The resulting deep purplish-red solution was then made slightly acid by dilute HCl, and the very finely divided precipitate separated and washed to neutrality by centrifuging. Dried at 55°, the product weighed 1.8 g., and consisted of reddish-brown micro-plates, decomposing about 230°. *Anal.* Calcd. for $C_{12}H_8N_2O_4$: C, 59.0; H, 3.30. Found: C, 58.9; H, 3.52.

Longer refluxing with alkali than in the case of 2-chlorophenazine-5,10-dioxide still leaves considerable residue when 2,7-dichlorophenazine-5,10-dioxide is so treated; prolonged refluxing over a period of ten days or more has not yielded a residue-free solution. Moreover, the analytical data for samples of 2,7-phenazindiol-5,10-dioxide recrystallized from glacial acetic acid have never been satisfactory. These various phenomena are being investigated, with the aim of determining whether they are due to instability of the compound under the given conditions, etc.

7-Chloro-2-phenazinol-5(?)-oxide.—A mixture of 1.5 g. of 2,7-dichlorophenazine-5-oxide[10], 200 cc. of ethanol, 120 cc. of distilled water and 40 g. KOH was refluxed overnight in a metal flask, and the cooled and filtered reddish-violet solution made slightly acid with dilute HCl. There were precipitated very small deep yellow needles weighing 1.0 g. after washing to neutrality and drying. These, after two recrystallizations from glacial acetic acid, began to decompose at about 260°. *Anal.* Calcd. for $C_{12}H_7ClN_2O_2$: C, 58.4; H, 2.86; Cl, 14.4. Found: C, 58.3; H, 3.11; Cl, 14.7.

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[CONTRIBUTION FROM THE RICHARDSON CHEMICAL LABORATORY OF TULANE UNIVERSITY]

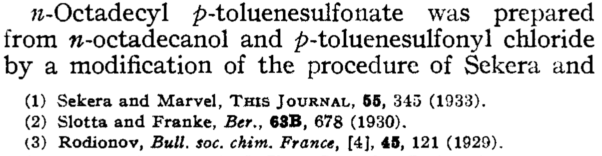
Alkylation with Long Chain *p*-Toluenesulfonates. I. Alkylation of Phenols with *n*-Octadecyl *p*-Toluenesulfonate

BY DAVID A. SHIRLEY AND WILLIAM H. REEDY

n-Octadecyl *p*-toluenesulfonate has been examined as an alkylating agent for phenols, and it has been found that the *n*-octadecyl aryl ethers are formed in 50 to 75% yields.

Esters of *p*-toluenesulfonic acid have been long established as alkylating agents for many organic types, including amines,[1,2,3] alkoxides,[4] phenoxides,[5] thiophenoxides,[6,2] Grignard reagents[4,7,8] and metallic salts.[1,9,10] The long chain (dodecyl and above) esters of *p*-toluenesulfonic acid have not been studied as alkylating agents except for the work of Sekera and Marvel[1] in 1933, who alkylated *n*-butylamine with dodecyl and hexadecyl *p*-toluenesulfonate and formed heptadecanonitrile from the hexadecyl ester and sodium cyanide.

We have undertaken in this Laboratory to examine the applicability of the long chain alkyl esters as alkylating agents. In this paper we are reporting the results of some experiments in which phenol and several phenolic types have been alkylated with *n*-octadecyl *p*-toluenesulfonate. The compounds alkylated were phenol, *o*- and *p*-nitrophenol, *p*-chlorophenol, *p*-cresol, α- and β-naphthol. The yields of octadecyl aryl ethers from the reaction varied from 51 to 75%.



n-Octadecyl *p*-toluenesulfonate was prepared from *n*-octadecanol and *p*-toluenesulfonyl chloride by a modification of the procedure of Sekera and Marvel[1,11] and we have obtained yields of the *n*-octadecyl ester of above 80%, an improvement over the earlier work by about 25%.

Experimental

***n*-Octadecyl *p*-Toluenesulfonate.**—Several modifications were made in the procedure given for the preparation of *n*-dodecyl *p*-toluenesulfonate.[11] To the cooled mixture of *n*-octadecyl alcohol, Eastman Kodak Co. white label (135 g.; 0.5 mole) and 300 g. of dry C.P. pyridine, 120 g. of *p*-toluenesulfonyl chloride was added. The mixture was stirred for 5 hours at a temperature below 15°. On pouring the mixture into one liter of ice-water the ester crystallized. It was collected on a Buchner funnel, washed several times with water, and sucked as dry as possible. It was purified as described previously from methanol. The yield of ester based upon the *n*-octadecyl alcohol used was 92%; m.p. 54–55°. This material was sufficiently pure for the work described below. After recrystallization from petroleum ether (b.p. 35–60°) using 5 ml. per 3 g., the melting point was 56° (reported,[11] 56°). The recovery was 90%.

Anal. Calcd. for $C_{25}H_{44}O_3S$: S, 7.55. Found: S, 7.46, 7.53.

***p*-Nitrophenyl *n*-Octadecyl Ether.**—In a 500-ml. three-necked, round-bottomed flask, equipped with a stirrer and a water condenser, were placed 7.5 g. (0.056 mole) of *p*-nitrophenol and 2.2 g. (0.055 mole) of sodium hydroxide dissolved in 100 ml. of water. To this mixture was then added 21.2 g. (0.050 mole) of *n*-octadecyl *p*-toluenesulfonate. The mixture was stirred and heated under reflux for about 20 hours. The hot reaction mixture was then poured into a 250-ml. separatory funnel and the water layer separated and discarded. The oil layer was washed with 6 *N* sodium hydroxide until a yellow color was no longer imparted to the alkaline wash layer. The organic material was then dissolved in benzene and washed twice with hot water. The benzene solution was cooled in an ice-bath, and the precipitated solid ether collected and dried on a Buchner funnel. This procedure yielded 11.4 g. of material melting from 68–71°. One recrystallization from ligroin (b.p. 65–90)) gave 11.1 g. of material melting at 70–71°. This corresponded to a 56.7% yield of ether based upon the ester.

Anal. Calcd. for $C_{24}H_{41}O_3N$: N, 3.58. Found: N, 3.65.

***p*-Aminophenyl *n*-Octadecyl Ether.**—In a 300-ml. round-bottomed flask were placed 5 g. (0.013 mole) of *p*-nitro-

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TABLE I

ALKYLATION OF PHENOLS WITH *n*-OCTADECYL *p*-TOLUENESULFONATE

Phenol used	Mole of phenol	Mole of ester	Yield of ether, %	M. p. of ether, °C.	Molecular formula of ether	Analyses, % Calcd.	Found
Phenol	0.063	0.050	54.8	48–49	$C_{24}H_{42}O$	C, 83.3	C, 83.1, 83.3
						H, 12.1	H, 12.4, 12.5
p-Cresol	.058	.050	50.5	49.5	$C_{25}H_{44}O$	C, 83.3	C, 83.5
						H, 12.2	H, 12.1
p-Chlorophenol	.053	.050	61.1	54–54.5	$C_{24}H_{41}ClO$	Cl, 9.31	Cl, 9.31, 9.26
o-Nitrophenol	.057	.050	74.6	39–40	$C_{24}H_{41}NO_3$	N, 3.58	N, 3.44
α-Naphthol	.052	.050	66.0	42–43	$C_{28}H_{44}O$	C, 84.8	C, 84.6, 84.6
						H, 11.2	H, 11.5, 11.6
β-Naphthol	.052	.050	55.3	64.5–65	$C_{28}H_{44}O$	C, 84.8	C, 84.4, 84.9
						H, 11.2	H, 11.0, 11.0
						Mol. wt., 396	Mol. wt., 396

phenyl *n*-octadecyl ether, 25 g. of stannous chloride dihydrate, and 150 ml. of glacial acetic acid. The mixture was heated at reflux temperature for about 4 hours. After cooling the solution was made basic by the addition of 6 *N* sodium hydroxide solution and filtered. The residue was then suspended in 200 ml. of 6 *N* hydrochloric acid and stirred for several minutes. The solid was then placed in 200 ml. of water (to which had been added 50 ml. of 6 *N* sodium hydroxide) and stirred. The mixture was again filtered with suction and washed several times with water and sucked as dry as possible. Recrystallization from petroleum ether gave a product melting at 64–66°. The solid was then dissolved in benzene and a small amount of decolorizing charcoal was added. The solution was heated and filtered and upon cooling in an ice-bath the *p*-aminophenyl *n*-octadecyl ether crystallized. It was collected and dried on a Buchner funnel. The 2.8 g. (melting point, 66–67°) obtained in this manner corresponded to a 61% yield.

Anal. Calcd. for $C_{24}H_{43}ON$: N, 3.87. Found: N, 3.86, 4.03.

Other Alkylation Reactions.—The phenols listed in Table I were all alkylated with *n*-octadecyl *p*-toluenesulfonate in general accordance with the procedure given above for *p*-nitrophenyl *n*-octadecyl ether.

NEW ORLEANS, LA. RECEIVED JULY 31, 1950

[CONTRIBUTION FROM THE RESEARCH LABORATORIES OF WALLACE & TIERNAN PRODUCTS, INC.]

The Reaction of Hydrazoic Acid with Thioether-sulfoxides: Synthesis of Sulfoximines

BY FERNANDA MISANI, T. W. FAIR AND L. REINER

The reaction of hydrazoic acid with thioether–sulfoxides in the presence of sulfuric acid as a catalyst yielded compounds which contained the characteristic configuration –S(O)(NH)–. The name sulfoximine is proposed for these compounds. The preparation and some of the properties of diamyl, diphenyl, methyl *p*-tolyl, methyl *p*-nitrophenyl and 4-aminophenyl methyl sulfoximines are described. In support of the assigned structure the results of the degradation of methionine sulfoximine previously isolated from nitrogen trichloride-treated prolamines are reviewed briefly and the formation of diphenyl N-acetylsulfoximine is described. The only sulfoximine which possessed convulsant properties was that derived from L-methionine.

A methionine derivative was isolated recently from nitrogen trichloride-treated prolamines[1,2,3] and it was shown by degradation studies that it differed from methionine in having an NH group and an oxygen atom directly attached to the sulfur atom.[2,4] This conclusion was reached on the basis of the following evidence: The elementary composition differed from that of methionine by one additional atom of each, hydrogen, nitrogen and oxygen. Hydrolysis of the compound with 57% hydriodic acid yielded one mole of methyl iodide and the thiolactone of homocysteine. Reduction with Raney nickel gave α-aminobutyric acid. Oxidation with hydrogen peroxide converted the compound into methionine sulfone and nitric acid. There was no appreciable decomposition when the compound was refluxed with 1 *N* hydrochloric acid for 1 hour but it was hydrolyzed by refluxing with 5 *N* sulfuric acid for 24 hours liberating one mole of ammonia and a number of ninhydrin-positive compounds the presence of which was demonstrated by paper chromatography. Thus the compound, just as methionine, contained an unsubstituted methyl group and an unsubstituted α-amino-γ-butyryl group attached to the sulfur atom. Consequently, the remaining three atoms (H, N and O) must be attached to the sulfur atom. Since ammonia was formed by hydrolysis and nitrate by oxidation, it was most likely that these atoms formed with the sulfur the configuration $=\!S\genfrac{}{}{0pt}{}{\rightarrow NH}{\rightarrow O}$. We further confirmed the existence of this hitherto unknown configuration, for which we propose the name "sulfoximine," by the synthesis of methionine sulfoximine from racemic methionine sulfoxide and hydrazoic acid.[5] The resulting compound was identical with that isolated from nitrogen trichloride-treated zein with respect to its analytical characteristics. It was, however, only half as toxic, presumably because it was prepared from D,L-methionine whereas the isolated compound was derived from L-methionine. In this paper we

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