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Alumina as Reagent. The One-step Conversion of Benzyl Chloride and Bromide into Dibenzyl Ether

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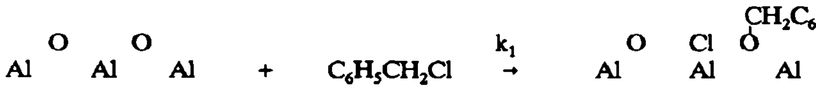
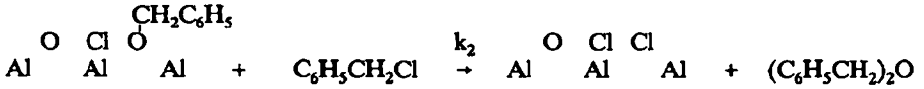
Abstract: Benzyl chloride and bromide react with alumina via a two-step mechanism to produce dibenzyl ether in good yield. Chemisorbed benzyloxy is the other major product of the reactions.

The surfaces of inorganic oxides such as alumina, silica gel, clays, and zeolites provide unusual environments for chemical transformations.[1] Alumina is particularly interesting in this regard because its surface is polar[2] and contains immobile, catalytic Brønsted and Lewis acidic (OH^-, Al^{+3}) and basic ($\underline{O}H^-$, O^{-2}) sites whose composition and nature can be altered by activation by heating.[3] Manifestations of these catalytic groups are numerous.[2b,4] Alumina also serves as a support for other reagents undergoing chemical transformations.[1a,b,5] Surprisingly, alumina may function as a reagent, providing both OH^- and O^{-2} in the conversion of benzyl chloride and bromide to dibenzyl ether by the two-step mechanism described in equations 1 and 2 (for O^{-2}).



$$\begin{array}{ccccc} & O & & O & \\ Al & & Al & & Al \end{array} + C_6H_5CH_2Cl \xrightarrow{k_1} \begin{array}{ccccc} & O & & Cl & \overset{CH_2C_6H_5}{O} \\ Al & & Al & & Al \end{array} \qquad (1)$$



$$\begin{array}{ccccc} & O & & Cl & \overset{CH_2C_6H_5}{O} \\ Al & & Al & & Al \end{array} + C_6H_5CH_2Cl \xrightarrow{k_2} \begin{array}{ccccc} & O & & Cl & Cl \\ Al & & Al & & Al \end{array} + (C_6H_5CH_2)_2O \qquad (2)$$

When a solution of benzyl chloride in hexanes was treated with unactivated Brockmann neutral alumina, which contains a surface layer of hydroxyl groups, for 17 hours at 25°, dibenzyl ether was formed in 69% yield (Table I, entry 1). HCl was also generated in this reaction, but little benzyl alcohol was formed. As expected for the two-step mechanism, there was a corresponding weight increase of the alumina due to deposition of Cl^- and benzyl (as $C_6H_5CH_2O$) on the surface.[6-8] Benzyl bromide also yielded dibenzyl ether on unactivated alumina (Table I, entry 5). The reaction of benzyl chloride on alumina previously activated at 400°, which contains a mixture of hydroxyl and oxide groups on its surface, also occurred (Table I, entry 8), but the yield of dibenzyl ether was considerably reduced and the proportion of surface-bound benzyloxy was considerably increased. Solvent did not seem to play a pivotal role in the reaction because it worked equally well when run in the absence of solvent (Table I, entries 3 and 4; compare to entry 1), while increased reaction temperature, unexpectedly, had a small, adverse effect on the formation of product (compare entries 1 and 6, Table I, for example). Finally, the formation of product was very fast at short reaction times, but slowed considerably at longer reaction times. This was undoubtedly due to the change in the nature of the surface during the course of the reaction. The surface area decreased by over 30% for the benzyl chloride reaction, for example, while it decreased by 80% for the benzyl bromide reaction.[9]

Table I. The Effect of Reaction Parameters on the Conversion of Benzyl Chloride into Dibenzyl Ether

entry	alumina[a,b]	reaction temperature(°C)	reaction time(hr)	R[c]	$[C_6H_5CH_2Cl]^d$	yield	corrected yield[e,f]
1	UA	25	17	.69	.33	48%	69%
2	UA	25	24	.63	.33	47%	72%
3	UA	25	3	.64	no solvent	37%	67%
4	UA	25	19	.64	no solvent	53%	74%
5[g]	UA	25	25	.46[h]	no solvent	39%	42%
6	UA	63	18	.70	.24	41%	54%
7	UA	85	71	.66	.30	16%	64%
8	A	25	23	.65	.32	18%	37%

(a) Brockmann neutral, activity 1 alumina. (b) UA = unactivated; A = activated at 400°C. (c) R = mmol of $C_6H_5CH_2Cl$/g of Al_2O_3. (d) In hexanes. (e) Based on recovered, unreacted $C_6H_5CH_2Cl$. (f) "Missing" material is due to chemisorbed $C_6H_5CH_2O$. (g) Reaction of $C_6H_5CH_2Br$. (h) mmol of $C_6H_5CH_2Br$/g of Al_2O_3.

Benzyl bromide is solvolyzed more rapidly in solution than is benzyl chloride,[10] but that was not the case on alumina.[11] On an alumina of given activity, benzyl bromide and chloride had comparable reactivity (Table II). The activity of the alumina did have a profound effect on the reactions, however. As the activity of the solid went up, the rate of reaction went down significantly for both substrates; of the benzyl substrate which had reacted, most remained chemisorbed to the surface in the form of benzyloxy. These effects correlate with the relative percentages of hydroxyl and oxide on the surface: when more oxide is present on the surface, the overall rate of reaction is smaller and the amount of chemisorbed $C_6H_5CH_2O^-$ is larger.

Other substrates reacted with alumina as well. *p*-Methoxybenzyl chloride reacted instantly with unactivated alumina, as evidenced by the appearance of a red color whose intensity was proportional to external HCl pressure.[12] Benzyl alcohol, which has a poor leaving group, was inert on unactivated alumina, but did yield dibenzyl ether under photochemical activation (eq. 3).[13] CCl_4, which is known to yield a variety of gaseous products when treated with alumina at elevated temperatures,[14] also reacted with alumina at room temperature[4a] in direct proportion to the oxide concentration on the surface. As the reacted CCl_4 was completely chemisorbed to the surface, the weight gain of the solid represents a simple method to measure oxide concentration.

Table II. Relative Reactivities of Benzyl Chloride and Bromide on Alumina[a]

Al_2O_3 activation temperature(°C)	relative % of surface nucleophiles[b]		benzyl halide (x=Cl or Br)	yield	corrected yield[c,d]
	OH	O			
100	93	7	Cl	23%	33%
			Br	21%	32%
200	76	24	Cl	10%	23%
			Br	13%	27%
700	20[e]	80[e]	Cl	3%	6%
			Br	5%	9%

(a) 2.50 mmol of benzyl halide/g of Al_2O_3 for 3 hr. at 25°C. (b) From reference 3. (c) Based on recovered, unreacted benzyl halide. (d) "Missing" material is due to chemisorbed $C_6H_5CH_2O$. (e) Extrapolated value.

$$\text{No Reaction} \xleftarrow{\Delta} C_6H_5CH_2OH \xrightarrow{h\upsilon} (C_6H_5CH_2)_2O \qquad (3)$$

Although O^{-2} and hydroxide behaved as nucleophiles in these reactions, their nucleophilicities must be moderated by coordination to surrounding aluminum ions. When surface O^{-2} and OH^- compete with other nucleophiles on the surface such as S^{-2},[5] which is a superior nucleophile, and alcohols,[15] which are modest nucleophiles, the latter nucleophiles react exclusively with benzyl chloride.

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6. H (as HCl) and O (as dibenzyl ether) were also lost from the surface.
7. Good material balances were obtained for these reactions.
8. A variety of techniques were used to characterize the surfaces: a) The weight gains were not due to adsorbed $C_6H_5CH_2Cl$, $(C_6H_5CH_2)_2O$ or $C_6H_5CH_2OH$ which were easily extracted from the surfaces. b) The surface areas of the alumina (151 m^2/g) were significantly reduced when treated with $C_6H_5CH_2Cl$ (101 m^2/g) and $C_6H_5CH_2Br$ (27 m^2/g). c) The acidity of the alumina [activated at 400° ($-3.0 \leq H_o \leq -8.2$)] was reduced when treated with $C_6H_5CH_2Br$ ($-8.2 \leq H_o \leq -13.2$) but remained the same when treated with $C_6H_5CH_2Cl$. d) The $C_6H_5CH_2Cl$- and $C_6H_5CH_2Br$- treated aluminas yielded HCl and HBr when treated with H_2O, as expected if AlCl and AlBr bonds are formed in reactions 1 and 2. e) Reflectance FTIR of a $C_6H_5CH_2Cl$-treated alumina after removal of $C_6H_5CH_2Cl$ and $(C_6H_5CH_2)_2O$ showed bands at 1497, 1454 and 1368 cm^{-1}. These bands are those expected for a benzyloxy species. f) ^{13}C SS NMR (1200 acquisitions) of $C_6H_5CH_2Cl$- treated alumina after removal of $C_6H_5CH_2Cl$ and $(C_6H_5CH_2)_2O$, both of which gave sharp resonances under these conditions, yielded a noisy spectrum with broad resonances at δ 158.9, 163.9, 170.0, 191.6 and 201.2. These bands may be indicative of a benzyloxy group having hindered rotation due to complexation of the aryl ring to an electron deficient Al ion.
9. Above 100°, the reaction became increasingly homolytic. By 143°, the reaction was completely homolytic in the presence or absence of O_2 affording: benzyltoluenes, diphenylmethane, benzaldehyde and 1,2-diphenylethane. No reaction occurred in the absence of alumina.
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11. If a solvolysis reaction is a substitution reaction in which the reaction medium (solvent) is also the nucleophile, the term is applicable to reactions described here.
12. The color is likely due to the reaction of HCl with chemisorbed *p*-$MeOC_6H_4CH_2O^-$.
13. A degassed sample in a quartz tube afforded 4% of dibenzyl ether (uncorrected) after 5 hr irradiation (Rayonet Reactor; 2537 Å lamps).
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