hydrolysis. The ester and alcoholic solution were then slowly poured into a large beaker of crushed ice and, after washing repeatedly with cold water until neutral to litmus and free from alcohol, the esters were dried over calcium chloride. The yields varied from 45% for the isopropyl esters to 95% for the chloroethyl and bromoethyl esters.

Because of the immiscibility of *n*-butyl alcohol and water, the theoretical amount of sodium was dissolved in an excess of *n*-butyl alcohol and this solution used instead of aqueous sodium hydroxide in the preparation of the butyl esters.

Attempts were made to prepare β-diethylaminoethyl *p*-alkoxybenzenesulfonates by (1) esterification of the sulfonyl chlorides by β-diethylaminoethanol, (2) coupling of chloroethyl and bromoethyl esters with diethylamine, and (3) reaction between sodium *p*-alkoxybenzenesulfonates and β-diethylaminoethyl chloride. None of these attempts produced the desired results.

All the *p*-alkoxybenzenesulfonic acid esters were found to be very soluble in benzene, ether, chloroform, acetone and dioxane, sparingly soluble in ligroin and insoluble in water. Most of them were difficult to obtain in crystalline form because of their tendency to supercool, and some were never solidified, even though cooled to −75° by Dry Ice and acetone. The melting points ranged from 5.0 to 47.5° and the boiling points from 165 to 204° at 1 mm. pressure. Sulfur determinations were made by the Parr bomb method. The results are given in Table II. Saponification equivalents were determined by the method of Shriner and Fuson[13] using *N* potassium hydroxide in diethylene glycol as a hydrolyzing agent. The saponification values, shown in Table II, were approximately the same before and after distillation and agreed fairly well with the theoretical molecular weights for the methyl, ethyl, *n*-propyl and *n*-butyl esters; those for the *i*-propyl esters were little more than half the theoretical value. The explanation for this latter irregularity has not been established. Low values for the chloroethyl and bromoethyl esters were due to hydrolysis of the chloro and bromo groups (compare Földi[10]).

(13) R. L. Shriner and R. C. Fuson, "The Systematic Identification of Organic Compounds," John Wiley and Sons, Inc., New York, N. Y., 1940, p. 118.

Limited attempts were made to ascertain whether or not the *p*-alkoxybenzenesulfonic acid esters had any physiological action. A 2% suspension of methyl *p*-methoxybenzenesulfonate in mineral oil was placed on the lower lid of a rabbit's eye, a drop of plain mineral oil being used in the other eye as a control. The animal showed some evidence of pain for about ten minutes, but no dilatation or anesthesia was apparent up to thirty minutes. A 2% suspension of the same ester in physiological saline (0.85% sodium chloride) was next used in a similar manner with the same results. A 2% suspension of *n*-butyl *p*-*n*-butoxybenzenesulfonate in physiological saline seemed to cause no discomfort to a rabbit, neither did it produce dilatation or anesthesia. Results using a 5% suspension of the same ester were the same. The animals when examined twenty-four and forty-eight hours after the experiments showed no damage to their eyes. It appears that the *p*-alkoxybenzenesulfonic acid esters have little or no anesthetic activity.

Acknowledgment.—The authors wish to express their appreciation to Dr. J. F. Lewis for valuable assistance rendered.

Summary

1. Using sodium *p*-hydroxybenzenesulfonate as a starting material, four series of *p*-alkoxybenzenesulfonic acid esters were prepared.

2. Methods of syntheses of these esters and the necessary intermediate compounds are outlined.

3. Physical and chemical characteristics of these compounds are described.

4. Experiments to give preliminary indications of the possible anesthetic activity of *p*-alkoxybenzenesulfonic acid esters on the eyes of rabbits were performed and no evidence of activity was obtained.

LEAVENWORTH, KANSAS RECEIVED DECEMBER 13, 1946

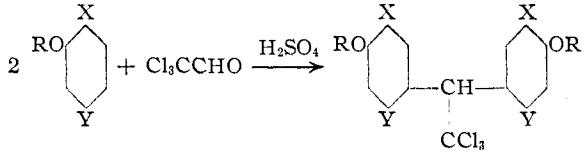
[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF NEW YORK UNIVERSITY]

Some Phenol–Chloral Condensations

BY JOSEPH B. NIEDERL AND AKSEL A. BOTHNER-BY[1]

The condensation of chloral with phenols may lead to oxygen heterocycles,[2] substituted phenyltrichloromethylcarbinols,[3] or diaryltrichloroethanes.[4] The latter reaction usually occurs in the presence of concentrated sulfuric acid, the products being phenol analogs of DDT. The value of these compounds and their ethers and esters as insecticides has been investigated by Stephenson and Waters,[5] who found that the free phenols and most of the esters have no activity, but that the lower ethers in some cases approach DDT in effectiveness.

In the present work it was decided to synthesize the chloral condensation products with thymol,[6] carvacrol, and a few of their alkyl ethers, according to the following scheme



Thymol: X = *i*-propyl, Y = methyl
Carvacrol: X = methyl, Y = *i*-propyl
R = H or alkyl

The ethers can be converted conveniently into diaryldichloroethenes by refluxing with alcoholic potassium hydroxide.[5,7] Both the ethers and the dehydrochlorinated compounds are easily obtained as pure crystalline substances with sharp melting points. It is suggested that they may be useful as

(1) Abstracted from the thesis of Aksel A. Bothner-By presented to the Graduate School of New York University, in partial fulfillment of the requirements for the degree of Master of Science, 1946. Presented before the Division of Organic Chemistry at the Atlantic City meeting of the American Chemical Society, April 15, 1947.

(2) Chattaway and Prats, *Anal. fis. quim.*, **26**, 75 (1928).

(3) Pauly and Schanz, *Ber.*, **56B**, 979 (1923).

(4) Zeidler and co-workers, *ibid.*, **7**, 1180 (1874).

(5) Stephenson and Waters, *J. Chem. Soc.*, 339 (1946).

(6) Jaeger, *Ber.*, **7**, 1197 (1874).

(7) Cristol and co-workers, THIS JOURNAL, **67**, 1495, 2222 (1945); **68**, 913 (1946).

TABLE I

CHLORAL CONDENSATION PRODUCTS

	Yield, %	M. p., °C.	Formula	Analyses %C Calcd.	%C Found	%H Calcd.	%H Found
			Trichloroethanes-				
Dicarvacrolyl, monohydrate	52	167.0–167.3	$C_{22}H_{29}O_3Cl_3$	59.00	58.94	6.53	6.66
Dicarvacrolyl, dimethyl ether	57	157–158	$C_{24}H_{31}O_2Cl_3$	62.93	63.08	6.83	6.82
Dithymolyl, dimethyl ether	52	114–115	$C_{24}H_{31}O_2Cl_3$	62.93	63.08	6.83	6.73
Dithymolyl, diethyl ether	59	73.6–74.0	$C_{26}H_{35}O_2Cl_3$	64.26	64.44	7.26	7.41
Dithymolyl, di-*n*-propyl ether	70	83.6–84.1	$C_{28}H_{39}O_2Cl_3$	65.43	65.49	7.65	7.63
Dithymolyl, dimyristyl ether	55	54–55	$C_{50}H_{83}O_2Cl_3$	73.01	73.27	10.17	10.22
Dithymolyl, diacetate	..	102.0–102.5	$C_{26}H_{31}O_4Cl_3$	60.77	60.60	6.08	5.93
Dibromodithymolyl	..	117–118	$C_{22}H_{25}O_2Cl_3Br_2$	44.96	44.74	4.29	4.50
			Dichloroethenes-				
Dicarvacrolyl, dimethyl ether	80	117.8–118.3	$C_{24}H_{30}O_2Cl_2$	68.40	68.22	7.18	7.40
Dithymolyl, dimethyl ether	85	103.8–104.5	$C_{24}H_{30}O_2Cl_2$	68.40	68.04	7.18	7.29
Dithymolyl, diethyl ether	77	100–101	$C_{26}H_{34}O_2Cl_2$	69.48	69.30	7.63	7.54
Dithymolyl, di-*n*-propyl ether	79	82.8–83.8	$C_{28}H_{38}O_2Cl_2$	70.43	70.13	8.02	7.93

derivatives in the identification of arylalkyl ethers.

Jaeger[6] in his article on the syntheses of dithymolyltrichloroethane and its acetate did not report the melting points. It was found that dithymolyltrichloroethane when recrystallized from absolute ethanol melts at 186° with decomposition, and the acetate at 102.0–102.5°. The free phenol also gives a crystalline dibromo derivative melting at 117–118°.

Table I gives the melting points and analyses of the compounds prepared. All melting points are uncorrected.

Experimental

Condensation Methods: Free Phenols and Phenol Ethers.—Concentrated sulfuric acid, diluted with one third its volume of glacial acetic acid is dropped slowly into a cooled mixture of the phenol and chloral in a two to one molar proportion until a solid or a gummy mass precipitates from the reaction mixture. The mass is washed thoroughly with cold water by decantation and then boiled with a large volume of water for several hours. The phenolic condensation products are recrystallized from 50–50 ethanol–water mixture, and crystallize with one mole of water of crystallization. The condensation products from the phenol ethers are recrystallized from 95% ethanol and contain no solvent of crystallization; yield was 52–80%.

Dehydrochlorination Methods.—The phenol ether condensation product (1 to 5 g.) is refluxed for two to six hours with 50 to 100 ml. of 30% ethanolic potassium hydroxide, and the solution poured into water. The ethene precipitates as an orange powder, and is recrystallized twice from 95% ethanol; yield 77–85%.

Preparation of Thymol Myristyl Ether.—32.0 g. (0.11 mole) of myristyl bromide, 22.5 g. (0.15 mole) of thymol and 6.0 g. (0.15 mole) of sodium hydroxide were refluxed with 15 ml. of water for ten hours. The water-insoluble layer was then washed and dried for three days over calcium chloride. Distillation gave a fraction boiling at 273–274° at 40 mm.; yield 30.5 g. or 83%.

The physical constants determined for the liquid were $n^{25}D$ 1.4859, d_{25} 0.8888. The molar refraction, calculated 111.2, found 111.5.

Anal. Calcd. for $C_{24}H_{42}O$: C, 83.17; H, 12.21. Found: C, 83.17; H, 12.10.

Summary

The condensation products of chloral with thymol, carvacrol and some of their alkyl ethers, together with the dehydrochlorinated derivatives of these have been prepared.

NEW YORK, N. Y. RECEIVED DECEMBER 19, 1946

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF NORTHWESTERN UNIVERSITY]

Replacement of Halogen by the Nitro Group in Halogenated Acetothiophenamides

BY HILL M. PRIESTLEY AND CHARLES D. HURD

Nitroso compounds of thiophene are unknown. This statement applies not only to nitrosothiophene but also to N-nitrosoaceto-2-thiophenamide, $C_4H_3S—N(NO)—COCH_3$. Steinkopf[1] attempted to prepare the latter compound but was unable to isolate any definite product.

It was reasoned that by employing 2-acetamido-3,5-dibromothiophene (I) instead of aceto-2-thiophenamide itself, the N-nitroso compound might be the more readily formed. As is known, no difficulty is encountered in the formation of the N-nitroso derivative of aceto-2,4-dibromoanilide. Hence, nitrous fumes, generated from arsenic trioxide and nitric acid, were passed into a solution of 2-acetamido-3,5-dibromothiophene in glacial acetic acid. A yellow compound of melting point 207° was easily isolated. The N-nitroso-N-aryl amides are of low melting point, readily explode, and cannot be kept for more than a few days. The yellow compound obtained possessed none of these properties and hence could not be the

(1) Steinkopf, *Ann.*, **403**, 25 (1914).