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Indirect Oxidative Deamination of Benzylamines to Benzaldehydes

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INDIRECT OXIDATIVE DEAMINATION OF BENZYLAMINES TO BENZALDEHYDES

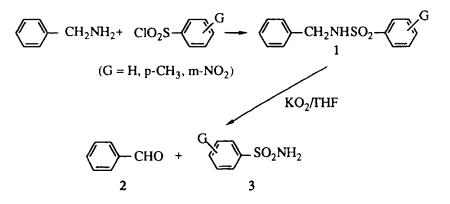
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Abstract: Treatment of N-benzylarenesulfonamide (1) with potassium superoxide yields benzaldehyde (2) and arenesulfonamide (3).

Deamination of benzylamine to benzaldehyde is achieved, in most cases, indirectly using various oxidants to make corresponding imines which could then be hydrolyzed in acidic conditions. ¹⁻³ We report a simple and convenient indirect method for the conversion of benzylamine to benzaldehyde (Scheme 1). As shown in Scheme 1, N-benzylarene-sulfonamide (1)⁴ prepared from benzylamine and arenesulfonyl chloride gives benzaldehyde (2), an oxidatively cleaved product, and arenesulfon-amide (3) in the presence of potassium superoxide ⁵⁻⁷ at room temperature.

Scheme 1



A general procedure of the present methodology is as follows: In a round-bottomed flask (50 mL) containing dry tetrahydrofuran (25 mL), equipped with a condenser connected to gas bubbler and a magnetic stirrer, potassium superoxide (510 mg, 57 mmol) was introduced. While passing oxygen-free nitrogen from the bottom of the solution, N-benzylbenzene-sulfonamide (470 mg, 19 mmol) was added. Soon vigorous formation of oxygen⁸ ensued for about 15 seconds and then subsided. During the whole reaction period, no liberation of heat was observed. As the reaction proceeded, concentration of both benzaldehyde and benzenesulfonamide ⁹ increased at the expense of N-benzylbenzenesulfonamide, determined by G. C. and ¹H NMR spectra.

Two points can be noted from the results of this reaction (in Table1). One is that the present method (Scheme 1) is limited and unique only to N-benzylarenesulfonamides (entry 1-6, Table 1) in reaction with

Entry	y Substrate	Product	Reaction Time(hr)	Yield* (%)
1	SO2NHCH2	PhCHO	24	88
2	H ₃ C- SO ₂ NHCH ₂	PhCHO	24	90
3	O ₂ N SO ₂ NHCH ₂	PhCHO	24	19
4	H ₃ C-CH ₂ NHSO ₂	p-CH ₃ -C ₆ H₄CHO	24	83
5	H ₃ CO-CH ₂ NHSO ₂ -C	p-OCH ₃ -C ₆ H ₄ CH0) 24	84
6	O ₂ N-CH ₂ NHSO ₂	p-NO ₂ -C ₆ H ₄ CHO) 24	85
7	SO ₂ NH -		20	0
8	SO ₂ NH(CH ₂) ₅ CH ₃		20	0
9	CONHCH ₂		20	0
10	CH ₂ NHCH ₂		8	0

Table 1. Synthesis of Benzaldehyde from the Reaction of N-Benzylbenzenesulfonamide and Related Compounds with KO₂

*: Determined by either G. C. or ¹H NMR spectrum.

potassium superoxide to give benzaldehyde and arenesulfonamide. Other compounds such as N-phenylbenzenesulfonamide (entry 7), N-hexylbenzenesulfonamide (entry 8), N-benzylbenzamide (entry 9), and dibenzylamine (entry 10) are inert in these reaction conditions. The other is the facile and unusual N-C bond cleavage of compound 1 by potassium superoxide. It is described in the literature that structure of compound 1 is quite stable to acid or base. In forcing conditions, however, S-N bond is usually cleaved rather than N-C bond. ^{10,11} In conclusion the unusual cleavage of N-benzylarenesulfonamide (1) by potassium superoxide (Scheme 1) presents an alternative methodology for the indirect oxidative deamination of benzylamine.

Mechanistic view points of this method are currently under investigation.

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