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

A Study of Aliphatic Sulfonyl Compounds. V. Neopentanesulfonyl Chloride[1]

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Two *beta* methyl groups are approximately as effective in hindering ethanolysis of an aliphatic sulfonyl chloride as one *alpha* methyl group. New aliphatic sulfonyl compounds of neopentane prepared are the sulfonyl chloride, the sulfonic acid sesquihydrate, the sulfonic anhydride, the ethyl sulfonate, several sulfonamides as characterizing derivatives, the γ-chlorosulfonyl chloride, several γ-chlorosulfonamides as characterizing derivatives, and the disulfonmorpholide.

It has been observed that an *alpha* methyl group[2] hinders ethanolysis of an aliphatic sulfonyl chloride considerably less than an analogously situated *beta* methyl group hinders similar bimolecular attack on a primary alkyl bromide, probably because the atomic size of sulfur is greater than that of carbon. From a study of variously substituted sulfonyl chlorides it has been shown that a *beta* methyl group[3] is only moderately effective in hindering ethanolysis and that two *gamma* methyl groups[4] offer practically no hindrance. In order to determine the effect of two *beta* methyl groups, neopentanesulfonyl chloride was prepared and studied.

Neopentanesulfonyl chloride was prepared by photochemical chlorosulfonylation[5] of neopentane and also by sulfonylation of the Grignard reagent[6] from neopentyl chloride. It undergoes alcoholysis in boiling ethanolic hydrogen chloride (k = 0.016 min.$^{-1}$) at approximately the same rate as octane-2-sulfonyl chloride (k = 0.014 min.$^{-1}$),[2] thereby showing that two *beta* methyl groups are approximately as effective[7] as one *alpha* methyl in hindering the attack of ethanol on the chlorosulfonyl group.

Ethyl neopentanesulfonate was prepared by reacting the sulfonic acid with diazoethane[2] and by alkylating the dry silver salt of the sulfonic acid with ethyl iodide. The rate of attack on this ester by boiling ethanolic hydrogen chloride (k = 0.011 min.$^{-1}$), being considerably slower than that on ethyl octane-1-sulfonate (k = 0.051 min.$^{-1}$),[2] suggests that there might be a relationship between the steric requirements of a sulfonyl chloride and those of the corresponding ethyl sulfonate and that the rate constant for ethyl octane-2-sulfonate (k = 0.041 min.$^{-1}$)[2] may be somewhat high,[8] although this apparent discrepancy might be attributable to a fundamental difference between esters of primary and secondary sulfonic acids. That solvolysis of ethyl neopentanesulfonate is only of minor importance in this attack was shown by a single determination with boiling ethanol (k = 0.002 min.$^{-1}$).

EXPERIMENTAL

Neopentanesulfonyl chloride from neopentyl chloride. The Grignard reagent (0.25 mole, 76% yield) from 35.5 g. (0.33 mole) of neopentyl chloride[9] (b.p. 84–85°) was added at −5° to 0° to 40.5 g. (0.30 mole) of sulfuryl chloride in ether solution[6] and the sulfonyl chloride produced was separated and fractionally distilled.[2] In this manner 12.0 g. (0.07 mole, 21% yield from neopentyl chloride, 28% from Grignard reagent) of neopentanesulfonyl chloride[10] was obtained, b.p. 43–44°/1 mm., n_D^{25} 1.4556, d_4^{25} 1.1529, M_D 40.21.

Anal. Calc'd for $C_5H_{11}ClO_2S$: C, 35.19; H, 6.50; S, 18.79; Cl, 20.77. Found: C, 35.00; H, 6.38; S, 18.74; Cl, 20.26.

Neopentanesulfonyl chloride from neopentane. Commercial neopentane (95 mol-% min., b.p. 9–10°) (90 g., 1.2 moles) was chlorosulfonylated[5] in 200 ml. of carbon tetrachloride at −5° to 0° in the light from a 150-watt General Electric Par 38 Projector Flood lamp with a mixture of 0.75 mole of chlorine[11] and 1.5 moles of sulfur dioxide[11] during a period of one hour. The sulfonyl chloride[10] was separated and fractionally distilled as described above, 42 g. (0.25 mole, 20% conversion) being obtained with the same physical properties as that obtained from the previously described Grignard route.

γ-Chloroneopentanesulfonyl chloride. After another chlorosulfonylation of neopentane (79 g., 1.1 moles) the rotameters were found to have been erratic, evidently a much larger proportion of chlorine having been used than had been intended. On fractional distillation of the reaction products, 52 g. (0.32 mole, 27% conversion) of neopentanesulfonyl chloride, b.p. 53–55°/2 mm., n_D^{25} 1.4454, and then 37.9 g. (0.19 mole, 17% conversion) of crude γ-chloroneopentane-

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[2] Scott and Lutz, *J. Org. Chem.*, **19**, 830 (1954).

[3] Scott and Heller, *J. Org. Chem.*, **20**, 1159 (1955).

[4] Scott and Gordon, *J. Org. Chem.*, **21**, 385 (1956).

[5] Reed, U. S. Patent 2,046,090; *Chem. Abstr.*, **30**, 5593 (1936).

[6] Cherbuliez and Schnauder, *Helv. Chim. Acta*, **6**, 249 (1923).

[7] It is the intent of this series of studies to show major differences caused by steric or polar effects; there is no significance attached to the difference between the rate constants cited here.

[8] This is being investigated.

[9] Neopentyl chloride was prepared according to Whitmore and Fleming, *J. Am. Chem. Soc.*, **55**, 4161 (1933) by photochemical chlorination of commercial neopentane at −5° to 0° and also in the vapor phase.

[10] That prepared by the Grignard route turned black and gave off an odor of SO_2 after overnight storage, while that made directly from the hydrocarbon kept indefinitely without signs of decomposition. Whatever impurity causes decomposition in the first case must be present in very small amounts.

[11] Based on rotameter flow.

sulfonyl chloride, b.p. 98–99°/2.8 mm., were obtained. Refractionation of this latter material yielded 22.3 g. (0.11 mole) boiling at 84–85°/1.8 mm., n_D^{25} 1.4847–1.4848. After three more fractional distillations, analysis of a sample (b.p. 78–79°/0.8 mm., n_D^{25} 1.4847), showed the chlorine content to be too low.[12] As it was not our object to produce this sulfonyl chloride at this time, no further attempts have been made to purify it. It was derivatized, however.

Anal. Calc'd for $C_5H_{10}Cl_2O_2S$: C, 29.28; H, 4.91; S, 15.63; Cl, 34.58. Found: C, 29.57; H, 5.02; S, 15.39; Cl, 33.34.

Characterizing derivatives of neopentanesulfonic acid and γ-chloroneopentanesulfonic acid. Several solid sulfonamides which were prepared from neopentanesulfonyl chloride and from γ-chloroneopentanesulfonyl chloride in the usual way are recorded in Table I. Equivalence of the neopentanesulfonyl chloride prepared by the two methods was further shown by there being no depression in melting point of a mixture of the piperidide from the chlorosulfonylated hydrocarbon (m.p. 89–90°) with that derived from the sulfonyl chloride produced from the Grignard reagent (m.p. 90–91°).

The residue from distilling neopentanesulfonyl chloride from a normal chlorosulfonylation of neopentane was shown to contain some disulfonyl chloride by isolation of the disulfonmorpholide from the reaction product of an excess of morpholine with the still residue. This derivative also is listed in Table I.

TABLE I

SOLID AMIDES OF NEOPENTANE-, NEOPENTANEDI-, AND γ-CHLORONEOPENTANE-SULFONIC ACIDS

		Analyses			
		Calculated		Found	
Derivative	M.P., °C.	C	H	C	H
Neopentanesulfon-					
n-Butylamide	54–55	52.14	10.21	52.24	10.14
Anilide	70.5–71.5	58.12	7.53	58.22	7.75
Benzylamide	89–91	59.76	7.95	59.85	7.89
Piperidide	90–91	54.76	9.65	55.02	9.46
Cyclohexylamide	90–91	56.62	9.93	56.82	10.11
Morpholide	113–114	48.85	8.66	48.86	8.73
Amide	122–123	39.71	8.67	39.94	8.63
Neopentanedisulfon-					
Morpholide	159–160	42.14	7.07	42.13	7.04
γ-Chloroneopentanesulfon-					
Benzylamide	63–64	52.26	6.58	52.74	6.83
Amide	85–86				
Morpholide	109–110	42.27	7.10	42.46	7.14

Neopentanesultone.[13] Hydrogen chloride was lost from crude γ-chloroneopentanesulfonic acid (6.8 g., 0.036 mole) [obtained by alcoholysis of 7.6 g. (0.037 mole) of crude γ-chloroneopentanesulfonyl chloride (b.p. 76°/0.4 mm., n_D^{25} 1.4804)] on heating at 160–170° under reduced pressure, and 2.8 g. (0.019 mole, 52% conversion) of yellow, crude, liquid neopentanesultone distilled over at 150–160°/18–20 mm. The product was partitioned between ether and water and the solid sultone obtained on evaporating the ether solution was recrystallized from carbon tetrachloride, m.p. 51.5–52°. Sultone formation established the position of the chlorine on the *gamma* carbon atom. This sultone has been reported previously (m.p. 50.5°, b.p. 108°/1 mm.) as having been prepared by dehydrating γ-hydroxyneopentanesulfonic acid derived from the γ-bromohydrin.[14]

Anal. Calc'd for $C_5H_{10}O_3S$: C, 40.21; H, 6.61. Found: C, 39.98; H, 6.71.

Ethyl neopentanesulfonate. Neopentanesulfonic acid,[15] obtained by bubbling hydrogen chloride into an ether slurry of the dry sodium[16] sulfonate procured through saponification of neopentanesulfonyl chloride, then filtering out the sodium chloride and evaporating the ether, was converted into the ethyl ester directly with ethereal diazoethane[2] (41% conversion) and by means of the silver salt with ethereal ethyl

TABLE II

ETHANOLYSIS OF NEOPENTANESULFONYL CHLORIDE[a]

Time mins.	RSO_2Cl[b] millimoles	RSO_2OEt[b] millimoles	RSO_2OH[c] millimoles	k, min.$^{-1}$
10	16.4	2.3	1.3	0.020
15	15.3	3.2	1.5	.018
20	14.9	3.4	1.7	.015
30	13.1	5.4	1.5	.014
30	12.3[d]	6.6[d]	1.1[e]	.016
45	9.5	4.1	4.7[f]	.017
45	10.2[d]	6.2[d]	3.6[e]	.015
60	7.3	4.9	7.8	.017
60	8.0[d]	5.6[d]	6.4[e]	.015
75	6.3	5.5	8.2	.015
75	6.4	4.9	8.7	.015
90	4.2	5.6	10.2	.017
			Average[g]	0.016

[a] Refluxed (*ca.* 84°) a mixture of 20 millimoles of RSO_2Cl, 34 millimoles of HCl, and 0.41 mole of EtOH. [b] Except as noted, from weight and refractive index of the distilled mixture of RSO_2Cl and ester from ether layer from partitioning between water and ether. Refractive index usually changed no more than 0.0003 on distilling *in vacuo* to remove chance impurities. [c] By stoichiometric difference from RSO_2Cl and ester, unless noted. [d] By stoichiometric difference from acid and from refractive index of distilled mixture of RSO_2Cl and ester from ether extract. [e] From titration of non-volatile acid. Heating avoided except for mild warming at end of vacuum evaporation. [f] From weight of residue from evaporating aqueous extract *in vacuo*. [g] Graphical average.

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[12] It has been observed that it is frequently difficult to prepare sulfonyl chlorides in general for which analyses show the proper amount of chlorine; the chlorine content of samples having identical physical properties sometimes will vary considerably.

[13] This preparation was carried out by Mr. Morgan S. Heller.

[14] Nilsson, Thesis, Lund University, 1946; *Brit. Abstr.*, AII, 137 (1948).

[15] The free acid is a hygroscopic, viscous liquid which readily forms a sesquihydrate which can be recrystallized from *n*-pentane, and which itself is quite hygroscopic. *Anal.* Calc'd for $C_5H_{12}O_3S \cdot {}^3/_2H_2O$: Neutr. equiv., 179.2. Found: Neutr. equiv., 178.9.

[16] Some of the other salts of neopentanesulfonic acid behave oddly. Earlier attempts to prepare the acid from the barium salt were abandoned when barium neopentanesulfonate was found to have an anomalously high solubility (15.6 g. in 100 g. of water at 25°) approaching that of barium nitrate. The potassium salt forms gels with fairly large volumes of methyl, ethyl, *n*-propyl, isopropyl, or *n*-butyl alcohols (no others were tried), although the sodium salt is readily recrystallized from ethanol.

From 15.8 g. of the sodium salt was obtained 14.8 g. of black, liquid residue from which was distilled by mild heating under a vacuum 2.5 g. of a liquid, boiling at 40–50°/3 mm., and leaving 12.0 g. of sulfonic acid residue. The distillate contained neither sulfur nor chlorine, was soluble in water, gave a positive hydroxamate test for alcohols, and reacted with acetyl chloride. It has not been further investigated.

TABLE III

ATTACK OF ETHANOLIC HYDROGEN CHLORIDE ON ETHYL NEOPENTANESULFONATE[a]

Time mins.	RSO_2OEt, millimoles Initial	Final[c]	RSO_2OH millimoles[d]	k[b], min.$^{-1}$
15	2.74	2.37	0.37	0.010
25	3.10	2.24	0.86	.013
40	6.05	3.72	2.33	.012
60	5.29	3.12	2.16	.009
			Average[e]	0.011

[a] Refluxed (*ca.* 84°) mixtures in proportions of 10 millimoles of ester, 17 millimoles of HCl, and 0.30 mole of EtOH. [b] Constant for combined attacks of HCl and EtOH. [c] By stoichiometric difference from RSO_2OH. [d] From differential titrations of aqueous extract for total acidity and chloride ion. [e] Graphical average.

iodide (69% conversion). The ethyl neopentanesulfonate had identical properties regardless of method of preparation, b.p. 62–63°/0.8 mm., n_D^{25} 1.4318, d_4^{25} 1.0567, *M*, 44.23.

Anal. Calc'd for $C_7H_{16}O_3S$: C, 46.64; H, 8.94. Found: C, 46.81; H, 8.77.

Neopentanesulfonic anhydride. On heating at 100° equivalent amounts of anhydrous silver neopentanesulfonate and neopentanesulfonyl chloride, a conversion of about 45% to neopentanesulfonic anhydride, m.p. 81–82°, was obtained.

Anal. Calc'd for $C_{10}H_{22}O_5S_2$: Neut. equiv., 143.20. Found: Neut. equiv., 143.78, 143.83.

Action of ethanolic hydrogen chloride at reflux on neopentanesulfonyl chloride and ethyl neopentanesulfonate. Ethanolysis of neopentanesulfonyl chloride and attack of ethanolic hydrogen chloride on the resulting ester were carried out in a manner similar to that earlier reported for other systems.[2,3] The data are recorded in Tables II and III.

Solvolysis of ethyl neopentanesulfonate. A solution of 0.450 g. (0.0025 mole) of ethyl neopentanesulfonate in 10 ml. (0.17 mole) of dry ethanol was refluxed for 3.0 hours, then partitioned between cold water and ether. Titration of the aqueous layer indicated that 0.0006 mole of sulfonic acid had been formed and that solvolysis had progressed 24% (k = 0.0015 min.$^{-1}$).

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