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.	Found
RS—C$_6$H$_5$	0.057	0.050	Petroleum ether (b.p. 35–60°)	80	55.5–56.5	$C_{24}H_{42}S$	8.84	8.76
RS—C$_6$H$_4$(CH$_3$)-*o*	.101	.100	Acetone	61	38–39	$C_{25}H_{44}S$	8.51	8.58
RS—C$_6$H$_4$—CH$_3$-*p*	.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.

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

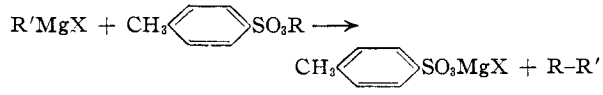
[CONTRIBUTION FROM THE RICHARDSON CHEMICAL LABORATORY OF TULANE UNIVERSITY]

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*-

(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.

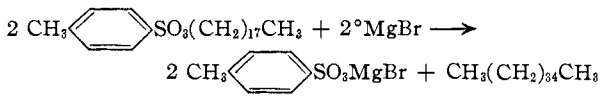
(3) H. Gilman and N. J. Beaber, THIS JOURNAL, **45**, 839 (1923); **47**, 518 (1925).

(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).

toluenesulfonate and *p*-tolylmagnesium bromide. The expected R–R′ hydrocarbon, *p*-*n*-octadecyltoluene, was isolated in only 10–15% yield.

Of greater interest, however, was the isolation in 12% yield of the 36-carbon atom, straight chain alkane, hexatriacontane. This hydrocarbon type is, as far as we know, a unique product from this type of reaction. We postulated that the formation of the hexatriacontane resulted from the interaction of *n*-octadecyl *p*-toluenesulfonate and magnesious bromide (°MgBr) as indicated in the equation.



We also postulated that the magnesious bromide was present in the reaction mixture as a component of the equilibrium between magnesium bromide from the Grignard reagent and excess magnesium metal also present.

$$2RMgX \rightleftharpoons R_2Mg + MgX_2 \quad (1)$$

$$MgX_2 + Mg \rightleftharpoons 2°MgX \quad (2)$$

The first equation is the well-known equilibrium of the Grignard reagent with dialkylmagnesium and magnesium halide.[6] The second equation, involving the formation of magnesious halide, was proposed originally by Gomberg and Bachmann[7] to explain the reactivity of the Mg + MgI_2 system used in the reduction of ketones to pinacols.

In order to test the postulate of the formation of hexatriacontane from magnesious halide and *n*-octadecyl *p*-toluenesulfonate, we prepared magnesious iodide from equivalent quantities of magnesium iodide and magnesium according to the procedure of Gomberg and Bachmann,[7] and allowed it to react with an equivalent quantity of sulfonate ester. From this reaction, we isolated hexatriacontane in 38% yield, and a similar reaction using magnesious bromide allowed formation of the hydrocarbon in 25% yield. These experiments indicate that the system Mg + $MgBr_2 \rightleftarrows 2°MgBr$ will carry out conversion of the *n*-octadecyl *p*-toluenesulfonate to hexatriacontane.

There remains, however, the question of the possible mechanisms of formation of the magnesious bromide in the reaction of ester with Grignard reagent. In addition to the possibility mentioned above of its formation from magnesium bromide and excess magnesium, a direct dissociation of the Grignard reagent $RMgX \rightleftarrows R° + °MgX$, might provide sufficient quantities of °MgX for reaction with the sulfonate ester in the indicated manner.

Some light has been thrown on this question by the studies of Gilman and Fothergill[8] on the reaction of Grignard reagents with benzophenone. These workers showed that in a reaction of *n*-butylmagnesium iodide with benzophenone in the presence of an equivalent amount of magnesium, benzopinacol was formed in 10–17% yield while in the absence of the metallic magnesium no pinacol was isolated. They interpreted these data to indicate that magnesious iodide formed in the presence of magnesium reduced benzophenone to benzopinacol, but the failure of this reaction in the absence of the magnesium indicated lack of appreciable dissociation of the Grignard reagent into free radicals and magnesious halide. In an examination of several Grignard types, only in the case of the triphenylmethylmagnesium chloride and bromide did formation of pinacol take place in the absence of magnesium, indicating dissociation of the Grignard reagent.

We have been able to rule out dissociation of the Grignard reagent as a factor involved in the formation of hexatriacontane from *n*-octadecyl *p*-toluenesulfonate. In an experiment in which carefully filtered *p*-tolylmagnesium bromide was allowed to react with *n*-octadecyl *p*-toluenesulfonate, none of the hexatriacontane was formed, indicating that excess magnesium was necessary for its formation.

In order to eliminate the possibility of hexatriacontane having been formed through the agency of some component of the reaction mixture other than magnesious bromide, we examined the reaction of the sulfonate ester with the two remaining known components of the Grignard reagent mixture, namely, magnesium and magnesium bromide. A 100-hour reflux period of magnesium turnings and sulfonate ester in ether allowed 98% recovery of the unchanged ester. In a similar reaction between magnesium bromide and an equivalent quantity of ester, no hexatriacontane was formed. Instead a 61% yield of *n*-octadecyl bromide was obtained. This product is not surprising in view of the reported[9] formation of alkyl iodides from alkyl *p*-toluenesulfonates and sodium iodide.

From these data we believe that the hexatriacontane formed in the reaction of *n*-octadecyl *p*-toluenesulfonate and *p*-tolylmagnesium bromide could only have arisen from the interaction of the sulfonate ester and magnesious bromide, and that the magnesious bromide arose as a component of the equilibrium between magnesium bromide and excess magnesium present in the Grignard reagent.

The question remains as to the exact mechanism of the reaction between sulfonate ester and magnesious halide. It is interesting to note that there is a formal resemblance between this reaction and the Wurtz reaction in which the magnesious halide acts as metallic sodium and the alkyl sulfonate as the alkyl halide. In this connection we treated *n*-octadecyl *p*-toluenesulfonate with metallic sodium in boiling xylene for eight hours and observed no formation of hexatriacontane, indicating that sodium was not in any sense equivalent to magnesious halide in its action on the sulfonate ester.

Experimental

Action of *p*-Tolylmagnesium Bromide on *n*-Octadecyl *p*-Toluenesulfonate.—*p*-Tolylmagnesium bromide was prepared in normal fashion from 84.6 g. (0.50 mole) of *p*-bromotoluene, 18 g. (0.75 g. atom) of magnesium and 200 ml. of dry ether. A solution of 106 g. (0.25 mole) of *n*-octa-

(6) H. Gilman, "Organic Chemistry," Vol. I, John Wiley and Sons, Inc., New York, N. Y., 1943, p. 497.

(7) M. Gomberg and W. E. Bachmann, THIS JOURNAL, **49**, 236 (1927).

(8) H. Gilman and R. E. Fothergill, *ibid.*, **51**, 3149 (1929).

(9) (a) W. Borsche and B. G. B. Scholten, *Ber.*, **50**, 596 (1917); (b) W. Borsche, H. Lowenstein and R. Quast, *ibid.*, **50**, 1339 (1917).

decyl *p*-toluenesulfonate[10] in 400 ml. of dry ether was added with stirring over a period of two hours. The reaction mixture was heated to reflux for three hours and then poured over a mixture of crushed ice and hydrochloric acid. A white ether-insoluble solid was filtered off and the ether layer was separated, dried and the ether evaporated. The residue was distilled at atmospheric pressure and four fractions were collected: (1) 6.3 g., b.p. 100–270°; (2) 17.1 g., b.p. 270–330°; (3) 18.7 g., b.p. 330–375°; and (4) 11.5 g., b.p. 375–380°. There was very little evidence of decomposition during distillation.

Isolation and Identification of Hexatriacontane.—The ether-insoluble white solid filtered from the above reaction mixture was 7.4 g. of hexatriacontane, m.p. 76.5–77°. Recrystallization of this material from petroleum ether (b.p. 30–60°) did not raise the melting point. The 7.4 g. represented a 11.8% yield based on the starting *n*-octadecyl *p*-toluenesulfonate. The melting point of hexatriacontane has been reported as 76°[11] and 76.5°.[12]

A synthetic sample of hexatriacontane was prepared by a 24-hour reflux of a benzene solution of *n*-octadecyl bromide and excess metallic sodium. The product melted at 76.5–77° and a mixed m.p. with the 76.5–77° melting material isolated above showed no depression.

Isolation and Identification of *p*-*n*-Octadecyltoluene.—The 11.5 g. constituting fraction 4 above was a white solid melting around room temperature. One recrystallization from petroleum ether (b.p. 30–60°) gave 7.4 g., m.p. 30–32°. *Anal.* Calcd. for $C_{25}H_{44}$: C, 87.1; H, 12.9. Found: C, 87.2; H, 12.7.

This compound was further identified by oxidation with aqueous alkaline potassium permanganate to terephthalic acid. The dimethyl ester of the terephthalic acid, m.p. 140°, was prepared and this gave no depression in m.p. when mixed with an authentic specimen, m.p. 140°. From 5 g. of starting hydrocarbon, there was obtained 0.8 g. of terephthalic acid and 2.6 g. of unreacted starting material was recovered.

Fraction 3 also contained some *p*-(*n*-octadecyl)-toluene since its oxidation with alkaline permanganate solution yielded terephthalic acid. The terephthalic acid from this oxidation was converted to its di-(*p*-nitrobenzyl) ester, m.p. 271°. The literature[13] reports this ester to melt at 263°; however, a sample of the di-(*p*-nitrobenzyl) ester prepared from an authentic specimen of terephthalic acid melted at 271° and a mixed m.p. showed no depression.

The total yield of *p*-*n*-octadecyltoluene was in the range of 10–15%.

Hexatriacontane from *n*-Octadecyl *p*-Toluenesulfonate and Magnesious Iodide.—A solution of 12.7 g. (0.1 g. atom) of iodine in 250 ml. of dry ether was added slowly with cooling and stirring to 2.43 g. (0.1 g. atom) of magnesium turnings in 50 ml. of ether. The mixture was stirred and heated to reflux for 15 minutes after completion of the addition. To the resulting solution was added over a 90-minute period a solution of 21.2 g. (0.05 mole) of *n*-octadecyl *p*-toluenesulfonate in 150 ml. of dry ether. The mixture was stirred and heated to reflux for an additional three hours. The reaction mixture was poured into a mixture of ice and dilute hydrochloric acid and the precipitated white solid (5.1 g.) removed by filtration. It melted at 73–75° and one recrystallization from petroleum ether gave 4.8 g. (38%) of hexatriacontane, m.p. 76.5–77°. Mixed m.p. of this sample with the authentic specimen and with the sample obtained from the Grignard reaction showed no depression.

The ether layer remaining from the above hydrolysis was dried and evaporated, and the residue recrystallized twice from ethanol to give 5.8 g. of a solid, m.p. 34°. The solid gave a positive alcoholic silver nitrate test for halogen. Hexatriacontane was formed by heating the product with sodium in benzene and it was concluded that it was *n*-octadecyl iodide. The m.p. of *n*-octadecyl iodide is 34°. The 5.8 g. isolated above is a 30% yield based on the starting *n*-octadecyl ester.

Formation of Hexatriacontane from Magnesious Bromide and *n*-Octadecyl *p*-Toluenesulfonate.—Magnesious bromide prepared from 16.0 g. (0.1 mole) of bromine and excess magnesium metal was allowed to react with 42.4 g. (0.1 mole) of *n*-octadecyl *p*-toluenesulfonate in ether solution as described above. There was isolated 6.1 g. (24%) of hexatriacontane, m.p. 76–76.5°.

Reaction of Magnesium Bromide and *n*-Octadecyl *p*-Toluenesulfonate.—Magnesium bromide was prepared from mercuric bromide and magnesium according to the procedure of Gomberg and Bachmann.[7] To a solution of about 0.1 mole of magnesium bromide in a mixture of ether and benzene was added 21.2 g. (0.05 mole) of *n*-octadecyl *p*-toluenesulfonate. The mixture was stirred and heated to reflux for about one hundred hours and then washed several times with water. The organic layer was evaporated to small volume, and cooling precipitated a solid product which was separated and recrystallized from ethanol. There was obtained 10.2 g. of a product, m.p. 30°. This material proved to be *n*-octadecyl bromide, since a mixed m.p. with an authentic specimen, m.p. 29°, gave no depression and heating with metallic sodium allowed formation of hexatriacontane as described above. The 10.2 g. of *n*-octadecyl bromide represented a 61% yield, based on *n*-octadecyl *p*-toluenesulfonate. No hexatriacontane could be found in the reaction products.

Reaction of Magnesium and *n*-Octadecyl *p*-Toluenesulfonate.—A 100-hour reflux period of equivalent quantities of magnesium and ester in ether solution did not cause a reaction to occur. Recovery of unchanged ester was 98%.

Reaction of Sodium and *n*-Octadecyl *p*-Toluenesulfonate.—A mixture of 2.0 g. of sodium and 200 ml. of xylene was stirred vigorously and heated to reflux while 21.2 g. (0.05 mole) of *n*-octadecyl *p*-toluenesulfonate was added. The mixture was refluxed for eight hours. It was then cooled and 10 ml. of alcohol added to destroy the sodium. Careful examination of the resulting solution indicated that no hexatriacontane was present.

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(10) D. A. Shirley and W. H. Reedy, THIS JOURNAL, **73**, 456 (1951).

(11) A. Gascard, *Ann. chim.*, **15**, 344 (1921).

(12) A. Oskerk, *J. Russ. Phys.-Chem. Soc.*, **46**, 411 (1914); *C. A.*, **8**, 3185 (1914).

(13) E. Lyons and E. E. Reid, THIS JOURNAL, **39**, 1721 (1917).