A Convenient Synthesis of Alkyl Halides from Carboxylic Acids

Sir:

The salts of a variety of metals and carboxylic acids upon treatment with halogens lead to the halogenative decarboxylation reaction RCOOM + $X_2 \rightarrow$ RX + MX + CO_2.[1] Of these reactions, that of the silver salt (generally termed the Hunsdiecker reaction) appears to be the most useful.[1] This reaction has the practical disadvantage that the silver salt must be relatively pure and must be scrupulously dry in order to obtain satisfactory yields. In the course of our studies[2] on the mechanism of the decomposition of the acyl hypobromite intermediate[1] in the Hunsdiecker reaction, we attempted to prepare this intermediate in another fashion. This has led to what appears to us to be a useful preparative method, as reagents and operations are much more convenient than the silver salt–bromine reaction.

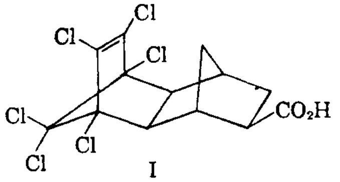
Treatment of a slurry of excess red mercuric oxide in a refluxing solution of an aliphatic carboxylic acid in carbon tetrachloride with approximately one equivalent of bromine in the dark led to excellent yields of the corresponding alkyl bromide. For example, treatment of 0.25 mole of stearic acid with 0.25 mole of bromine and 0.19 mole of red mercuric oxide in 150 ml. of carbon tetrachloride for one hour gave a 93% yield of crude heptadecyl bromide, m.p. 22° (lit.[3] m.p. 32° for pure material). The presumable stoichiometric equation is as follows:

$$2\ RCOOH + HgO + 2\ Br_2 \longrightarrow 2\ RBr + HgBr_2 + H_2O + 2\ CO_2 \qquad (1)$$

Since our original observation, the reaction has been found to go in fair to excellent yields with cyclopropanecarboxylic acid and bromine,[4] with 9,10-dihydro-9,10-ethano-9-anthroic acid with bromine in carbon tetrachloride and with iodine in cyclohexane,[5] with lauric acid and bromine,[6] with stearic acid and iodine,[6] and in poor yield to give 1,3-dibromopropane from glutaric acid.[6] No γ-butyrolactone was found in the latter case.

The reaction gave poor yields with benzoic acid and bromine. Tetrachloroethane may also be used as solvent.[4] Silver oxide may not be substituted for mercuric oxide, and reaction in light gives polybromination.

When either *exo-* (I) or *endo*-5,6,7,8,9,9-hexachloro-1,2,3,4,4a,5,8,8a-octahydro-*exo-endo*-1,4,5,8-dimethano-2-naphthoic acid (II)[2] was treated under these conditions, a mixture of 71% *exo*-(III) and 29% *endo*-bromides (IV)[2] was formed. This is precisely the same mixture of bromides obtained from the silver salt of either acid with bromine.[2] This suggests that both procedures lead to the same intermediate RCOOX. The reaction may involve the existence of the mercuric salt although (a) it has been reported[1a] that mercury salts of acids such as stearic acid do not give good yields following the normal Hunsdiecker reaction, and (b) glutaric acid does not give γ-butyrolactone, whereas the silver (and presumably the mercury) salt gives the lactone. It seems most likely that the mercuric oxide gives a positive halogen species,[7] which reacts with the carboxylic acid to give the acyl hypohalite. If this is the case, and if equation (1) represents the stoichiometry of the reaction, we do not understand why the water formed does not interfere with the reaction as it apparently does in the Hunsdiecker procedure where glassware and chemicals need to be scrupulously dry.[1] In any case, the preparative value of this procedure lies in its convenience and simplicity in comparison to those procedures involving preparation of silver or mercury salts.



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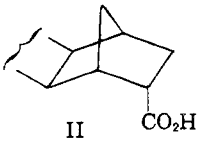

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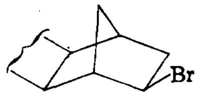
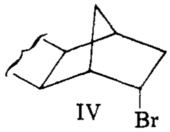


III



IV

Acknowledgment. The authors are indebted to Professor John S. Meek, D. T. Osuga, P. W. Jennings and Miss J. S. Nelson for permission to mention their work previous to publication. W. C. F. is further indebted to the Shell Development Company and the University of Colorado for research fellowships.

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Received October 21, 1960

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(1) For leading references see: (a) H. Hunsdiecker and C. Hunsdiecker, *Ber.*, **75**, 291 (1942); (b) R. G. Johnson and R. K. Ingham, *Chem. Revs.*, **56**, 219 (1956); (c) C. V. Wilson, *Org. Reactions*, **9**, 332 (1957).

(2) S. J. Cristol, J. R. Douglass, W. C. Firth, Jr., and R. E. Krall, *J. Am. Chem. Soc.*, **82**, 1928 (1960).

(3) For comparable results with the silver salt see: J. W. H. Oldham, *J. Chem. Soc.*, 100 (1950).

(4) J. S. Meek and D. T. Osuga, unpublished work.

(5) J. S. Meek and P. W. Jennings, unpublished work.

(6) S. J. Cristol and J. S. Nelson, unpublished work.

(7) W. Brenshede and H.-J. Schumacher, *Z. physikal. Chem.*, **29B**, 356 (1935); *Z. anorg. Chem.*, **226**, 370 (1936).