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KO$_2$/crown ether: a novel catalytic system for the hydrosilation and Tishchenko reaction of aromatic aldehydes

Franck Le Bideau,[a] Thibaud Coradin,[b] Didier Gourier,[b] Josette Hénique[a]
and Edmond Samuel[a],*

[a]*UMR 7576 CNRS, Ecole Nationale Supérieure de Chimie de Paris, 11 rue Pierre et Marie Curie,
75231 Paris Cedex 05, France*
[b]*UMR 7574 CNRS, Ecole Nationale Supérieure de Chimie de Paris, 11 rue Pierre et Marie Curie,
75231 Paris Cedex 05, France*

Abstract

A new catalytic system KO$_2$/18-crown-6 ether is reported to lead, in the presence of Et$_3$SiH, to hydrosilation and Tishchenko reaction of aromatic aldehydes. The nature of the products obtained are shown to depend on aldehydes and experimental conditions. © 2000 Elsevier Science Ltd. All rights reserved.

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It is widely known that the superoxide ion [O$_2$]$^-$ exhibits an exceptional reactivity both in the fields of chemistry and biology.[1] However, to the best of our knowledge, its participation in catalysis has been mentioned only at one occasion.[2]

In this work we show that KO$_2$ in the presence of 18-crown-6 ether[3] is an active catalyst for the hydrosilation of aromatic aldehydes and for promoting the Tishchenko reaction.[4]

In the presence of triethylsilane and catalytic amounts of KO$_2$ and 18-crown-6, various aromatic aldehydes **1** were converted to a mixture of products **2** and **3** (Scheme 1). Compound **2** is the hydrosilation product while **3** is formed from the aldehyde by the Tishchenko reaction.
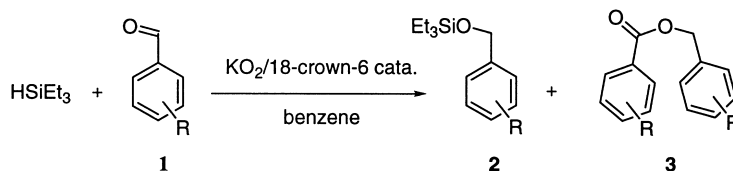
Scheme 1.

* Corresponding author. Tel: 33 1 44 27 66 98; fax: 33 1 43 26 00 61; e-mail: samuel@ext.jussieu.fr

The reaction of aldehyde **1a** (*p*-anisaldehyde) (Table 1) has been studied under various experimental conditions. We found that KO_2/18-crown-6 (14%/7%) were the optimal proportions of catalyst components to carry the reaction to completion (entries 1 and 2). At room temperature, the reaction time is 20 h while at 40°C the same amount of products is obtained after only 1 h (entries 2 and 3). Increasing the silane amount to 1.5 equivalents relative to the aldehyde led to the hydrosilylated product exclusively (entries 4 and 5). Hexane and THF can be used instead of benzene without significant change in the product distribution (entries 6 and 7).

Table 1
Reactivity of *p*-anisaldehyde under various experimental conditions

entry	Et₃SiH	KO₂/18-crown-6	solvent	Cond.	Conc.	R = OMe	
						2[a]	**3**[a]
1[b]	1 eq.	7%/7%	benzene	r.t. 20 h.	2M/paa	62	16
2	idem	14%/7%	idem	idem	idem	72	28
3	idem	idem	idem	40°C 1 h.	idem	75	25
4	idem	idem	idem	idem	4M/paa	86	14
5	1.5 eq.	idem	idem	idem	idem	100	0
6	idem	idem	THF	idem	idem	100	0
7	idem	hexane	hexane	idem	idem	95	5

a) *Ratio of product based on the ^{1}HNMR of the crude mixture*

b) *Unreacted starting material : 22%.*

The catalytic reaction was also examined using different substrates **1** (Table 2) and triethylsilane (1.5 equiv.) in the presence of KO_2 (14%) and 18-crown-6 (7%) in benzene. After 1 h at 40°C, compounds **2** and **3** were isolated by flash chromatography (entries 1–5) or detected by the ^{1}H NMR spectra of the crude reaction mixture (entries 6 and 7). The results show that compounds having an electron withdrawing group on the aromatic ring (entries 6 and 7) are not reactive and only small amounts of products **2** and **3** were observed. The Tishchenko process is favorable when the aromatic ring has a stronger electron withdrawing group (entries 4–6) giving **3** as the predominant product with benzaldehyde and *m*-anisaldehyde.

Under the same conditions, pivalaldehyde gave 78% yield of the compound resulting exclusively from hydrosilation. For saturated aldehydes possessing an α hydrogen, we observed an aldol

Table 2
Influence of the aromatic substituent R on the process

entry	1	R	conditions	2	3
1	1b	p-NMe$_2$	Isolated yields	85	0
2	1a	p-OMe	idem	90	0
3	1c	o-OMe	idem	86	0
4	1d	m-Me	idem	56	32
5	1e	H	idem	29	69
6	1f	m-OMe	^{1}HNMR, SM. left	1	2
7		o-Me, p-Br, p-NO$_2$	idem	traces	traces

reaction leading to a conjugated aldehyde. These last results confirm the strong basic character of the superoxide ion.[1]

Different silanes (Ph$_3$SiH, Ph$_2$CH$_3$SiH, C$_6$H$_{11}$(CH$_3$)$_2$SiH) were also used under the above reaction conditions and gave similar results judging from the ^{1}H NMR spectra of the crude reaction mixtures. The reactivity of dimethylethoxysilane ((CH$_3$)$_2$(CH$_3$CH$_2$O)SiH) in the presence of catalytic amounts of KO$_2$ (14%) and 18-crown-6 (7%) was examined in situ in deuterated benzene. Two products resulting from redistribution,[5,6] dimethylsilane ((CH$_3$)$_2$SiH$_2$) and dimethyldiethoxysilane ((CH$_3$)$_2$(CH$_3$CH$_2$O)$_2$Si), were observed by ^{1}H NMR spectra of the crude reaction mixture with no starting material left.

Replacing KO$_2$ with KOH yields essentially the same products. This can consequently be explained in terms of the anionic activation of the Si–H bond by different salts as mentioned by Corriu[7] or Hosomi.[8] However, Corriu reported more drastic reaction conditions (80°C in DMF) while Hosomi was only successful with alkoxysilanes which are known to be more reactive than the corresponding trialkylsilanes used in this work. Thus it can be admitted that the Si–H bond is weakened by anionic coordination of the catalyst (O$_2^-$ or OH$^-$) to give 4 (Scheme 2). The activated silane 4 would then readily rearrange with the aldehyde to give 5. Two pathways are conceivable at this stage. In path a, the hydrosilylated product 2 would be obtained directly from 5. In path b, a cascade of two rearrangements via 6 and 7 would lead to compound 3.

Further work in this area is being pursued with a view to apply the above reaction to other substrates.

Typical procedure (Table 2, entry 1): Triethylsilane (3 mmol) was added, at room temperature, to a solution of 4-dimethylaminobenzaldehyde (2 mmol) and KO$_2$/18-crown-6 ether (14%/7%) in benzene (1 mL). After 30 min at 40°C, the reaction mixture was concentrated. The residue was flash chromatographed, affording the corresponding hydrosilylated product 2 [(petroleum ether:dichloromethane (50:50)].

^{1}H NMR (200 MHz, CDCl$_3$) δ 7.28 (2H, d, *J* 8.0 Hz), 6.77 (2H, d, *J* 8.0 Hz), 4.69 (2H, s), 2.98 (6H, s), 1.00 (9H, t, *J* 2.0 Hz), 0.67 (6H, q, *J* 2.0 Hz); ^{13}C NMR (50 MHz, CDCl$_3$) δ 149.9, 129.3, 127.7, 112.5, 64.7, 40.7, 6.7, 4.5; IR (neat): 2954, 2907, 2876, 1617, 1524, 1549, 1348, 1072, 809,
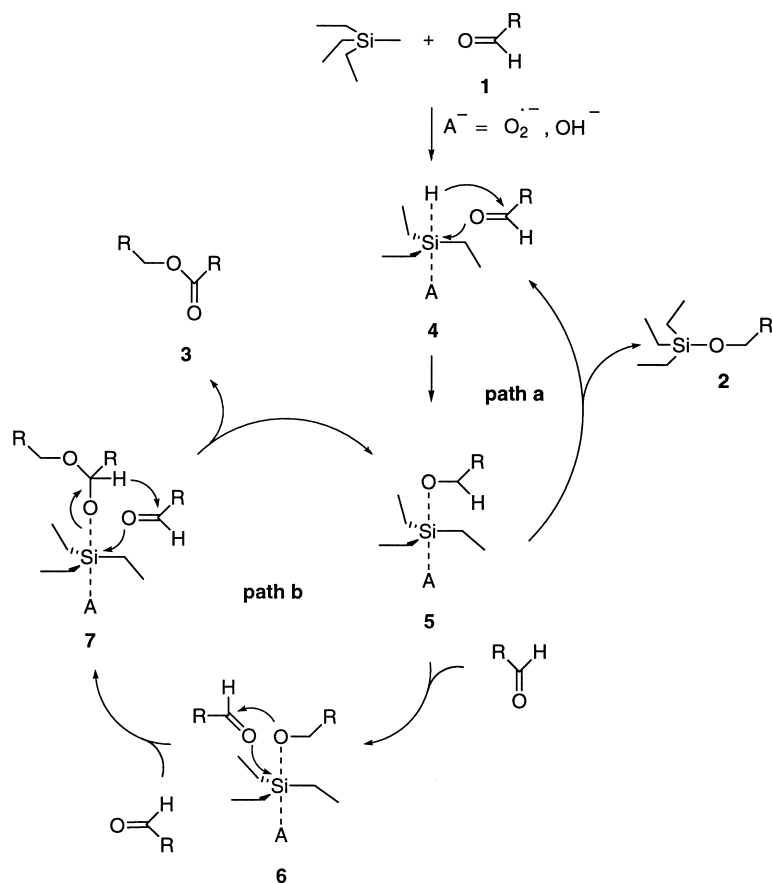
Scheme 2.

744 cm^{-1}; MS 265, 134, 118, 90, 59 (*m/z*). Anal. calcd for C$_{15}$H$_{27}$NOSi: C, 67.87; H, 10.24; N, 5.27. Found: C, 67.74; H, 10.45; N, 5.26.

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