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# The Benzil Dicyanohydrin Rearrangement Analogy with the Benzil–Cyanide Reaction

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In the course of our studies,[1] we found that benzil dicyanohydrin **2** is easily obtained (75% yield) by the reduction of benzoyl cyanide **1** with aqueous acidic $TiCl_3$ solution (Scheme 1).

This report notes the formation of mandelonitrile benzoate (**3**), in quantitative yield, from the reaction of **2** with potassium carbonate in *t*-BuOH. Besides the synthetic aspect of this transformation, the result is of added interest in view of the fact that the intermediacy of **3** has been repeatedly invoked in the benzil–cyanide reaction,[2-5] though **3**, *per se*, has never been isolated, either in alcoholic or in aprotic solvents.

The benzil–cyanide reaction has been widely studied owing to the similarity with the benzoin condensation and the renewed interest in reactions which generate protected cyanohydrins for use in nucleophilic acylations.[6-10]

The reaction gives a variety of products, depending on the solvent used (Scheme 2).

In alcoholic solvents, cleavage to benzaldehyde and to the corresponding ester takes place,[2,5] whereas, in DMSO, stilbenediol benzoate (**4**) is the sole product formed.[3] Although **3** has never been isolated, carbanion **B** was proposed as the common intermediate leading to the observed products.

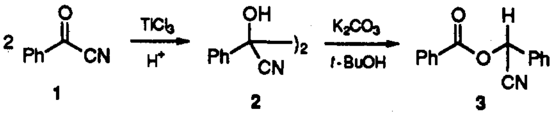
An obvious analogy can be drawn between the mechanism proposed in Scheme 2 and the one we suggest for the rearrangement of **2** to **3** (Scheme 3).

**A**, formed by hydrogen cyanide loss from **2**, rearranges to the stabilized carbanion **B**, which then abstracts a hydrogen from the solvent, *t*-BuOH, to give **3** in quantitative yield. The catalytic nature of the reaction is ensured by the formation of *tert*-butoxy anion, which regenerates **A** from **2**.

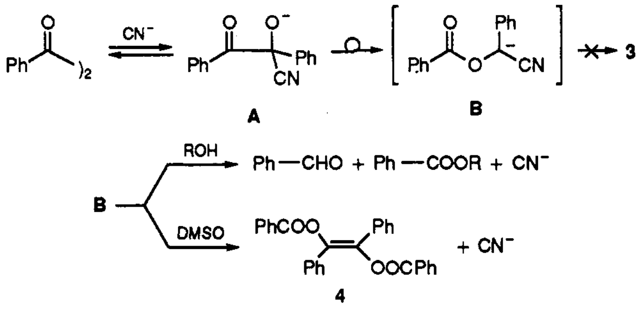
When MeOH was used, instead of *t*-BuOH, under comparable experimental conditions, benzaldehyde and methyl benzoate were formed from **2**,[11] exactly as it occurs in the benzil–cyanide reaction. Furthermore, in the presence of a catalytic amount of $K_2CO_3$, **3** was quantitatively methanolized to PhCHO and PhCOOMe within a few minutes at 25 °C.

These results, in our opinion, simply reflect the different reactivity, under basic catalysis, of the two alcohols used as solvents: the low nucleophilicity of *tert*-butoxy anion hampers the subsequent alcoholysis of **3**, whereas methoxy anion easily promotes the resulting cleavage of **3** (Scheme 3).

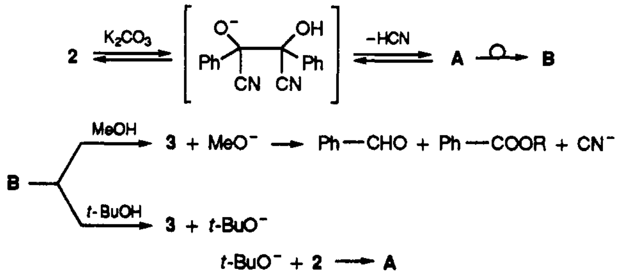
**Scheme 1**



**Scheme 2**



**Scheme 3**



Even though the cleavage of benzil by cyanide ion has been extensively studied in protic (MeOH, EtOH, and PrOH) and aprotic (DMSO) solvents, to our knowledge, an investigation of this reaction in *t*-BuOH has never been reported.

In order to verify our hypothesis, benzil was treated with potassium cyanide in *t*-BuOH. Because of the low solubility of the salt in this solvent, 60% of the starting benzil was left unreacted though **3** and **4** were recovered in 18 and 15% yields, respectively, as the sole reaction products.

These findings strongly support that **3** is indeed the intermediate in the benzil–cyanide reaction, as well as in the rearrangement of **2**. The success of its isolation merely results from the inertness of the tertiary alcohol to undergo transesterification with **3**.

## Experimental Section

$^1H$ NMR spectra of $CDCl_3$ solutions were recorded with a 250-MHz Bruker Model AC-250 instrument: $Me_4Si$ served as an internal standard. IR spectra of mineral oil mulls were recorded with a Perkin-Elmer Model E-177 instrument. Mass spectra were recorded with a Hitachi-Perkin-Elmer Model RMU-6D spectrometer operated at 70 eV. Melting points (uncorrected) were measured with a Kofler apparatus.

**Preparation of Mandelonitrile Benzoate (3).** A mixture of **2** (0.66 g, 2.5 mmol) and potassium carbonate (0.2 g, 1.4 mmol) in *t*-BuOH (20 mL) was stirred at 30 °C for 4 h. After that time

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[11] Benzaldehyde and methyl benzoate were formed in 35 and 65% yield, respectively.

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the insoluble salts were filtered off, the filtrate was concentrated under reduced pressure, and the residue, recrystallized from hexane/ethyl ether (1:1), gave **3** in quantitative yield (0.59 g, colorless plates): mp 61 °C (lit.[12] 61 °C); IR (Nujol)[2] $\nu_{max}$ 1725 (C=O), 1320 and 1090 (C–O–C) cm$^{-1}$; MS, *m/z* 237 (M$^+$, 20), 116 (31), 105 (100), 89 (8), 77 (23), 51 (12). $^1$H NMR (CDCl$_3$) $\delta$ 6.68 (1H, s, CH), 7.5–8.1 (10 H, m, Ph H).

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