[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, RENSSELAER POLYTECHNIC INSTITUTE]

The Decomposition of Optically Active 2-Octanesulfonyl Chloride[1]

BY HARRY F. HERBRANDSON, WILLIAM S. KELLY AND JOHN VERSNEL

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Optically active 2-octanesulfonyl chloride has been prepared and its decomposition to 2-chlorooöctane and sulfur dioxide under various conditions has been studied. The 2-chlorooöctane obtained from the thermal decomposition in the absence of solvent, in diphenyl ether, in the presence of ultraviolet light, and in the presence of peroxide is in each case racemic and probably results from a free radical reaction. The 2-chlorooöctane obtained from the decomposition in N,N-dimethylformamide as solvent is optically active and results from inversion and partial racemization at the active center. An ionic mechanism is suggested for this reaction.

Alkanesulfonyl chlorides undergo thermal decomposition to the alkyl chloride, alkene, sulfur dioxide and hydrogen chloride. The reaction has been of value in determining the position of the sulfonyl chloride group which results from the chlorosulfonation of hydrocarbons.[2]

Various factors can exert an influence on the course of the reaction. Asinger[3] reported that the best yields of alkyl chloride resulted when the alkanesulfonyl chlorides were decomposed in a 30–35% solution in a solvent of b.p. 140–150°. The use of aromatic hydrocarbon solvents has been found to minimize the formation of olefin,[4] whereas Friedel–Crafts type catalysts[5] increase the formation of olefins.[3] Peroxides[6] and ultraviolet light[3,6b] markedly lower the temperature of decomposition of the alkanesulfonyl chlorides. An α-phenyl group apparently favors the decomposition.[7] Limpricht has reported the decomposition of phenylmethanesulfonyl chloride on heating above its melting point and Kharasch has reported an unsuccessful attempt to prepare 1-phenyl-1-ethanesulfonyl chloride.

In view of the free radical nature of the chlorosulfonation reaction[8] which by a side reaction can yield alkyl chloride as well, it seemed desirable to study the reaction of an optically active alkanesulfonyl chloride to determine whether or not racemization, consistent with the intermediate formation of a free radical,[9] did occur in the course of the decomposition. Because of the availability of optically active 2-octyl compounds, *d*- and *l*-2-octanesulfonyl chlorides were synthesized and their decompositions studied under a variety of conditions.

2-Octanesulfonyl chloride of $[\alpha]^{20}\mathrm{D}$ $-0.72°$ (homogeneous) was obtained by the oxidative chlorination of 2-octanethiol[10] which had been prepared through the bromide and isothiouronium salt from 2-octanol of $[\alpha]^{20}\mathrm{D}$ $-7.7°$. Alternatively, the sulfonyl chloride, $[\alpha]^{20}\mathrm{D}$ $+0.87°$ (homogeneous) was prepared by the oxidative chlorination[11] of 2-octyl thiocyanate[12] of $[\alpha]^{20}\mathrm{D}$ $+44.8°$. The rotations observed in these transformations permit an assignment of $[\alpha]\mathrm{D} \sim 1.3°$ for optically pure 2-octanesulfonyl chloride assuming no racemization in the oxidative chlorination reaction.[13] The extremely low specific rotation for the compound is noteworthy. The oxidative chlorination reactions in no case use strongly basic conditions which might lead[16] to racemization. Furthermore, that there is extensive racemization in the formation of the sulfonyl chloride is also rendered unlikely by the relatively high rotations of $-20.7°$ and $+4.2°$ for 2-chlorooöctane from the decompositions of the sulfonyl chloride in a reaction which has been shown to involve partial racemization (see below).

Table I presents the results obtained from the decomposition of racemic 2-octanesulfonyl chloride under various conditions, and Table II presents the results obtained with the optically active compound.

Evidence for a free radical mechanism in certain of the decomposition reactions of 2-octanesulfonyl chloride is apparent. The isolation of racemic 2-chlorooöctane from the peroxide-catalyzed, the radiation-induced and the thermal decomposition in diphenyl ether and in the absence of solvent is consistent with the intermediate formation of the 2-octyl radical. As has been noted earlier,[3,6] the

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[1] This work was supported in part by the Office of Naval Research and in part by a grant from the R.P.I. Research Fund.

[2] J. H. Helberger, *Die Chemie*, **55**, 172 (1942); F. Asinger, *Ber.*, **77B**, 191 (1944); J. H. Helberger, G. Manecke and H. M. Fischer, *Ann.*, **562**, 23 (1949); A. P. Terent'ev and A. I. Gershenovich, *Zhur. Obshchei Khim.*, **23**, 209, 215 (1953).

[3] F. Asinger, W. Schmidt and F. Striegler, U. S. Dept. Comm., O. T. S. Report, *PB* 850 (1941).

[4] Italian Patent 390,187 (July 31. 1941); *Chem. Zentr.*, **113**, **II**, 2848 (1942).

[5] W. E. Truce and C. W. Vriesen, THIS JOURNAL, **75**, 5032 (1953).

[6] (a) H. J. Schumacher and J. Stauff, *Die Chemie*, **55**, 341 (1942); (b) M. A. Smook, E. T. Pietski and C. F. Hammer, *Ind. Eng. Chem.*, **45**, 2731 (1953).

[7] H. Limpricht, *Ber.*, **6**, 532 (1873); M. S. Kharasch, E. M. May and F. R. Mayo, *J. Org. Chem.*, **3**, 189 (1938).

[8] M. S. Kharasch, T. H. Chao and H. C. Brown, THIS JOURNAL, **62**, 2393 (1940).

[9] C. Walling, "Free Radicals in Solution," John Wiley and Sons, Inc., New York, N. Y., 1957, p. 24.

[10] C. Ziegler and J. M. Sprague, *J. Org. Chem.*, **16**, 621 (1951).

[11] T. B. Johnson and I. B. Douglas, THIS JOURNAL, **61**, 2548 (1939).

[12] W. G. Rose and H. L. Haller, *ibid.*, **58**, 2648 (1936).

[13] Kenyon, *et al.*,[14] prepared 2-octyl thiocyanate of $[\alpha]^{20}\mathrm{D}$ 61.8°[12] from 2-octyl *p*-toluenesulfonate, a reaction which should not have involved any racemization. The *p*-toluenesulfonate had been prepared in turn from 2-octanol of $[\alpha]^{20}\mathrm{D}$ $+9.70°$ by reactions which wuuld not involve racemization. Since the maximum rotation which has been reported for 2-octanol is $[\alpha]^{25}\mathrm{D}$ $10.3 \pm 0.3°$,[15] the 2-octanol of Kenyon, *et al.*, and hence the 2-octyl thiocyanate of $[\alpha]^{20}\mathrm{D}$ 61.8° must have been $94 \pm 3\%$ optically pure. Thus the rotation of optically pure 2-octyl thiocyanate must be $[\alpha]^{20}\mathrm{D}$ $66 \pm 2°$. The oxidative chlorination of 2-octyl thiocyanate does not involve the asymmetric carbon, so the thiocyanate of $[\alpha]^{20}\mathrm{D}$ $+44.8°$ and the sulfonyl chloride of $[\alpha]^{20}\mathrm{D}$ $+0.87°$ in the experiments cited above must be $69 \pm 2\%$ optically pure with a rotation for optically pure 2-octanesulfonyl chloride of 1.3°.

[14] J. Kenyon, H. Phillips and V. P. Pittman, *J. Chem. Soc.*, 1072 (1935).

[15] N. Kornblum, L. Fishbein and R. A. Smiley, THIS JOURNAL, **77**, 6261 (1955).

[16] W. von E. Doering and L. K. Levy, *ibid.*, **77**, 509 (1955).

TABLE I

THE THERMAL DECOMPOSITION OF RACEMIC 2-OCTANESULFONYL CHLORIDE

Conditions	Initial decompn. temp., °C.	Temp. maintained, °C.	RCl, %	Olefin, %	RSO_2Cl recovd., %
Diphenyl ether solvent	165	165–170	27	41	. .
Diphenyl ether solvent	. .	190	43	30	. .
No solvent	155	155–170	60	31	. .
300 watt lamp	. .	120		No reacn.	
Hg vapor lamp	100	135–140	13	21	13
Hg vapor lamp	100	135–140	37	11	34
Hg vapor lamp	100	140–145	71	10	14
Benzoyl peroxide (0.0013 mole/mole RSO_2Cl)	85	115–120	16	0	81
Benzoyl peroxide (0.024 mole/mole RSO_2Cl)	85	120	21	0	60
Benzoyl peroxide (0.042 mole/mole RSO_2Cl)	85	115–120	24	0	70
N,N-Dimethylformamide +12% LiCl solvent		120	52	. .	. .

TABLE II

THE THERMAL DECOMPOSITION OF OPTICALLY ACTIVE 2-OCTANESULFONYL CHLORIDE

$[\alpha]^{20}D$[a]	Conditions	Decompn. temp., °C.	RCl, %	Olefin, %	RSO_2Cl Recovd., %	$[\alpha]^{22}D$[a] of RCl
+0.8°	Diphenyl ether solvent	165	50	. .	. .	0
+1.21[b]	No solvent	165–170	86	. .	. .	0
−0.72	Hg vapor lamp	140–145	70	6	13	0
−0.72	Benzoyl peroxide (0.054 mole/mole RSO_2Cl)	115–120	20	. .	71	0
−0.72	N,N-Dimethylformamide solvent	130–135	23	. .	. .	+ 4.2°
+4.42[c]	N,N-Dimethylformamide solvent	130	27	20	. .	−20.7[d]
+0.83	N,N-Dimethylformamide solvent +12% LiCl	120–125	59	. .	. .	0

[a] Rotations measured on the homogeneous compound. [b] Rotation measured in benzene solution at 27°. [c] Rotation measured in benzene solution at 25°. This sample of 2-octanesulfonyl chloride was contaminated with (+)-2-octyl thiocyanate. [d] Rotation measured in benzene at 25°.

diminution in the temperature required for decomposition in the presence of peroxides or ultraviolet light points to a free radical mechanism. For the thermal reaction, the initiating step may well be that represented by equation 1 instead of 2 as suggested by Smook[6b] in view of the relative strengths of the C–S and S–Cl bonds,[17] whereas in the presence of peroxides the initiating step would be represented by equation 3. Reaction 5 is reversible and in the presence of a high concentration of sulfur dioxide, as is the case with the chlorosulfonation reaction, shifts to the left.[6a,18]

Initiating:

$$RSO_2Cl \longrightarrow R\cdot + \cdot SO_2Cl \quad (1)$$

and/or

$$RSO_2Cl \longrightarrow RSO_2\cdot + Cl\cdot \quad (2)$$

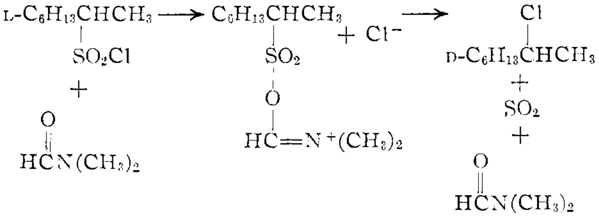
$$RSO_2Cl + R'\cdot \longrightarrow RSO_2\cdot + R'Cl \quad (3)$$

Propagating:

$$RSO_2Cl + R\cdot \longrightarrow RSO_2\cdot + RCl \quad (4)$$

$$RSO_2\cdot \rightleftharpoons R\cdot + SO_2 \quad (5)$$

A different type of decomposition from which arises optically active 2-chlorooctane occurs in N,N-dimethylformamide solution. The 2-chlorooctane results from inversion at the asymmetric carbon, a fact which suggests that the decomposition in this solvent is ionic. Acyl halides are known to react with N,N-dimethylformamide to give O-acyl derivatives,[19] and aromatic sulfonyl chlorides react with primary carboxamides at the oxygen in a step intermediate to the dehydration to nitriles.[20] Reaction of the 2-octanesulfonyl chloride in a similar way should form a reactive cation that would be susceptible to nucleophilic attack by chloride ion with inversion of configuration at the asymmetric carbon.



$$\text{L-}C_6H_{13}\underset{\underset{\underset{\underset{HCN(CH_3)_2}{\overset{\|}{O}}}{+}}{SO_2Cl}}{CH}CH_3 \longrightarrow C_6H_{13}\underset{\underset{\underset{HC{=}N^+(CH_3)_2}{|}}{\underset{|}{\underset{O}{SO_2}}}}{CH}CH_3 + Cl^- \longrightarrow \text{D-}C_6H_{13}\overset{Cl}{\overset{|}{C}}HCH_3 + SO_2 + \underset{HCN(CH_3)_2}{\overset{O}{\overset{\|}{}}}$$

Since the maximum rotation that has been reported for 2-chlorooctane is $[\alpha]^{20}D$ 36.15°,[21] extensive racemization has occurred in the course of the reaction. However, 2-chlorooctane is completely racemized by lithium chloride in dimethylformamide at 135° for one hour, so the observed racemization presumably takes place subsequent to the formation of the 2-chlorooctane from the sulfonyl chloride. The recovery of chloride from the decomposition in dimethylformamide was less than 30% which may in part be attributable to an elimination reaction catalyzed by this solvent.[22]

Experimental

d,l-2-Octanesulfonyl Chloride.—This compound, b.p. 92.5–93.5° (0.2 mm.), $n^{25}D$ 1.4598 (lit.[23] b.p. 90° (1 mm.),

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[17] L. Pauling, "The Nature of the Chemical Bond," 2nd ed., Cornell University Press, Ithaca, N. Y., 1945, p. 53.

[18] H. J. Schumacher and C. Schott, *Z. physik. Chem.*, **193**, 343 (1944).

[19] H. K. Hall, Jr., THIS JOURNAL, **78**, 2717 (1956).

[20] C. R. Stephens, E. J. Bianco and F. J. Pilgrim, *ibid.*, **77**, 1701 (1955).

[21] H. Brauns, *Rec. trav. chim.*, **65**, 799 (1946).

[22] N. Kornblum and R. K. Blackwood, THIS JOURNAL, **78**, 4037 (1956).

[23] R. B. Scott, Jr., and R. E. Lutz, *J. Org. Chem.*, **19**, 830 (1954).

n^{25}_{D} 1.4599), was prepared by the oxidative chlorination of 2-octanethiol.[10]

l-2-Octanesulfonyl Chloride.—The preparation of this compound from *l*-2-octanol[24] of $[\alpha]^{20}_{D}$ −7.7° (homogeneous) was similar to the preparation of the racemic compound. The product had a b.p. 93–95° (0.3 mm.), n^{26}_{D} 1.4593, d^{20}_{4} 1.053, and $[\alpha]^{20}_{D}$ −0.72° (homogeneous).

d-2-Octanesulfonyl Chloride.—*l*-2-Bromoöctane,[25] $[\alpha]^{20}_{D}$ −29° (homogeneous), was converted to *d*-2-octyl thiocyanate, b.p. 111–111.5° (9 mm.), n^{20}_{D} 1.4633, $[\alpha]^{20}_{D}$ +44.8° (homogeneous) (lit.[12] b.p. 98.5–99.0° (4 mm.), n^{20}_{D} 1.4635), 27 g. (0.16 mole) of which was chlorinated below 25° in a solution of 150 ml. of glacial acetic acid and 20 ml. of cold water until an excess of chlorine was evident. The solution was poured into ice-water, and the organic phase was extracted with benzene, washed with sodium sulfite solution, and dried. Distillation gave a first fraction, b.p. 62–80° (7 mm.), n^{22}_{D} 1.4356, α^{20}_{D} −7.47° (homogeneous), which was presumably largely *l*-2-chloroöctane (lit.[26] b.p. 68° (22 mm.), n^{20}_{D} 1.4267). After an intermediate fraction was removed, the major portion of the material distilled at 119–121° (7 mm.), α_{D} +3.1° (homogeneous). This was redistilled to give 23 g. (0.113 mole, 71%) of *d*-2-octanesulfonyl chloride, n^{22}_{D} 1.4582, $[\alpha]^{20}_{D}$ +0.87° (homogeneous).

In another preparation, *l*-2-bromoöctane, $[\alpha]^{20}_{D}$ −31.5° (homogeneous), was converted through the isothiouronium salt to *d*-2-octanesulfonyl chloride, b.p. 82° (0.05 mm.), n^{20}_{D} 1.4621, $[\alpha]^{27}_{D}$ +1.21° (*c* 2.4, benzene).

The Decomposition of 2-Octanesulfonyl Chloride.—The decompositions were carried out in Claisen flasks fitted with drying tubes, appropriate receivers and gas-bubbling apparatus for observing the decomposition. In some instances the sulfur dioxide and hydrogen chloride were collected as silver sulfite and chloride, which were distinguished by the solubility of the former in nitric acid.

The decompositions were carried out as recorded in Tables I and II. After the evolution of gas ceased, the contents of the flasks were fractionated *in vacuo* to separate the products. From the decompositions carried out in purified[27] N,N-dimethylformamide[28] as a solvent, the products were obtained by dissolving in benzene, washing with water, drying and distilling.

The Racemization of d-2-Chloroöctane.—A lithium chloride–N,N-dimethylformamide solution (15 ml., mole ratio 1.0:4.5) was added to 3.00 g. of *d*-2-chloroöctane, $[\alpha]^{20}_{D}$ +30.1° (homogeneous), and the solution was heated to 135°. After one hour at this temperature, 8 ml. was withdrawn, dissolved in ether, washed with water, dried and distilled. Racemic 2-chloroöctane, 0.89 g., b.p. 76–77° (28 mm.), n^{18}_{D} 1.4250, was obtained.

Irradiation of *l*-2-chloroöctane, $[\alpha]^{20}_{D}$ −2.61° (homogeneous), with ultraviolet light for 4.5 hr. at 135–140° led to the recovery of *l*-2-chloroöctane of unchanged specific rotation.

TROY, NEW YORK

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[24] J. Kenyon in "Organic Syntheses," Coll. Vol. I, 2nd ed., John Wiley and Sons, Inc., New York, N. Y., 1944, p. 418.

[25] C. M. Hsueh and C. S. Marvel, THIS JOURNAL, **50**, 855 (1928).

[26] A. J. H. Housa, J. Kenyon and H. Phillips, *J. Chem. Soc.*, 1700 (1929).

[27] G. R. Leader and J. F. Gormley, THIS JOURNAL, **73**, 5731 (1951).

[28] We are grateful to the Rohm and Haas Co. for a generous gift of this compound.

[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF THE UNIVERSITY OF NOTRE DAME]

Reactions of Free Radicals with Aromatics. I. The Unimportance of the "Identity Reaction" with Benzylic Radicals[1]

BY ERNEST L. ELIEL, PHIL H. WILKEN,[2] FABIAN T. FANG AND SAMUEL H. WILEN

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The decomposition of acetyl peroxide in optically active 2-phenylbutane gives rise to an optically inactive dimer, but the recovered 2-phenylbutane is only slightly racemized, indicating that the "identity reaction" [(i), shown below, R = 2-phenyl-2-butyl, X = H] does not proceed to a major extent. The absence of identity reaction requires that the peroxide-induced hydrogen abstraction from toluene-*α*-*d* should proceed with a reasonable over-all isotope effect, and that the same should be true, contrary to a previous report, for *p*-xylene-*α*-*d*. This was verified.

By "identity reaction"[3] is meant the reaction of a molecule R–X with the corresponding radical R· according to the equation

$$\text{R–X} + \text{R}\cdot \longrightarrow \text{R}\cdot + \text{R–X} \qquad \text{(i)}$$

Although the identity reaction does not result in any net chemical change, it may be detected under certain circumstances. Thus if R–X is optically active due to asymmetry of R at its point of attachment to X, the radical R· will be incapable of maintaining optical activity[4] and the identity reaction will lead to racemization of R–X. The identity reaction may also manifest itself in labeled molecules, *e.g.* Brown and Russell[5] have shown that the

$$C_6H_5CH_2D + C_6H_5CHD\cdot \longrightarrow C_6H_5CH_2\cdot + C_6H_5CHD_2 \qquad \text{(ii)}$$

identity reaction does not occur in the free-radical chlorination of several hydrocarbons and, in particular, that reaction ii does not occur in the course of the free-radical chlorination of toluene-*α*-*d* to benzyl chloride. Wang and Cohen,[6] using a variation of the labeling technique, have recently proved that little or no identity reaction occurs in the course of the dimerization reaction of diphenylmethyl radicals in the presence of diphenylmethane (eq. i, R = $(C_6H_5)_2CH\cdot$, X = H), except in the presence of chain-transfer agents. In contrast, it has been reported[7] that in the reaction of *p*-xylene-*α*-*d* with benzoyl peroxide, an identity reac-

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[1] Presented in part before the Division of Organic Chemistry of the American Chemical Society at Minneapolis, Minn., September 14, 1955, and before the Petroleum Chemistry Division at Atlantic City, N. J., September 20, 1956.

[2] Part of this work is from the Ph.D. thesis of P.H.W., Peter C. Reilly Fellow, 1952–1953; Socony-Mobil Fellow, 1953–1954.

[3] This type of reaction is described by W. A. Waters, "The Chemistry of Free Radicals," Oxford University Press, 2nd ed., London, England, 1948, p. 19 but the terminology is our own: Preprints, Division of Petroleum Chemistry, Am. Chem. Soc., **1** (3), 195 (1955).

[4] *Cf.* E. L. Eliel in M. S. Newman's "Steric Effects in Organic Chemistry," John Wiley and Sons, Inc., New York, N. Y., 1956, pp. 140–142. A particularly clear-cut demonstration of this point has recently been provided by D. F. DeTar and C. Weiss, THIS JOURNAL, **79**, 3045 (1957).

[5] H. C. Brown and G. A. Russell, *ibid.*, **74**, 3995 (1952). For a similar demonstration in bromination, see K. B. Wiberg and L. H. Slaugh, *ibid.*, **80**, 3033 (1958).

[6] C. H. Wang and S. G. Cohen, *ibid.*, **79**, 1924 (1957).

[7] J. I. Cadogan, V. Gold and D. P. N. Satchell, *J. Chem. Soc.*, 561 (1955).