# Interaction of levoglucosenone with malononitrile

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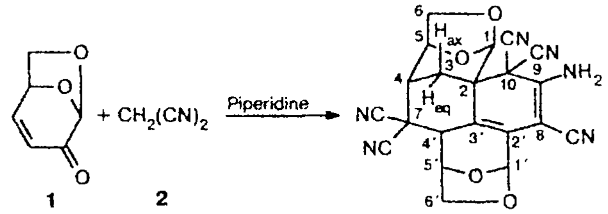
Levoglucosenone reacts with malononitrile to form a product with a complex structure, which contains two levoglucosenone molecules and three malononitrile molecules. The conclusion about the structure of the product was based on the data of NMR, IR, and UV spectroscopy and mass spectrometry. The suggested reaction mechanism involves cascade cyclization.

**Key words:** levoglucosenone, malononitrile, cascade cyclization.

It is known that levoglucosenone (1) reacts with C—H-acids in the presence of bases to form addition products at the C=C bond.[1–3] The reaction of compound **1** with nitromethane is a more complex process in which two molecules **1** and one nitromethane molecule are involved.[4] The reaction of compound **1** with malononitrile studied in this work is even more complex.

In the presence of piperidine, levoglucosenone (**1**) reacts with an equimolar amount of malononitrile (**2**) to form a product to which structure **3** was assigned based on the data of NMR, IR, and UV spectroscopy and mass spectrometry (Scheme 1).

**Scheme 1**



1 2 3

The [1]H NMR spectrum has two sets of signals, which correspond to the protons of two different carbohydrate fragments. The signals of one set with the chemical shifts of 2.11 ($H(3)_{eq}$), 2.85 ($H(3)_{ax}$), 3.13 (H(4)), 5.24 (H(5)), and 5.96 ppm (H(1)) are similar in shape and spin-spin coupling constants to the signals for the protons of the hydrocarbon fragments of molecules in which the six-membered ring is closed as a result of attack of 1,3-binucleophiles on the C=C bond and the carbonyl group of levoglucosenone.[5–7] The signals at δ 5.06 (H(5′)) and 5.83 (H(1′)) correspond, apparently, to the second carbohydrate fragment. The doublet at 4.46 ppm and the multiplet in the region of 3.98—4.13 ppm (3 H) correspond to four protons H(6) of both fragments. In addition, the spectrum has a singlet at δ 4.29, which is assigned to H(4′), and a broadened singlet at δ 7.5 (2 H), which is interpreted as a signal for the amino group.

The conclusion about the presence of the amino group is confirmed by the IR spectral data. The IR spectrum has bands typical of vibrations of the amino group at 3420, 3340, and 3220 cm$^{-1}$ ($\nu NH_2$) as well as at 1640 cm$^{-1}$ ($\delta NH_2$) and a band at 2220 cm$^{-1}$, which corresponds to the conjugated nitrile group. All the aforesaid suggest the presence of the enaminonitrile $C(NH_2)=C(CN)$ fragment in the molecule. However, the UV spectrum has an absorption band with a maximum at 342 nm, which is apparently indicative of an extension of the conjugation chain compared to the normal enaminonitrile fragment ($\lambda_{max}$ = 260—270 nm).[8] Apparently, this is also the cause of the slight shift of the vibration frequency of the nitrile group in the IR spectrum (2220 cm$^{-1}$ compared to 2180—2190 cm$^{-1}$, which is typical of enaminonitriles[8]). In addition, the IR spectrum has a low intensity band at 2260 cm$^{-1}$, which suggests the presence of the nonconjugated nitrile group as well.

The [13]C NMR spectrum shows 21 signals among which six signals are observed in the region of 110—115 ppm, which is typical of nitrile groups. This suggests that the molecule of the product results from the interaction of two molecules **1** with three malononitrile molecules. This suggestion is also confirmed by the mass spectrum (M = 414) under the assumption that two water molecules are eliminated in the course of this interaction.

The structure of **3** gives excellent agreement with all the above data. Besides, the formation of this compound

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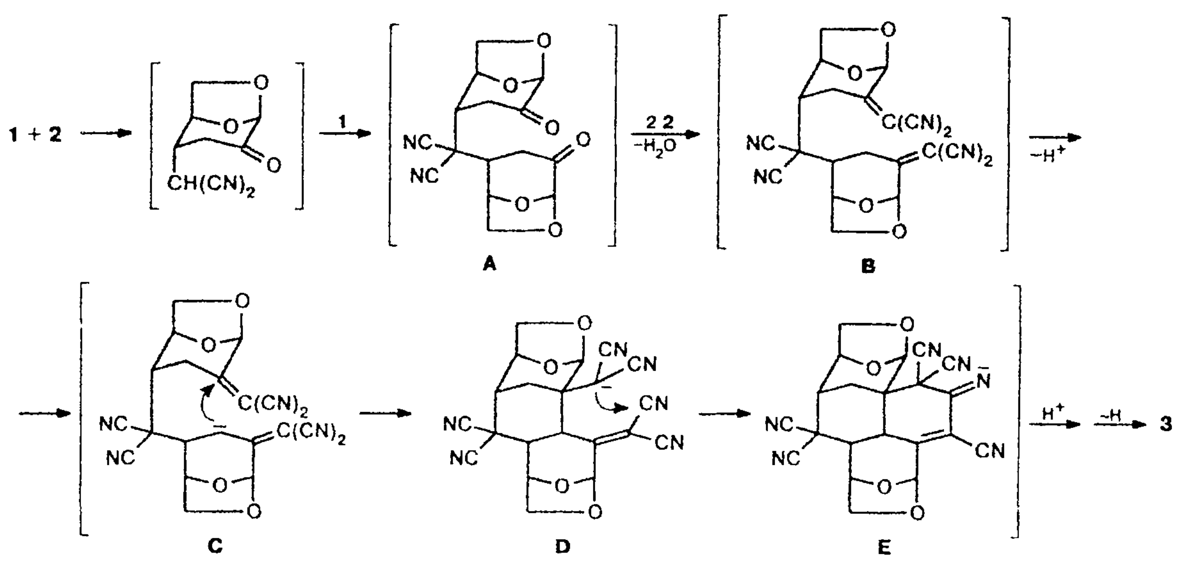
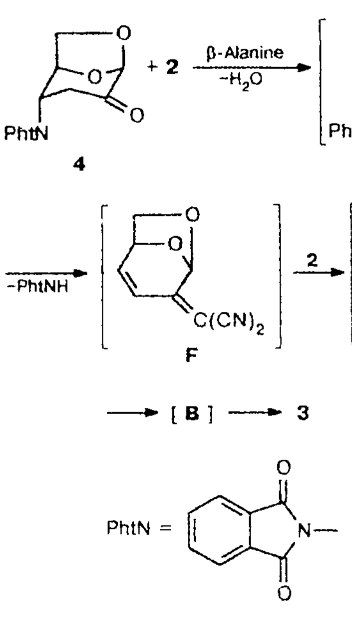
Scheme 2



can be adequately explained by assuming the mechanism shown in Scheme 2.

Apparently, a malononitrile molecule (**2**) originally adds to two levoglucosenone molecules (**1**). Then, bis-adduct **A** enters into the Knoevenagel condensation with two molecules **2** to form intermediate **B**. After proton abstraction, the latter apparently undergoes the "anionic cascade" of conversions **C** → **D** → **E** accomplished by addition of the proton and the [1,5]-shift of the hydrogen atom to form compound **3**.

Scheme 3



Interestingly, the same adduct **3** was also formed in the reaction of malononitrile (**2**) with the product of addition of phthalimide to levoglucosenone **4**[9] in the presence of catalytic amounts of β-alanine. The reaction mechanism proposed is shown in Scheme 3.

In conclusion, it should be noted that the reactions of malononitrile with α,β-unsaturated ketones are often rather complex processes.[10] However, to our knowledge, "three-to-two" adducts analogous to compound **3** are not known in the literature.

## Experimental

The NMR spectra were recorded on a Bruker AM-300 instrument (300.13 MHz for $^1$H and 75.47 MHz for $^{13}$C). The IR spectrum was obtained on a Specord M-80 instrument. The UV spectrum was recorded on a Specord UV-VIS instrument. The mass spectrum was measured on a Kratos MS-30 spectrometer with direct introduction of the sample into the ion source.

**Synthesis of adduct 3 by the reaction of levoglucosenone (1) with malononitrile (2).** Piperidine (1 drop) was added to a solution of compound **1** (0.63 g, 5 mmol) and nitrile **2** (0.33 g, 5 mmol) in EtOH (4 mL) at 30 °C. After 5 min, an oily precipitate formed, which solidified after 30 min. The precipitate was ground, filtered off, thoroughly washed three times with hot EtOH, and dried. The resulting product was obtained as a yellowish powder in a yield of 0.46 g (66% with respect to the amount of malononitirile used), decomp. temp. > 250 °C.

**Synthesis of adduct 3 by the reaction of the adduct 4 with malononitrile (2).** A suspension of compound **4** (1.36 g, 5 mmol), nitrile **2** (0.5 g, 7.5 mmol), and β-alanine (10 mg) in EtOH (20 mL) was refluxed for 6 h and cooled. The precipitate was separated and chromatographed on a column with silica gel in a benzene—AcOEt mixture. Compound **3** was obtained in a yield of 0.56 g (54%). $^1$H NMR (acetone-$d_6$), δ: 2.11 (dm, 1 H, H(3)$_{eq}$, $J$ = 13.9 Hz); 2.85 (dd, 1 H, H(3)$_{ax}$,

$J$ = 13.9 and 3.9 Hz); 3.13 (distort.q, 1 H, H(4)); 3.98—4.13 (m, 3 H, $H(6')_A$, $H(6')_B$, $H(6)_A$); 4.29 (s, 1 H, H(4')); 4.46 (d, 1 H, $H(6)_B$, $J$ = 8.3 Hz); 5.06 (dm, 1 H, H(5'), $J$ = 4.6 Hz); 5.24 (m, 1 H, H(5)); 5.83 (s, 1 H, H(1')); 5.96 (d, 1 H, H(1), $J$ = 1.9 Hz); 7.50 (br.s, 2 H, $NH_2$). $^{13}C$ NMR (DMSO-$d_6$), δ: 28.6 (C(3)); 39.2 (C(7)); 40.0 (C(4)); 42.8 (C(2)); 47.3 (C(10)); 47.6 (C(4')); 68.1, 69.0 (C(6), C(6')); 73.4 (C(8)); 71.9, 74.2 (C(5), C(5')); 95.9, 101.4 (C(1), C(1')); 110.3, 110.4, 111.2, 114.0, 114.3, 115.1 (5 CN, C(3')); 130.7 (C(2')); 144.6 (C(9)). IR (KBr), ν/$cm^{-1}$: 3420, 3340, 3220 (ν$NH_2$); 2260, 2220 (CN); 1640 (δ$NH_2$); 1580 (C=C). UV (MeCN), $\lambda_{max}$/nm: 342 (ε 9600). MS (EI, 70 eV), $m/z$ ($I_{rel}$ (%)): 414 $[M]^+$ (10), 388 (41), 312 (64), 235 (100), 210 (36), 209 (97), 148 (41).

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# Interaction of ferrocenecarbaldehyde with zinc tetrahydroborate and its derivatives

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Ferrocenecarbaldehyde was reduced to methylferrocene upon interaction with zinc tetrahydroborate in THF. The reactions proceeded rapidly (5—10 min) in high yields (*ca.* 90%). Analogous results were obtained when a mechanically activated mixture of zinc chloride and sodium tetrahydroborate or the complex of zinc tetrahydroborate with dibenzo-18-crown-6, $2Zn(BH_4)_2 \cdot$ DB-18-C-6, was used in the reaction.

**Key words:** ferrocenecarbaldehyde, methylferrocene, reduction, zinc tetrahydroborate, complex $2Zn(BH_4)_2 \cdot$ DB18C6, mechanochemistry.

Alkylferrocenes find application as efficient combustion stabilizers, antiknock compounds, and motor oil additives as well as in some other fields.[1] The procedure most generally employed for the preparation of alkylferrocenes involves reduction of acetyl derivatives of ferrocene with lithium aluminum hydride in the presence of $AlCl_3$. Recently, it was found that carbonyl derivatives of ferrocene were reduced to form the corresponding alkylferrocenes upon interaction with a mixture of zinc chloride and zinc tetrahydroborate or zinc chloride and sodium tetrahydroborate in THF for 8—10 h.[2,3]

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