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A Convenient Synthesis of 1,2-Naphthalic Anhydride[1]

Melvin S. Newman,* Balram Dhawan,[2] Mohamed M. Hashem,[2]
V. K. Khanna,[2] and James M. Springer[2]

Chemistry Department, The Ohio State University,
Columbus, Ohio 43210

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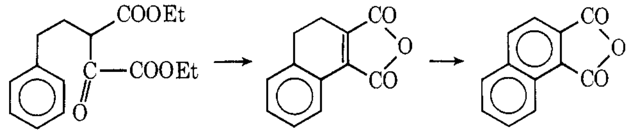
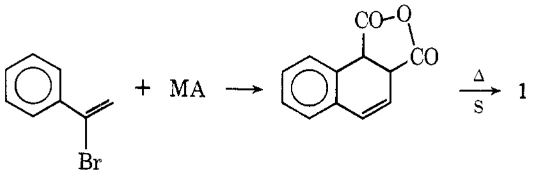
1,2-Naphthalic anhydride (1) has long been used for the elaboration of compounds in the benz[*a*]anthracene series.[3] An early synthesis of 1 involved cyclization of ethyl 3-carboethoxy-2-oxo-5-phenylpentanoate (2) to 3,4-dihydronaphthalene-1,2-dicarboxylic acid anhydride (3) followed by aromatization by heating with sulfur.[4] Later, 1,2-dihydronaphthalene-1,2-dicarboxylic anhydride (4), together with a small amount of 1, were prepared by heating α-bromostyrene (5) with maleic anhydride[5] but no developmental work on this route to 1 has been reported. An attempt to convert β-bromostyrene to 4 by heating with maleic anhydride failed.[6] We have tried to use α-chlorostyrene instead of 5 but obtained none of the desired 4. In this note we record our observations on an improved preparation of 1 by the styrene route.



2 3 1

We have converted styrene dibromide to 5, by using phase transfer catalysis.[7] In the final dehydrogenation of 4 by heating with sulfur, we have found that the 1 produced always contains some sulfur compound which is not removed by recrystallization. However, by boiling 1 in aqueous alkali, acidification, and cyclization to the anhydride pure sulfur-free 1 can be obtained in satisfactory overall yield.



5 4

In our opinion it is much easier to prepare quantities of 1 by the styrene route than by the earlier cyclization of the keto diester[4] as it is relatively simple to carry out the reactions involved on a large (2–3 mol) scale.

Experimental Section

α-Bromostyrene (5). In the best experiment, a solution of 336 g of bromine in 250 ml of CHCl$_3$ was added to a cooled (ca. 5 °C) solution of 208 g of freshly distilled styrene in 250 ml of CHCl$_3$. The temperature was not allowed to rise above 15 °C but cooling to 5 °C near the end is not advisable because the product will crystallize prematurely. After all of the bromine was added the reaction mixture was allowed to stand at room temperature for 1 h. The solvent was then removed to constant weight on a rotary evaporator. The yield of styrene dibromide is practically quantitative.

In the best of many runs, a solution of the crude styrene dibromide thus obtained in 800 ml of benzene was added fairly rapidly to a well-stirred mixture at 70 °C of 528 g of KOH, 800 ml of water, and 10 g of Aliquat 336.[8] The mixture was held at reflux for 3 h.[9] After cooling, the benzene layer was washed with water and saturated salt solution, passed through a cone of anhydrous MgSO$_4$, and fractionally distilled to afford 301 g (82.7%) of 5, bp 80–83 °C (10 mm). In other similar runs which varied in detail yields of 52–79% were obtained. The yield is somewhat dependent on the skill of the operator in conducting a rapid distillation. If the distillation is conducted too slowly thermal decomposition occurs and the yield is lower. The use of a hot salt bath and a free flame to hasten distillation is recommended.[10]

1,2-Naphthalic Anhydride (1). In the best of many runs, a solution of 408 g of 5 and 326 g of maleic anhydride in 1.5 l. of xylene was refluxed for 48 h (to ensure escape of most of the HBr formed). The solvent was then distilled and the residue was rapidly vacuum distilled to yield crude 4, bp 150–165 °C (1 mm), which was immediately placed in a Claisen flask with 71 g of sulfur. The mixture was heated rapidly to 230–235 °C with a salt bath and held at this temperature for 1 h, then at 250 °C for 1 h. Rapid vacuum distillation afforded 300 g (69%) of crude 1, mp in the 160–164 °C range. The yields in this step varied from 63 to 75% (small-scale run). This product contains sulfur-containing impurities and cannot be effectively purified by crystallization. The best method of purification involved heating at reflux for 4 h 131.5 g of crude 1 with excess 20% NaOH. On acidification of the filtered solution followed by heating of the acid with 1 l. of (Ac)$_2$O, there was obtained 116.9 g (89%) of 1 in three crops. The melting points lay in the 165–167 °C range and this material was suitable for further work. No sulfur was present as shown by the absence of *m/e* over 198.

Registry No.—1, 5343-99-7; 4, 60224-29-5; 5, 98-81-7; styrene, 100-42-5; styrene dibromide, 93-52-7; maleic anhydride, 108-31-6.

References and Notes

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(9) Refluxing for longer times results in the formation of larger amounts of phenylacetylene, bp below 75 °C (10 mm).
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The Chemistry of a Ketene–Sulfur Dioxide Adduct. 3. Reactions with Azines

Zenon Lysenko and Madeleine M. Joullié*

Department of Chemistry, University of Pennsylvania,
Philadelphia, Pennsylvania 19174

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The cycloadditions of imines with ketene–sulfur dioxide adduct (1)[1b,c] to give substituted thiazolidin-4-one 1,1-dioxides was described in earlier publications,[1a,b] and extended by Kagan et al.[2] to substituted ketenes. More recently, Bellus reported that ketenes containing carbanion stabilizing substituents, generated in situ in the presence of sulfur dioxide,