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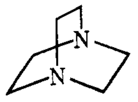
Communications

Halogen–Amine Complexes in Chemical Synthesis. 1. The Oxidation of Alcohols by 1,4-Diazabicyclo[2.2.2]octane·$2Br_2$ Complex

Summary: 1,4-Diazabicyclo[2.2.2]octane·$2Br_2$ complex employed with additional amine shows promise as a new reagent to oxidize benzyl alcohol to benzaldehyde in high yields, and potential to oxidize secondary alcohols to ketones in the presence of primary alcohols.

Sirs: We are initiating a study of the properties of halogen–amine complexes as reagents in chemical synthesis. In particular, we are examining the Br_2 complexes of 1,4-diazabicyclo[2.2.2]octane (**1**, commonly called Dabco) and similar bicyclic tertiary amines in the quinuclidine (**2**) system.[1]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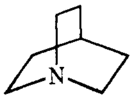
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The Dabco·$2Br_2$ complex first reported by Herrick[2a] is readily prepared by combining carbon tetrachloride solutions of the amine and bromine.[2b] This complex is a nonhygroscopic yellow solid that is very stable "on the shelf". It decomposes at 155–160 °C. Unlike the well-known pyridine perbromide complex described by Williams[3] as "a red crystalline solid, decomposing slowly in moist air and smelling strongly of bromine", the Dabco·$2Br_2$ complex is not affected by ordinary exposure to light, air, or water, and has no offensive odor of bromine or amine. Thus, Dabco·$2Br_2$ is a source of active

Table I. Alcohol Oxidation

	Reactants, mmol			Conditions			Products				
							mmol				
Entry	Dabco·$2Br_2$ complex	Dabco	Alcohol	Solvent[a]	Reaction temp, °C	Reaction time, h	Recovered alcohol	Product, aldehyde or ketone	Product + recovered alcohol	Material balance	% yield
					Benzyl Alcohol						
1	0.499	1.505	2.00	CH_3CN	25	52	1.00	0.81	1.81	91	81
2	0.501	1.502	1.98	CH_3CN	50	6.5	1.35	0.86	2.21	112	86
3	0.498	1.512	1.04	CH_3CN	50	89	0.41	0.56	0.97	93	56
4	0.478	1.523	1.98	CH_2Cl_2	Reflux	11	1.07	0.93	2.00	101	97
5	0.501	1.512	2.04	CH_2Cl_2	Reflux	18	1.16	0.96	2.12	104	96
					Cyclohexanol						
6	0.508	0.529	2.07	CH_3CN	50	3.0 (15.5)[b]	1.31 (1.26)	0.72 (.71)	2.03 (1.97)	98 (95)	71 (70)
7	0.557	1.539	2.19	CH_3CN	50	2.7	1.59	0.71	2.30	105	64
8	0.500	1.615	2.07	CH_3CN	25	69.5	1.83	0.17	2.00	97	17
9	0.498	0	2.02	CH_3CN	50	3.0	1.60	0	1.60	79	0
					Cyclopentanol						
10	0.499	0.476	2.09	CH_3CN	50	3.0	1.55	.52	2.07	100	52
					2-Pentanol						
11	0.513	1.630	2.01	CH_3CN	50	16.0	1.35	0.26	1.61	80	26
12	0.504	0.589	2.20	CH_3CN	50	3.0	1.76	0.36	2.12	96	36
					1-Heptanol						
13	0.504	0.506	2.02	CH_3CN	50	3.2	1.54	0.09	1.63	81	10
					1-Butanol						
14	0.499	0.557	1.99	CH_3CN	50	3.0	1.43	0.11	1.54	77	11
15	0.505	1.526	2.05	CH_3CN	50	19.3	1.22	0	1.22	59	0

[a] The volume of solvent was 2 mL for all reactions except for the benzyl alcohol runs where 4 mL was used. [b] Values in parentheses refer to the same reaction mixture after a longer reaction time.

bromine that can be manipulated conveniently, precisely, and safely.

The high stability of Dabco·$2Br_2$, however, is accompanied by a low solubility in a variety of solvents and a low reactivity of its bromine. This undoubtedly accounts for the fact that this complex has not been explored as a new reagent with general application in chemical synthesis. We have found, however, that, if Dabco·$2Br_2$ is employed with additional Dabco the reactivity of the bromine is enhanced, perhaps as a result of conversion of Dabco·$2Br_2$ into a more soluble species, or one that contains a more active form of bromine.[4] Thus, we are able to report our preliminary results for the oxidation of alcohols by Dabco·$2Br_2$ in Table I. Table I reflects the optimum conditions for oxidations found thus far (see supplementary material).

The alcohol oxidations were planned on the assumed stoichiometries of eq 1 or 2 illustrated by the oxidation of benzyl alcohol.

$$2C_6H_5CH_2OH + \text{Dabco}\cdot 2Br_2 + 3\text{Dabco} = 2C_6H_5CHO + 4\text{Dabco}\cdot HBr \quad (1)$$

$$2C_6H_5CH_2OH + \text{Dabco}\cdot 2Br_2 + \text{Dabco} = 2C_6H_5CHO + 2\text{Dabco}\cdot 2HBr \quad (2)$$

For these exploratory studies the oxidations were carried out with 100% excess alcohol. Thus, with Dabco·$2Br_2$ as the limiting agent, an equimolar mixture of unreacted alcohol and product aldehyde or ketone should be obtained for a 100% yield. A material balance was calculated as the percent of the starting alcohol accounted for as product or unreacted alcohol. Generally, the material balance is very good which means that few competing reactions are occurring. Thus, in spite of the slow rates, the reaction yields mainly one product. This is particularly important in deciphering the mechanism of these reactions and other oxidations of alcohols by active bromine.[5] The oxidation of secondary alcohols by bromine in the presence of silver salts gives ketones and/or tetrahydrofurans depending on the reaction conditions.[6] In our studies, no GLC product peaks other than the expected aldehyde or ketone were observed; however, we have not yet rigorously determined that small yields of other products are observable under our conditions of analysis. The very low yields of aldehydes from the primary alcohols suggest that Dabco·$2Br_2$ with added Dabco can be used as a selective oxidizing agent for secondary and benzylic -OH groups.[7,8]

Materials. All alcohols, solvents, and bromine were analytical reagents or spectroquality materials and were used without further purification. Dabco, obtained as a gift from The Chemical Additives Division of Air Products and Chemicals, Inc., was purified by distillation with benzene to remove water, precipitation of Dabco by addition of hexane to the dry benzene residue, followed by recrystallization two or three times from dry benzene/hexane. Dabco·$2Br_2$ was prepared in stock quantities by adding a solution of 10 mL of Br_2 (5% excess) in 200 mL of CCl_4 dropwise over a period of 1–2 h to a vigorously stirred solution of 10.4 g of Dabco in 200 ml of CCl_4. After the mixture stirred for 30 min, the complex was collected in a sintered-glass funnel, washed twice with CCl_4, and placed on a watch glass to dry for 24 h. The complex is very insoluble in a variety of common solvents and cannot be recrystallized. No special precautions are necessary to handle or store the complex.

General Procedure. To a mixture of 0.5 mmol of Dabco·$2Br_2$ and 1.5 mmol of Dabco was added 2.0 mmol of alcohol and 2.0 mL of solvent. The reaction flask was fitted with a serum cap for low temperature runs and a reflux condenser with $CaCl_2$ drying tube for high temperature runs. The flask was wrapped with aluminum foil to keep out light. Under constant magnetic stirring at the temperature indicated by Table I, the reaction was allowed to proceed until the yellow color of the solid complex changed to the white color of the solid Dabco hydrobromide.[9] Then, at room temperature the reaction mixture was filtered through a sintered-glass funnel to collect the Dabco hydrobromide solid which was washed with solvent. To the filtrate was added an internal standard (1.0 mmol of chlorobenzene or bromobenzene) and solvent to afford a 10-ml total volume. This solution was then analyzed by GLC for unreacted alcohol and product ketone or aldehyde by the usual procedure which involves relative peak areas, an internal standard, and a standard solution.

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Supplementary Material Available. Thirteen additional entries to Table I including results for other solvents (C_6H_6, $CHCl_3$, CCl_4, CH_3OH) and additional reactions in CH_3CN and CH_2Cl_2 at different temperatures and molar ratios of reactants (1 page). Ordering information is given on any current masthead page.

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Acidities of Anilines and Toluenes

Summary: The p*K*s in dimethyl sulfoxide solution of *p*-CN, *p*-$PhSO_2$, *p*-PhCO, *p*-F_3CSO_2, and *p*-NO_2 toluenes have been found to plot linearly against the p*K*s of the corresponding anilines; from these data, and the Hammett ρ for meta-substituted anilines ($\rho = 5.67$), it is estimated that ρ for substituted toluenes is ~12 and that the p*K* for toluene in a dipolar aprotic solvent is ~42.

Sir: Acidity data are sparse for anilines and toluenes, two fundamental classes of very weak organic acids. Absolute acidities for a number of meta- and para-substituted anilines have been measured potentiometrically in dimethyl sulfoxide (Me_2SO),[1,2] and by the H_- technique in Me_2SO–H_2O mixtures.[3] Relative acidities of a number of anilines have been determined in liquid ammonia,[4a] and these have been put on an absolute scale.[4b]