Tetrahedron Letters,Vol.25,No.43,pp 4989-4992,1984 0040-4039/84 $3.00 + .00
Printed in Great Britain

AIR OXIDATION OF IN SITU OBTAINED CARBANIONS IN KOH-DME-CROWN SYSTEM

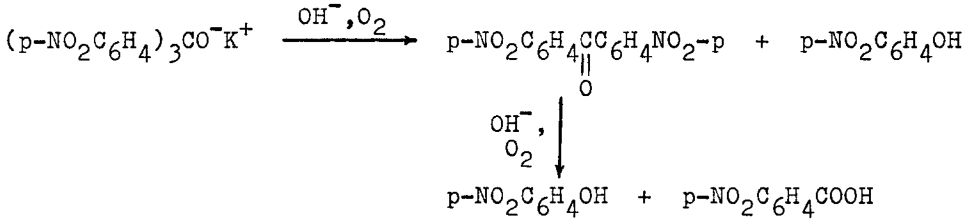
G.A.Artamkina, A.A.Grinfel'd, I.P.Beletskaya*
Department of Chemistry, Moscow State University, GSP, SU-119899, USSR

Summary: KOH(NaOH)-dimethoxyethane-18-crown-6-O_2 system has been found to be efficient for generation and oxidation of carbanions, obtained from monoarylmethanes.

Recently we have shown that carbanions from tri- and diarylmethanes can be generated and oxidized to triarylcarbinols (70-95%) or diarylketones (85-100%) in KOH-DME-18-crown-6 system$^{1)}$.

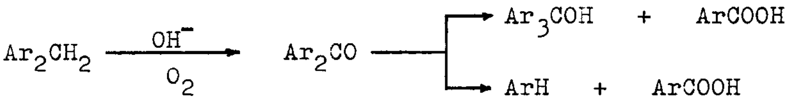
$$Ar_3CH \xrightarrow{OH^-} Ar_3C^- \xrightarrow{O_2} Ar_3COH \qquad (1)$$

An interesting observation was made for the reaction of $(p\text{-}NO_2Ph)_3CH$: the reaction products depended on the duration of the reaction. Prolonged oxidation gave $p\text{-}NO_2PhOH$ and $p\text{-}NO_2PhCOOH$ instead of $(p\text{-}NO_2Ph)_3COH$. In the case of $(p\text{-}NO_2Ph)Ph_2CH$ the products of deeper oxidation were $p\text{-}NO_2PhOH$ and Ph_2CO.



$$\begin{tikzcd}(p\text{-}NO_2C_6H_4)_3CO^-K^+ \arrow[r, "OH^-{,}O_2"] & p\text{-}NO_2C_6H_4\overset{\overset{}{}}{\underset{\|}{\underset{O}{C}}}C_6H_4NO_2\text{-}p + p\text{-}NO_2C_6H_4OH \arrow[d, "OH^-{,}\ O_2"'] \\ & p\text{-}NO_2C_6H_4OH + p\text{-}NO_2C_6H_4COOH\end{tikzcd} \qquad (2)$$

The nature of M in MOH may also affect the degree of oxidation. With LiOH only $(p\text{-}NO_2Ph)_3COH$ can be obtained, while in the presence of KOH deeper oxidation may be achieved. For diarylmethanes the oxidative cleavage of formed diarylketones on prolongation of oxidation leads to arylcarbonic acids and triarylcarbinols or phenols depending on the nature of Ar'.



$$Ar_2CH_2 \xrightarrow[O_2]{OH^-} Ar_2CO \rightarrow \begin{cases} Ar_3COH + ArCOOH \\ ArH + ArCOOH \end{cases} \qquad (3)$$

We have tried to extend this method of oxidation over monoarylmethanes. It turned out that $p\text{-}NO_2PhMe$ was oxidized in KOH(excess)-DME-O_2 system even in the absence of crown, though in its presence the reaction rate was higher. The yield of the reaction strongly depended on the concentration of $p\text{-}NO_2PhMe$. At small concentrations of nitrotoluene ($C < 0.5$ M) p-NO_2PhCOOH can be obtained in an excellent yield (for example, C=0.13 M, 3.5 hrs, 20°, 94%), but at $C > 0.5$ M there are many by-products, and tar. The pressure increase to $P_{O_2}=10$ atm facilitates the reaction which proceeds under such conditions giving high yields of acid in other solvents too even in the absence of crown. The best results were achieved in the mixture of benzene-DMSO (9:1). The yields of p-NO_2PhCOOH at 10 atm, $C_0=0.26$ M in 6 hrs were 75% in DME, 92% in benzene-DMSO and 80% in MeOH. We have shown that p-NO_2PhCHO was oxidized under such conditions very rapidly and with quantitative yield, but p-NO_2PhCH_2OH was oxidized more slowly and the yield was virtually the same as that of p-NO_2PhMe oxidation.

Oxidation of o-NO_2PhMe in KOH-DME system gives no more than 50% of o-NO_2PhCOOH (along with tar) (Table 1). The addition of phase-transfer catalysts (18-crown-6, Bu_4NBr) does not suppress the by-product formation. Moreover, the oxidation rate gradually decreases probably due to the formation of water.

Various m- and p-halogentoluenes (with the exception of p-FPhMe) can be

$$HalC_6H_4CH_3 \longrightarrow HalC_6H_4COOH \qquad (4)$$

oxidized in KOH-DME-Crown system but the reaction rate is slow even at 60°. However, there are no by-products in this case (the conversion of HalPhMe is equal to the yield of HalPhCOOH). The yield was about 20% in 5 hrs (Hal=m-F, m-Cl, m-Br, p-Cl, p-Br), but in 35 hrs p-BrPhCOOH and p-ClPhCOOH were isolated with 73 and 76% yields respectively. Halogentoluenes could not be oxidized without a catalyst.

The results of α-, β- and γ-picoline oxidation are of special interest. Oxidation of β-picoline is the most difficult, which complies with its acidity. The yield of the corresponding acid is only 25% even at 80° in t-BuOK-DME-crown system. But oxidation of γ- and α-picolines gives isonicotinic and picolinic acids with high yields (80-85% in 96 hrs, 25°). It is worth a notice that γ-picoline may be oxidized without a solvent. The rate of the reaction is very low (14% in 18 hrs at 60°), but the selectivity is very high (>90% of the acid).

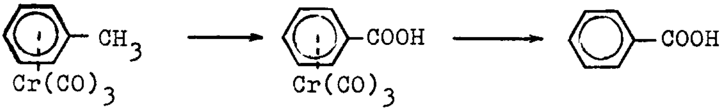
It turned out that even methylnaphthalenes could be oxidized in the KOH-DME-crown system. For α-methylnaphthalenes this fact has only theoretical interest, because the maximum yield of the acid is only 25%, while β-naphthalene carboxylic acid is obtained with high yield (80% in 96 hrs at 20° or 60% in 6-8 hrs at 60°). Thus methylnaphthalenes are the terminal case in the studied series with respect to pK_a for carbanion generation in the proposed system. Accordingly toluene cannot be oxidized under such conditions, only traces of benzoic acid found after prolonged heating. We succeded in toluene

Table 1. Oxygen oxidation of monoarylmethanes in alkali media

Hydrocarbon	Concentration M	T° C	Solvent	Alkali	Catalyst	Time h	Product	Yield, %
p-$NO_2C_6H_4CH_3$	0.127	20	DME	KOH	18-c-6	3.5	p-nitrobenzoic acid	94
-"-	0.25	20	C_6H_6-DMSO	KOH	-	6	-"-	92$^{a)}$
-"-	0.25	20	CH_3OH	NaOH	-	6	-"-	80$^{a)}$
o-$NO_2C_6H_4CH_3$	0.127	20	THF	NaOH	18-c-6	5	o-nitrobenzoic acid	50$^{b)}$
γ-picoline	0.5	25	DME	KOH	18-c-6	96	isonicotinic acid	80
-"-	-	60	γ-picoline	KOH	-	18	-"-	90$^{c)}$
α-picoline	0.5	25	DME	KOH	18-c-6	96	picolinic acid	85
β-picoline	0.5	60	DME	t-BuOK	18-c-6	12	nicotinic acid	25
β-methylnaphthalene	0.5	70	DME	KOH	18-c-6	6	β-naphthoic acid	60
α-methylnaphthalene	0.5	60	DME	KOH	18-c-6	96	α-naphthoic acid	25

a) Oxygen pressure - 10 atm.
b) Conversion 53%.
c) Conversion 14%.

oxidation having transformed it into a chromtricarbonyl complex.



(5)

Benzoic acid (70%) and its complex with $Cr(CO)_3$ (17%) were isolated from the reaction mixture after 25 hrs at 60° (the overall yield was 87%). The latter compound is easily decomposed during extraction (without oxidizing agent).

As can be seen from the scheme deprotonation or oxidation of generated carbanions may be the limiting stage of the process. In most investigated

$$RH \xrightleftharpoons{B} R^- + BH^+ \xrightarrow{O_2} R'COOH \qquad (6)$$

reactions (probably with the exception of p- and o-NO_2PhCH_3) the first stage is the rate-determining one. Though the concentration of carbanions is very small, they are easily oxidized due to their high nucleophilicity.

Probably in some cases this method of oxidation of CH-acids via carbanions will have clear advantages because of its simplicity.

Obviously, the intermediate products in the monoarylmethane oxidation should be the corresponding alcohols and aldehydes. However, no traceable amounts of them were detected during analysis of the reaction mixtures, which pointed to their fast conversion into acids. Since oxygen oxidation of aldehydes and alcohols in alkali media is a poorly investigated field, we studied it in the KOH - DME system.

It turned out that aromatic aldehydes and alcohols (and also alcohols, giving non-enolizating aldehydes, such as neopentyl alcohol) were easily oxidized in the KOH - DME system by oxygen at 20°, giving the corresponding acids with nearly quantitative yields (Table 2). It was shown that under the studied conditions aldehydes easily underwent the Cannizzaro reaction; possibly the aldehyde oxidation proceeded via fast Cannizzaro reaction with subsequent oxygen oxidation of the formed alcohol.

Table 2. Oxidation of aromatic aldehydes and alcohols in the KOH-DME-O_2 system at 20°C

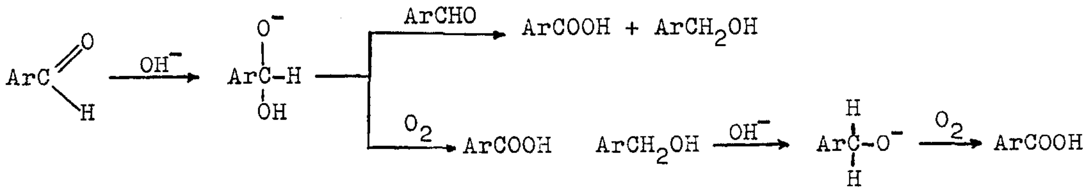
№	Substrate	Reaction time, hrs	Acid yield, %
1	PhCHO	3 - 3.5	100
2	$p\text{-}NO_2C_6H_4CHO$(1)	4	92 - 96
3	$m\text{-}NO_2C_6H_4CHO$	4	94 - 96
4	$p\text{-}CH_3OC_6H_4CHO$	4	95 - 97
5	$p\text{-}BrC_6H_4CHO$	4	93 - 96
6	$PhCH_2OH$	3 - 3.5	100
7	$p\text{-}CH_3OC_6H_4CH_2OH$	6 - 8	96
8	$p\text{-}NO_2C_6H_4CH_2OH$	8	60*
9	$p\text{-}NO_2C_6H_4CH_2OH$+(1) /1:1/	8	75
10	$p\text{-}NO_2C_6H_4CH_2OH$+(1) /1:2/	8	95
11	$(CH_3)_3CCH_2OH$	12 - 14	80 - 85
12	Ph_2CHOH	0.5-1.5	90 - 95**

*) The reaction is accompanied by tar-formation.

**) Benzophenone is the reaction product.

***) Addition of (1) prevents tar-formation.

The oxidation probably involves formation of alkoxide or tetrahedral intermediates at the key stage, which are oxidized by oxygen or aldehyde molecule.



REFERENCES

1. G.A.Artamkina, A.A.Grinfel'd, I.P.Beletskaya, Izv.Akad.Nauk SSSR, ser. khim., 1983, № 2, 383-391.

(Received in Russia 19 June 1984)