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A Study of Aliphatic Sulfonyl Compounds. IV. Neopentylmethanesulfonyl Chloride[1]

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The absence of a steric effect from two *gamma* methyl groups on the rate of ethanolysis of an aliphatic sulfonyl chloride and on the rate of attack by ethanolic hydrogen chloride on the corresponding ethyl ester has been demonstrated.

A new aliphatic sulfonyl chloride, 2,2-dimethylbutane-4-sulfonyl chloride, the corresponding sulfonyl fluoride, and the ethyl ester and several characterizing amides of the corresponding sulfonic acid have been prepared.

As a methyl group in the *beta* position is only moderately effective in hindering ethanolysis of an aliphatic sulfonyl chloride,[2] it was supposed that one more distantly situated would have no appreciable influence on reactions of sulfonyl chlorides with bases having steric requirements no greater than those of ethanol. Neopentylmethanesulfonyl chloride, having two *gamma* methyl groups, was used as a model to test the validity of this assumption.

Neopentylmethanesulfonyl chloride, from sulfonylating the Grignard reagent from neopentylcarbinyl chloride,[3] undergoes ethanolysis in an excess of boiling (approximately 84°) ethanolic hydrogen chloride at about the same rate ($k = 0.092$ min.$^{-1}$) as that determined for octane-1-sulfonyl chloride ($k = 0.089$ min.$^{-1}$),[4] thereby verifying the assumption that *gamma* methyl groups are ineffective in hindering ethanolysis.

Rate constants during ethanolysis are influenced by rate of reflux; for example, at a slow rate of reflux during ethanolysis of neopentylmethanesulfonyl chloride, the average temperature was 81.8° ($k = 0.076$ min.$^{-1}$), whereas at a very rapid rate of reflux, it was 85.7° ($k = 0.103$ min.$^{-1}$). Prior to this investigation, occasional measurements indicated that the temperature of reflux approximates 84° with the simmering water bath normally used. Probably 0.092 min.$^{-1}$, determined for approximately 84° by means of the Arrhenius equation, is the most representative rate constant[5] for comparing neopentylmethanesulfonyl chloride with other sulfonyl chlorides previously reported.[2,4,6]

The ethyl ester of neopentylmethanesulfonic acid was prepared by reacting the acid with diazoethane and by reacting the silver salt of the acid with ethyl iodide; only the latter method yielded analytically acceptable material, however. Attack on this ester by an excess of boiling ethanolic hydrogen chloride ($k = 0.051$ min.$^{-1}$) occurs as readily as that on ethyl octane-1-sulfonate ($k = 0.051$ min.$^{-1}$),[4] further confirming the conclusion that *gamma* methyl groups are too far removed

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

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

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

[5] The average rate constant determined from several experiments in which the temperature was not observed is 0.088 min.$^{-1}$, substantially in agreement with this calculated value. (The calculated value for 83.5° also is 0.088 min.$^{-1}$.)

[6] There is no significance attached to the difference between the rate constants for neopentylmethane- and octane-1-sulfonyl chlorides, it being the intent in these studies to show major differences. Presently, rates are being determined at lower temperatures for a select few of the sulfonyl chlorides investigated, to determine if steric or polar factors influence the energy of activation of alcoholysis.

from the seat of reaction to influence appreciably the rate. A single determination made of the rate of alcoholysis of ethyl neopentylmethanesulfonate in an excess of boiling ethanol (k = 0.003 min.$^{-1}$) indicates that probably solvolysis is only a minor contributor to the attack on the ester by ethanolic hydrogen chloride.

EXPERIMENTAL

4-Chloro-2,2-dimethylbutane. Ethylene was absorbed in a cold[7] (−30° to −20°) *n*-pentane solution of *tert*-butyl chloride in the presence of aluminum chloride according to Schmerling.[8] The product, 4-chloro-2,2-dimethylbutane, obtained in 25% yield, was fractionally distilled, b.p. 116–117.5°/759 mm., $n_{\rm D}^{20}$ 1.4158 (lit.[8] b.p. 115°/760 mm., $n_{\rm D}^{20}$ 1.4160;[9] b.p. 115°, $n_{\rm D}^{20}$ 1.4161), and characterized as the anilide of γ,γ-dimethylvaleric acid, m.p. 138–139° (lit.[8] m.p. 138–139°), obtained by the action of phenyl isocyanate on the Grignard reagent, and as the 3,5-dinitrobenzoate, m.p. 80–81° (lit.[8,10,11] m.p. 83.5°), of 3,3-dimethyl-1-butanol obtained by oxidation of the Grignard reagent, and as the α-naphthylamine addition product, m.p. 132–133° (lit.[8,10] m.p. 132.5–133°), of the dinitrobenzoate. However, treating the Grignard reagent with mercuric chloride yields a mercuri chloride melting at 178–180°, which is considerably higher than the 133–133.5° reported for this compound by Whitmore.[9]

In view of this discordance between the reported and the observed values for the melting point of the mercuri chloride, and of the possibility of rearrangement during the Schmerling synthesis, 4-chloro-2,2-dimethylbutane also was prepared from neopentylcarbinol[12] derived from neopentylmagnesium chloride[13] and formaldehyde. Thionyl chloride in the presence of pyridine[14] did not bring about conversion of the carbinol into the chloride; however, the general method of heating with hydrochloric acid in the presence of zinc chloride[15] was satisfactory. Physical constants (b.p. 117–118°, $n_{\rm D}^{20}$ 1.4156) for the resultant chloride are in agreement with those of the chloride obtained from *tert*-butyl chloride and ethylene. The mercuri chloride prepared from the Grignard reagent made from this carbinol-derived chloride melted at 178–180°, as did a mixture of this mercuri chloride and that prepared *via* *tert*-butyl chloride and ethylene. As Whitmore gave neither the method of preparation nor the physical properties of the alcohol used for his reported synthesis of 4-chloro-2,2-dimethylbutane, it is not possible to duplicate the exact procedure outlined by him.

Anal. Calc'd for $C_6H_{13}ClHg$: Cl, 11.04. Found: Cl, 11.49, 11.42.

2,2-Dimethylbutane-4-sulfonyl chloride. One mole (121 g.) of 4-chloro-2,2-dimethylbutane was converted into the Grignard reagent (68% by titration) which was added slowly at 0° to 5° to vigorously stirred ethereal sulfuryl chloride (1.1 moles) according to the method of Cherbuliez.[3] Fractional distillation, through a 36 cm. × 16 mm. Vigreux column fitted with partial condensation still head, of the residue from evaporating the water-washed ether solution yielded 62.3 g. (0.34 mole) of neopentylmethanesulfonyl chloride, m.p. 43–44°, b.p. 60–61°/1 mm., a conversion of 34% based on the alkyl chloride. The distilland was stabilized with crystals of potassium carbonate.

Anal. Calc'd for $C_6H_{13}ClO_2S$: C, 39.02; H, 7.10; S, 17.36; Cl, 19.20. Found: C, 39.12; H, 6.94; S, 17.41; Cl, 18.95.

Characterizing derivatives of 2,2-dimethylbutane-4-sulfonic acid. The amide and several substituted amides were prepared in the usual manner from neopentylmethanesulfonyl chloride and ammonia or the appropriate amine in ether. Their properties are recorded in Table I.

TABLE I

AMIDE DERIVATIVES OF 2,2-DIMETHYLBUTANE-4-SULFONIC ACID

		Analyses			
		Calc'd		Found	
Derivative	M.P., °C.	C	H	C	H
Isopropylamide	74.5–75	52.11	10.20	52.38	10.07
n-Butylamide	76.5–77.5	54.26	10.47	54.39	10.23
Isobutylamide	83–83.5	54.26	10.47	54.41	10.57
n-Propylamide	84–85	52.11	10.20	52.60	9.96
Amide	96–97	43.61	9.15	43.72	8.84
Morpholide	104.5–105.5	51.03	8.99	51.02	8.76
Cyclohexylamide	118.5–119.5	58.21	10.19	58.55	9.89
Benzylamide	121–122	61.14	8.29	61.41	7.99

2,2-Dimethylbutane-4-sulfonyl fluoride. Neopentylmethanesulfonyl chloride (5.0 g., 0.027 mole) was refluxed for two hours with 15.0 g. (0.26 mole) of potassium fluoride in 100 ml. of water according to the method developed by Salzberg.[16] There was obtained 2.0 g. (0.012 mole, 44% conversion) of sulfonyl fluoride, distilled through a Vigreux column from potassium carbonate, with b.p. 53–54°/2.3 mm., $n_{\rm D}^{25}$ 1.4077, d_4^{25} 1.0811, $M_{\rm D}$ 39.3.

Anal. Calc'd for $C_6H_{13}FO_2S$: C, 42.84; H, 7.79. Found: C, 43.21; H, 7.54.

Ethyl 2,2-dimethylbutane-4-sulfonate. The dried silver salt of the sulfonic acid from alcoholysis of neopentylmethanesulfonyl chloride was converted into the ethyl ester by means of ethyl iodide,[17] conversion being about 61% based on the free sulfonic acid. The sweet smelling liquid, fractionally distilled in the same manner as the sulfonyl chlo-

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(7) Maximum absorption occurred at a lower temperature than the −15° to −10° noted by Schmerling.[8]

(8) Schmerling, *J. Am. Chem. Soc.*, **67**, 1152 (1945).

(9) Whitmore and Bernstein, *J. Am. Chem. Soc.*, **60**, 2626 (1938).

(10) Sutter, *Helv. Chim. Acta*, **21**, 1266 (1938).

(11) Huston and Agett, *J. Org. Chem.*, **6**, 123 (1941).

(12) B.p. 140–142°, $n_{\rm D}^{23}$ 1.4160 (lit.[10] b.p. 140–143°;[11] b.p. 141–143°, $n_{\rm D}^{23}$ 1.4160; and Malinovskii, Volkova, and Morozova, *Zhur. Obshchei Khim.*, **19**, 114 (1949) give b.p. 140–142°, $n_{\rm D}^{15}$ 1.4323). The carbinol was characterized as the 3,5-dinitrobenzoate and as the α-naphthylamine addition product of that ester. Melting points of these derivatives agreed with those of the derivatives obtained *via* *tert*-butyl chloride and ethylene, and no depression was observed on melting correspondent mixtures of these derivatives. The α-naphthylurethan of the carbinol melted at 81.5–82°, which corresponds with the 83° reported by Whitmore.[9]

(13) Neopentyl chloride, b.p. 84–85.5°/760 mm., $n_{\rm D}^{20}$ 1.4040 [Whitmore and Fleming, *J. Am. Chem. Soc.*, **55**, 4161 (1933) give b.p. 84.4°/760 mm., $n_{\rm D}^{20}$ 1.4042], was prepared by liquid phase photochemical chlorination of neopentane.

(14) On following Whitmore's directions,[9] a copious tarry residue and a high-boiling liquid (boiling range 220–260°) resulted. Apparently the liquid was the chlorosulfite, for, upon refluxing it with quinoline hydrochloride as suggested by the work of Gerrard and Tolcher, *J. Chem. Soc.*, 3640 (1954), sulfur dioxide was evolved. However, this treatment gave only the original alcohol.

(15) Copenhaver and Whaley, *Org. Syntheses*, Coll. Vol. I, (2nd ed.), 142 (1941).

(16) Salzberg, U. S. Patent, 2,276,097, March 10, 1942 [*Chem. Abstr.*, **36**, 4662 (1942)].

(17) The ester prepared by reacting the free acid with diazoethane was not analytically acceptable even after repeated fractional distillation. Carbon and hydrogen contents were considerably low and the density and refractive index were consistently high.

TABLE II

ETHANOLYSIS OF 2,2-DIMETHYLBUTANE-4-SULFONYL CHLORIDE[a]

Temp. °C.	Time mins.	RSO_2Cl, Initial	millimoles Final[d]	RSO_2OEt[b] millimoles	RSO_2OH[c] millimoles	k, min.$^{-1}$
81.7	5	4.995	3.377	1.604	0.014	0.078
81.7	10	4.992	2.334	2.593	0.066	0.076
81.7	15	4.987	1.631	3.130	0.225	0.075
81.7					Average[e]	0.076
85.7	10	4.892	1.766	2.821	0.306	0.102
85.7	15	4.992	1.056	3.309	0.628	0.104
85.7					Average[e]	0.103

[a] Refluxed at indicated temperature; 5 millimoles of RSO_2Cl with 13 millimoles of HCl, and 0.25 mole of EtOH. [b] By stoichiometric difference from RSO_2OH and RSO_2Cl. [c] From total acidity and chloride ion content of aqueous extract. Checked by titration of non-volatile acid. [d] From chloride ion content of hydrolyzate of RSO_2Cl and ester in ether layer from partitioning between water and ether. Checked with values from stoichiometric difference from RSO_2OH and refractive index of totally distilled RSO_2Cl and ester in ether extract. [e] Graphical average.

TABLE III

ATTACK OF ETHANOLIC HYDROGEN CHLORIDE ON ETHYL 2,2-DIMETHYLBUTANE-4-SULFONATE[a]

Time mins.	RSO_2OEt, Initial	milli-moles Final[d]	RSO_2OH[b] milli-moles	k,[c] min.$^{-1}$
5	5.013	3.861	1.153	0.052
10	5.029	3.016	2.013	0.051
15	5.059	2.286	2.773	0.053
25	5.044	1.501	3.543	0.048
			Average[e]	0.050

[a] Refluxed (*ca.* 84°) 5 millimoles of ester with 12 millimoles of HCl and 0.44 mole of EtOH.

[b] From titration of non-volatile acid.

[c] Constant for combined attacks of HCl and EtOH.

[d] By stoichiometric difference from RSO_2OH.

[e] Graphical average.

ride, had the following properties: b.p. 90°/1 mm., n_D^{25} 1.4337, d_4^{25} 1.0276, M_D 49.2.

Anal. Calc'd for $C_8H_{18}O_3S$: C, 49.45; H, 9.34. Found: C, 49.35; H, 9.16.

Action of ethanolic hydrogen chloride at reflux on 2,2-dimethylbutane-4-sulfonyl chloride and the correspondent ethyl ester. Rates of ethanolysis of 2,2-dimethylbutane-4-sulfonyl chloride and attack of ethanolic hydrogen chloride on the resultant ester were determined in a manner similar to that earlier reported for other systems.[2,4] The data are presented in Tables II and III.

Solvolysis of ethyl 2,2-dimethylbutane-4-sulfonate. The rate of solvolysis of the sulfonic ester by ethanol was estimated by refluxing a mixture of 0.9768 g. (5.027 millimoles) of ethyl neopentylmethanesulfonate and 19.7 g. (0.43 mole) of dry ethanol for 302 mins. Titration of the aqueous extract indicated formation of 3.24 millimoles of acid, representing 65% reaction (k = 0.003 min.$^{-1}$).

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