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ALKYLATION WITH LONG CHAIN *p*-TOLUENESULFONATES. V. ANIONIC DISPLACEMENT REACTIONS OF *n*-OCTADECYL *p*-TOLUENESULFONATE[1]

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As a part of a program of evaluation of reactions of long chain *p*-toluenesulfonates with a variety of organic types (1), we have examined the reaction of *n*-octadecyl *p*-toluenesulfonate with a series of anions in mixed water-alcohol solvent. The anionic displacement reactions of simple short chain esters and carbohydrate esters of *p*-toluenesulfonic acid are well known (2). Two cases are found in the literature of similar reactions of long chain esters. In one of these Sekera and Marvel (3) report the formation of *n*-hexadecyl cyanide in high yield from *n*-hexadecyl *p*-toluenesulfonate and potassium cyanide in aqueous solution. The second is an observation made earlier in this laboratory in connection with other work in which *n*-octadecyl bromide was formed in 61% yield from the *n*-octadecyl ester and magnesium bromide in refluxing ether solvent (4).

We have examined the reaction of *n*-octadecyl *p*-toluenesulfonate with the following ions in water-alcohol mixed solvent: CN^-, CNS^-, I^-, CH_3COO^-, $S^=$ and SH^-. In all cases the corresponding *n*-octadecyl derivative was formed in above 75% yield and in two cases above 90%. In several cases it was demonstrated that a higher yield was obtained in water-alcohol solvent mixture than in pure alcohol. Also in our hands the aqueous potassium cyanide system used by Sekera and Marvel (3) did not produce appreciable quantities of *n*-octadecyl cyanide, while a 10% water–90% ethanol solvent allowed formation of the product in 86% yield. An experiment using potassium cyanide in absolute alcohol gave only a 36% yield of *n*-octadecyl cyanide and also a 28% yield of *n*-octadecyl ethyl ether.

Phthalimide was converted to N-*n*-octadecylphthalimide in 85% yield. Also sodiomalonic ester and sodioacetoacetic ester were alkylated. The *n*-octadecyl derivatives of these latter two compounds were hydrolyzed to eicosanoic acid and methyl *n*-nonadecyl ketone in over-all yields of around 50%.

EXPERIMENTAL[4]

n-Octadecyl cyanide. A mixture of 21.2 g. (0.05 mole) of *n*-octadecyl *p*-toluenesulfonate, 6.5 g. (0.10 mole) of potassium cyanide, and 100 ml. of a 90% ethanol–10% water mixture was heated under reflux for 1.5 hours. The reaction mixture was added to 100 ml. of water and the layers were separated. The aqueous layer was washed with ether and the organic

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[4] All melting and boiling points are uncorrected.

layer and ether extracts were combined. The volatile solvents were removed by distillation and the residue was crystallized from acetone to give 12.1 g. (86%) of *n*-octadecyl cyanide, m.p. 42–43°. A second crystallization from acetone did not raise the melting point. This compound has been reported to melt at 42° (5) and 42.5–43.5° (6).

In a reaction using the same amount of reactants in absolute alcohol there was obtained 36% of *n*-octadecyl cyanide and 28% of *n*-octadecyl ethyl ether, b.p. 158–162° at 0.80–0.85 mm., m.p. 30.5–31.5°. The ether was identical (mixture melting point) with a sample prepared from sodium ethoxide and *n*-octadecyl bromide (47% yield), m.p. 31–32°. *n*-Octadecyl ethyl ether has been reported (7) but no melting point is given. In other attempted reactions in which the reagents were heated without a solvent, with water as a solvent for 6 hours, and with water as a solvent for 22 hours, only in the last case was *n*-octadecyl cyanide formed and then only in small yield.

Table I summarizes results of displacement reactions with other anions.

TABLE I

ANIONIC DISPLACEMENT REACTIONS WITH *n*-OCTADECYL *p*-TOLUENESULFONATE

REACTANT	SOLVENT	PRODUCT $R = (CH_2)_{17}CH_3$	YIELD, %	M.P. OF PRODUCT, °C.
KCNS	Ethanol (90%)	RCNS	96	27–27.5[a]
KI	Ethanol	RI	79	33.5–34.5[b]
CH_3COOK	Ethanol (95%)	CH_3COOR	85	32–32.5[c]
Na_2S	Ethanol (95%)	R_2S	100	70–71[d]
KSH	Ethanol (95%)	RSH	76	32–32.5[e]
$C_6H_4(CO)_2NH$	None[f]	$C_6H_4(CO_2)NR$	82	78–80[g]
$Na^+(CH_3COCHCOOEt)^-$	Ethanol	RCH_2COCH_3[h]	43[i]	59–61[j]
$Na^+[CH(COOEt)_2]^-$	None	RCH_2COOH	45[k]	73–75[l]

[a] Frewing, *Proc. Roy. Soc.* (*London*), **A 182**, 270 (1944) reports m.p. 27°. [b] Numerous literature reports give the melting point at about this temperature. [c] This compound was identical (mixture m.p.) with a sample prepared by acetylation of *n*-octadecyl alcohol with acetic anhydride. [d] Reported values of this m.p. range from 62–64° [Barry, O'Rourke, and Twomey, *Proc. Roy. Irish Acad.*, **51B**, 223 (1947); *Chem. Abstr.*, **42**, 4133 (1948)] to 68–69° [Hunter, *Iowa State Coll. J. Science*, **15**, 215 (1941); *Chem. Abstr.*, **36**, 4474 (1942)]. A sample prepared by Reedy [Shirley and Reedy, *J. Am. Chem. Soc.*, **73**, 4886 (1951)], m.p. 63.5–64.5°, was recrystallized once from absolute ethanol and once from ether to give a product m.p. 69.5–70.5° which showed no depression in m.p. when mixed with the above sulfide. [e] Undepressed m.p. when mixed with a commercial sample. [f] The reactants were heated with anhydrous sodium carbonate to 190–210° for 0.5 hour. [g] The N-*n*-octadecylphthalimide was hydrolyzed to *n*-octadecylamine, m.p. 51–54° which in turn was acetylated with acetic anhydride to the acetamino derivative, m.p. 81–82° in 87% over-all yield. The m.p. of N-*n*-octadecylacetamide is reported as 79.5–80° by Adam and Dyer, *J. Chem. Soc.*, **127**, 70 (1925). [h] The ethyl *n*-octadecylacetoacetate was not isolated but was hydrolyzed with aqueous sodium hydroxide solution to the methyl ketone. [i] The yield is over-all to the methyl ketone. [j] A m.p. of 61° is reported by Holmes and Morgan, *J. Soc. Chem. Ind.* (*London*), **44**, 108 T (1925). This ketone was converted to its *semicarbazone*, m.p. 128–129°. The semicarbazone is reported by Cyamada, *Science Repts. Tôhoku Imp. Univ., First Ser.*, **18**, 625 (1939) [*Chem. Abstr.*, **24**, 2446 (1930)], m.p. 130°. [k] The intermediate ethyl *n*-octadecylmalonate was hydrolyzed and decarboxylated in dilute alcoholic potassium hydroxide solution. The yield is the over-all yield. [l] This compound is reported by several workers and melts at about 74–76°.

SUMMARY

An evaluation of the reaction of *n*-octadecyl *p*-toluenesulfonate with a variety of anions has shown that the displacement reaction $ArSO_3R + X^- \rightarrow RX + ArSO_3^-$ can be carried out in high yield.

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