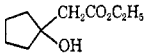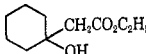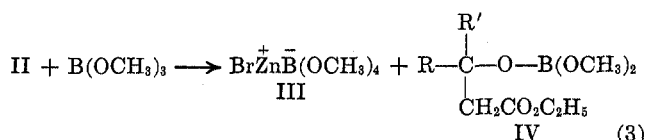<div align="center">

TABLE II

REACTION OF CARBONYL COMPOUNDS WITH ZINC AND ETHYL BROMOACETATE AT 25°

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Carbonyl compd	Product	Tetrahydrofuran–trimethyl borate	Benzene	Lit.[c]
Acetaldehyde	$CH_3CHOHCH_2CO_2C_2H_5$	95	65	
Butyraldehyde	$CH_3(CH_2)_2CHOHCH_2CO_2C_2H_5$	97 (90)	80	25
Isobutyraldehyde	$(CH_3)_2CHCHOHCH_2CO_2C_2H_5$	98 (89)	95	35
Crotonaldehyde	$CH_3CH=CHCHOHCH_2CO_2C_2H_5$	98 (90)	89	60
Benzaldehyde	$C_6H_5CHOHCH_2CO_2C_2H_5$	(95)	(84)	61
Phenylacetaldehyde	$C_6H_5CH_2CHOHCH_2CO_2C_2H_5$	90	70	
Acetone	$(CH_3)_2COHCH_2CO_2C_2H_5$	90 (85)	90	
Cyclopentanone	(structure: cyclopentane ring with $CH_2CO_2C_2H_5$ and OH)	93 (87)	50	40[d]
Cyclohexanone	(structure: cyclohexane ring with $CH_2CO_2C_2H_5$ and OH)	85 (80)	80	56

[a] All products gave analytical data and spectra in accordance with the assigned structures. [b] Glpc yields. Isolated yields in parentheses. [c] Reference 1 unless otherwise noted. [d] V. N. Ipatieff, J. E. Germain, and H. Pines, *Bull. Soc. Chem. Fr.*, 259 (1951).

not isolated. Instead a precipitate assumed to be the zinc salt III is formed, presumably by reaction of II with excess trimethyl borate (eq 3). Hydrolysis of the

$$
\text{II} + \text{B(OCH}_3)_3 \longrightarrow \overset{+}{\text{Br}}\overset{-}{\text{Zn}}\text{B(OCH}_3)_4 + \underset{\underset{\text{CH}_2\text{CO}_2\text{C}_2\text{H}_5}{|}}{\overset{\overset{\text{R}'}{|}}{\text{R}-\text{C}-\text{O}-\text{B(OCH}_3)_2}}
$$
$$
\text{III} \qquad\qquad\qquad \text{IV} \qquad (3)
$$

boron ester IV during work-up then gives the β-hydroxy ester.

As expected, the advantage of using trimethyl borate is most apparent when the carbonyl compound is especially susceptible to base-catalyzed condensations. Thus the reactive aldehydes, acetaldehyde and phenylacetaldehyde, and the reactive ketone, cyclopentanone, give clearly increased yields with the trimethyl borate procedure. With less reactive carbonyl compounds, the procedure utilizing benzene at 25° gives comparable yields. With either procedure, the yields are much higher than those obtained at reflux temperatures.

Experimental Section

All experiments were conducted using unactivated 20 mesh zinc metal. Ethyl bromoacetate was distilled under reduced pressure and stored under a nitrogen atmosphere. Trimethyl borate was distilled from calcium hydride and stored under nitrogen. All carbonyl compounds were distilled shortly before use. Tetrahydrofuran and benzene, reagent grades, were used directly. Glpc analyses were performed on a SE-30 silicon oil column using appropriate internal standards.

Reactions Using Tetrahydrofuran–Trimethyl Borate Solvent.— The following procedure for the conversion of benzaldehyde into ethyl 3-phenyl-3-hydroxypropionate is representative. Zinc metal (6.54 g, 100 mg-atoms) was put in a 250-ml round-bottom flask equipped with septum inlet and magnetic stirring bar and maintained under a static nitrogen pressure. The flask was immersed in a water bath at 25° and a solution of 10.6 g (100 mmol) of benzaldehyde in 25 ml of tetrahydrofuran and 25 ml of trimethylborate was injected. Stirring was initiated and 11.1 ml (100 mmol) of ethyl bromoacetate was injected all at once. The reaction mixture was stirred for 12 hr at which time all of the zinc was consumed (with the other aldehydes and ketones studied, complete reaction was achieved in 5 hr or less). The reaction mixture was hydrolyzed by the addition of a solution containing 25 ml of concentrated ammonium hydroxide (to dissolve zinc salts) and 25 ml of glycerine (to dissolve boric acid). The organic phase was separated and the aqueous layer extracted with three 25-ml portions of ether. The combined organic extracts were dried and subjected to vacuum distillation to obtain 18.5 g (95% yield) of ethyl 3-phenyl-3-hydroxypropionate, bp 105° (0.2 mm).

Reactions Using Benzene as Solvent.—An identical procedure was utilized except an equal volume of benzene was substituted for the tetrahydrofuran–trimethyl borate solvent.

Cyanuric Chloride. A Novel Laboratory Hydrochlorinating Reagent for Alcohols

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This note reports on the investigation of cyanuric chloride with alcohols with the aim of extending the SNi type of reaction, already well known. In an attempt to prepare 2,4,6-trimethyl-*s*-triazine by the reaction of a methanolic solution of sodium methoxide with cyanuric chloride, methyl chloride was unexpectedly obtained in 92% yield along with a 100% yield of cyanuric acid.

A search of the literature revealed that only two earlier reports in 1834[1] and 1886[2] had briefly mentioned the occurrence of a similar reaction in the absence of sodium methoxide or other bases, but they gave no experimental details. More recent investigators[3] reporting the preparation of trialkyl-*s*-triazines by similar methods

(1) J. Liebig, *Ann. Pharm.*, **10**, 1 (1834).

(2) P. Klason, *J. Prakt. Chem.*, **34**, 152 (1886).

(3) (a) J. R. Dudley, J. T. Thurston, F. C. Schaefer, D. H. Hansen, C. J. Hull, and P. Adams, *J. Amer. Chem. Soc.*, **73**, 2986 (1951); (b) J. R. Dudley, J. T. Thurston, F. C. Schaefer, C. J. Hull, D. H. Hansen, and P. Adams, *ibid.*, **73**, 2999 (1951); (c) J. R. Dudley, U. S. Patent 2,510,564 (1950); (d) A. J. Matuszko and M. S. Chang, *J. Org. Chem.*, **27**, 677 (1962).

TABLE I
HYDROCHLORINATION OF PRIMARY, SECONDARY, AND
TERTIARY ALCOHOLS WITH CYANURIC CHLORIDE[a,b]

Alcohol (mol)	Cyanuric chloride (mol)	Base (mol)	% yield, RCl
CH₃OH		NaOCH₃	
2.5	0.5	0.5	92
3.0	0.5		72
C₂H₅OH			
5.4	0.5		70
n-C₃H₇OH			
4.2	0.5		65
n-C₄H₉OH			
3.4	0.5		41
		NaOBu	
2.5	0.5	0.5	34
t-C₄H₉OH			
3.4	0.5		56
Allyl alcohol			
7.8	0.5		43
n-C₅H₁₁OH			
4.0	0.5		44
2-C₅H₁₁OH			
1.7	0.73		29
3.4	0.50		57
3-C₅H₁₁OH			
0.85	0.49		38
C₆H₅CH₂OH			
3.0	0.5		71

a The reaction temperature is the boiling point of the alcohol and the reaction time is 1–1.5 hr. *b* The chlorides were identified by their ir and nmr spectra.

$$\text{(1)}$$
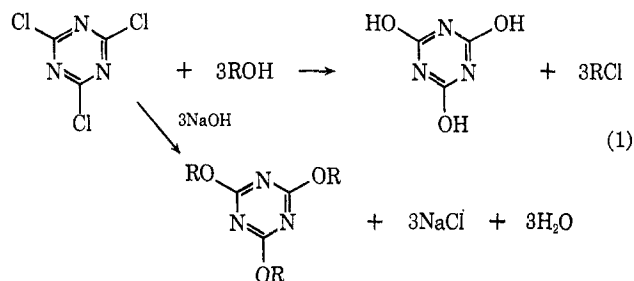
lides as seen for the case of methanol and *n*-butyl alcohol in Table I. The results of Table I also indicate that cyanuric chloride can be conveniently used to hydrochlorinate primary, secondary, and tertiary alcohols. 2- and 3-pentanol are hydrohalogenated to their respective chlorides without isomerization as is not true for zinc chloride–HCl hydrochlorination (Table II). Thionyl chloride–pyridine[4] also gives no isomerization as shown for 2-pentanol in Table II.

Experimental Section

A typical preparation involves heating the alcohol (2–20 mol) to 10–20° below its boiling point and then slowly adding powdered cyanuric chloride (1 mol). A Dry Ice trap should be connected *via* a rubber tube to the top of the reflux condenser in order to trap the low boiling chlorides. After the addition (*ca.* 1–1.5 hr), the reaction mixture is cooled, filtered, and distilled. If complete conversion to the chloride is desired,

TABLE II
HYDROCHLORINATION OF 2-PENTANOL USING VARIED METHODS

ROH	Cyanuric chloride	ZnCl₂	HCl (concd)	SOCl₂	Pyridine	Temp, °C	Time, hr	% yield	Isomer, % 2-Chloro	3-Chloro
2-Pentanol										
3.4	0.5					117	1	57	100	
1.0		2.0	2.0			78	1–2	68	38	62
0.547				0.848	0.552	5–10	1	48	100	
0.25			0.50			86–95	1–2	27	76	24

completely ignored the hydrochlorination reaction of the alcohols.

The results of the investigation indicate that cyanuric chloride under the appropriate conditions can be used as a convenient hydrochlorinating reagent for alcohols giving no isomerization as is also true with other SNi reagents.[4–9] Cyanuric chloride has the advantage that it can be conveniently handled and requires no added base such as sodium alkoxide or pyridine.[4–6] The alcohol can be completely converted to the chloride by using an excess of cyanuric chloride under anhydrous conditions. The crude chloride is simply isolated by filtration and then purified by distillation. The presence of sodium hydroxide changes the reaction so that trialkyl-cyanurates are produced.[3] The presence of sodium alkoxide has little effect on the reaction to give alkyl ha-

excess cyanuric chloride should be added. See Table I for molar quantities used.

**Base-Induced α-Sulfonylation of
Aryl Alkanesulfonates**

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In the course of our investigations utilizing sulfur-stabilized carbanions for synthetic purposes,[1] it has been

(4) F. C. Whitmore and F. A. Karnatz, *J. Amer. Chem. Soc.*, **60**, 2536 (1938).
(5) E. S. Lewis and C. E. Boozer, *ibid.*, **74**, 308 (1952).
(6) L. H. Sommer, H. D. Blankman, and P. C. Miller, *ibid.*, **76**, 803 (1954).
(7) K. L. Oliver and W. G. Young, *ibid.*, **81**, 5811 (1959).
(8) K. B. Wiberg and T. N. Shryne, *ibid.*, **77**, 2774 (1955).
(9) S. J. Rhoads and R. E. Michel, *ibid.*, **85**, 585 (1963).

(1) (a) W. E. Truce and F. E. Roberts, *J. Org. Chem.*, **28**, 961 (1963); (b) W. E. Truce and L. W. Christensen, *Tetrahedron*, **25**, 181 (1969); (c) W. E. Truce and D. J. Vrencur, *J. Org. Chem.*, **35**, 1226 (1970); (d) H. Fukuda, F. F. Frank, and W. E. Truce, *ibid.*, **28**, 1420 (1963).