sodium dichromate in acetic acid[9,10], by sodium hypochlorite[11], potassium hypochlorite[12], or by potassium hypobromite[13].

The oxidation reaction with sodium dichromate, although easy to be carried out in a laboratory, implies a certain risk level due to the addition of the oxidant in solid form. This technique was reported the first time by Ray and Rieveschl[9,10] as early as 1943 and again 1955, announcing a yield of 74%. The application of other oxidants, like NaOCl and KOCl, does not improve the outcome (21% and 60%, respectively). By use of KOBr, Ilina et al.[13] achieved a

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considerable reduction of the reaction time from originally 4 hours to about 30 minutes, and at the same time the yield increased to 78%.

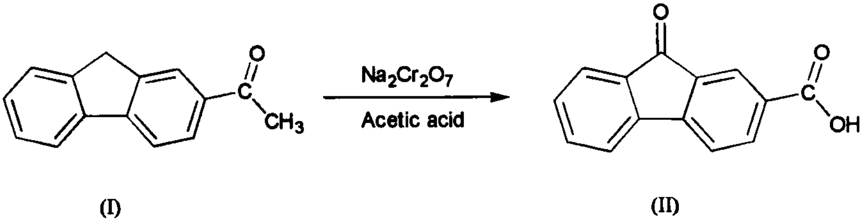

FIG. 1. Oxidation reaction of 2-acetylfluorene with sodium dichromate in acetic acid.

Nevertheless is the use of sodium dichromate even more practical than what is known from halogens and hydroxides.

Now, we report the oxidation reaction of (I) with sodium dichromate in acetic acid (see FIG. 1), obtaining a considerable increase of the product yield up to 98.5%. This is reached by way of a new apparatus design, which enables a modified addition of the oxidant to the prime material. As the oxidation reaction with sodium dichromate requires high reactant concentrations, we choose an addition-chamber design as shown in FIG. 2. This chamber contains the oxidant, and is fit into one of the joints of the two-necked round-bottom flask. As only the vapor of the solvent gets into contact with the oxidant, the addition is sufficiently slow, maintaining constant the solvent volume.

Commercial 2-acetylfluorene (Aldrich) and sodium dichromate dihydrate ($Na_2Cr_2O_7 \cdot 2H_2O$) were used without previous purification. 1 g ($4.8 \cdot 10^{-3}$ mol) of (I) as well as 13 ml of glacial acetic acid are placed in a 200 ml round-bottom reaction flask, equipped with a reflux condenser, an addition-chamber (see FIG. 2), a heating jacket and a magnetic stirrer. The mixture was heated gently, while 9 g (0.03 mol) of sodium dichromate dihydrate, previously ground to a fine powder, were put into the addition-chamber, and the solution was brought to reflux. The vapor of the solvent slowly dissolves the oxidant, and the solution descends in the same measure toward the reaction mixture for about 45 to 60 minutes.. Afterwards, 4 ml of acetic anhydride is added

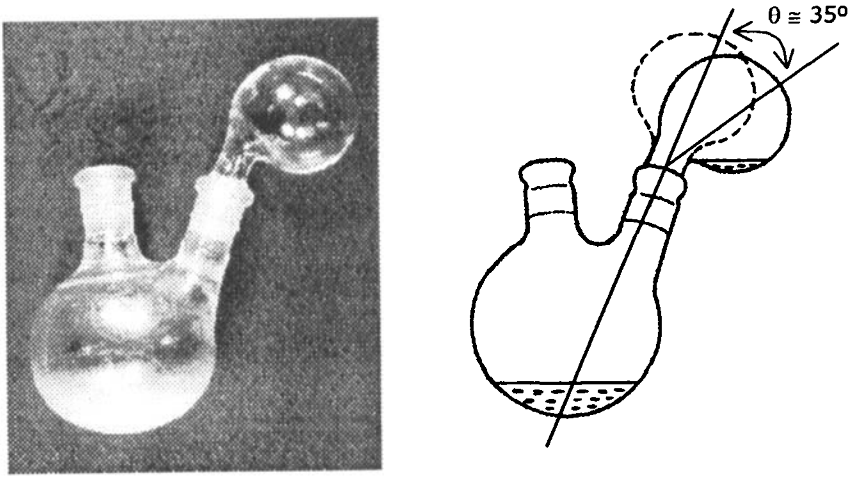

FIG. 2. Two-necked round bottom reaction flask with addition-chamber of the oxidant (left). The inclination of the addition-chamber against the flask axis by an angle θ is shown on the right, which creates the reservoir of the oxidant.

cautiously through a dropping funnel, permitting a time of 8 hours for reflux, followed by the addition of 180 ml of hot water. A suspension forms, which is stirred for 15 minutes. Filtered on a Büchner funnel, the filtrate is washed with 5 ml of hot water. The product recrystallizes in ethanol, and is than vacuum-dried leaving a yield of 1.06 g (corresponding to a yield of 98.5%). The melting point of the product was measured to be $336\text{-}338^0$ C[11,13]. No oxidation by-products occur, which is particularly interesting in the light of the tedious purification procedures of previous techniques.

The reaction process does not require particular security measures, is clean and carried through with low-cost prime materials. The described design is advantageous in applications, where high concentrations, and slow continuous additions with constant solvent volumes are required.

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Received in the USA 12/8/99