extracts were washed with aqueous sodium bicarbonate (2½%, 20 cc.) and water (25 cc.). Removal of the ether left about 1.5 g. of a brown oil, a third of which was distillable at 19 mm. (b.p. about 140°); part of this distillate crystallized (m.p. 70–75°). Viscous gummy residues remained from both distillations.

The base-insoluble products from several experiments of this type were combined and distilled. The first fraction ($n_D^{26.5}$ 1.4642, b.p. 75–77° at 20 mm.) was unsaturated toward both bromine and permanganate and apparently was a mixture of nitrogen-containing and nitrogen-free ketones.

Anal. Calc'd for Ia ($C_8H_{13}NO_3$): C, 56.16; H, 7.66; N, 8.18. Calc'd for $C_8H_{12}O$: C, 77.38; H, 9.75. Found: C, 72.1; H, 9.65; N, 3.09.

This material formed a mixture of two 2,4-dinitrophenylhydrazones (m.p. 210–212° and 147.5–149.5°) which were separated by virtue of the much greater solubility of the lower-melting derivative in methanol. Several recrystallizations of the latter (red flakes from methanol) gave a product melting at 152.0–152.7° (dec.). The analytical data suggested that this was the 2,4-dinitrophenylhydrazone of $C_8H_{12}O$, which may be the acetyl analog of III.

Anal. Calc'd for $C_{14}H_{16}N_4O_4$: C, 55.25; H, 5.30; N, 18.42. Found: C, 55.46; H, 5.20; N, 18.63.

The solid isolated during distillation of the base-soluble reaction products melted at 81.0–82.2° after two sublimations at 0.15 mm. The white crystals decolorized both permanganate and bromine and were unstable, completely melting within two months. The instability and analytical value for nitrogen suggest that the solid may be 3,5-dimethylisoxazolone, the 5-methyl analog of IV.

Anal. Calc'd for $C_5H_7NO_2$: N, 12.38. Found: N, 11.7.

SCHOOL OF CHEMISTRY
UNIVERSITY OF MINNESOTA
MINNEAPOLIS 14, MINNESOTA

An Empirical Method for Prediction of the Boiling Points of Halomethanes

JACK HINE AND STANTON J. EHRENSON[1]

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We have found that the boiling point of a halomethane may be estimated fairly reliably by adding to the boiling point of methane (−161.37°) certain parameters for each fluorine, chlorine, bromine, and iodine atom present and another parameter if the halomethane is a methyl halide, methylene dihalide, or haloform. Thus

$$\text{b.p. } (^\circ\text{C.}) = -161.37 + n_F X_F + n_{Cl} X_{Cl} + n_{Br} X_{Br} + n_I X_I + X_{CH_n} \quad (1)$$

where n_F, n_{Cl}, n_{Br}, and n_I are the number of fluorine, chlorine, bromine and iodine atoms in the molecule, X_F, X_{Cl}, X_{Br}, and X_I are the parameters for the four halogens and X_{CH_3}, X_{CH_2} and X_{CH} are the parameters for mono-, di-, and tri-halomethanes, respectively.

Optimum values for the seven parameters were obtained from a least squares treatment using all of the reliable boiling point data available in the literature through September, 1955. Of the 69 possible halomethanes, boiling points for 52 have been reported. Five of these values were ignored since they were either determined at a pressure considerably below 760 mm. or were for compounds reported to boil with decomposition. The data on fluorodiiodomethane was also ignored for the reason to be described shortly. Of the remaining 46 boiling points (ranging from −128 to 190°) 16 appeared to have been determined with particular care, and were given double weight in the least squares treatment. These include all of the 14 compounds listed by Timmermans.[2]

The numerous arithmetic and algebraic operations involved in the summations over the 46 sets of data and solution of the resultant seven simultaneous equations in seven unknowns were accomplished by use of a high speed computer, Engineering Research Associates, model 1101. The values obtained for the parameters are listed below to the nearest hundredth of a degree.

$$X_F = 7.15,\ X_{Cl} = 59.06,\ X_{Br} = 87.15,\ X_I = 125.02,$$
$$X_{CH_3} = 77.68,\ X_{CH_2} = 85.99, \text{ and } X_{CH} = 46.79$$

It was then found that equation (1) and the parameters above gave estimated boiling points that differed from the 46 boiling points used by an average of 2.4° (standard deviation 3.4°) and from the 16 particularly reliable boiling points by an average of 1.7° (s. d. 2.0°). Only 4 of the 46 compounds deviated by more than 6.3°. These were CHF_3 and CH_2F_2 which boiled 10.9 and 9.5° higher than expected and CF_3Br and CF_3I which boiled 6.9° and 7.1° lower than expected. The deviations for CHF_3 and CH_2F_2 may be due to hydrogen bonding. Although better agreement could probably be obtained by use of an additional parameter for fluorine, this was not attempted.

Equation (1) predicts a boiling point of 142.6° for $CHFI_2$. The only boiling points recorded in the literature for this compound are 100.3°[3] and 50° at 50 mm.[4] The latter boiling point may be extrapolated to about 122° at 760 mm. Thomas, however, has reported that $CHFI_2$ boils at 78° at 65 mm. (equivalent to about 147° at 760 mm.).[5]

For the other 5 of our 52 compounds, boiling points were estimated by extrapolation to 760 mm. and were found to deviate from those predicted from equation (1) by an average 4.5°.

A referee has pointed out that the halogen parameters closely parallel the absolute boiling points of

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[1] Eastman Kodak Fellow, 1955–1956.

[2] Timmermans, *Physico-Chemical Constants of Pure Organic Compounds*, Elsevier Publishing Company, New York, N. Y., 1950, pp. 210–229.

[3] Ruff, Bretschneider, Luchsinger, and Miltschitzky, *Ber.*, **69**, 299 (1936).

[4] Haszeldine, *J. Chem. Soc.*, 4259 (1952).

[5] Thomas, Ph.D. Thesis, Georgia Institute of Technology, Atlanta, Georgia, 1953, p. 18.

the elemental halogens. In fact from the linear equation

$$X_{hal} = 0.317 \text{ b.p.}_{hal} - 18.5°$$

our X_{hal} values may be calculated with no deviation of as much as 2°.

While it is not usually possible to predict the boiling points of unknown organic compounds with the accuracy found in the present case, we believe that organic chemists frequently overlook gross deviations between expected and actual boiling points. In one of the most striking examples known to us, a liquid boiling at 14.5° is reported to be $Br_2C(OCH_3)_2$,[6] a compound that should boil at around 200°.

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School of Chemistry
Georgia Institute of Technology
Atlanta, Georgia

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[6] Feist, *Z. angew. Chem.*, **35**, 489 (1922).

Triethylamine Salts in the Preparation of Esters from Active Halogen Compounds

Walter T. Moreland, Jr.

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The formation of acyloxy derivatives from compounds which contain halogen substituents adjacent to a carbonyl group or aromatic ring has long been utilized for the preparation of solid derivatives of carboxylic acids.[1,2] Favored reagents have been compounds such as *p*-nitrobenzyl halides[1] and substituted phenacyl halides.[2] More recently, this type reaction has been useful in the field of corticoid hormones for the introduction of C_{21}-oxygen functions into 20-ketosteroids *via* the corresponding C_{21}-iodo derivatives.[3]

Typical conditions have involved treatment of the halogen compound with the sodium or potassium salt of the desired acid in solvents such as acetone, alcohols, or (for acetoxy derivatives) acetic acid. The choice of solvents has been necessarily limited by wide differences in the solubilities of the two reactants and, frequently, varying amounts of water have been incorporated to give increased solubility of the salt component.[1-5] In steroid preparations anhydrous conditions have often been used, necessitating a large excess of the acetate salt and prolonged refluxing of the resulting heterogeneous reaction mixture. Recent improvements include the use of dry acetone and potassium acetate freshly prepared from potassium bicarbonate and acetic acid[4] and the use of potassium acetate in a mixture of acetone, water, and acetic acid such that homogeneity is obtained.[5]

Salts other than those of the alkali metals in this type reaction apparently have received little attention. Methylammonium salts have been mentioned,[2b] catalytic amounts of triethylamine in the presence of a sodium salt have been used,[6] and there is at least one example of the use of a triethylammonium salt in benzene.[7]

The present study demonstrates a general utility for triethylammonium salts in this type reaction, making possible the preparation of the desired esters in excellent yields and high purity in a variety of solvents. The reaction is carried out by mixing the solvent, acid, and triethylamine in appropriate quantities and adding the halogen compound. The resulting clear solution is allowed to stand at room temperature or refluxed depending on the reactivity of the halogen compound and the solvent

TABLE I

Esters from Active Halogen Compounds Using Triethylammonium Salts in Acetone[a]

Halide, 0.02 mole; Acid, 0.175 mole; $(C_2H_5)_3N$, 0.109 mole

Acid	Ester Yield, %[b,c]	M.P., °C. Obs.[c]	M.P., °C. Lit.
PHENACYL BROMIDE			
Benzoic	85	119–121	118.5[e]
Benzilic	87	121–125	125.5[f]
Salicylic	86	106–108	110[g]
p-PHENYLPHENACYL BROMIDE			
Acetic	86	109–111	111[h]
Benzoic	93	168–170	167[e]
p-NITROBENZYL CHLORIDE			
Acetic	54[d]	78–79	78[h]
Benzoic	68[d]	85–87	88–89[e]

[a] Unless otherwise stated the reactions proceeded in one hour at room temperature. [b] Based on starting halide. [c] The reported yields and physical constants represent the crude products obtained directly from the reaction mixture. [d] Refluxed two hours in the presence of 0.2 g. of sodium iodide. [e] Ref. 8, p. 146. [f] Ref. 8, p. 156. [g] Ref. 8, p. 158. [h] Ref. 8, p. 180.

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[1] Reid, *J. Am. Chem. Soc.*, **39**, 124 (1917).

[2] (a) Reid, *et al.*, *J. Am. Chem. Soc.*, **41**, 75 (1919); **42**, 1043 (1920). (b) Drake and Bronitsky, *J. Am. Chem. Soc.*, **52**, 3715 (1930).

[3] See for example: Romo, Rosenkranz and Sondheimer, *J. Am. Chem. Soc.*, **76**, 5169 (1954); Djerassi and Lenk, *J. Am. Chem. Soc.*, **75**, 3493 (1953).

[4] Rosenkranz, Pataki, Kaufmann, Berlin, and Djerassi, *J. Am. Chem. Soc.*, **72**, 4084 (1950).

[5] Ruschig, *Chem. Ber.*, **88**, 878 (1955).

[6] Tharp, *et al.*, *Ind. Eng. Chem.*, **39**, 1300 (1947).

[7] Cromwell and Starks, *J. Am. Chem. Soc.*, **72**, 4108 (1950).

[8] Huntress and Mulliken, *Identification of Pure Organic Compounds, Order I*, John Wiley & Sons, Inc., New York, 1941.