The Addition of Nitrotoluenes to Aldehydes

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$$R\text{-}CH_3 + B \rightleftharpoons R\text{-}CH_2^- + BH^+$$

$$R\text{-}CH_2^- + HC(=O)\text{-}R' \longrightarrow R\text{-}CH_2\text{-}CH(O^-)\text{-}R'$$

$$R\text{-}CH_2\text{-}CH(O^-)\text{-}R' + BH^+ \longrightarrow R\text{-}CH_2\text{-}CHOH\text{-}R' + B$$

(R = nitrophenyls)

The addition of 2-nitrotoluene and 4-nitrotoluene to formaldehyde has recently been reported by Wesslén [1] and the reaction between these nitrotoluenes and a variety of aldehydes by the present author.[2] This communication will briefly summarize our successful additions and also point at some of the limitations of the reaction.

Tri-[3] and di-nitrotoluenes [3,4] are known to react with aldehydes under basic conditions. The reactions are believed to involve formation of a carbanion and its addition to the aldehyde: see the right column. 2- and 4-Mononitrotoluenes are less acidic than the di- and tri-nitrotoluenes, and the addition of the mononitro compounds to aldehydes is not realized in conventional solvents. However, the basicity of small anionic bases as hydroxide or alkoxide ions is considerably larger in polar, aprotic solvents as dimethyl sulfoxide (DMSO) and dimethyl formamide (DMF) than in protic, polar solvents.[5] The addition of mononitrotoluenes to various aldehydes was therefore tried in DMSO and DMF. Table 1 shows the results.

Wesslén [1] used 2.8 moles CH_2O per mole nitrotoluene and obtained the corresponding 2-nitrophenyl-1,2-propanediol as the major product. By working with equimolecular amounts of the two reactants, we obtained the 2-nitrophenylethanol as the main product (run 1).

Table 1. $RCH_3 + R'CHO \xrightarrow[DMSO]{B} RCH_2\text{—}CHOHR'$

Run	R	R	Starting concentrations, moles/l DMSO	Yield in per cent	
				Based on starting material	Based on reacted material
1	2-Nitrophenyl	H[a]	5	24[b]	61
2	2-Nitrophenyl	Phenyl	1	31	
3	2-Nitrophenyl	Phenyl[c]	0.18	12	
4	2-Nitrophenyl	4-Methoxy-phenyl	2	24	59
5	2-Nitrophenyl	4-Cyano-phenyl	0.6	18	
6	2-Nitrophenyl	2-Nitro-phenyl	1	9	
7	2-Nitrophenyl	2-Furyl	4.8	53	
8	4-Nitrophenyl	H	7	41	
9	4-Chloro-2-nitrophenyl	H	5	21	
10	4-Chloro-2-nitrophenyl	Phenyl	5	48	

Base: NaOEt in EtOH, concentration 1—5 mole %.

[a] Formaldehyde-source: paraformaldehyde.

[b] 10 % yield (based on reacted material) of 2-(2-nitrophenyl)-1,3-propanediol was also obtained.

[c] In DMF, base concentration 87 mole %.

The relative high yields of 1,2-diarylethanols obtained by reacting nitrotoluenes with benzaldehydes (runs 2—6) are in contrast to the results of Russell and Becker.[6] They reacted aromatic aldehydes with aryl compounds containing active methyl groups and isolated only the corresponding stilbenes. Their reactions were run with more than 100 mole % of base, and this is probably one reason for their high yield of the elimination product (see below).

When 2-nitrotoluene and formaldehyde were reacted with larger amounts of base present, three products were isolated in addition to 2-(2-nitrophenyl)ethanol: sodium formate, methanol, and 2-nitrostyrene. The presence of the two first of these products shows that a Cannizzaro reaction competes with the addition of nitrotoluene to the aldehyde. In the case of nitrotoluene and formaldehyde, the latter reaction is favoured in the competition. However, when 2-nitrotoluene was reacted with the highly reactive 4-nitrobenzaldehyde in DMSO with sodium ethoxide as base, only 4-nitrobenzyl alcohol was isolated together with 4-nitrobenzoic acid, showing the Cannizzaro reaction to be the favoured one in that case.

The 2-nitrostyrene is probably formed from 2-(2-nitrophenyl)-ethanol by a base-catalysed elimination of water. 2-(2-Nitrophenyl)ethanol is stable towards elimination under acidic conditions: After 30 min of reflux with 10 % aqueous H_2SO_4, only starting material (80 %) was isolated.

Attempts to add the nitrotoluenes to aliphatic aldehydes as acetaldehyde or butyraldehyde under these conditions have all failed, due to the rapid aldol condensation of the aldehyde. The addition of 2- and 4-mononitrotoluenes to aldehydes is thus restricted to aldehydes without α-hydrogen atoms and to aldehydes whose Cannizzaro reaction does not compete too well with the nitrotoluene for the base.

The reaction is under further investigation.

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Equilibrium Studies of Polyanions

15. Vanadates in the "Instability Range" at 40°C

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In 1956 Rossotti and Rossotti [1] published an emf study on vanadates in the acidic ionic medium 1 M $(H^+, Na^+)ClO_4$ in which z, the average charge per vanadium atom, and B, the total (analytical) concentration of vanadium, were varied as follows: $+1 \geq z \geq -1.6$ and $0.0025\ M \leq B \leq 0.0200$ M. They could explain their data assuming that the ion VO_2^+, on decreasing $[H^+]$ forms the complexes $H_2V_{10}O_{28}^{4-}$, $HV_{10}O_{28}^{5-}$ and $V_{10}O_{28}^{6-}$.

Later on Brito and Ingri [2] studied the behavior of vanadates in the alkaline medium 0.5 M $Na(Cl^-,OH^-)$ covering the range $-1 \geq z \geq -2$ and 0.6 mM $\leq B \leq$ 80 mM. Using graphical methods they could explain their data assuming the species HVO_4^{2-}, $HV_2O_7^{3-}$, $V_3O_9^{3-}$, and VO_3^-. However, recent calculations [3] of the same data using Letagropvrid [4] indicate that a still better fit is obtained by adding the complexes $V_2O_7^{4-}$, $V_4O_{13}^{6-}$, and $V_4O_{12}^{4-}$; this reduces $\sigma(z)$, the standard deviation, from 0.012 (for 4 species) to 0.009 (for 7 species). Thus it seems that the metavanadates ($z = -1$) are both tri- and tetranuclear.

The present note concerns a similar study carried out a few years ago at 40°C with 0.5 M Na(Cl) medium, in which B ranged from 0.018 M to 0.100 M and z