

Procedures and Data

3,4-Dicyanomaleic Anhydride, A New Dienophile

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Abstract. Thermolysis of 2,3-dicyano-bicyclo[2,2,1]hept-5-ene-2,3-dicarboxylic anhydride (**6**) at 580–590 °C or of 3,4,5,6-

tetraazidophthalic anhydride (**9**) at 110 °C affords 3,4-dicyanomaleic anhydride (**1**).

Although dienophile reactivity depends amongst other factors on the structure of the diene as well, the nature and position of substituents may be used as the main guideline to new reactive dienophiles. Carbonyl substituents and/or cyano groups are a common structural feature of reactive dienophiles [1], [2], and Diels–Alder cycloaddition reactions of maleic anhydride [3] and of polycyanoethenes [4] are well documented. For example cyclic structures such as in maleic anhydride or maleimide have been found to be generally more activating than the two cyano groups in 1,2-dicyanoethenes [5]. Thus the combination of a cyclic anhydride moiety with two cyano groups such as in 3,4-dicyanomaleic anhydride (**1**) should produce a reactive dienophile. Here we report two independent syntheses of **1**, a new member of the cyanocarbon family.

Synthesis from Diethyl 2,3-Dicyanomaleate (**3**)

Diethyl 2,3-dicyanofumarate (**2**) [6] was photochemically isomerized to give diethyl 2,3-dicyanomaleate (**3**). The *Z*-compound **3** proved to be easily isomerized back to **2** in the presence of even weak nucleophiles such as bromide anions (in KBr pellets for IR-spectroscopy) or alkaline glass surfaces. Similarly attempts to hydrolyze **3** to give the corresponding *Z*-diacid or its salts failed, decomposition products were formed instead.

To prevent isomerization of the *Z*-configuration, we used a route *via* the Diels–Alder adduct **4** obtained from (**3**) and cyclopentadiene. This compound then could be hydrolyzed by methanolic KOH to give the dipotassium salts **5** which in turn was cyclized by acetyl chloride affording anhydride **6**. Gas phase thermolysis of **6** at 580–590 °C gave the desired 3,4-dicyanomaleic anhydride (**1**) in 38% yield.

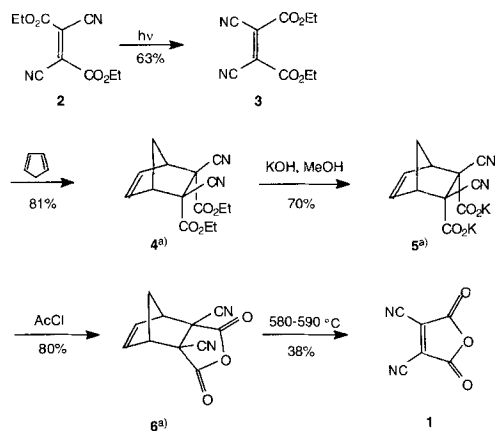
Anhydride **1** is purified by sublimation to give colorless crystals which melt at 185 °C (dec.). The compound is sensitive to moisture and other nucleophiles and has an irritating effect on mucous membranes.

Synthesis from 3,4,5,6-Tetrachlorophthalic Anhydride (**7**)

Thermolytic decomposition of 1,2-diazidobenzene occurs by ring cleavage between C-1 and C-2 and affords the open-chain compound 1,4-dicyanobutadiene [7].

Under the assumption that a similar reaction of 3,4,5,6-tetraazidophthalic anhydride (**9**) would proceed by cleavage of the benzene ring preferentially between C-3/C-4 and C-5/C-6, this reaction should give anhydride **1** together with one equivalent of cyanogen and four equivalents of nitrogen.

The synthesis of 3,4,5,6-tetraazidophthalic acid (**8**) from 3,4,5,6-tetrachlorophthalic anhydride (**7**) and sodium azide has been reported in a short communication with only scarce



a) compounds 4 - 6 are mixtures of *exo*-*endo* isomers.

Scheme 1

(lg ϵ) = 236 nm (3.94). ^{13}C NMR (CD_3CN , 100.6 MHz): δ/ppm = 107.80, 127.91, 157.38. –MS (70 eV, EI) $m/z(\%)$ = 149 (1) [M^+], 148 (10) [M^+], 105 (5), 104 (69), 78 (6), 77 (6), 76 (100), 50 (12).
 $\text{C}_6\text{N}_2\text{O}_3$ calcd.: C 48.67 N 18.92
(148.1) found: C 48.96 N 18.76.

3,4,5,6-Tetraazidophthalic Anhydride (9)

In a 500 mL round-bottomed flask with magnetic stirrer and drying tube kept at 25 °C by a water bath, 2.32 g (8.12 mmol) of finely ground 3,4,5,6-tetrachlorophthalic anhydride was dissolved in 40 mL of abs. DMSO. After complete solution, 2.7 g (0.042 mol) of finely ground sodium azide was added in one portion with rapid stirring. The sodium azide dissolved to give a slightly turbid orange solution, and after a few minutes a colourless precipitate began to separate. The mixture was stirred for 3 hours and then diluted with 200 ml of ice-water. The yellow-orange precipitate was filtered off and washed twice with ice-water. On acidification the filtrate deposited an additional precipitate, which together with the first crop was dissolved in 100 ml of cold 1N KOH. After a few minutes a clear yellow solution was obtained which was filtered and acidified with cold conc. HCl. For easier filtration, the off-white precipitate was kept in the refrigerator overnight, filtered by suction until still damp, transferred together with the filter to a 500 ml round bottomed flask and dissolved with slow stirring at r.t. (water cooling!) in 200 ml of acetic anhydride. To prevent decomposition of the azide, the flask and the stir bar must have a smooth unscratched surface. After 16 h the bar was removed, and the volatile components completely distilled off at 25 °C/0.05 Torr (ca. 4 h). –IR (neat): ν/cm^{-1} = 2110, 1850, 1820, 1767, 1430, 1380, 1290, 1260, 1205, 1145, 915, 880, 810, 740. ^{13}C NMR (CD_3CN , 100.6 MHz): δ/ppm = 119.66, 130.98, 133.70, 161.02. The dry residue (2.33 g, 7.47 mmol, 93%) was dissolved in 50 ml of abs. toluene in a 100 ml round bottomed flask with

reflux condenser which was connected *via* drying tube and a gas washing bottle (1N KOH) to a gasometer. After 2 h reflux 638 ml (28.5 mmol, 95%) of nitrogen were evolved and cyanide and cyanate anion could be detected in the KOH solution. The toluene was evaporated at 30 °C/0.1 Torr, and sublimation of the remaining solid at 120 °C/0.01 Torr afforded 0.39 g (2.64 mmol, 35%) of the anhydride **1**.

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