[CONTRIBUTION FROM THE RICHARDSON CHEMICAL LABORATORY OF TULANE UNIVERSITY]

ALKYLATION WITH LONG CHAIN *p*-TOLUENESULFONATES. IV.[1] ALKYLATION OF ALCOHOLS AND AMINES WITH *n*-OCTADECYL *p*-TOLUENESULFONATE[2]

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As a part of a general study of alkylation reactions of long chain *p*-toluenesulfonate esters, we have undertaken to examine the reaction of *n*-octadecyl *p*-toluenesulfonate with alcohols and amines. In previous papers (1) we have reported results of alkylation studies on phenols, thiophenols, and mercaptans. Aqueous alkaline media, found effective in earlier work, resulted in low yields of octadecyl ethers when alcohols were treated in this manner. Mixtures of alcohol, *n*-octadecyl *p*-toluenesulfonate, and anhydrous sodium carbonate heated to around 150° allowed formation of the corresponding *n*-octadecyl ethers in yields of 30 to 80%.

$$ROH + CH_3C_6H_4SO_3(CH_2)_{17}CH_3 \rightarrow RO(CH_2)_{17}CH_3 + CH_3C_6H_4SO_3H$$

Equimolar amounts of ethylene glycol and *n*-octadecyl ester gave both mono- and di-*n*-octadecyl ethers of ethylene glycol in 56 and 25% yield, respectively. Other alcohols alkylated were 2-octanol, 1-butanol, 1-octanol, 1-octadecanol, benzyl alcohol and β-hydroxyethyl mercaptan.

Sekera and Marvel (2) investigated the alkylation of *n*-butylamine with dodecyl and hexadecyl *p*-toluenesulfonate and found both mono- and di-alkylation from equimolar quantities of ester and amine. We have extended this work to include the reaction of *n*-octadecyl *p*-toluenesulfonate with aniline, *m*-chloroaniline, *n*-butylamine, *p*-toluidine, *p*-nitroaniline, β-naphthylamine, and diphenylamine. In the first three amines listed, both mono- and di-alkylation products were isolated. As in the case of alcohol alkylation total yields in all cases except *p*-nitroaniline were in the range of about 30 to 70%.

EXPERIMENTAL

Ethylene glycol n-octadecyl and di-n-octadecyl ethers. A mixture of 42.5 g. (0.10 mole) of *n*-octadecyl *p*-toluenesulfonate [prepared as described earlier (1)], 7.20 g. (0.11 mole) of ethylene glycol, and 10.6 g. (0.10 mole) of anhydrous sodium carbonate was stirred at a temperature of 170–185° for a period of four hours. Water was allowed to distil from the reaction flask. Evolution of carbon dioxide was noted and the mixture took on a light brown coloration. A solution of 4.0 g. of sodium hydroxide in 100 ml. of water was added and the mixture heated at reflux for 15 minutes. The brown oily layer was washed twice with hot 3 *N* hydrochloric acid, followed by two washings with hot water. The organic product was treated with 200 ml. of hot ethanol and the resulting two layers were separated by

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[1] Preceding paper: Shirley and Reedy, *J. Am. Chem. Soc.*, **73**, 4886 (1951).

[2] 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.

decantation. The ethanol solution was cooled to 20°, precipitating a crystalline solid which, on separation by filtration and recrystallization from acetone, yielded a small quantity of di-*n*-octadecyl ether, m.p. 60.5–61.5°. On further cooling the solution to 8°, a waxy solid was obtained which, after filtration and recrystallization from acetone, yielded 17.6 g. (56%) of white ethylene glycol *n*-octadecyl ether, m.p. 51.5–52.5°.

Anal. Calc'd for $C_{20}H_{42}O_2$: C, 76.4; H, 13.5.

Found: C, 76.2; H, 13.5.

The ethanol-insoluble solid from above was recrystallized from acetone, yielding 7.1 g. (25%) of white ethylene glycol di-*n*-octadecyl ether, m.p. 56.5–57°.

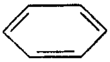
Anal.[3] Calc'd for $C_{38}H_{78}O_2$: C, 80.5; H, 13.9.

Found: C, 81.1; H, 14.3.

A total of 81% of the *n*-octadecyl *p*-toluenesulfonate was utilized in the alkylation of ethylene glycol.

TABLE I

n-OCTADECYL ETHERS

COMPOUND, R = $CH_3(CH_2)_{17}$—	YIELD[a], %	M.P., °C[b]	B.P., °C./MM.	MOLECULAR FORMULA	ANALYSES			
					Carbon		Hydrogen	
					Calc'd	Found	Calc'd	Found
$CH_3(CH_2)_6CH_2OR$	67	35–36		$C_{26}H_{54}O$	81.6	81.5[c]	14.2	14.2[c]
$CH_3(CH_2)_2CH_2OR$	60	29	152/0.7	$C_{22}H_{46}O$	80.9	81.0	14.2	14.3
ROR	67	62–63		$C_{36}H_{74}O$[d]				
 CH_2OR	40	28.5–29	199/1.0[e]	$C_{25}H_{44}O$	83.3	83.5	12.3	12.3
$RS(CH_2)_2OR$	44	68–69		$C_{38}H_{78}OS$[f]				

[a] Yields based on reagent present in smaller molar proportion. [b] All products had a final recrystallization from ethanol. [c] Analysis by W. A. Reeves. [d] Identified by undepressed mixture melting point with an authentic sample of di-*n*-octadecyl ether. [e] Previously reported: b.p. 250°/15 mm. British Patent 393,937 [*Chem. Abstr.*, **27**, 5752 (1933)]. [f] *Anal.* Calc'd: S, 5.50. Found: S, 5.46.

1-Octadecyl 2-octyl ether. 2-Octanol (0.30 mole or 39 g.), 84.9 g. (0.20 mole) of *n*-octadecyl *p*-toluenesulfonate, and 20 g. of anhydrous sodium carbonate were stirred at 120° for 18 hours. Sodium hydroxide solution (200 ml., 10%) was added and the mixture was refluxed for one hour. The organic product was washed four times with hot water, yielding a waxy material melting around room temperature. Cooling a solution of the product in a mixture of acetone and ether resulted in precipitation of a solid which, after separation and recrystallization from petroleum ether, yielded 8.0 g. of di-*n*-octadecyl ether, m.p. 61–62°. The filtrate, after removal of the solvent, was distilled at reduced pressure, yielding 22.9 g. (30%) of a light yellow oily liquid, 1-octadecyl 2-octyl ether, boiling at 206° (pressure 1.8 mm.).

Anal. Calc'd for $C_{26}H_{54}O$: C, 81.6; H, 14.2.

Found: C, 81.7, H, 14.3.

Other alcohols were converted to the *n*-octadecyl ethers with the results listed in Table I.[4]

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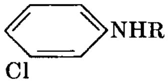
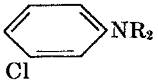
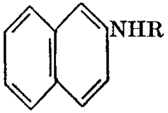
[3] Analysis by F. C. Canter.

[4] Unless otherwise noted all carbon and hydrogen analyses were carried out by the Galbraith Microanalytical Laboratories, Knoxville, Tennessee.

TABLE II

n-OCTADECYLAMINES

COMPOUND $R=CH_3(CH_2)_{17}-$	YIELD,[a] %	M.P., °C.	SOLVENT FOR RECRYSTN.	MOLECULAR FORMULA	ANALYSES					
					Carbon		Hydrogen		Other	
					Calc'd	Found	Calc'd	Found	Calc'd	Found
	15	79–80	Methanol	$C_{24}H_{42}N_2O_2$					N, 7.17	7.18, 7.21
 [b]	37	63–63.5	Petroleum ether	$C_{25}H_{45}N$	83.5	83.6	12.6	12.8	N, 3.90	3.94, 3.88
	34[c]	51–52	Methanol	$C_{24}H_{42}ClN$					Cl, 9.33	9.35,[d] 9.23
	25[c]	56–56.5	Ethanol	$C_{42}H_{78}ClN$					Cl, 5.61	5.49,[e] 5.62
	29	48–49	Methanol	$C_{30}H_{47}N$	85.4	85.4	11.2	11.1	N, 3.32	3.28, 3.33
$CH_3(CH_2)_3NHR$	17[f]	41–43	Methanol-water	$C_{22}H_{47}N$[g]					N, 4.30	4.28, 4.31
$CH_3(CH_2)_3NR_2$	42[f]	38–38.5	Methanol-ether	$C_{40}H_{83}N$	83.1	83.2	14.5	14.2	N, 2.42	2.53, 2.54
	41	67–68.5	Methanol	$C_{28}H_{45}N$	85.0	85.2	11.5	11.6	N, 3.54	3.58, 3.61

[a] All yields based on n-octadecyl p-toluenesulfonate. [b] Reported in Swiss Patent 207,448 [*Chem. Abstr.*, **35**, 8310 (1941)]. Preparation and properties not given. [c] Total alkylation amounted to 59% based on starting ester. [d] Analysis by M. J. Danzig. [e] Analysis by G. Chuchani. [f] Total alkylation was 59%. [g] A completely pure product could not be isolated.

N-n-Octadecylaniline and N,N-di-n-octadecylaniline. Aniline (0.05 mole or 4.7 g.), *n*-octadecyl *p*-toluenesulfonate (0.05 mole, 21.2 g.), and 2.7 g. of anhydrous sodium carbonate were stirred in a 300-ml. three-necked flask at 140–150° for 18 hours. The brown product was washed four times with hot water, dried, and then treated with two successive portions of hot methanol, the solution being decanted from the insoluble material. Cooling the methanol solution in an ice-bath precipitated a purple-colored solid which was separated, dried, and then dissolved in ether. Dry hydrogen chloride was passed into the ether solution, forming an insoluble amine hydrochloride (m.p., 96–99°). Treatment of the ether-insoluble salt with dilute aqueous sodium hydroxide (boiling five minutes), followed by recrystallization of the organic solid from methanol, yielded 1.9 g. N-*n*-octadecylaniline, m.p. 52.5–53° (11% yield). The melting point of N-*n*-octadecylaniline has been previously reported as 42° (3).

Anal. Calc'd for $C_{24}H_{43}N$: C, 83.4; H, 12.5; N, 4.05.
Found: C, 83.5; H, 12.3; N, 4.08, 4.11.

A purple color in the methanol-insoluble material from above was removed by precipitation of a hydrochloride in ether solution (m.p. 109–113°) and reconversion to the amine with dilute sodium hydroxide solution. Recrystallization of the light tan solid from a mixture of methanol and ether resulted in 9.3 g. of N,N-di-*n*-octadecylaniline, m.p. 52–53° (62% yield).

Anal. Calc'd for $C_{42}H_{79}N$: C, 84.3; H, 13.3; N, 2.34.
Found: C, 84.4; H, 13.3; N, 2.38, 2.39.

The above reaction represents a 73% utilization of the *n*-octadecyl *p*-toluenesulfonate. A mixture melting point of the mono- and di-alkylated products showed a sharp depression.

In a second reaction (0.1 mole of ester, 0.1 mole of aniline, and 5.3 g. of anhydrous sodium carbonate) in which the reactants were stirred at 120–140° for two hours, yields of 25% of the mono-*n*-octadecyl compound and 17% of the di-*n*-octadecyl compound were obtained.

Results of the alkylation of other amines by similar procedures are summarized in Table II.

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SUMMARY

Alkylation of a series of alcohols by *n*-octadecyl *p*-toluenesulfonate allows formation of the corresponding *n*-octadecyl ethers in yields ranging from 30 to 80%.

Alkylation of a series of aliphatic and aromatic primary amines gives mixtures of N-*n*-octadecyl and N,N-di-*n*-octadecyl derivatives in total yields ranging in general from 30 to 70%.

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REFERENCES

(1) Shirley and Reedy, *J. Am. Chem. Soc.*, **73**, 458 (1951); **73**, 4885 (1951).
(2) Sekera and Marvel, *J. Am. Chem. Soc.*, **55**, 345 (1933).
(3) Adler, Haskelberg, and Bergmann, *J. Chem. Soc.*, 576 (1940).