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THE CONVERSION OF CARBOXYLIC ACIDS INTO ACID BROMIDES ON BBr_3-MODIFIED ALUMINA

Satinder Bains, James Green, Lay Choo Tan, Richard M. Pagni,* and George W. Kabalka*

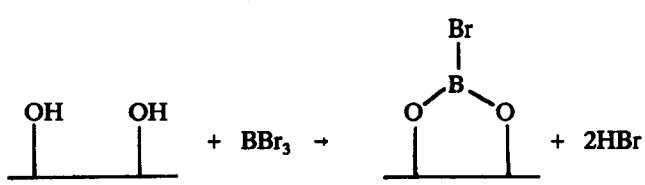
Department of Chemistry, University of Tennessee, Knoxville, Tennessee 37996-1600 U.S.A.

Abstract: Carboxylic acids are converted into acid bromides on alumina which has been modified with boron tribromide. A different reaction occurs in solution.

Acid chlorides are versatile reagents for the synthesis of esters, amides, ketones, and other carbonyl-containing compounds.[1] Acid bromides are less commonly used for these reactions because, unlike acid chlorides, relatively few preparative procedures are available and those that are require brominating agents which are not readily available.[2] We wish to report a new method to prepare acid bromides which is simple to use, versatile, and employs readily available chemicals. The procedure involves treating carboxylic acids with boron tribromide which has been chemisorbed onto alumina (BBr_3/Al_2O_3) (eq.1).

$$RCOOH + BBr_3/Al_2O_3 \rightarrow RCOBr \qquad (1)$$

BBr_3/Al_2O_3 is prepared by treating alumina, which has been activated at 400°C,[3] with a 1.0 M solution of BBr_3 in hexane for 0.5 hours at 0°C.[4] The ratio of the BBr_3 solution to Al_2O_3 is adjusted so that 1 mmol of BBr_3 is chemisorbed per gram of alumina. Copious quantities of gaseous HBr are liberated in the reaction. The reagent, which fumes in air, contains boron (^{11}B SS NMR: broad singlet at 7.1 ppm relative to $NaBPh_4$ at δ = 0 ppm) and has considerable acidity ($H_o \leq$ - 13.2).[5] Based on the weight increase of the solid and the (assumed) loss of bromide generated in the chemisorption reaction as HBr, each chemisorbed boron contains one boron-bromine bond (eq. 2)[6] which is the active agent in the formation of acid bromides.



(2)

The reactions, which give moderate to excellent yields of products (Table 1), are run by treating the corresponding carboxylic acids with BBr_3/Al_2O_3 in a 1:1 molar ratio of acid to BBr bonds, ordinarily at room temperature. The reactions can be run in the absence of solvent if the carboxylic acid is a liquid and in solution if the acid is a solid. No starting carboxylic acids were recovered from the reactions.

Table 1. Synthesis of Acid Bromides by the Reaction of Carboxylic Acids with BBr_3/Al_2O_3.[a]

Acid	Solvent[b]	Temperature (°C)	% Yield of Product[c]
Hexanoic	None	RT	67%
Decanoic	Benzene	RT	64%
Benzoic	Benzene	60°	65%
1-Adamantaneacetic	Benzene	RT	70%
p-Nitrophenylacetic	CH_3CN[d]	RT	59%
3-Bromopropionic	CH_2Cl_2	RT	84%
2-Benzoylbenzoic	CH_2Cl_2	RT	86%

a) 40 mmol of RCOOH + 40g of BBr_3/Al_2O_3 (1 mmol BBr_3/g of Al_2O_3) for 20 hours. b) When a solvent was used in the reaction, 100 ml was used. c) Acid bromides, which gave satisfactory spectral data, were converted to methyl esters for yield determinations. d) Acetonitrile reacts with BBr_3/Al_2O_3 in the absence of the carboxylic acid.

Interestingly, reaction of hexanoic acid with neat BBr_3 did not afford the corresponding acid bromide. Instead, the acid was partially converted to the hexanoic boric anhydride (eq. 3).[7] This result illustrates again that chemistry on a solid may take a markedly different route than the seemingly identical reaction in solution.[8]

$$3CH_3(CH_2)_4COOH + BBr_3 \xrightarrow{\text{solution}} (CH_3(CH_2)_4CO_2)_3B + 3HBr \quad (3)$$

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5. The indicator method described in Tanaba, K. *Solid Acids and Bases*; Academic Press: New York, 1970 was used to determine the acidity of the solid.
6. A 1:1 admixture of chemisorbed B and BBr_2 can yield a weight increase identical to that of BBr.
7. This type of chemistry has been reported previously: Yur'ev, Y.K.; Belyakova, Z.V.; Kostetskii, P.V.; Prokof'ev, A.I. *Zh. Obshch. Khim.* **1960**, *30*, 415.
8. This work was supported by the Research Corporation and the Department of Energy.

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