TABLE III

Physical Properties of the Di-*n*-alkyl Sulfates $(RO)_2SO_2$

				Analysis					
				C		H		S	
R	Formula	B.P.[a]	M.P.[a]	Calcd.	Found	Calcd.	Found	Calcd.	Found
Butyl	$C_8H_{18}O_4S$	96–98/3 mm.							
Hexyl	$C_{12}H_{26}O_4S$	123–126/3 mm.							
Decyl	$C_{20}H_{42}O_4S$		37.5–38.0	63.44	63.45	11.19	10.91	8.47	8.37
Dodecyl	$C_{24}H_{50}O_4S$		47.8–48.5	66.30	66.42	11.59	11.49	7.37	7.28
Tetradecyl	$C_{28}H_{58}O_4S$		57.5–58.0	68.51	68.80	11.91	11.84	6.53	6.46
Hexadecyl	$C_{32}H_{66}O_4S$		66.5–67.0	70.27	70.15	12.16	12.31	5.86	5.31
Octadecyl	$C_{36}H_{74}O_4S$		70.0–70.5	71.70	71.88	12.37	12.17	5.32	5.24

[a] Boiling points and melting points are uncorrected.

Anschutz thermometer suspended in a 10 × 70 mm. test tube was placed in the tube. The test tube was suspended in a 20 × 50 mm. vial by means of a notched cork ring, the vial serving as an air bath. The vial was immersed in a 400-ml. beaker filled with water which was heated and stirred by a magnetic stirrer hot plate.

The temperature of the water bath was slowly raised (about 2 degrees per minute) and readings were made every 30 sec. The thermometer readings were then plotted against time. The cooling curve was obtained by removing the water bath after the temperature had been raised well above the melting point and thermometer readings were made at thirty second intervals.

Another procedure employed was to suspend a second Anschutz thermometer in the water bath and take readings of the thermometer in the tube at intervals of one degree change of the water bath temperature. In some respects this procedure is superior as the rate of heating or cooling has less effect on the curve obtained.

The transition point (conversion from crystalline solid or clear isotropic liquid to the turbid mesomorphic stage) was marked by a break in the heating and cooling curves. As would be expected the melting point or freezing point (conversion of turbid mesomorphic stage to clear isotropic liquid or crystalline solid) did not involve as marked a temperature change and consequently not as distinct a break in the curves obtained. In general, there was good agreement in the results obtained from the heating and cooling curves, but the cooling curves gave better results at the freezing point.

Melting points were checked using a Fisher-Johns apparatus. The results agreed within the range of accuracy obtainable by this method, and are in substantial agreement with the melting points previously published.

We are indebted to Dr. Arthur Montgomery of the Lafayette College Department of Geology for assistance in the study of these compounds with the use of a polarizing microscope.

Lafayette College
Easton, Pa.

St. John's University
Brooklyn, N. Y.

A New Synthesis of *cis*-9,10-Epoxyoctadecane

Leonard L. Gelb,[1] William S. Port, and Waldo C. Ault

Received July 3, 1958

Boeseken and Belinfante[2] in a four step synthesis prepared *cis*-9,10-epoxyoctadecane by epoxidation of *cis*-9,10-octadecene which they obtained by the reduction of oleyl iodide with a copper-zinc couple in acetic acid.

We have prepared *cis*-9,10-epoxyoctadecane by a new three step synthesis. Oleyl alcohol was converted to oleyl tosylate, and the latter was cleaved with $LiAlH_4$ to *cis*-9,10-octadecene which was then epoxidized with peracetic acid to give the desired compound in 47% over-all yield.

The geometrical structure of the *cis*-9,10-epoxyoctadecane was verified by the appearance in its infrared absorption spectrum of a peak at 825 cm.$^{-1}$ which Shreve *et al.*[3] reported to be characteristic of *cis* epoxides, and by the absence of a peak at 893 cm.$^{-1}$ which they reported to be characteristic of *trans* epoxides. A peak was also observed at 905 cm.$^{-1}$ which was shown to be present in *cis*-9,10-epoxyoctadecanol and absent in *trans*-9,10-epoxyoctadecanol. This new peak was obscured in previous work with the isomeric epoxystearic acids and esters[3] by the COO vibrations in this region.

Table I lists the physical properties of *cis*-9,10-epoxyoctadecane and its intermediates.

EXPERIMENTAL

Oleyl alcohol. Commercial oleyl alcohol, Cachalot 0-8 grade, obtained from M. Michel and Co.[4] was purified by the method of Swern, *et al.*[5] The cuts boiling between 184–187° at 4.5 mm., n_D^{25} 1.4590, iodine value 93.5 (purity 98.6%) were used to make the tosylate. Infrared analysis showed this material to contain about 2% elaidyl alcohol.[3]

Synthesis of oleyl tosylate. The procedure of Shirley[6] was followed essentially, except that the *p*-toluenesulfonyl chloride was added as a pyridine solution. After the reaction mixture had been stirred at 10 ± 2° for 6 hr., it was poured into cold water and transferred to a separatory funnel. The upper oil layer was washed with two successive portions of cold methanol. The lower (tosylate) layer from these extractions was drained into a round-bottom flask, and the pyridine and methanol were removed *in vacuo* under a

---

(1) Fellow of National Renderers Association.

(2) J. Boeseken and A. H. Belinfante, *Rec. trav. chim.*, **45**, 914 (1926).

(3) O. D. Shreve, M. R. Heether, H. B. Knight, and D. Swern, *Anal. Chem.*, **23**, 277 (1951).

(4) Reference to commercial products does not imply endorsement by the United States Department of Agriculture over similar products not mentioned.

(5) D. Swern, H. B. Knight, and T. W. Findley, *Oil & Soap*, Vol. **XXI**, 133 (1944).

(6) D. A. Shirley and W. H. Reedy, *J. Am. Chem. Soc.*, **73**, 458 (1951).

TABLE I

PROPERTIES OF *cis*-9,10-EPOXYOCTADECANE AND ITS INTERMEDIATES

Compound	B.P., °C./Mm.	M.P.,[a] °C.	F.P.,[a] °C.	Iodine Values Calcd.	Iodine Values Found	n_D^{25}	n_D^{35}
Oleyl alcohol[b]	184–187/4.5	—	—	94.8	93.5	1.4590	—
Oleyl tosylate	—	—	−30	60.2	59.7	1.4904	1.4866
cis-9,10-Octadecene	109/0.1	—	−35[c]	100.8	99.0	1.4448[c]	1.4410
cis-9,10-Epoxyoctadecane	—	22–23[d]	22	0.0	0.8[e]	1.4432	1.4395

[a] Uncorrected. [b] Contains 2% *trans* by infrared absorption[3] and 1–4% saturates (from iodine values). [c] Reported by Elsner and Paul[7] to be −30.5° and 1.4450, respectively. Reported by Boeseken and Belinfante[2] to be −15° and 1.4483 at 20°, respectively. [d] Reported by Boeseken and Belinfante[2] to be 0°. [e] Trace of *trans* olefin (determined by infrared analysis).

stream of nitrogen. The resulting tosylate (iodine value 54–57) was poured into three times its volume of diethyl ether and was refrigerated overnight. A white precipitate (m.p. 115–117°, 2.67% N, 7.01% S, water soluble), possibly the octadecenyl pyridinium complex of *p*-toluenesulfonic acid, was filtered out. (The presence of pyridine hinders the precipitation.) When the ether was removed, the yield of oleyl tosylate was 65%. Iodine value 59.7 (calcd. 60.2), n_D^{25} 1.4904.

Anal. Calcd. for $C_{25}H_{42}O_3S$: C, 71.04; H, 10.02; S, 7.59. Found: C, 68.21; H, 9.22; S, 7.15.

Cleavage of oleyl tosylate. A solution of 8.4 g. (0.02 mole) of oleyl tosylate dissolved in 60 ml. of distilled tetrahydrofuran (dried over sodium) was added in 1 hr. to a vigorously stirred, refluxing mixture of 1.2 g. of $LiAlH_4$ in 100 ml. of tetrahydrofuran. Agitation and refluxing were continued for a total of 10 hr. At the end of 5 and 7 hr., respectively, additional 0.3-g. portions of $LiAlH_4$ were added. This maneuver improved the yield of octadecene considerably. During the reflux period the refractive index of the oil (after the solvent from a 5 ml. sample had been evaporated) was observed to drop from 1.4904 to 1.4455 at 25°. Longer refluxing did not lower the refractive index.

Excess $LiAlH_4$ was decomposed in the usual manner with ethyl acetate, metallic complexes were decomposed with dilute HCl, and the organic layer was extracted with ether and separated. The ethereal layer was washed with cold water until acid free, dried over $CaSO_4$, and the solvents distilled off. The crude yield of *cis*-9,10-octadecene was 5.0 g. (100%).

Some purification was achieved by adsorption of the crude oil on a column of activated alumina and elution with diethyl ether. On removal of the ether from the eluate, 4.6 g. (92% recovery) of colorless oil was obtained which had an iodine value of 96.5 (calcd. 100.8), n_D^{25} 1.4452. A second alumina treatment raised the iodine value to 98.5 and lowered the refractive index to 1.4448 without loss in yield.

Anal. Calcd. for $C_{18}H_{36}$: C, 85.63; H, 14.37. Found: C, 85.81; H, 13.96.

On a larger scale, 168.8 g. (0.4 mole) of oleyl tosylate were reduced by the same method and purified by distillation to give an 85% yield of 98.6% pure *cis*-9,10-octadecene, n_D^{35} 1.4410, b.p. 109°/0.1 mm., iodine value 99.0.

Epoxidation to cis-9,10-epoxyoctadecane. The procedure of Findley, Swern, and Scanlan[8] for the epoxidation of unsaturated fatty materials with peracetic acid was employed. The yield of *cis*-9,10-epoxyoctadecane was 82%, m.p. (uncorr.) 22–23°, n_D^{35} 1.4395.

Anal. Calcd. for $C_{18}H_{36}O$: C, 80.52; H, 13.52; Oxirane O, 5.96. Found: C, 80.43; H, 13.22; Oxirane O,[9] 5.86.

Acknowledgment. We wish to thank C. R. Eddy and his staff at the Eastern Utilization Research and Development Division for the infrared analyses.

EASTERN UTILIZATION RESEARCH
AND DEVELOPMENT DIVISION
UNITED STATES DEPARTMENT OF AGRICULTURE
PHILADELPHIA 18, PA.

Synthesis of Possible Neuromuscular Blocking Agents Related to Succinylcholine[1]

KENNETH T. MECKLENBORG AND MILTON ORCHIN

Received July 3, 1958

Succinylcholine iodide (Ia), a neuromuscular blocking agent, exhibits a depolarizing action at the myoneural junction, which cannot be antagonized by cholinesterase inhibitors. It has been reported[2]

$$[CH_2CO_2CH_2CH_2N^+(CH_3)_2RX^-]_2$$

Ia, R = CH_3, $X^- = I^-$ Ib, R = *p*-nitrobenzyl, $X^- = Br^-$ that the related compound, Ib, exhibits a nondepolarizing action similar to that of the naturally occurring (+)-tubocurarine, which can be antagonized by cholinesterase inhibitors. The reversal of physiological action observed with Ib was attributed to the added bulk placed at the nitrogen centers of Ib.

In the present investigation compounds related to succinylcholine iodide have been prepared. In one series, bulky groups were added at the nitrogen atom (Table I, Formula I). In a second series (Formula II), the quaternary nitrogen was incorporated in a ring system with two carbon atoms separating the nitrogen and oxygen atoms whereby the spacing between quaternary nitrogens, characteristic of many active neuromuscular agents, was preserved. In a third series (Formula III)

---

(7) B. B. Elsner and P. F. M. Paul, *J. Chem. Soc.*, 3156 (1953).

(8) T. W Findley, D. Swern, and J. T. Scanlan, *J. Am. Chem. Soc.*, **67**, 412 (1945).

(9) A. J. Durbetaki, *Anal. Chem.*, **28**, 2000 (1956).

(1) Taken in part from the Ph.D. thesis of Kenneth T. Mecklenborg. Present address, Research Laboratories, Standard Oil of Indiana, Whiting, Ind.

(2) L. Randall, E. Giuliano, B. Kappell, and E. Allen, *J. Pharmacol. Exptl. Therap.*, **105**, 16 (1952).