

NOVEL FORMATION OF AROMATIC NITRILES BY FRIEDEL-CRAFTS
REACTION IN NITROMETHANE

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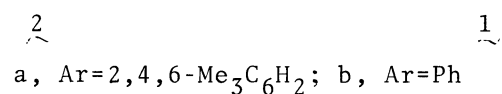
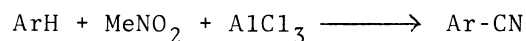
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Mesitylene and benzene gave the corresponding nitriles by reaction with anhydrous aluminum chloride and nitromethane at 80°C, together with the corresponding aldoximes.

During the course of a study on some Friedel-Crafts reactions of mesitylene in nitromethane, we found the formation of 2,4,6-trimethylbenzotrile (1a) as a by-product.

Such a formation of nitrile has never been reported, but it has been reported that reaction of benzene with nitromethane and anhydrous aluminum chloride gave benzaldoxime and N-benzylideneaniline.¹⁾ Thus, nitrile is considered to be produced through dehydration of aldoxime by aluminum chloride.

Therefore, mesitylene (2a) was allowed to react with anhydrous aluminum chloride and nitromethane under several conditions. The reaction mixture was poured into cold water, made alkaline with aqueous sodium hydroxide, and steam-distilled. After extraction of the distillate with dichloromethane, the extract was chromatographed on silica gel to isolate 1a, mp 48-48.5°C (lit,²⁾ 50-52°C). The results are summarized in Table. Since 1a sublimates easily, the isolated yields are underestimated values.



In Run 2, syn-, mp 123-124.5°C (lit,³⁾ 124°C), and anti-2,4,6-trimethylbenzaldoximes, mp 173-176°C (lit,³⁾ 179°C), were also obtained. The structures were confirmed by NMR.⁴⁾

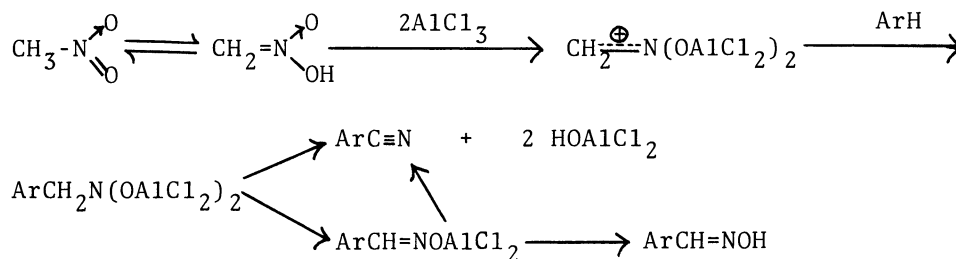
Table. Yields of benzonitriles (1)

Run	ArH (mmol)	AlCl ₃ (mmol)	MeNO ₂ (mmol)	Temp. (°C)	Time (hr)	Yield of <u>1</u> (mmol)
1	<u>2a</u> 80	30	80	80	5	<u>1a</u> 11.5 ^{a)}
2	<u>2a</u> 50	110	230	80	6	<u>1a</u> 3.5 ^{a)} , 17.3 ^{a)}
3	<u>2a</u> 50	100	458	80-100	30	<u>1a</u> 20.2 ^{a)}
4	<u>2b</u> 50	100	458	80	24	<u>1b</u> 3.0 ^{a)} , 14.0 ^{b)}

a) Isolated yield. b) Determined by NMR.

Run 3 gave 2,4,6-trimethylaniline as a by-product, which is considered to be formed through the Beckmann rearrangement of 2,4,6-trimethylbenzaloxime. Benzene (2b) gave also benzonitrile (1b) in a low yield.

From the results, the reaction pathway is considered as follows.



Thus, nitromethane should be avoided as a solvent in Friedel-Crafts reactions of very activated aromatics. The present reaction is considered to be used for one-step preparation of nitriles from activated aromatics.

References

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(Received September 2, 1974)