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**Procedures and Data** 

# 3,4-Dicyanomaleic Anhydride, A New Dienophile

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**Abstract.** Thermolysis of 2,3-dicyano-bicylo[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 3,4dicyanomaleic 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 3,4dicyanomaleic 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 Zcompound 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  $185 \,^{\circ}C$  (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 3,4,5,6tetraazidophthalic 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

experimental details [8]. We adapted that procedure in order to handle 2–3 g of **8** safely. Cyclization of **8** by reaction with acetic anhydride at room temperature gave anhydride **9**. After complete removal of acetic anhydride and acetic acid *in vacuo* at room temperature the raw anhydride **9** was thermolyzed in absolute toluene at reflux temperature. After 2 h 95% of the theoretical amount of nitrogen had evolved, and 35% of **1** was isolated by sublimation *in vacuo*. The formation of cyanogen was proved by passing the gas through aqueous 1N potassium hydroxide and detection of cyanide and cyanate anion. For safety reasons we recommend that azido compounds **9** and **8** do not come into contact with ground or otherwise scratched surfaces or be handled when dry (see also [9]). Every mechanical stress of the dry anhydride **9** by loose objects such as spatulae or magnetic stirrers should be avoided.



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## Experimental

IR: Perkin-Elmer 298. – NMR: Bruker WM 400 (400 and 100.6 MHz for <sup>1</sup>H and <sup>13</sup>C, res.). – MS: Finnigan MAT 44S. – *m.p.* (uncorrected): Dr. Tottoli apparatus of Fa. Büchi.

#### Diethyl 2,3-Dicyanomaleate (3)

Before use the irridiation apparatus was treated with 6N HCl for 16 h, thoroughly washed with distilled water and dried at 110 °C. 2.78 g (12.5 mmol) of diethyl 2,3-dicyanofumarate [6] in 250 ml of absol. dichloromethane were degassed by ultrasound and then saturated with argon. After irridiation for 2.25 h (Philips HPK 125W, Duran 5O filter) at r.t. under nitrogen, the solvent was removed at 20 °C/0.05 Torr and the partly crystalline residue purified by sublimation at 60 °C/0.01 Torr. Yield: 1.83 g (8.24 mmol, 66%) of colourless crystals containing 4% of the educt. *m.p.* 46 °C,  $n_D^{23}$  1.4650 (supercooled liquid). – IR (neat): v/cm<sup>-1</sup> = 2980, 1740, 1600, 1465, 1440, 1370, 1285, 1190, 1070, 1010, 850, 770, 720. – UV/Vis (dichlormethane):  $\lambda_{max}$ 

 $\begin{array}{l} (\lg \varepsilon) = 238 \ \text{nm} \ (4.06). - \ ^1\text{H} \ \text{NMR} \ (\text{CDCl}_3, 400 \ \text{MHz}): \ \delta/\text{ppm} = 1.37 \ (t, \ 6\text{H}), \ 4.39 \ (q, \ 4\text{H}). - \ ^{13}\text{C} \ \text{NMR} \ (\text{CDCl}_3, \ 100.6 \ \text{MHz}): \\ \delta/\text{ppm} = 13.71, \ 64.86, \ 111.30, \ 125.55, \ 157.54. \\ C_{10}\text{H}_{10}\text{N}_2\text{O}_4 \ \ \text{calcd.:} \ \ \text{C} \ 54.05 \ \ \text{H} \ 4.54 \ \ \text{N} \ \ 12.61 \\ (222.2) \ \ \text{found:} \ \ \text{C} \ 54.02 \ \ \text{H} \ 4.74 \ \ \text{N} \ \ 12.34. \end{array}$ 

## 2,3-Dicyano-bicylo[2,2,1]hept-5-ene-2,3-dicarboxylic Anhydride (6)

To 1.5 g (6.76 mmol) of diethyl 2,3-dicyanomaleate (**3**) in 65 ml of absol. dichloromethane (dried over Al<sub>2</sub>O<sub>3</sub>, activity super I) was added 0.45 g (6.8 mmol) of freshly distilled cyclopentadiene in 5 ml of absol. dichloromethane. After 16 h at r.t. a solution of 850 mg (12.9 mmol) of 100% KOH in 10 ml of absol. methanol (dried over Mg) was added all at once with stirring at r.t.. The initial blue color of the mixture soon faded, and after 1.5 h a white precipitate of the dipotassium salts appeared. After 3 days under argon, the dipotassium salts were filtered off, air-dried for 8 h and after being finely ground, dried over P<sub>4</sub>O<sub>10</sub> at 80 °C and 0.05 Torr for additional 8 h. A yield of 1.61 g (5.23 mmol, 82%) of a chamois-coloured salt was obtained, which according to its NMR spectra consisted of the dipotassium salts (70% endo, endo, 15% exo, exo and 15% exo, endo).

2.0 g (6.5 mmol) of the finely ground dipotassium salts 5 were placed in 500 ml three-necked round bottom flask which had been thoroughly dried by heating under argon. After addition of 150 ml of acetyl chloride at r.t. the mixture was stirred for 20 h, all compounds volatile at 50 °C/0.05 Torr were removed, and the solid residue was sublimed at 140-150 °C/ 0.002 Torr. After 8 h the yield of white amorphous material was 1.11 g (5.19 mmol, 80%) of 6, containing 77% of endo, endoand 23% of exo, exo-dicarboxylic anhydride [10]. m.p. 198 °C. -IR (KBr):  $v/cm^{-1} = 2255, 1870, 1800, 1460, 1330, 1285, 1260,$ 1220, 1200, 1040, 990, 960, 910, 890, 800, 750, 680. - <sup>1</sup>H NMR  $(D_{6}\text{-}acetone, 400 \text{ MHz}): \delta/\text{ppm} (endo, endo-anhydride) = 2.23$ (dm, 1H), 2.29 (dt, 1H), 4.16–4.20 (m, 2H), 6.61 (t, 2H); (exo, exo-anhydride) = 1.83 (dm, 1H), 1.99 (dt, 1H), 4.03-4.07 (m, 2H), 6.85 (t, 2H).  $-{}^{13}$ C NMR (D<sub>6</sub>-acetone, 100.6 MHz):  $\delta$ /ppm (endo, endo-anhydride) = 44.61, 52.69, 55.49, 114.75, 138.01, 163.13; (exo, exo-anhydride) = 44.61, 57.15, 57.49, 114.58, 139.92, 163.85.

$C_{11}H_6N_2O_3$	calcd .:	C 61.69	H 2.82	N 13.08
(214.2)	found:	C 62.02	H 2.88	N 12.95.

#### 3,4-Dicyanomaleic Anhydride (1)

The flash pyrolysis apparatus consisted of a 20 ml evaporating flask directly connected to an empty horizontal quartz tube (450 mm × 20 mm) heated in an oven of 400 mm length. The exit of the pyrolysis tube was connected to two traps, the first one cooled by ice, the second by liquid nitrogen. During pyrolysis the central section (ca. 100 mm) of the tube had a temperature of 580–590 °C. At a pressure between  $6.5 \times 10^{-5}$  and  $1 \times 10^{-4}$  Torr 1.92 g (8.97 mmol) of anhydride **6** was heated in the evaporating flask to ca. 180 °C. After 8 h the chamois-coloured mixture of **1** and **6** in the ice-cooled trap was transferred under dry argon to a sublimation apparatus, and 0.51 g (3.4 mmol, 38%) of **1** was isolated by sublimation at 50 °C/0.002 Torr. *m.p.* 185 °C (decomp.). – IR (KBr):  $\nu/cm^{-1} = 2230, 2180, 1990, 1910, 1850, 1800, 1240, 1050, 940, 720. – UV/Vis (acetonitrile): <math>\lambda_{max}$ 

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

#### 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):  $v/cm^{-1} = 2110, 1850,$ 1820, 1767, 1430, 1380, 1290, 1260, 1205, 1145, 915, 880, 810, 740.  $-^{13}$ C NMR (CD<sub>3</sub>CN, 100.6 MHz):  $\delta$ /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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