2,3-Naphthalenedicarboxylic Anhydride

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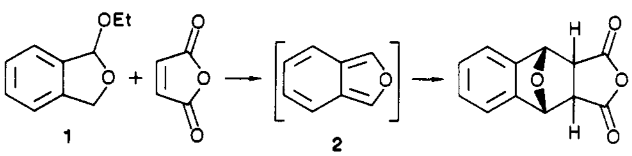
The title compound is useful for the generation of the very reactive naphthol[2,3-*c*]furan.[1] Until a few years ago the corresponding diacid was sold, but it has become either prohibitively expensive or unavailable. Carlson[2] has indicated that the precursor needed for the *Organic Syntheses* preparation[3] is no longer sold. This method also requires a stirred pressure reactor, equipment not found in many laboratories. Another preparation of the diacid, described several years ago by Cava et al.,[4] utilizes commercially available $\alpha,\alpha,\alpha',\alpha'$-tetrabromo-*o*-xylene, NaI, and maleic anhydride and gives product in ca. 60% yield.[2,4]

A simple alternative procedure is described that furnishes the anhydride in high yield, starting from the acetal **1**. The synthesis of **1** from phthalide has been reported



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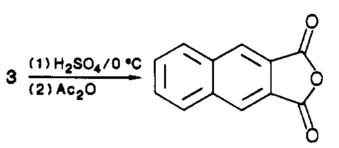

4 (2)

earlier.[5] The utility of **1** as a precursor of isobenzofuran (**2**) is well established.[1b] Reaction of **1** (via **2**) with maleic anhydride takes place simply upon heating a solution of the two materials, as first descried by Naito,[6] to afford cycloadduct **3** (exo + endo). It is convenient for the present purpose to reflux equimolar amounts of **1**, maleic anhydride, and acetic anhydride[8] in chlorobenzene (bp 131 °C) for ca. 24 h. Vacuum evaporation of the solvent affords **3** in essentially quantitative yield as a colorless solid that has the equilibrium composition (exo/endo = ca. 95/5).[9]

While several related materials are readily dehydrated under acidic conditions,[11] there have also been reports[11–13] of difficulties with this step. Cycloadduct **3** was especially recalcitrant in this respect, and many of the reagents examined gave either recovered starting material, decomposition, or side reactons.[14] However, when solid **3** was added to ice-cold concentrated H_2SO_4, stirred for a few minutes, and then poured onto crushed ice, aromatized product was isolated in essentially quantitative yield by filtration and vacuum drying.[17] It is important to cool the H_2SO_4 prior to the addition of **3** to prevent discoloration. The IR spectrum suggested that diacid was formed, presumably in varying amounts depending upon contact time with the aqueous acid. This material was therefore heated in acetic anhydride to effect ring closure and recrystallization. Pure crystalline **4** was isolated in 89% yield.

This sequence complements Cava's method[4] and, in principle, can be extended to substituted derivatives through the use of the corresponding phthalides or other substituted isobenzofuran precursors.

Experimental Section

Cycloadduct 3. A mixture of the acetal **1** (1.96 g, 12 mmol), maleic anhydride (1.29 g, 13.1 mmol), and 1.25 mL (13.2 mmol) of acetic anhydride in 19 mL of chlorobenzene was refluxed for 24 h. Removal of the solvent (rotary evaporation with heating followed by vacuum pump) gave 2.54 g (98%) of the cycloadduct **3**, identified by comparison of the ^{1}H NMR spectrum with that of known material; the product was a mixture of exo (ca. 95%) and endo (ca. 5%) isomers.[6]

2,3-Naphthalenedicarboxylic Anhydride (4). An Erlenmeyer containing 35 mL of concentrated H_2SO_4 and a stir bar was placed in an ice bath. Solid **3** (2.82 g) was added in portions over 5 min, and stirring was continued an additional 15 min. Most of the solid was in solution at this point. This mixture was then poured onto ca. 100 g of ice, with swirling. After 0.5 h the product was suction filtered and then dried in a vacuum desiccator over P_2O_5 to a constant weight (2.76 g, 98–106%, depending upon the extent of hydrolysis to diacid). A portion of this product, 2.60 g, was taken up in ca. 25 mL of acetic anhydride, refluxed for a few minutes (some darkening observed), and then allowed to stand

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(6) Naito, K.; Rickborn, B. *J. Org. Chem.* **1980**, *45*, 4061. The maleic anhydride adducts of isobenzofuran had been described earlier by Wiersum and Mijs,[7] who used a retro-Diels–Alder reaction to isolate the reactive diene.

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(8) The acetic anhydride serves the purpose of scavenging the ethanol coproduct generated along with isobenzofuran in the 1,4-elimination of **1**, thereby preventing the alcohol from opening the anhydride ring of the desired product **3**.

(9) The kinetically controlled reaction of **2** with maleic anhydride exhibits modest preference for the endo adduct, which is converted to the favored exo material fairly rapidly at 131 °C; the rates of endo and exo equilibration have been examined by Tobia.[10]

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(14) The following reagents/conditions were explored: (a) $ZnBr_2$/HOAc/Ac_2O, discoloration, slight dehydration; (b) Me_3SiI, prepared in situ from Me_3SiCl and NaI,[15] in DMF at 100 °C, no reaction; (c) Me_3SiI in acetonitrile at reflux[11] for up to 70 h gave up to 70% of the anhydride **4**, along with significant amounts of reduction product (1,2,3,4-tetrahydro-2,3-naphthalenedicarboxylic anhydride) and recovered *endo*-**3**, which appears to be stable under these conditions; (d) Me_3SiBr in refluxing acetonitrile, no reaction, **3** recovered; (e) NaOAc in refluxing Ac_2O, 4 h, no reaction; (f) 24-h reflux in Ac_2O containing concentrated HCl, ca. no reaction; (g) 4-h reflux in Ac_2O containing *p*-toluenesulfonic acid, ca. 25% **4**, remainder **3**; (h) trifluoroacetic acid in $CHCl_3$, 22-h reflux, no reaction; and (i) trifluoromethanesulfonic acid (0.15 equiv) in refluxing Ac_2O, 26 h, partial dehydration, dark coloration. The triflic acid attempt (i) was based on the report of Christophel and Miller[13] that trimethylsilyl trifluoromethanesulfonate provided a convenient, if rather expensive, solution to the problem of dehydration of the cycloadduct of naphthoquinone and 1,3-diphenylisobenzofuran.

Decomposition products (darkening) were not identified, but it should be noted that electron-withdrawing groups (cyano,[16a] acetyl[16b]) may lead to C–C rather than C–O bond cleavage under acidic conditions.

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(16) (a) Bremner, J. B.; Hwa, Y. *Aust. J. Chem.* **1971**, *24*, 1307. (b) Keay, B. A.; Rajapaksa, D.; Rodrigo, R. *Can. J. Chem.* **1984**, *62*, 1093.

(17) The use of concentrated H_2SO_4 for this dehydration was modeled after a procedure described by Newman and Cella.[18] We wish to thank Scott Whitney for calling our attention to this application.

(18) Newman, M. S.; Cella, J. A. *J. Org. Chem.* **1973**, *38*, 3482.

0022-3263/88/1953-2353$01.50/0

at room temperature overnight. Crystals of 4 were obtained (2.11 g, 89%), mp 250–252 °C (lit.[12] mp 250–251 °C).

It is not necessary to dry rigorously the diacid/anhydride prior to the recrystallization step. Repetition of the experiment, starting with 2.36 g of 3 and omitting the vacuum drying of the filtrand, gave 1.93 g (89%) of pure 4 as a single crop from acetic anhydride (washed with ether).

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Registry No. 1, 75802-19-6; 3 (stereoisomer 1), 109428-59-3; 3 (stereoisomer 2), 114027-87-1; 4, 716-39-2; maleic anhydride, 108-31-6; 1,2,3,4-tetrahydro-2,3-naphthalenedicarboxylic acid anhydride, 29811-05-0.

Diastereoselective Alkylation of 3-Acylimidazolidin-2-ones: Synthesis of (*R*)- and (*S*)-Lavandulol

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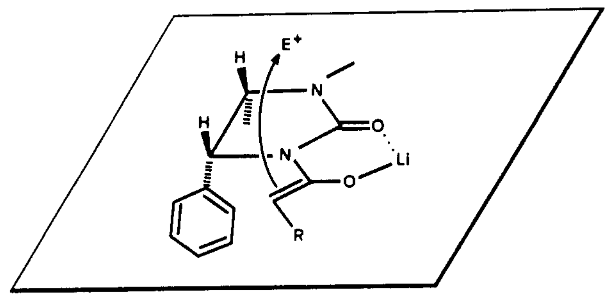
In connection with our general interest in the search for new approaches to prenyl compounds,[1] we developed a procedure incorporating one prenyl unit at a time, through the alkylation of the Li dianion of 3-methyl-2-butenoic acid.[2] This methodology provides terpenes with the lavandulyl skeleton, since this dianion undergoes alkylation predominantly at C-2.[3,4] Owing to the increasing importance of optically active monoterpenes,[5] their asymmetric synthesis through chiral auxiliaries has attracted interest.[6]

Herein we report a new method for asymmetric alkylation that we believe has considerable potential in the synthesis of prenyl compounds. This process, outlined in Scheme I, appears to offer many advantages, including high efficiency, procedural simplicity, predictable configuration of the introduced stereogenic center, and mildness of the reaction conditions. The utility of chiral auxiliaries in the alkylation of carboxylic acid derivatives has been recently reported;[7] we now exploit the use of the readily accessible imidazolidin-2-ones 4*R*,5*S* **1a** and 4*S*,5*R* **1b**[8] (Figure 1).

1a 1b

Figure 1.



Chiral auxiliary	Priority	Configuration of the new chiral center
1a (4R,5S)	E < R	R
	E > R	S
1b (4S,5R)	E < R	S
	E > R	R

Figure 2.

In our approach to the enantiomerically pure lavandulol,[9] the lithium anion of **1a** is acylated with 3-methyl-2-butenoyl chloride, to obtain **2a** in high yield. After treatment of **2a** with an equimolar amount of LDA in THF at −78 °C, the alkylation is performed at the same temperature[10] with 1-bromo-3-methyl-2-butene, to afford **3a** in 83% yield.

The diastereoselection of the reaction can be determined by ^{1}H NMR spectroscopy, by observing the doublet of the CHPh proton of the auxiliary moiety, which shows different chemical shifts in the two diastereomers. An asymmetric induction ≥95% can be assumed if only one diastereomer is recognizable in the ^{1}H NMR spectrum.[11] A 96:4 diastereomeric ratio is determined from the ^{13}C NMR spectrum[12] and successively confirmed by reduction of the alkylated product **3a** with lithium aluminum hydride (LAH) to afford (−)-lavandulol (**4a**), $[\alpha]_D$ −10.04°,[9a] a value corresponding to 92% ee. The synthetic sequence starting

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