An Improved Synthesis of 1,8-Naphthaldehydic Acid

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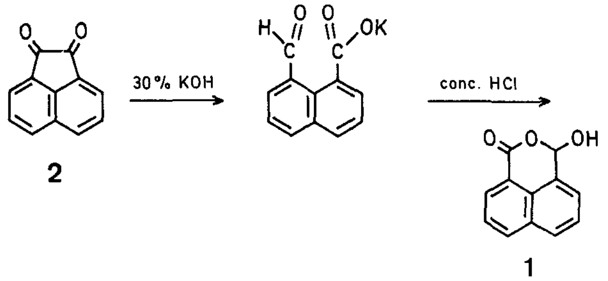
Although naphthaldehydic acid (**1**) has been an important chemical intermediate[1] for a long time, its method of preparation is still unreliable and not suited for large scale work.

Preparation of **1** by the alkaline cleavage of acenaphthenequinone (**2**) with aqueous potassium hydroxide was first reported by Graebe and Gfeller[2]. According to their procedure, **2** and 30% aqueous potassium hydroxide are heated together for a period of ten minutes by immersing the reaction vessel in an oil bath preheated to 150°.



Though the authors reported "almost quantitative" yields of **1**, other investigators experienced considerable variation in results. Cason and Wordie[3] reported that no **1** was obtained when the procedure of Graebe and Gfeller "was followed rigorously", the chief product being 1,8-naphthalic acid. Under milder conditions, 10 minutes on a steam-bath, they obtained **1**, but the results were variable, separation of naphthalic acid was necessary, and the average yield of **1** was only about 50%. As discussed by Cason and Wordie[3], other workers also experienced varying results. Thus, Zink[4] reported an 82% yield of **1**, and the formation of some naphthalic acid, while Fuson and Munn[5] obtained 68–73% yield of **1** but did not report the formation or separation of 1,8-naphthalic acid by-product. The method of Fuson and Munn gave in our hands a 75% yield of product less than 70% pure by G.L.C.

Further inquiry showed that the reaction occurs at ~93° (previous workers[2, 4, 5] who recommended immersing a reaction flask into an oil bath kept at 150°, were actually operating at an internal temperature of 108°), at which temperature optimum yields are achieved within 30–45 minutes. Even when an 87% yield of 90% naphthaldehydic acid could thus be occasionally obtained, the yields varied over a wide range. They greatly depended upon contact between phases, size and shape of acenaphthenequinone crystals, stirring rate, etc. Furthermore, in agreement with Cason and Wordie[3], a small increase in reaction time or in temperature resulted in formation of higher amounts of 1,8-naphthalic acid.

This note describes a new and facile synthesis of **1**, utilizing dimethyl sulfoxide as co-solvent. With this co-solvent, the reaction can be performed at room temperature. A lower temperature helps to minimize the main side-reaction, that of oxidation of **1** to naphthalic anhydride. In addition to eliminating the wide variation in yields encountered in prior processes, the product is obtained in improved purity and consistently high yield.

The two phases, 45% aqueous alkali and dimethyl sulfoxide, are only slightly miscible. Furthermore, acenaphthenequinone is poorly soluble in either phase. This presents several options for carrying out the reaction, each with its advantages and disadvantages. The procedure found to be the most reliable and easy to scale-up is that using sufficient amounts of solvent and alkali to dissolve an appreciable amount of the starting material **2**. Its only drawback is the relatively high dilution. Neither the concentration, nor the amount of potassium hydroxide could be decreased without loss in yield and purity of the product. However, the reaction mixture separates into two layers upon completion of reaction. The alkali solution is easily separated and can be recycled. As the excess base is removed (in the lower layer), the amount of hydrochloric acid needed for neutralization of the organic phase is greatly reduced. Under the preferred condition, the product thus precipitated is already of sufficient purity as not to require further purification. This is the main advantage of the more dilute system.

The optimum temperature range was that of 28–34°. A drop of 5–10% in yield of **1** would occur at 50°, and of 30% and more with prolonged heating at 85°. Furthermore, poor yield would also alter the clean phase separation between the organic solution containing the product and the product-free alkali solution. In such cases potassium salt of **1** would precipitate, necessitating redissolution and handling of large amounts of acid.

Not all dipolar aprotic solvents were found satisfactory. Thus, use of dimethylformamide as co-solvent produced **1** in only 24% yield.

Sodium hydroxide was found to be not as suitable as potassium hydroxide: with sodium hydroxide under optimum conditions the yield of **1** dropped to 26% with a 33% recovery of the starting material.

1,8-Naphthaldehydic Acid (1):

To a suspension of acenaphthenequinone (20 g, 0.11 mol) in dimethyl sulfoxide (258 g), 45% aqueous potassium hydroxide (418.5 g) was added all at once under vigorous stirring. After stirring at room temperature (internal temperature 29–34°) for 8 h, the reaction mixture was poured into a separatory funnel. The clear bottom layer of potassium hydroxide solution (352 g) was discarded and the top dark layer was diluted with ~450 ml of water, to a total volume of 700 ml. One gram of celite was added and the solution was filtered. After neutralizing with conc. hydrochloric acid (about 16 ml was required) to pH 6–7 and stirring for 1 h, the solid was filtered and washed with three 100 ml portions of water. The solid was dried at 60° in a vacuum oven; yield: 19.01 g (86% of theory; purity by G.L.C.[6] 98.6%); m.p. 168–169°.

A sample of the above material (5 g) was crystallized from xylene (90 ml); yield: 4.85 g (97%, purity by G.L.C.[6] 99.8%) of analytically pure **1**; m.p. 170–171° (Cason and Wordie[3] report m.p. 169–171°, after four recrystallizations).

$C_{12}H_8O_3$	calc.	C 72.0	H 4.0
(199.2)	found	72.2	4.1

I.R. (Nujol): ν_{max} = 3275 (OH), 1680 (CO) cm^{-1}.

^{1}H-N.M.R. (DMSO-d_6): δ = 7.07 (s, 1H), 8.80 (s, 1H), 7.75–8.58 (m, 6H$_{arom}$).

U.V. (CH_3OH): λ_{max} = 310 nm (ε = 7225).

A more concentrated system, employing five time higher concentrations than the one described above (i.e., 56 g of DMSO and 93 g of 45%-potassium hydroxide for 20 g of **1**) still gave a high yield of **1** (74% after recrystallization), provided good mixing was assured. In this variation a solid phase is present throughout (first the non-dissolved **2**, then the potassium salt of **1**), in addition to the two liquid phases. Consequently, the yield and the purity of the product would still depend on crystal size, rate of stirring, etc.

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[6] The purity of all the samples was obtained from G.L.C. analysis. Gas liquid chromatography was performed on a Hewlett-Packard 7620 A Research Chromatogaph using OV-17 silicon column at 240° with *o*-terphenyl as internal standard.