TABLE II

Sulfone	Yield, %	M.p., °C.	Analyses, % Calcd. C	Calcd. H	Found C	Found H
$CH_3SO_2CH_2Cl$	37	57.2–58.2[a]				
$CH_3SO_2CHCl_2$	56	72.0–73.3	14.73	2.47	14.83	2.38
$CH_2ClSO_2CH_2Cl$	36	69.4–70.5[b]	14.73	2.47	14.84	2.54
$CH_2ClSO_2CHCl_2$	67	Clear, colorless liquid[c]	12.16	1.53	12.11	1.53
$CH_3SO_2CCl_3$	62	173.8–174.2	12.16	1.53	12.35	1.77
$CH_2ClSO_2CCl_3$	66	49.8–50.0	10.36	0.87	10.37	0.83
				Cl, 61.11		Cl, 61.1
$CHCl_2SO_2CHCl_2$	[d]	103.8–104.5	10.36	0.87	10.30	0.91
				Cl, 61.11		Cl, 61.1
$CHCl_2SO_2CCl_3$	13	36.2–36.4[e]	9.02	0.38	9.06	0.40
$CCl_3SO_2CCl_3$	36	35.7–36.0[e]	7.98	0.00	8.04	0.06
$(CH_3)_3CSO_2CCl_3$	17	130.2–130.8	25.07	3.79	25.05	3.82
$CH_3SO_2CF_3$	40	Clear, colorless, odorless liquid[f]	16.22	2.04	15.94	2.01
$CH_3SO_2CClF_2$	62	21.0–21.6[g]	14.60	1.84	14.71	1.79
$CH_2ClSO_2CF_3$	46	[h]	13.16	1.10	13.13	1.09

[a] Literature value, 56°.[4] [b] Literature value, 70.5–72°[13]; mixed m.p. with $CH_3SO_2CHCl_2$, 44–64°. [c] B.p. 96° (2 mm.), n^{20}_4 1.5303, d^{20}_4 1.7010, f.p. −35°. [d] Obtained by oxidation of a mixture of $CH_2ClSCCl_3$ and $CHCl_2SCHCl_2$ followed by fractional crystallization from petroleum ether (b.p. 60–70°). [e] Mixed m.p. of these two compounds was below room temperature. [f] B.p. 128.9° (737 mm.), n^{20}_D 1.3486, d^{20}_4 1.5141, f.p. 14.0°. [g] B.p. 165.1° (760 mm.), n^{20}_D 1.4050, d^{20}_4 1.5685. [h] B.p. 139.9° (751 mm.), n^{20}_D 1.3859, d^{20}_4 1.6533, f.p. −90°.

connected to a Dry Ice trap. One hundred and six grams of products (about 30 g. of pentachlorodimethyl sulfide and 76 g. of α,α,α,α'-tetrachlorodimethyl sulfide), b.p. 55–60° (4 mm.), obtained in several chlorinations of dimethyl sulfide with sulfuryl chloride were combined and added to the flask over a period of 10 minutes. The flask was warmed in a water-bath at 95° for 30 minutes, and then the condenser was replaced with a delivery tube extending into a receiver cooled in ice water. Warming at 95° was continued until distillation stopped. Rectification of the product boiling below room temperature in a Podbielniak Hyd-Robot low-temperature fractionation apparatus gave 9.3 g. (about 45% yield) of pentafluorodimethyl sulfide, b.p. 0.8–1.3° (760 mm.). Qualitative analysis showed that it contained sulfur and fluorine but no chlorine. The molecular weight found by the vapor density method was 152.7 and 153.3; calculated molecular weight, 152.1.

Oxidation to Sulfones.—A solution of the sulfide in glacial acetic acid was added with stirring and external cooling to a solution of chromic oxide in glacial acetic acid (approx. molar ratio, 2.5 CrO_3:1.0 sulfide). The reaction mixture was heated to 95° and kept there for 15 minutes to one hour. The solution was poured into ice water and neutralized with sodium hydroxide. The resulting sulfone was filtered off or extracted with chloroform and it was recrystallized usually from petroleum ether (b.p. 60–70°). Results in these oxidations are tabulated below.

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LAFAYETTE, INDIANA

[CONTRIBUTION FROM THE PURDUE UNIVERSITY]

Alkylation of Certain Phenolic Compounds[1]

BY ED. F. DEGERING, HAROLD J. GRYTING AND P. A. TETRAULT

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A series of alkylated cresols and chlorophenols has been prepared by the alkylation of *o*-cresol, *p*-cresol, *o*-chlorophenol and *p*-chlorophenol with capryl, cetyl and lauryl alcohols. *o*-Cresol was also alkylated with *n*-decyl alcohol and 1-octanol. The 4-capryl-2-methylphenol and 4-(2-decyl)-2-methylphenol were ring acylated with chloroacetyl chloride. Certain physical properties of these compounds are tabulated. The compounds described herein, some of which are of themselves good germicides,[2] were prepared as intermediates in the synthesis of phenolic-quaternary-ammonium type germicides.

Alkylation and alkylation of phenols have been discussed, respectively, by Shreve[3a] and Price.[3b]

It is also known that zinc chloride catalyzes alkylation of phenols with alcohols in the para-position and, where that is impossible, in the ortho-position without substantial rearrangements to meta-derivatives which are often obtained with aluminum chloride. Rearrangements of alkyl groups from primary to secondary generally occur, however, in zinc chloride-catalyzed alkylations of this type.[4]

Experimental

The alkylation of *o*-cresol with cetyl alcohol in the presence of zinc chloride for the preparation of a mixture of alkylphenol isomers, in which 4-(2-cetyl)-2-methylphenol predominates, is typical of the reactions we have utilized in the synthesis of the alkylcresols and alkylchlorophenols whose physical properties are recorded in the accompanying table.

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[1] Abstract of a portion of a thesis submitted to the Faculty of Purdue University by Harold J. Gryting in partial fulfillment of the requirements for the degree of Doctor of Philosophy, June, 1947. This project was sponsored by the Alrose Chemical Company, Providence, Rhode Island.

[2] Ed. F. Degering, H. J. Gryting and P. A. Tetrault, unpublished work.

[3] (a) P. H. Groggins, "Unit Processes in Organic Synthesis," Chapter by R. N. Shreve, pp. 485–532 (1938); (b) C. C. Price, *Chem. Revs.*, **29**, 37 (1941); also R. Adams, "Organic Reactions," Vol. III, John Wiley and Sons, Inc., New York, N. Y., 1946.

[4] L. H. Flett, U. S. Patent 2,205,947 (June 25, 1940).

TABLE I

PHYSICAL CONSTANTS OF CERTAIN MONO-ALKYL CRESOLS AND MONO-ALKYL CHLOROPHENOLS

Phenol[b, j]	B.p., °C.	B.p., Mm.	d_{20}	$n^{20}D$	*MR* Calcd.	*MR* Found	Conversion, %	Carbon, % Calcd.	Carbon, % Found	Hydrogen, % Calcd.	Hydrogen, % Found
4-Methyl-2-(2-octyl)	140.4	6	0.9319	1.5057	69.41	69.97	69.7	81.83	81.2	10.99	11.0
2-Methyl-4-(2-octyl)[a]	133.5	2	0.9324	1.5069	69.41	70.08	60.7	81.83	82.04	10.99	10.85
4-Chloro-2-(2-octyl)[f]	147.9	4	1.0302	1.5181	69.70	70.62	33	69.87	70.24	8.73	8.88[h]
2-Chloro-4-(2-octyl)	139.4	5	1.0248	1.5117	69.70	70.25	17.5	69.87	70.5	8.73	8.77[i]
2-(2-Dodecyl)-4-methyl[g]	175	2	0.9089	1.4955	87.91	88.54	36	82.59	83.10	11.69	11.81
4-(2-Dodecyl)-2-methyl	157.5	2	.9113	1.4976	87.91	88.63	44.5	82.59	82.64	11.69	11.65
4-Chloro-2-(2-dodecyl)	182	2.5	.9772	1.5037	88.11	89.89	15	72.87	73.6	9.87	9.94
2-Chloro-4-(2-dodecyl)	164	2	.9656	1.4995	88.11	90.04	40.3	72.87	73.1	9.87	9.7
2-(2-Cetyl)-4-methyl[g]	222.5	7	.8992	1.4914	106.41	107.03	67.7	83.12	82.94	12.15	12.0
4-(2-Cetyl)-2-methyl	174.5[m]	1	.8981	1.4916	106.41	107.08	51	83.12	83.3	12.15	12.1
2-(2-Cetyl)-4-chloro	197[n]	2	.9635	1.5015	106.61	107.78	39	74.91	75.10	10.57	10.57
4-(2-Cetyl)-2-chloro	176	0.75	.9549	1.4967	106.61	107.91	25.5	74.91	75.2	10.57	10.8
4-(2-Decyl)-2-methyl	150–153	2.25	.9215	1.5017	78.71	79.92	60	82.20	82.16[p]	11.36	11.33
Ketone[b, j]											
Chloromethyl-5-(2-octyl)-2-hydroxy-3-methylphenyl[c, l]	186–188	3.0	1.0486	1.5188	85.31	85.85	..	d_1			
2-Chloroethyl-5-(2-octyl)-2-hydroxy-3-methylphenyl[c]	184–187	2.4–5	1.0345	1.5055	89.93	89.13	77.8	d_2			
Chloromethyl-5-(2-decyl)-2-hydroxy-3-methylphenyl[c]	176–177	1.8	1.0301	1.5184	94.51	95.49	97	d_3			

[a] This compound was prepared by alkylation of *o*-cresol with 2-octanol and also with 1-octanol. [b] All boiling points are corrected. [c] These compounds were prepared by the Friedel–Crafts reaction of the corresponding alkylcresol with chloroacetyl chloride or chloropropionyl chloride. [d] (1, 2 and 3). Chlorine analyses, calcd.: 11.95, 11.40 and 10.92; found: 11.25, 10.23 and 10.35, respectively. These compounds lost HCl on rectification. Quaternary ammonium compounds prepared from two of them were analyzed for better identification: from d_1, the pyridinium chloride (m.p. 200–200.5°). This cpd. was obtained from alkylation, chloromethylation, and quaternary salt formation, starting with both capryl alcohol and 1-octanol. Calcd.: N, 3.74; C, 70.4; H, 8.0; found: N, 3.85, 3.56; C, 70.53; H, 8.30; from d_3, the pyridinum chloride (m.p. 186–187°), calcd.: N, 3.45; found: N, 3.28. [f] This compound was previously reported by Klarmann.[5] [g] This compound is claimed by Flett[4] as a constituent of the mixture obtained by alkylating *o*-cresol with a mixture of the alcohols obtained from coconut oil. [h] Chlorine, calcd.: 14.74, found: 14.8. [i] Chlorine, calcd.: 14.74, found: 14.5. [j] Predominantly compound indicated as would be predicted by normal directional influences of OH, CH_3 and Cl; presence of isomers in presently undetermined amount as well as corresponding lower and higher molecular weight compounds from other alcohols probably present as impurities is indicated. [k] Taken from a central portion flat during re-rectification after previous distillation and rectification using a five-foot helix packed column. [l] Ferric chloride positive phenol test indicates ring acylation rather than the usual alcohol type ester forming acylation. [m] 180.5° at 1.5–2 mm. [n] 184.5° at 1 mm. [o] 183° at 1¼ mm. [p] Additional data: C, 81.20, 83.35; H, 11.51, 11.97.

Cetyl alcohol (242.3 g., Givaudan–Delawanna, m.p. 48–49°) and *o*-cresol (216 g., Eastman, Technical grade) were stirred with 216 g. of zinc chloride while the mixture was heated at 175–180° for 25 hours. The product was washed, dried and rectified. Seventy-six grams of *o*-cresol (b.p. 58° at 4 mm.) and 6 g. of cetyl alcohol (b.p. 152° at 4 mm., m.p. 48–49°) were recovered. The bulk of the product was collected at 203.5 to 208.5° at 3.5 to 4 mm. ($n^{20}D$ 1.4916–1.4934). The largest fraction (b.p. 206.5–207.5° at 3.5–4 mm.) was re-rectified in a 5-foot, helix packed column: a sample, b.p. 174.5° at 1 mm., or 180.5° at 1.5–2.0 mm., was analyzed. Calcd.: C, 83.12; H, 12.15. Found: C, 83.3; H, 12.1. This product gave a positive ferric chloride test for a phenol and is presumably predominately the 4-(2-cetyl)-2-methylphenol isomer. Approximately 40 g. of solid remained from the original distillation. This was crystallized several times from ethanol yielding white flakes (b.p. 223° at 3 mm., m.p. 53–54°) which gave negative ferric chloride tests for a phenol and analyzed as: C, 81.4, 81.2; H, 12.92, 13.2%. The conversion to the monoalkyl derivative (calcd.: C, 83.12; H, 12.15) was 51 and 14% to the by-product which may be the dicetyl ether according to C and H analysis (calcd.: C, 81.65; H, 12.62). The latter compound was also obtained in the reaction of *o*-chlorophenol with cetyl alcohol with removal of chlorine. Hence it appears that the chlorine atom or the methyl group in the ortho-position to the hydroxyl group may be removed by heating in the presence of zinc chloride.

The solid from the reaction of cetyl alcohol with *o*-chlorophenol and also from the reaction of cetyl alcohol with *o*-cresol, which from C and H analyses at least corresponds to the dicetyl ether (1,2-dicetoxybenzene), is of interest as indicated since the compound does not contain chlorine. The condensation of cetyl alcohol with itself is ruled out on the grounds that the product was not obtained from *p*-cresol and *p*-chlorophenol with cetyl alcohol in similar experiments, although a high boiling oil free of chlorine was obtained from each of these, which may have been the corresponding 1,4-dicetoxy compounds. Further elucidation of the structure of this compound as well as certain others listed herein are contemplated utilizing infrared spectrophotometric methods.

A special manometer based on the vapor pressure of a constantly boiling liquid (dibutyl phthalate) was designed and assembled for accurate pressure determination in the rectification of several of these compounds under reduced pressure. A diagram of this is shown in Fig. 1. This manometer followed precisely even small changes in pressure which could not be noticed on the Zimmerli type gages. Its use is recommended where precise pressure control is inconvenient.

Discussion

In most of these alkylations a smaller quantity of the corresponding ether (no reaction with $FeCl_3$, the test for the phenolic group) boiling lower than the C-alkyl derivative was obtained. These and higher alkylated products, obtained in varying amounts according to the ratio of the alcohol to the phenolic compound, were not analyzed except in the instances noted.

The alkyl phenols tabulated with physical constants (Table I) are believed to be essentially the isomers indicated, as predicted from the directive influence of substituents on the benzene nucleus. However, the rectification curves indicate the prob-

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(5) E. G. Klarmann, THIS JOURNAL, **55**, 2576 (1933).

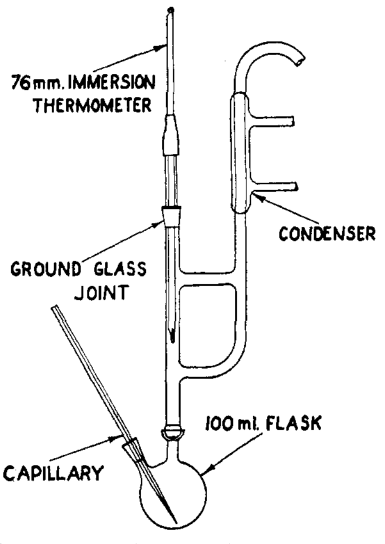

Fig. 1.—Special boiling liquid manometer.

ability of presence of an undetermined amount of isomeric compounds. Samples for physical constants were taken after two rectifications following the initial distillation and thus probably represent more nearly the correct constants for the isomer indicated than is illustrated from the rectification curves.

Figure 2 indicates three fractions, presumably close boiling decyl-*o*-cresol isomers. The largest fraction was re-rectified for physical constants data on the predominant isomer, postulated to be the 2-methyl-4-(2-decyl)-phenol.

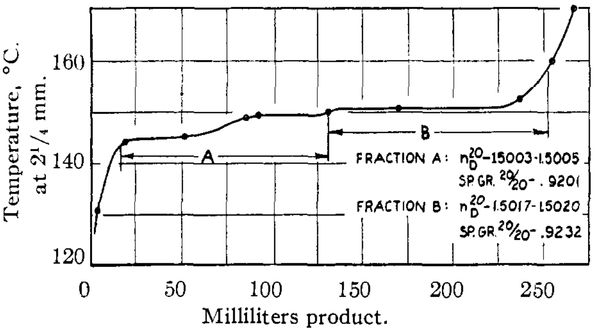

Fig. 2.—Rectification curve for alkylation of *o*-cresol with decyl alcohol.

The alkylations of *o*-cresol with 2-octanol and with 1-octanol resulted in identical C-alkyl products for the main compound as evidenced by their rectification curves and the physical constants of the products. (The solid quaternary ammonium salts prepared from their chloromethyl derivatives gave identical melting points and that of the mixture was not depressed.) The rearrangement of the carbon skeleton to give identical compounds as major product from primary and secondary alcohols may follow the olefin rearrangement[6a,b] cited previously or a carbonium ion mechanism.

(6) (a) A. W. Francis, *Chem. Revs.*, **42**, 111 (1948); (b) R. Huston and I. Kaye, THIS JOURNAL, **64**, 1577 (1942).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF UTAH]

Condensation of Naphthols with Formaldehyde and Primary Amines[1]

BY W. J. BURKE, MARTIN J. KOLBEZEN[2] AND C. WAYNE STEPHENS[3]

Condensation of 2-naphthol with formaldehyde and representative aliphatic and alicyclic primary amines resulted in 2,3-dihydro-2-substituted-1H-naphth[1.2-e]-*m*-oxazines or N,N-bis-(2-hydroxy-1-naphthylmethyl)-amines depending upon reaction conditions. The naphthoxazines were readily split by acid to yield the corresponding 1-substituted-aminomethyl-2-naphthols. Typical reactions of these compounds were investigated. Related studies were made with 1-naphthol.

Study of the condensation of representative phenols with formaldehyde and primary aliphatic amines indicates that the substituent ortho to the phenolic hydroxyl group plays an important role in determining the course of the reaction.[4] In view of this and the known peculiarities of the naphthols, the investigation has been extended to include this class of related compounds.

The condensation of naphthols with formaldehyde and secondary amines has been studied in several laboratories.[5–9] Reaction of piperidine and formaldehyde with 1- and 2-naphthol has been shown to result in the introduction of a piperidinomethyl group into the 1-position of 2-naphthol and into the 2-position of 1-naphthol. Preformed methylene-bis-amines can be used in place of formaldehyde and secondary amines in the reaction with 2-naphthol.[10] The mechanism of the reaction of 2-naphthol with both N-methylolamines and methylene-bis-amines has been studied by Lieberman and Wagner.[11]

In the present work reaction of 2-naphthol with formaldehyde and methylamine in a molar ratio of 1:2:1, respectively, in methanol solution at 60° was found to result in a 98% yield of 2,3-dihydro-2-methyl-1H-naphth[1.2-e]-*m*-oxazine (I). Benzyl-, cyclohexyl- and *n*-butylamine gave similar results. Upon treatment of I with hot aqueous hydrochloric acid, formaldehyde was liberated and the hydrochloride of 1-methylaminomethyl-2-naphthol (V) formed. Condensation of V with formaldehyde in the presence of base brought about reconversion to I.

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(1) Presented in part before the Organic Division of the American Chemical Society in Chicago in September, 1950.

(2) Wallace MacFarlane Fellow, 1948–1949, and University of Utah Research Committee Fellow, 1949–1950.

(3) University of Utah Research Committee Fellow, 1951.

(4) W. J. Burke, R. P. Smith and Carl Weatherbee, THIS JOURNAL, **74**, 602 (1952).

(5) F. Bayer and Company, German Patent 89,979; *Chem. Zentr.*, **68**, **I**, 576 (1897).

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(11) S. V. Lieberman and E. C. Wagner, *ibid.*, **14**, 1001 (1949).