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DEOXYBENZOINS FROM AROMATIC ALDEHYDES

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Aromatic aldehydes were easily converted into the corresponding deoxybenzoins by treatment with methyl thiocyanate in the presence of tributylphosphine, followed by addition of sodium hydride.

Recently, we have reported a novel disproportionation reaction of aromatic aldehydes —— that is, the reaction of aromatic aldehydes with methyl thiocyanate in the presence of tributylphosphine afforded both S-methyl thiobenzoates **3** and phenylacetonitriles **4** in good yields.[1] Pursuing the synthetic utility of this reaction, we intended to synthesize cyanodeoxybenzoins **9** from aromatic aldehydes in one pot by condensation of **3** and **4** which were derived from the above disproportionation reaction. However, the result showed that unexpected products, deoxybenzoins **8** were obtained as major products accompanied by minor products of **9**. Now, we wish to describe herein this unprecendented reaction.

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. To the reaction mixture was added sodium hydride (50 % dispersion in oil; 50 mg, 1 mmol) and 2 ml of N,N-dimethylformamide. The resulting solution was stirred for 2 h at room temperature, quenched with dil HCl, and extracted with chloroform. The extract was concentrated and then worked up by preparative TLC upon silica-gel using a 4 : 1 mixture of benzene and hexane as eluant to afford **8** and **9** in 61 % and 5 % yields, respectively.

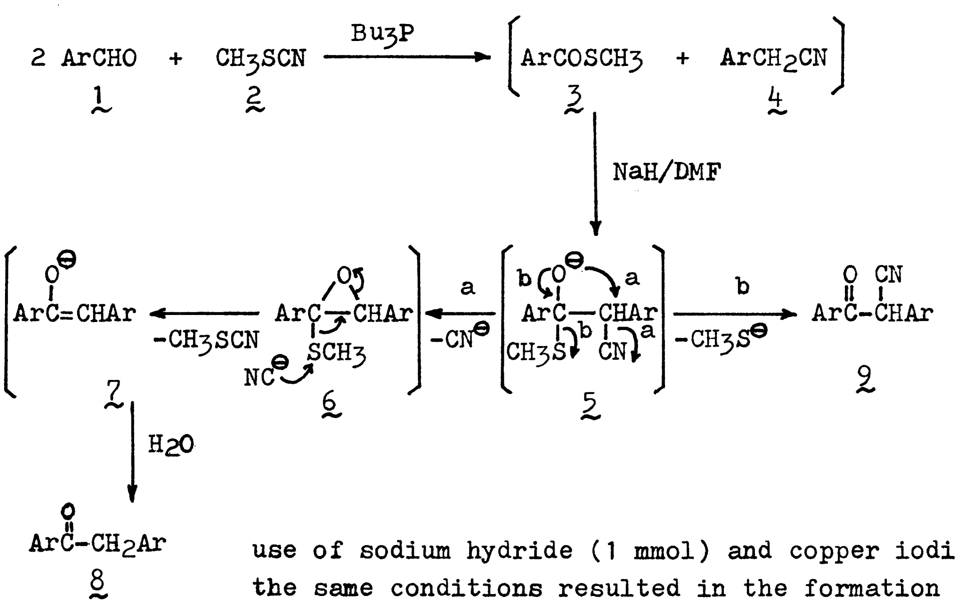
Table 1 Compounds **8** and **9** from Aromatic Aldehydes (yield %[a])

Entry	ArCHO	$ArCOCH_2Ar$ **8**	ArCOCH(CN)Ar **9**
1	Benzaldehyde	61	5
2	p-Tolualdehyde	45	24
3	m-Tolualdehyde	40	— b
4	p-Anisaldehyde	38	— b
5	p-Nitrobenzaldehyde	28	— b
6	Piperonal	— b	31

a) Isolated yields based on the starting aromatic aldehydes. b) Not isolated.

In a similar manner, various aromatic aldehydes were converted into the corresponding **8** and **9**. The results obtained are summarized in Table 1. It was also found that the yields of **8** and **9** were fairly dependent on the reaction temperature.[2] In exceptional case of piperonal (Entry 6) only **9** was obtained.

The reaction can be explained by assuming a key intermediate **5**, which is derived from the condensation of **3** and **4**, disproportionation products of aromatic aldehydes **1**. Compound **8** is formed from **5** via intermediates **6** and **7** with the elimination of methyl thiocyanate,[3] while **5** loses methylthio anion to give **9**, normal condensation product.



Many methods to synthesize deoxybenzoins have appeared in the literature,[4] but the present procedure provides a new method to prepare deoxybenzoins directly from aromatic aldehydes. It is also noteworthy that the coupled use of sodium hydride (1 mmol) and copper iodide (1 mmol) under the same conditions resulted in the formation of dibenzoylphenylmethane.[5]

References

1) M.Kurauchi, T.Imamoto, and M.Yokoyama, Tetrahedron Lett., 22, 4985 (1981).

2) After the addition of sodium hydride, the condensation reaction was carried out at 0 °C to afford **8** and **9** in 50 % and 29 % yields, respectively. In a similar manner, **8** (43 %) and **9** (29 %) were obtained in Entry 2; **8** (35 %) and **9** (31 %) in Entry 3.

3) Compound **9** is not a precursor of **8** because **8** could not be formed by the reaction of **9** with sodium ethylmercaptide.

4) D.A.Ballard and W.M.Dehn, J.Am.Chem.Soc.,54,3969(1932); S.S.Jenkins, J.Am.Chem. Soc.,55,703(1933); C.F.H.Allen and W.E.Barker, Org.Syn.,Coll.Vol.,2,156(1950); F.Krohnke and I.Vogt, Ann.Chim.,589(1954); K.Maeda, I.Moritani, T.Hosokawa, and S.Murakami, Tetrahedron Lett.,797(1974); Y.Sawaki and Y.Ogata, J.Am.Chem.Soc., 99, 6313 (1977); T.Mukaiyama and Y.Echigo, Chem.Lett.,49(1978); G.A.Olah and D.Meidar, Synthesis,671(1978); K.Deuchert, V.Hertenstein, S.Huenig, and G.Wehner, Chem.Ber.,112,2045(1979).

5) The corresponding dibenzoylphenylmethanes were obtained in 37 % yield from benzaldehyde and in 27 % yield from p-methoxybenzaldehyde.

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