hydroxide in 7 cc. of diethylene glycol gave 0.87 g. (78%) of crude acidic material. Vacuum sublimation and recrystallization from aqueous alcohol gave white needles, m.p. 120.5–121.5° (121°)[15] indicating that the compound was cyclopentenecarboxylic acid. The ultraviolet absorption spectrum of the acid in 95% ethanol indicated[16] that the double bond was in the α,β-position, $\lambda_{\text{max.}}$ 2210 Å., ϵ, 9200.

Treatment of 1.00 g. of the nitrile with 15 cc. of 10% hydrogen peroxide, 2 cc. of 10% sodium hydroxide and 20 cc. of acetone gave 0.98 g. (82%) of crude cyclopentene amide, m.p. 161–182°. Vacuum sublimation and recrystallization from methanol raised the m.p. to 206–208°.

Anal. Calcd. for C_6H_9ON: C, 64.84; H, 8.16. Found: C, 64.94; H, 7.94.

Fractions b to e were distilled through a Claisen flask equipped with a wide bore sausage-shaped receiver. Four arbitrary fractions were taken. The first three fractions were then purified by fractional crystallization from petroleum ether (b.p. 60–70°) to give 6.5 g. of tetramethylsuccinonitrile, m.p. 168–170° (combined yield with previously separated material, 44.5 g. (40.7%)), 15.1 g. (13.6%) of 1,1'-dicyano-1,1'-bicyclopentyl, m.p. 94–96° and 19.0 g. (17.2%) of the mixed nitrile (III), m.p. 69.5–70.5.

Anal. Calcd. for $C_{10}H_{14}N_2$: C, 74.06; H, 8.68; N, 17.21. Found: C, 73.96; H, 8.78; N, 17.16.

The fourth fraction, a heavy oil, b.p. 135–145° (0.5 mm.), amounted to 6.8 g. This apparently contains an addition product containing two molecules of cyclopentanenitrile plus one of isobutyronitrile since hydrolysis of 1.00 g. of this oil with 2.0 g. of potassium hydroxide in 10 cc. of diethylene glycol gave 0.83 g. (68%) of crude acid, m.p. 182–192°. Vacuum sublimation and recrystallization from toluene gave a m.p. of 199.5–201.5°.

Anal. Calcd. for $C_{16}H_{24}O_6$: C, 61.52; H, 7.74. Found: C, 61.52; H, 7.72.

BROOKLYN, NEW YORK RECEIVED MAY 8, 1951

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(15) E. Urion, *Compt. rend.*, **190**, 1512 (1930).

(16) For a comparison of absorption spectra of α,β-unsaturated acids, see C. G. Overberger and C. W. Roberts, THIS JOURNAL, **71**, 3618 (1949). See also H. E. Ungnade and I. Ortega, *ibid.*, **73**, 1564 (1951).

[CONTRIBUTION FROM THE RICHARDSON CHEMICAL LABORATORY OF TULANE UNIVERSITY]

Alkylation with Long Chain *p*-Toluenesulfonates. II. Reaction of *n*-Octadecyl *p*-Toluenesulfonate with Mercaptans and Thiophenols[1]

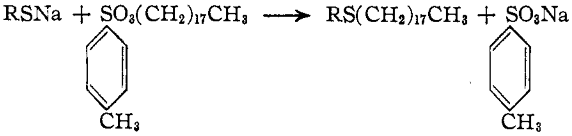
BY DAVID A. SHIRLEY AND WILLIAM H. REEDY

n-Octadecyl *p*-toluenesulfonate has been examined as an alkylating agent for a variety of mercaptans and thiophenols. The *n*-octadecyl aryl and alkyl thioethers were produced in yields ranging from 40 to 85%.

We have underway in this Laboratory a program of systematic evaluation of long chain aliphatic *p*-toluenesulfonates as alkylating agents for a variety of organic types. In the first paper, we reported the alkylation of phenols with *n*-octadecyl *p*-toluenesulfonate.[2] The *n*-octadecyl aryl ethers were formed in 50–75% yields.

It was next undertaken to alkylate mercaptans and thiophenols with *n*-octadecyl *p*-toluenesulfonate, and it was found that corresponding thioethers could be obtained in yields in the range of 40 to 85% all but one being obtained in above 60% yield. The compounds alkylated were thiophenol, *p*-nitrothiophenol, *o*- and *p*-thiocresol, *n*-butyl, decyl, dodecyl and octadecyl mercaptans, and 1,2-ethanedithiol. The results of these experiments are summarized in Table I.

$$RSH + NaOH \longrightarrow RSNa + H_2O$$



$$RSNa + SO_3(CH_2)_{17}CH_3 \longrightarrow RS(CH_2)_{17}CH_3 + SO_3Na$$

Several of the thioethers were oxidized to sulfones by conventional methods.

Experimental

The *n*-octadecyl *p*-toluenesulfonate used in this work was prepared as described earlier.[2]

***p*-Nitrophenyl *n*-Octadecyl Sulfide.**—*p*-Nitrothiophenol[3] (16.0 g. or 0.103 mole) was added to a solution of 4.1 g. (0.102 mole) of sodium hydroxide in 150 ml. of water. *n*-Octadecyl *p*-toluenesulfonate (42.4 g. or 0.100 mole) was then added and the resulting mixture stirred and heated to reflux for 20 hours. The hot mixture was placed in a separatory funnel and the aqueous layer separated. The oily layer was washed two times with hot 3 *N* aqueous sodium hydroxide solution, two times with hot 3 *N* hydrochloric acid, and finally several times with hot water. The remaining organic material was recrystallized once from methanol and once from petroleum ether (b.p. 70–90°) to give 26.3 g. (65% yield) of *p*-nitrophenyl *n*-octadecyl sulfide melting at 68–69°.

Anal. Calcd. for $C_{24}H_{41}NO_2S$: S, 7.87. Found: S, 7.89.

The mercaptans and thiophenols listed in Table I were alkylated with *n*-octadecyl *p*-toluenesulfonate in general accordance with the procedure given above.

***p*-Aminophenyl *n*-Octadecyl Sulfide.**—A solution of 10 g. of stannous chloride dihydrate in 100 ml. of glacial acetic acid was added to a solution of 5.0 g. (0.012 mole) of *p*-nitrophenyl *n*-octadecyl sulfide in 100 ml. of glacial acetic acid. The resulting mixture was heated to boiling for 30 minutes and then poured into 100 ml. of 6 *N* hydrochloric acid. The white solid which precipitated on cooling was collected by filtration and suspended in water. The mixture was made alkaline with excess 6 *N* sodium hydroxide and benzene added to dissolve the organic material. The benzene layer was separated and washed two times with water. Most of the benzene was removed by distillation, and ethanol was added to the hot solution. Cooling precipitated 3.2 g. (70% yield) of amine melting at 70–71°.

Anal. Calcd. for $C_{24}H_{43}NS$: S, 8.48. Found: S, 8.44.

***p*-Nitrophenyl *n*-Octadecyl Sulfone.**—A mixture of 5.0 g. (0.012 mole) of *p*-nitrophenyl *n*-octadecyl sulfide, 4.0 g. (0.025 mole) of potassium permanganate, and 200 ml. of glacial acetic acid was heated to reflux temperature for three hours. Sodium bisulfite solution and hydrochloric acid were added to destroy excess potassium permanganate and manganese dioxide. The mixture was added to excess ice-water and the precipitated solid collected by filtration. The product was recrystallized from ethanol and the yield of sulfone, melting at 82–83°, was 4.0 g. (74%).

Anal. Calcd. for $C_{24}H_{41}NO_4S$: S, 7.29. Found: S, 7.36.

Phenyl *n*-Octadecyl Sulfone.—Phenyl *n*-octadecyl sulfide (5.0 g. or 0.0138 mole) was oxidized to the sulfone as de-

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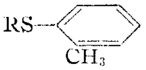
[1] A report of work done under contract with the U. S. Department of Agriculture and authorized by the Research and Marketing Act. The contract is being supervised by the Southern Regional Research Laboratory of the Bureau of Agricultural and Industrial Chemistry.

(2) D. A. Shirley and W. H. Reedy, THIS JOURNAL, **73**, 458 (1951).

(3) C. C. Price and G. W. Stacy, *ibid.*, **68**, 499 (1946).

TABLE I

ALKYL AND ARYL *n*-OCTADECYL SULFIDES

Compound R = $CH_3(CH_2)_{17}$	Mole of thiol	Mole of ester	Solvent for recrystallization[a]	Yield,[b] %	Melting point, °C.	Molecular formula	Sulfur analyses, % Calcd.	Sulfur analyses, % Found
	0.057	0.050	Petroleum ether (b.p. 35–60°)	80	55.5–56.5	$C_{24}H_{42}S$	8.84	8.76
	.101	.100	Acetone	61	38–39	$C_{25}H_{44}S$	8.51	8.58
	.101	.100	Petroleum ether (b.p. 35–60°)	85	52.5–53	$C_{25}H_{44}S$	8.51	8.49
$RS(CH_2)_3CH_3$	.100	.100	Acetone	74	29–30	$C_{22}H_{46}S$	9.36	9.11
$RS(CH_2)_9CH_3$	.103	.100	Methyl ethyl ketone	70	44–45	$C_{28}H_{58}S$	7.51	7.56
$RS(CH_2)_{11}CH_3$	.104	.100	Methyl ethyl ketone	73	50.5–51.5	$C_{30}H_{62}S$	7.05	7.14
$RS(CH_2)_{17}CH_3$	.105	.100	Benzene	62	63.5–64.5[c]	$C_{36}H_{74}S$	5.92	5.99

[a] All products were recrystallized once from ethanol or methanol and one or two times from the solvent listed in this column. [b] All yields are based on starting *n*-octadecyl *p*-toluenesulfonate. [c] The m.p. of *n*-octadecyl sulfide has previously been reported as 62–64°[5] and 98–99°.[6]

scribed above. The product, formed in 57% yield, melted at 61–62°.

Anal. Calcd. for $C_{24}H_{42}O_2S$: S, 8.12. Found: S, 7.93.

Di-*n*-octadecyl Sulfone.—Di-*n*-octadecyl sulfide (5.0 g. or 0.0093 mole) was oxidized as described previously. The product, m.p. 103–104°, was formed in 43% yield.

Anal. Calcd. for $C_{36}H_{74}O_2S$: S, 5.61. Found: S, 5.46.

The melting point of octadecyl sulfone has been reported previously as 98–99°[4] and 105.5–106.5°.[5]

***p*-Aminophenyl *n*-Octadecyl Sulfone.**—Three grams (0.0068 mole) of *p*-nitrophenyl *n*-octadecyl sulfone was reduced with 7.0 g. (0.031 mole) of stannous chloride in acetic acid in accordance with the procedure outlined above for the reduction of *p*-nitrophenyl *n*-octadecyl sulfide. There was obtained 2.0 g. (72% yield) of amine melting at 110–112°.

Anal. Calcd. for $C_{24}H_{43}NO_2S$: S, 7.83. Found: S, 7.70.

19,22-Dithiatetracontane.—An attempt to produce the dithio ether from 1,2-ethanedithiol and two equivalents of *n*-octadecyl *p*-toluenesulfonate by the general procedure outlined above gave a mixture of compounds which could not be separated. A 43% yield of the dithioether was obtained by the procedure given below. A mixture of 2.4 g. (0.025 mole) of 1,2-ethanedithiol, 28.0 g. (0.066 mole) of *n*-octadecyl *p*-toluenesulfonate, and 5.0 g. (0.048 mole) of solid sodium carbonate was heated with occasional stirring for ten hours at 120–130°. Hot water was added to the mixture, and the resulting two liquid layers separated. The oily layer was washed several times with hot water. The organic layer was recrystallized from ethanol, triturated with 200 ml. of ether, and then recrystallized from a mixture of equal parts of petroleum ether (b.p. 35–60°) and petroleum ether (b.p. 70–90°). There was obtained 8.5 g. (43%) of white solid, m.p. 70–72°.

Anal. Calcd. for $C_{38}H_{78}S_2$: S, 10.70. Found: S, 10.83.

Acknowledgment.—The authors wish to express appreciation to Dr. K. S. Markley of the U. S. Department of Agriculture, Southern Regional Research Laboratory, New Orleans, for his valuable advice and assistance.

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[4] V. C. Barry, L. O'Rourke and D. Twomeny, *Proc. Roy. Irish Acad.*, **51B**, 223 (1947).

[5] B. A. Hunter, *Iowa State College J. Sci.*, **15**, 215 (1941) [*C. A.*, **36**, 4474 (1942)].

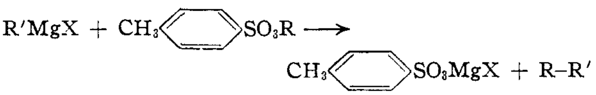
[CONTRIBUTION FROM THE RICHARDSON CHEMICAL LABORATORY OF TULANE UNIVERSITY]

Alkylation with Long Chain *p*-Toluenesulfonates. III.[1] Reaction of *n*-Octadecyl *p*-Toluenesulfonate with *p*-Tolylmagnesium Bromide[2]

BY DAVID A. SHIRLEY AND WILLIAM H. REEDY

Reaction of *n*-octadecyl *p*-toluenesulfonate with *p*-tolylmagnesium bromide allows formation of *p*-*n*-octadecyltoluene and hexatriacontane. It is proposed that the hexatriacontane was formed by the action of magnesious bromide on the octadecyl *p*-toluenesulfonate, and that the magnesious bromide came from the interaction of magnesium bromide and excess magnesium present in the Grignard reagent. Evidence for this proposal includes (a) observed formation of hexatriacontane from octadecyl *p*-toluenesulfonate and magnesious bromide, and (b) absence of hexatriacontane in the reaction product of octadecyl ester and Grignard reagent containing no magnesium metal.

The reaction of lower alkyl esters of *p*-toluenesulfonic acid and Grignard reagents has been studied extensively by Gilman and co-workers[3] and Marvel and co-workers.[4,5] This reaction, which is illustrated below, allows formation of the hydrocarbon, R–R′, in yields varying from a few per cent. to about 60%.



As a part of a general program of evaluation of long chain alkyl *p*-toluenesulfonates as alkylating agents for a variety of types,[1] we initiated an examination of the reaction of the Grignard reagent with the long chain ester. Selected for initial study was the reaction of *n*-octadecyl *p*-

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[1] Preceding paper; D. A. Shirley and W. H. Reedy, THIS JOURNAL, **73**, 4885 (1951).

[2] Presented before the Sixth Southwest Regional Meeting of the American Chemical Society, San Antonio, Texas, December 9, 1950.

[3] H. Gilman and N. J. Beaber, THIS JOURNAL, **45**, 839 (1923); **47**, 518 (1925).

[4] S. S. Rossander and C. S. Marvel, *ibid.*, **50**, 1491 (1925).

[5] J. W. Copenhaver, M. F. Roy and C. S. Marvel, *ibid.*, **57**, 1312 (1935).