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# A NOVEL DISPROPORTIONATION REACTION OF AROMATIC ALDEHYDES INVOLVING C-C BOND FORMATION

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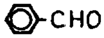
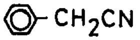
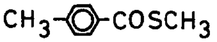
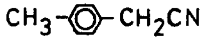
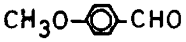
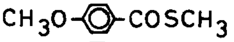
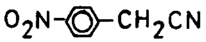
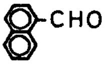
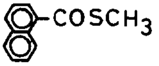
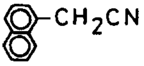
Summary: The reaction of aromatic aldehydes with methyl thiocyanate in the presence of tributylphosphine afforded both S-methyl thiobenzoates and phenylacetonitriles via a novel disproportionation pathway involving carbon-carbon bond formation.

In our study directed toward the synthesis of heterocycles by using methylthio group[1], it was found that benzaldehyde reacted with methyl thiocyanate in the presence of tributylphosphine to give both S-methyl thiobenzoate and phenylacetonitrile in good yields. We now report a hitherto unknown disproportionation reaction of aromatic aldehydes with methyl thiocyanate.

A typical experimental procedure is as follows: to an ice-cold mixture of benzaldehyde (212 mg, 2 mmol) and tributylphosphine (0.27 ml, 1.1 mmol) was added methyl thiocyanate (0.073 ml, 1 mmol) dropwise with a syringe under argon. After the addition had been completed, stirring was continued for 1 h at 0 °C and for an additional 2 h at ambient temperature. The reaction mixture was worked up by preparative TLC upon silica-gel using a 2 : 1 mixture of benzene and hexane as eluant to afford S-methyl thiobenzoate and phenylacetonitrile in 47 % and 35 % yields, respectively.

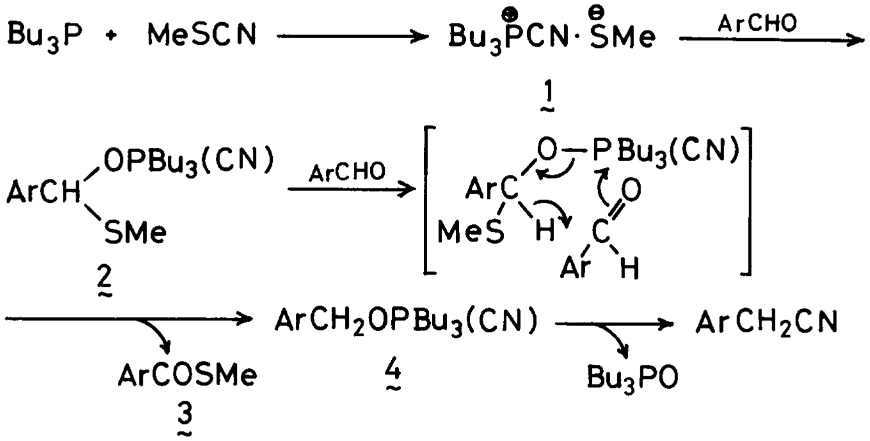
Table 1. Reaction of Aromatic Aldehydes with Methyl Thiocyanate in the Presence of Tributylphosphine

| Entry | Ar-CHO | Ar-COSCH$_3$ [a)] | Yield | Ar-CH$_2$CN [a)] | Yield |
|---|---|---|---|---|---|
| 1 |  |  | 47 % |  | 35 % |
| 2 |  |  | 47 % |  | 45 % |
| 3 |  |  | 16 % |  | 31 % |
| 4 b) |  |  | 22 % |  | not isolated |
| 5 |  |  | 15% |  | 32% |

a) All the products gave satisfactory ir, nmr, and mass spectra.
b) The reaction was carried out in dry THF.

In a similar manner, various aromatic aldehydes were converted into the corresponding disproportionation products. The results are summarized in Table 1.

This interesting disproportionation reaction may proceed through the following pathway. Methyl thiocyanate is initially activated by tributylphosphine to generate salt 1, which, in turn, attacks aromatic aldehyde to form a key intermediate 2. This species 2 then reacts with another molecule of aldehyde with hydride transfer to give 4 with loss of a stable thiol ester 3. The intermediary 4 is immediately converted into arylacetonitrile with the elimination of tributylphosphine oxide.



It is interesting to notice that p-chlorobenzaldehyde reacts with methyl thiocyanate under the same conditions to give 2-cyano-2,3-bis(p-chlorophenyl) oxirane$^2$ in 51 % yield instead of expected disproportionation products.

The most striking characteristic of this reaction is the disproportionation by coupled use of methyl thiocyanate and tributylphosphine as the reagent$^3$. This is compared with the well known Cannizzaro and Tischtschenko reactions which use a metal hydroxide or alkoxide as the catalyst. Another noteworthy fact is that aromatic aldehydes are converted to nitriles with one additional carbon.

We are now examining the scope and limitation of this novel reaction.

## References and Notes

(1) M.Yokoyama, M.Kurauchi, and T.Imamoto, Tetrahedron Lett., 2285 (1981).

(2) White prisms of mp 119-120 °C (recry. from ethanol); nmr ($CDCl_3$) δ 7.48 (s, 4H), 7.45 (s, 4H), 4.15 (s, 1H); mass m/e 289 ($M^+$), 254, 149, 114; ir (KBr) 2230 cm$^{-1}$ (w), 1400 (m), 1095 (s), 830 (s), 805 (s), 720 (m).

(3) The reaction of carboxylic acids with phenyl thiocyanate in the presence of tributylphosphine has been reported in the literature: P.A.Grieco, Y.Yokoyama, and E.Williams, J. Org. Chem., 43, 1283 (1978).

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