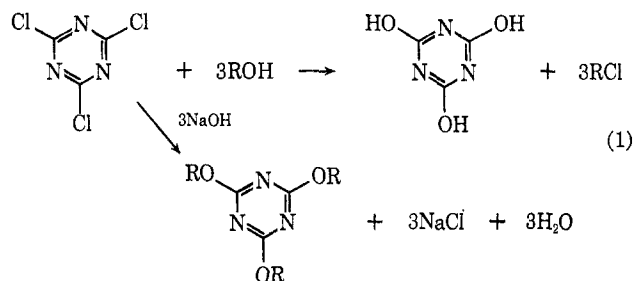TABLE I

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.

$$
\begin{array}{c}
\text{(cyanuric chloride)} + 3ROH \longrightarrow \text{(cyanuric acid)} + 3RCl \\[4pt]
\Big\downarrow\; 3NaOH \\[4pt]
\text{(trialkyl cyanurate)} + 3NaCl + 3H_2O
\end{array}
\tag{1}
$$

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 trialkylcyanurates 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).

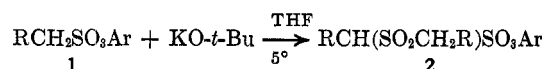(9) S. J. Rhoads and R. E. Michel, *ibid.*, **85**, 585 (1963).

(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).

TABLE I

$RCH(SO_2CH_2R)SO_3Ar$

Compd no.	Compd R	Compd Ar	Mp, °C	Yield,[a] %	Calcd, % C	Calcd, % H	Calcd, % S	Found, % C	Found, % H	Found, % S
3	C_6H_5	C_6H_5	174–175	69	59.70	4.52	15.94	59.59	4.55	15.74
4	C_6H_5	$p\text{-}C_7H_7$	160–160.5	60	60.60	4.84	15.40	60.86	5.10	15.13
5	C_6H_5	$p\text{-}BrC_6H_4$	155–156	59[b]	49.98	3.56	13.35	49.70	3.68	13.20
6	$p\text{-}ClC_6H_4$	C_6H_5	154–155	62[c]	51.00	3.50	13.60	51.22	3.71	13.35
7	$p\text{-}C_7H_7$	C_6H_5	160–161	52	61.40	5.14	14.90	61.20	5.22	14.67

[a] Isolated, purified material, yield not optimized. [b] Br analyses: calcd, 16.58; found, 16.29. [c] Cl analyses: calcd, 15.02; found, 15.00.

found that when aryl alkanesulfonates (1) are treated with potassium tert-butoxide in tetrahydrofuran, α-sulfonylation of the sulfonic esters occurs to give 2 in good yield (Table I). This transformation bears a formal resemblance to the Claisen condensation of carboxylic

$$RCH_2SO_3Ar + KO\text{-}t\text{-}Bu \xrightarrow[5°]{THF} RCH(SO_2CH_2R)SO_3Ar$$
$$1 \qquad\qquad\qquad\qquad\qquad\qquad 2$$

resemblance to the Claisen condensation of carboxylic esters. Also, there seemingly is only one other reported preparation of an α-alkylsulfonylsulfonate.[2] The latter preparative method, which proceeds through a sulfene dimer, could not be extended to esters of α-toluenesulfonic acids; hence, these two procedures complement one another for the preparation of this novel class of α-sulfonylated sulfonic esters.

The large steric requirements of potassium tert-butoxide minimize transesterification.[3] In addition, tetrahydrofuran alone is a desirable solvent; when tert-butyl alcohol–tetrahydrofuran was used as a mixed solvent system the yield of condensation product was markedly decreased.[4] It has been suggested that the observed increased reactivity of anions in tetrahydrofuran is due to preferential solvation of the cation.[5] The superiority of phenolic esters in this condensation is illustrated by the substantial recovery of starting material when neopentyl α-toluenesulfonate is subjected to the reaction conditions.

Characterization of the condensation products is based on chemical properties, elemental analyses, molecular weight determinations, infrared spectra and well-defined proton magnetic resonance spectra. The nmr spectrum is especially noteworthy. For compound 3 in

$$\underset{H_C}{Ph\overset{H_C}{\underset{H_B}{\overset{|}{C}}}(SO_2\overset{H_A}{\underset{|}{C}}\text{—}Ph)SO_3Ph}$$

3
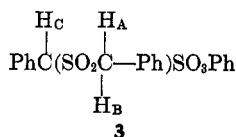
deuteriochloroform the methylene protons, H_A and H_B, give rise to a four-line AB pattern centered at δ 4.68 with $J_{AB} = 13.8$ cps, and the methyne proton, H_C, gives a singlet at δ 5.40. In contrast, the spectrum of 3 in acetone-d_6 consists of a singlet for the methylene protons at δ 4.82 and a singlet at δ 6.41 for the methyne proton. [The solvent dependence of the splitting of the meth-

ylene protons (H_A and H_B) may be due to a preferred conformation of the sulfonylsulfonate, which allows intramolecular hydrogen bonding in $CDCl_3$, while in acetone, a better hydrogen-bonding solvent, intermolecular hydrogen bonding negates this conformational preference.] The same nmr solvent dependency was found for the other α-sulfonylsulfonates.

Although this sulfonylation reaction constitutes a sulfonic ester analog of the Claisen condensation, the mechanistic sequences may be different. With carboxylic esters an intermediate such as 8 has experimental support.[6] However, available data relating to similar displacements on sulfonate esters would make a pentacoordinated intermediate, such as 10, somewhat unlikely.[7] One alternative mechanism would be simple S_N2 displacement by 9 on an unionized ester molecule to afford the product directly. Other mechanisms may also be postulated,[8] however, at this time there is little data available to support such speculation.
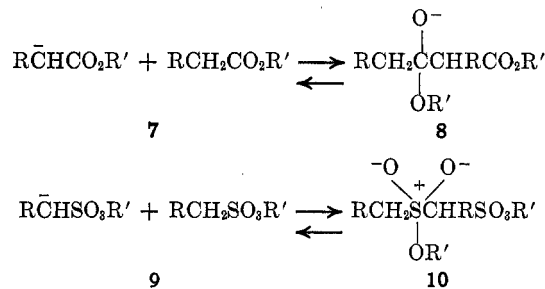
Experimental Section

All melting points are uncorrected. The nmr spectra were obtained in $CDCl_3$ or acetone-d_6 using a Varian A-60 spectrometer with TMS = 0. Microanalyses and molecular weight determinations were performed by Dr. C. S. Yeh and staff. Potassium tert-butoxide was purchased from MSA Corporation and purified by sublimation. Reagent grade THF was distilled from LAH prior to use. The para-substituted α-toluenesulfonyl chlorides were prepared by known methods and the phenols were used as commercially obtained.

General Procedure for the Preparation of Aryl α-Toluenesulfonates.—To a solution of 0.10 mol of triethylamine (Matheson Coleman and Bell reagent) and 0.10 mol of phenol in 200 ml of benzene under nitrogen at 5–10° was slowly added with cooling and stirring a solution of 0.10 mol of α-toluenesulfonyl chloride in 50 ml of tetrahydrofuran. The mixture was stirred for an additional hour, and the precipitated triethylamine hydrochloride was filtered. The filtrate was washed several times with dilute hydrochloric acid, dried over sodium sulfate, and then

(2) G. Opitz, M. Kleeman, D. Bucher, G. Walz, and K. Rieth, *Angew. Chem., Int. Ed. Engl.*, **5**, 594 (1966). Following completion of our work, a related system was reported by Y. Shirota, T. Nagai, and N. Tokura, *Tetrahedron*, **25**, 3193 (1969).

(3) L. A. Paquette and L. S. Wittenbrook, *J. Amer. Chem. Soc.*, **89**, 4483 (1967).

(4) For example, the yield of product 4 was 60% in THF as compared to 4% in tert-BuOH–THF (90:10).

(5) H. Feuer and B. F. Vincent, Jr., *J. Org. Chem.*, **29**, 939 (1964), and references cited therein.

(6) C. R. Hauser and B. E. Hudson, Jr., *Org. React.*, **1**, 266 (1942).

(7) (a) C. A. Bunton and Y. F. Frei, *J. Chem. Soc., London*, 1872 (1951); (b) R. V. Vizgert, *Usp. Khim.*, **32**, 3 (1963); (c) E. T. Kaiser and O. R. Zaborsky, *J. Amer. Chem. Soc.*, **90**, 4626 (1968).

(8) Sulfene ($Ph\overline{C}HSO_2^+$) formation accompanied by its novel trapping via the precursory carbanion ($Ph\overline{C}HSO_3Ar$) can be envisioned.

evaporated under reduced pressure. The resulting solid was recrystallized from 95% ethanol to afford white crystalline product.

Phenyl α-Toluenesulfonate.—α-Toluenesulfonyl chloride (19.06 g, 0.10 mol) gave 16.8 g (68%) of phenyl α-toluenesulfonate, mp 84.5–85.5°.

Anal. Calcd for $C_{13}H_{12}O_3S$: C, 62.90; H, 4.85; S, 12.05. Found: C, 62.98; H, 4.98; S, 12.16.

p-Tolyl α-Toluenesulfonate.—α-Toluenesulfonyl chloride (15.0 g, 0.079 mol) afforded 16.2 g (78%) of p-tolyl α-toluenesulfonate, mp 87–88°.

p-Bromophenyl α-Toluenesulfonate.—α-Toluenesulfonyl chloride (15.0 g, 0.079 mol) gave 19.3 g (75%) of p-bromophenyl α-toluenesulfonate, mp 84–85°.

Phenyl p-Methyl-α-toluenesulfonate.—p-Methyl-α-toluenesulfonyl chloride (10.0 g, 0.049 mol) gave 10.5 g (83%) of phenyl p-methyl-α-toluenesulfonate, mp 98–99°.

Phenyl p-Chloro-α-toluenesulfonate.—p-Chloro-α-toluenesulfonyl chloride (20.2 g, 0.09 mol) afforded 16.0 g (67%) of phenyl p-chloro-α-toluenesulfonate, mp 81–82.5°.

General Procedure for the Preparation of α-Sulfonylsulfonates.—To 150 ml of THF under nitrogen at 5–10° was added 0.030 mol of sublimed KO-t-Bu. This mixture was allowed to stir for 15 min after which 0.028 mol of the sulfonate ester in 50 ml of THF was added dropwise. After stirring for 8 hr at room temperature, 0.030 mol of glacial acetic acid was added and the mixture filtered. The solid was washed with four 50-ml portions of THF; the combined filtrates were evaporated *in vacuo*. The resulting solid was taken up in chloroform and the chloroform solution washed with three 50-ml portions of water and with 50 ml of a saturated sodium chloride solution and dried over Na_2SO_4 and the chloroform evaporated *in vacuo* leaving a white solid, which was recrystallized from absolute ethanol.

Phenyl α-(Benzylsulfonyl)-α-toluenesulfonate (3).—Phenyl α-toluenesulfonate (7.45 g, 0.030 mol) afforded 4.45 g (69%) of **3** (Table I): nmr (acetone d_6) δ 4.85 (s, 2), 6.40 (s, 1), 7.48 (m, 15); mol wt, calcd, 408; found, 405.

p-Tolyl α-(Benzylsulfonyl)-α-toluenesulfonate (4).—p-Tolyl α-toluenesulfonate (10.0 g, 0.039 mol) gave 4.85 g (60%) of **4** (Table I): nmr (acetone-d_6) δ 2.32 (s, 3), 4.77 (s, 2), 6.30 (s, 1), 7.35 (m, 14); mol wt, calcd, 416; found, 422.

p-Bromophenyl α-(Benzylsulfonyl)-α-toluenesulfonate (5).—p-Bromophenyl α-toluenesulfonate (10.0 g, 0.0306 mol) gave 4.32 g (59%) of **5** (Table I): nmr (acetone-d_6), δ 4.75 (s, 2), 6.38 (s, 1), 7.45 (m, 14); mol wt, calcd, 487; found, 477.

Phenyl α-(p-Chlorobenzylsulfonyl)-p-chloro-α-toluenesulfonate (6).—Phenyl p-chloro-α-toluenesulfonate (7.94 g, 0.028 mol) yielded 4.09 g (62%) of **6** (Table I): nmr (CDCl₃) δ 4.75 (q, 2), 5.30 (s, 1), 7.50 (m, 13); mol wt, calcd, 471; found, 475.

Phenyl α-(p-Methylbenzylsulfonyl)-p-methyl-α-methyl-α-toluenesulfonate (7).—Phenyl p-methyl-α-toluenesulfonate (6.0 g, 0.23 mol) gave 2.10 g (52%) of **7** (Table I): nmr (acetone-d_6) δ 2.40 (d, 6), 4.75 (s, 2), 6.30 (s, 1), 7.33 (m, 13); mol wt, calcd, 430; found, 428. A small amount of phenyl p-methyl-α-toluenesulfonate, 1.00 g (17%), was also recovered.

Attempted Reaction of Potassium *tert*-Butoxide with Neopentyl α-Toluenesulfonate.—Neopentyl α-toluenesulfonate (5.09 g, 0.021 mol) and KO-t-Bu (2.80 g, 0.025 mol) were stirred in 100 ml of dry THF under nitrogen at 5° for 14 hr. After careful acidification of the reaction mixture with glacial acetic acid (1.50 g, 0.025 mol), the solution was filtered, the solid was washed with three 50-ml portions of THF and the combined filtrates were evaporated *in vacuo*. The resulting white solid was recrystallized from 95% EtOH to afford 3.86 g (76%) recovery of starting ester.

Registry No.—**3,** 17074-71-4; **4,** 25894-34-2; **5,** 25894-35-3; **6,** 25894-36-4; **7,** 25957-56-6; phenyl α-toluenesulfonate, 10271-81-5; p-tolyl α-toluenesulfonate, 25894-38-6; p-bromophenyl α-toluenesulfonate, 25894-39-7; phenyl p-methyl-α-toluenesulfonate, 25894-40-0; phenyl p-chloro-α-toluenesulfonate, 25894-41-1.

Formation of an α-Chlorovinylamine and Its Interconversion to a Ketenimmonium Salt

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While studying the reactions of enamines with inorganic halides,[1] we observed a reaction that should be of interest to organic chemists. Phosphorus trichloride reacts with 2-methylpropenylidenebisdimethylamine (1) to form first a one-to-one complex which we believe to have structure 2 (see Scheme I). The proton nmr of

SCHEME I

$$PCl_3 + Me_2C{=}C(NMe_2)_2 \underset{\text{fast}}{\rightleftharpoons} Cl_2PCMe_2\overset{+}{C}(NMe_2)_2Cl^-$$
$$1 \qquad\qquad 2$$

$$\downarrow \text{slow}$$

$$Me_2NPCl_2 + Me_2C{=}C\overset{NMe_2}{\underset{Cl}{\diagup\diagdown}}$$
$$3 \qquad\qquad 4$$

$$Cl^- \bigg\Vert Ag^+$$

$$Me_2C{=}\overset{+}{C}{=}NMe_2$$
$$5$$

2 displays a broadened singlet at τ 6.50 consistent with amidinium N-methyl protons and a broadened doublet at τ 7.98 (J = 8.6 Hz) consistent with C-methyl protons coupled to phosphorus. Compound 2 was not isolated and is known only by its nmr. This spectrum disappears in 24–72 hr depending on temperature and concentration, and new resonances, a doublet[2] at τ 7.15 (J = 12.5 Hz) and sharp singlets at τ 7.63 and 8.22 in the ratio 1:1:1, are generated. This secondary reaction mixture was separated by preparative vpc into components 3 corresponding to the doublet above and 4 corresponding to the two sharp singlets. Compound 3 was shown to be dichloro(dimethylamino)phosphine by vpc and proton nmr comparison with an authentic sample prepared by equilibrating phosphorus trichloride with tris(dimethylamino)phosphine[3]. Compound 4, a colorless, distillable, thermally unstable liquid was prepared more conveniently by reaction of 1 with dichlorophenylphosphine. Although the reaction was slower, the products, chloro(dimethylamino)-phenylphosphine and 4, have sufficiently different volatilities to allow separation *via* simple fractional distillation.

Subtracting the elements of the phosphorus containing products from those of the starting materials permits only a limited number of alternatives for the structure of 4. Furthermore, hydrolysis of 4 yields N,N-dimethylisobutyramide which seemed to exclude most reasonable possibilities except the structure shown

(1) H. Weingarten and J. S. Wager, *Chem. Commun.*, 854 (1970).

(2) Demonstrated by decoupling experiments on a Varian Model HA-100 spectrometer.

(3) J. R. Van Wazer and L. Maier, *J. Amer. Chem. Soc.*, **86**, 811 (1964).