[CONTRIBUTION FROM THE CHEMISTRY LABORATORY OF THE UNIVERSITY OF ALABAMA]

A Study of Aliphatic Sulfonyl Compounds. VI. Camphane-10-sulfonyl Chloride[1]

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The apocamphyl group of camphane-10-sulfonic acid has been shown to have approximately the same effect on the reactivity of the sulfonyl chloride and the ethyl ester as previously had been determined for the *tert*-butyl group of the analogous neopentanesulfonic acid. New aliphatic sulfonyl compounds prepared are camphane-10-sulfonyl chloride, and as characterizing derivatives, the ethyl ester, benzylamide, and morpholide of the corresponding sulfonic acid. New evidence has been presented indicating that hydrogen chloride does not catalyze ethanolysis of aromatic sulfonyl chlorides.

In the preceding report of this series[3] it was shown that the *beta* methyl groups of neopentanesulfonyl chloride are approximately as effective in hindering ethanolysis of an aliphatic sulfonyl chloride as the *alpha* methyl and hexyl groups of octane-2-sulfonyl chloride. In as much as steric considerations suggest that groups larger than methyl for which freedom of rotation is restricted should have an effect similar to methyl, the reactivities of camphane-10- and neopentanesulfonyl chlorides have been compared.

Camphane-10-sulfonyl chloride was prepared from the corresponding sodium sulfonate obtained by modified Wolff-Kishner reduction of *dl*-camphor-10-sulfonic acid.[4] This sulfonyl chloride undergoes alcoholysis in excess boiling ethanolic hydrogen chloride at about the same rate ($k = 0.018$ min.$^{-1}$) as neopentanesulfonyl chloride ($k = 0.016$ min.$^{-1}$),[3] justifying the supposition that the larger grouping of the rigid bicyclic structure has approximately the same effect as noted for the analogously situated methyl groups of the neopentane system.

Because of the possibility that hydrogen chloride, which is a primary reaction product, might catalyze alcoholysis of sulfonyl chlorides as Goubau[5] supposed, the practice of incorporating hydrogen chloride in the ethanol used was adopted at the onset of these investigations to minimize any effects that might be caused by variations in its concentration. Although this procedure is satisfactory for the purpose intended, it remained of interest to determine if hydrogen chloride catalyzes alcoholysis at reflux, especially as Tommila[6] concluded that it has no effect at lower temperatures. Accordingly, the rates of ethanolysis of benzenesulfonyl chloride with added hydrogen chloride were determined at 34° and at reflux (approx. 84°) ($k = 0.0031$ and 0.14 min.$^{-1}$, resp.). These results are in agreement with those obtained by Tommila[6] at 0°, 15°, and 25° without added hydrogen chloride[7] ($10^3k = 0.088$, 0.44, and 1.23 min.$^{-1}$, resp.), the Arrhenius equation being applicable over the range from 0° to 84° as shown in Fig. 1.[8] It is interesting to note that benzenesulfonyl chloride undergoes ethanolysis at reflux faster than any of the aliphatic sulfonyl chlorides

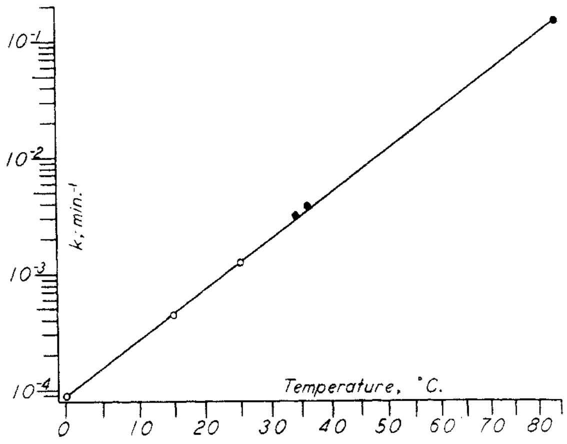

FIG. 1.—ETHANOLYSIS OF BENZENESULFONYL CHLORIDE AT VARIOUS TEMPERATURES. Open circles, without added hydrogen chloride (data from Tommila).[6] Filled circles, with added hydrogen chloride.

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(3) Scott and McLeod, *J. Org. Chem.*, **21**, 388 (1956).

(4) In a private communication, Dr. Pelham Wilder, Jr., Dep't of Chem., Duke Univ., Durham, N. C., reports having previously carried out the synthesis outlined in connection with a different study.

(5) Goubau, *Bull. classe sci. Acad. roy. Belg.*, 233 (1911).

(6) Tommila and Hirsjärvi, *Acta Chem. Scand.*, **5**, 659 (1951).

(7) Goubau[5] observed an apparent drift in his ethanolysis rate constants. Although this drift was attributed to hydrogen chloride catalysis, it is more probably the result of his having based his calculations on acidity titrations without taking into consideration the increasing acidity from slow solvolytic attack on the sulfonic ester concurrent with the more rapid attack by hydrogen chloride, which occasions no change in acidity. His report of an increase in the rate of ethanolysis of aromatic sulfonyl chlorides caused by addition of hydrogen chloride was not observed by us. It is possible that moisture was not entirely excluded in each of his ethanolyses.

(8) Having shown that hydrogen chloride does not catalyze ethanolysis of an aromatic sulfonyl chloride, it remains to be shown in the case of aliphatic ones. This presently is being investigated.

TABLE I
ETHANOLYSIS OF CAMPHANE-10-SULFONYL CHLORIDE[a]

Experiment	Time[b] mins.	RSO_2Cl[c] millimoles	RSO_2OEt[c] millimoles	RSO_2OH[d] millimoles	k_1, min.$^{-1}$	k_2, min.$^{-1}$[e]
A	27	6.3	2.7	1.1	0.017	0.020
	40	4.8	3.1	1.7	.018	.022
	50	4.0	3.2	2.4	.018	.023
	60	3.3	3.2	3.6	.019	.024
B	41	4.5	3.0	2.5	.019	
				Average	0.018	

[a] A mixture of 10 millimoles of RSO_2Cl refluxed (*ca.* 84°) with 14 millimoles of HCl and 0.24 mole of EtOH in A, with 68 millimoles of HCl and 0.45 mole of EtOH in B. [b] Starting with first drop of condensate, and ending 10 secs. after immersion in ice, when no further condensation was noted. [c] From weight of residue and Cl ion content of hydrolyzate of residue from the vacuum evaporation of the ether layer from partitioning between water and ether. [d] From Cl ion content and total acidity of aqueous extract. To minimize standardization errors, $AgNO_3$ standardized against NaOH with common sample of HCl. [e] From $B = \frac{k_1A_0}{k_2 - k_1}(e^{-k_1t} - e^{-k_2t})$, in which B = conc'n ester at time t, A_0 = init. conc'n RSO_2Cl. Values of k_2 are only approximate but of same order as directly determined ones in Table II.

TABLE III
ETHANOLYSIS OF BENZENESULFONYL CHLORIDE

Experiment[a]	Temperature °C.	Time mins.	RSO_2Cl[b] millimoles	RSO_2OEt[c] millimoles	RSO_2OH[d] millimoles	k, min.$^{-1}$
A	Reflux[e]	8	5.2	7.1	2.9	0.134
		15	1.5	6.1	7.6	.156
				Average		0.145
B	36[f]	180	3.8	3.3	0.5	0.0037
C	34[f]	163	3.7	2.5	0.1	0.0035
		320	2.3	3.7	0.3	.0032
		564	1.1	4.4	0.8	.0031
				Average		0.0031

[a] In A, 15.2 millimoles of $PhSO_2Cl$, 19 millimoles of HCl, and 0.26 mole of EtOH. In B, 7.6 millimoles of $PhSO_2Cl$, 12 millimoles of HCl, 0.17 mole of EtOH. In C, 6.3 millimoles of $PhSO_2Cl$, HCl and EtOH as in B. [b] From Cl ion content after saponifying ether layer from partitioning between water and ether. [c] By stoichiometric difference from other components. [d] From Cl ion content and total acidity of aqueous extract. [e] Approximately 84°. [f] ±0.3°.

TABLE II
ETHANOLIC HYDROGEN CHLORIDE ATTACK ON ETHYL CAMPHANE-10-SULFONATE[a]

Time mins.	RSO_2OEt[b] millimoles	RSO_2OH[c] millimoles	k, min.$^{-1}$[d]
10	4.5	0.8	0.015
20	3.8	1.5	.016
30	3.3	1.7[e]	.016
40	2.6	2.6	.017
		Average	0.016

[a] Refluxed (*ca.* 84°) a mixture of 5 millimoles of ester, 14 millimoles of HCl, 0.24 mole of EtOH. [b] From wgt. of residue after vacuum evaporation of ether layer from partitioning between water and ether. [c] From Cl ion content and total acidity of aqueous extract. [d] Constant for combined attacks of HCl and EtOH; based on RSO_2OH. [e] By stoichiometric difference from ester recovered.

thus far investigated.[3,9-11] This suggests that an α,β-unsaturated sulfonyl chloride such as ethylenesulfonyl chloride will be found to be highly reactive and the corresponding sulfonates very active alkylating agents.

The attack on ethyl camphane-10-sulfonate (prepared by alkylating the silver salt of the acid with ethyl iodide) by boiling ethanolic hydrogen chloride (k = 0.016 min.$^{-1}$) is significantly slower than on the ethyl ester of octane-1-sulfonic acid (k = 0.051 min.$^{-1}$),[9] again showing that ethyl sulfonates of sterically hindered sulfonic acids are less active alkylating agents than those of straight chain sulfonates. In order to make certain that solvolysis continues to play the minor role shown in the case of the other ethyl sulfonates investigated, a single determination of the rate of alcoholysis of ethyl camphane-10-sulfonate in ethanol at reflux (k = 0.001 min.$^{-1}$) was made. Although it is possible that hydrogen chloride might catalyze the solvolysis it is doubtful that its effect would be manifold.

EXPERIMENTAL

Camphane-10-sulfonyl chloride. After a mixture of 157 g. (0.67 mole) of commercial *dl*-camphor-10-sulfonic acid (m.p. 200–202°), 67 g. (1.4 moles) of solid 85% sodium hydroxide, and 55 ml. (0.9 mole) of 85% hydrazine hydrate in 500 ml. of diethylene glycol had been gently refluxed for one hour, the temperature was raised to 195–210° by distilling off water and excess hydrazine, and refluxing was continued for another seven hours at this temperature. The sodium camphane-10-sulfonate, which crystallized from the cooled mother liquor, was filtered off, washed with water,

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(9) Scott and Lutz, *J. Org. Chem.*, **19**, 830 (1954).
(10) Scott and Heller, *J. Org. Chem.*, **20**, 1159 (1955).
(11) Scott and Gordon, *J. Org. Chem.*, **21**, 385 (1956).

acetone, or alcohol and dried, about 150 g. (0.62 mole) of the crude salt being obtained. By using the residual diethylene glycol in a subsequent reduction, the dissolved sodium camphanesulfonate is recoverable.[12] To 100 g. (0.42 mole) of the crude salt, 200 g. (0.96 mole) of phosphorus pentachloride[13] was added at 10–20° in small increments with stirring. After hydrolysis of excess pentachloride, 40 g. (0.17 mole, 38% conversion based on camphorsulfonic acid) of crude camphane-10-sulfonyl chloride was obtained.[14] The product melted at 82–84° after recrystallization from 2,2,4-trimethylpentane.

Anal. Calc'd for $C_{10}H_{17}ClO_2S$: S, 13.54; Cl, 14.98. Found: S, 13.66; Cl, 14.75.

Characterizing derivatives of camphane-10-sulfonic acid. The *morpholide* of camphane-10-sulfonic acid was prepared in the usual way from the sulfonyl chloride; it melts at 191–193°.

Anal. Calc'd for $C_{14}H_{25}NO_3S$: S, 11.16. Found: S, 10.7.

The melting point of this morpholide is significantly higher than that of *dl-camphor-10-sulfonmorpholide*,[15] which melts at 137–140°, although the related sulfonyl chlorides melt closely together.[16]

The *benzylamide* of camphane-10-sulfonic acid was similarly prepared; it melts at 114–115°.

Anal. Calc'd for $C_{17}H_{25}NO_2S$: C, 66.39; H, 8.20. Found: C, 66.66; H, 8.36.

Ethyl camphane-10-sulfonate. A mixture of 28 g. (0.086 mole) of dry silver camphane-10-sulfonate, prepared from the free sulfonic acid[17] and moist silver oxide, and 20 ml. (0.25 mole) of ethyl iodide in 300 ml. of acetonitrile, was refluxed gently for an hour. On cooling and diluting to one liter with cold water, 13 g. (0.053 mole, 61% conversion) of crude ethyl camphane-10-sulfonate was obtained which melted at 66–68° after several recrystallizations from 2,2,4-trimethylpentane.

Anal. Calc'd for $C_{12}H_{22}O_3S$: C, 58.48; H, 9.01. Found: C, 58.64; H, 9.14.

Action of ethanolic hydrogen chloride on camphane-10-sulfonyl chloride, the corresponding ethyl ester, and benzenesulfonyl chloride. Rates of ethanolysis of camphane-10-sulfonyl chloride and attack of ethanolic hydrogen chloride on the resultant ester were determined at reflux, and the rates of ethanolysis of benzenesulfonyl chloride at different temperatures were determined in a manner similar to that earlier reported for other systems.[9,10]

Solvolysis of ethyl camphane-10-sulfonate. A solution of 10.0 millimoles of ethyl camphane-10-sulfonate in 0.24 mole of ethanol was refluxed for 7.5 hours. Titration of the aqueous solution after partitioning the reaction products between ether and cold water, indicated that 4.5 millimoles of sulfonic acid were formed ($k = 0.0014$ min.$^{-1}$) and evaporation of the ether yielded 1.305 g. (5.3 millimoles) of unreacted ester ($k = 0.0013$ min.$^{-1}$).

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(12) Mr. Jesse A. Giles of this Laboratory reports nearly quantitative conversions under these conditions.

(13) Actually, no more pentachloride is needed when addition of a small amount fails to cause a visible reaction ("fizz").

(14) A small amount of a heavy oil, which may be 10-chlorocamphane saturated with the sulfonyl chloride, settled out after hydrolysis of excess pentachloride and was carefully excluded. A similar material was noted on treating the sulfonyl chloride at room temperature with aluminum chloride.

(15) It was not determined if this is a known compound.

(16) *dl*-Camphor-10-sulfonyl chloride, m.p. 80–82°, is rather unstable, decomposing slowly even in a closed container and hydrolyzing rapidly in moist air, whereas camphane-10-sulfonyl chloride is relatively stable, showing no signs of decomposition or hydrolysis after several weeks in an open container. A mixture of the two sulfonylchlorides melted at 65°.

(17) Crude camphane-10-sulfonic acid, obtained in 79% conversion on evaporation of its ether solution prepared by bubbling hydrogen chloride into a slurry of the sodium salt in ether, is a liquid in contrast to camphor-10-sulfonic acid (m.p. 200–202°). Although the reduced acid and its salts appear to be unreported in the literature, they were not analyzed.