an authentic sample of dehydroabietic acid[1] no depression of melting point could be observed.

Dehydroabietic Methyl Ester.—The methyl ester of dehydroabietic acid was prepared in the usual manner by esterification with diazomethane. It separated from methyl alcohol as needles that melted at 62–63°; $[\alpha]^{20}D$ +60° in 2% absolute alcohol. *Anal.* Calcd. $C_{21}H_{30}O_2$: C, 80.20; H, 9.62; OCH_3, 9.88. Found: C, 80.37, 80.11; H, 9.85, 9.78; OCH_3, 10.17. No depression of melting point was observed when this sample was mixed with an authentic sample of dehydroabietic methyl ester.[1]

Lactonized Dihydroabietic Acid.—The ether solution, obtained from the extraction of sulfo-dehydroabietic acid from the crude sulfonation product, was washed with water and then evaporated to dryness. The residue was recrystallized from alcohol. It separated as rectangular plates which melted at 130–131°; $[\alpha]^{20}D$ −4° in 2% absolute alcohol. *Anal.* Calcd. for $C_{20}H_{32}O_2$: C, 78.88; H, 10.60. Found: C, 78.92, 78.87; H, 10.53, 10.75. When mixed with lactonized dihydroabietic acid isolated from catalytically prepared pyroabietic acid,[1] no lowering of the melting point could be observed.

Tetrahydrohydroxyabietic Acid.—A solution of 0.3 g. of the lactone isolated above, in 10 cc. of 10% *n*-butyl alcoholic potassium hydroxide, was refluxed for four hours. The *n*-butyl alcohol was distilled with steam. The residue was diluted with 100 cc. of water and this solution was then extracted three times with ether. The aqueous solution was made acid to litmus by careful addition of 10% acetic acid. The product was extracted

with ether, the extract washed with water, and then the ether evaporated to dryness. The residue crystallized from dilute methyl alcohol as thick needles that melted at 164–165° when dried at room temperature; $[\alpha]^{20}D$ +35° in 2% absolute alcohol. *Anal.* Calcd. for $C_{20}H_{34}O_3$: C, 74.47; H, 10.63. Found: C, 74.51, 74.25; H, 10.78, 10.73.

When this compound was mixed with tetrahydro-hydroxyabietic acid from catalytically prepared pyroabietic acid[5] no lowering of the melting point could be observed.

Summary

1. Dehydroabietic acid and dihydroabietic acid as the lactone have been isolated from pyroabietic acid prepared without the aid of a catalyst.

2. No tetrahydroabietic acid or dihydroabietic acid, $[\alpha]^{20}D$ +108°, previously found in catalytically prepared pyroabietic acid, could be isolated from pyroabietic acid prepared by heat alone.

3. The one hundred hour heating period, heretofore used for the non-catalytic conversion of *l*-abietic acid into pyroabietic acid, may be shortened to three or four hours by increasing the temperature from the customary 250 to about 330°.

WASHINGTON, D. C.   RECEIVED DECEMBER 2, 1938

Alkoxyalkyl Derivatives of Resorcinol

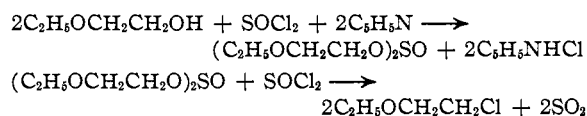BY CHARLES D. HURD AND GEORGE W. FOWLER[1]

Alkylresorcinols have been studied extensively as germicides, but this work has not been extended to include the effect of an ether linkage in the alkyl chain. Accordingly, the present study was directed toward the synthesis of 4-alkoxyalkylresorcinols and resorcinol alkoxyalkyl monoethers, since it is known[2] that the germicidal behavior of 4-alkylresorcinols and resorcinol alkyl monoethers is comparable.

The reaction: $RO(CH_2)_nX + NaOC_6H_4OH \rightarrow NaX + RO(CH_2)_nOC_6H_4OH$ was investigated for the synthesis of the monoethers. It was successful with alkoxyalkyl bromides, but unsuccessful with β-ethoxyethyl chloride or β-ethoxyethyl sulfite. In view of Swallen and Boord's experience[3] with β-ethoxyethyl chloride and sodium

phenoxide, the very slow reaction with sodium resorcinolate was anticipated; but the negligible yield from the sulfite was unexpected, because phenyl β-ethoxyethyl ether was synthesized satisfactorily by this method

$$(C_2H_5OCH_2CH_2O)_2SO + C_6H_5ONa \longrightarrow$$
$$C_6H_5OCH_2CH_2OC_2H_5 + C_2H_5OCH_2CH_2OSO_2Na$$
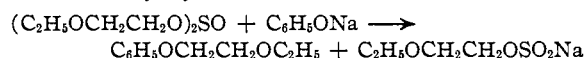
The sulfite approach was attractive since the sulfite[4] is an intermediate in the formation of the chloride from the alcohol.

$$2C_2H_5OCH_2CH_2OH + SOCl_2 + 2C_5H_5N \longrightarrow$$
$$(C_2H_5OCH_2CH_2O)_2SO + 2C_5H_5NHCl$$
$$(C_2H_5OCH_2CH_2O)_2SO + SOCl_2 \longrightarrow$$
$$2C_2H_5OCH_2CH_2Cl + 2SO_2$$

Four of the monoethers, $m\text{-}RO(CH_2)_nOC_6H_4OH$, wherein R = ethyl or *n*-butyl and *n* = 2 or 3, were prepared from the bromides. Smaller quantities of the diethers, $C_6H_4(O—(CH_2)_n—OR)_2$,

(1) Parke, Davis and Company Research Fellow, 1935–1937.

(2) Klarmann, Gatyas and Shternov, THIS JOURNAL, **53**, 3397 (1931).

(3) Swallen and Boord, *ibid.*, **52**, 651 (1930).

(4) Voss and Blanke, *Ann.*, **485**, 258 (1931).

separated by their insolubility in alkali, were formed concurrently.

Three of the monoethers were tested for their germicidal efficiency: resorcinol β-ethoxyethyl ether (A), resorcinol β-butoxyethyl ether (B), resorcinol γ-butoxypropyl ether (C). Compound B was moderately effective toward *B. typhosus*.
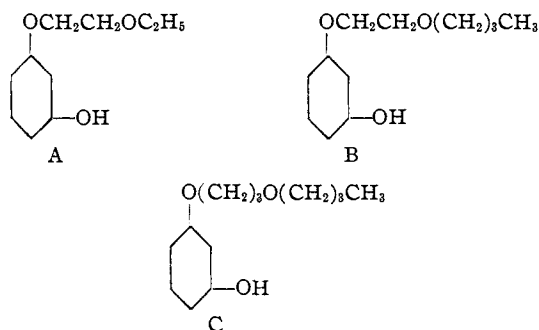
Its effective dilution in five minutes at 20° was one part in 800. C showed little effect at a dilution of 1–500, and A showed little effect at 1–200. All three ethers were ineffective toward *Staph. aureus* in five minutes at 37° at the maximum concentration tested, namely, one part in 500. The phenol coefficients from these data are listed in Table I. Included also are data for

TABLE I

COMPARISON OF PHENOL COEFFICIENTS OF RESORCINOL ALKOXYALKYL MONOETHERS AND THE CORRESPONDING RESORCINOL ALKYL MONOETHERS

Resorcinol monoether	*B. typhosus* at 20°	at 37°	*Staph. aureus* at 37°
β-Ethoxyethyl	2.5	..	5
n-Pentyl[a]	..	38	36
β-Butoxyethyl	10	..	5
n-Heptyl[a]	..	21	330
γ-Butoxypropyl	6	..	5
n-Octyl[a]	..	2.3	580

[a] Klarmann, Gatyas and Shternov, This Journal, 53, 3402 (1931).

the resorcinol alkyl monoethers, wherein the alkyl corresponds in size to the aliphatic portion of A, B, and C, *i. e.*, pentyl, heptyl and octyl, respectively. It will be seen that the last three ethers were much more effective against *Staph. aureus*. The relative inefficiency of the alkoxyalkyl ethers seems to be correlated with their appreciable solubility in water.

Several approaches to the 4-alkoxyalkylresorcinols, $RO(CH_2)_nC_6H_3(OH)_2$, were considered but all had their limitations. Except for low yields and difficulty of purification, Claisen's

plan of "C-alkylation"[5] seemed feasible. The unsaturated halide used here was δ-methoxycrotyl bromide, made from butadiene: CH_3OCH_2-$CH=CHCH_2Br + NaOC_6H_4OH \xrightarrow{\text{benzene}} NaBr$ $+ CH_3OCH_2CH=CHCH_2C_6H_3(OH)_2$. Much of the desired compound polymerized to a tetramer during purification in a molecular still. Possibly this could have been inhibited by hydrogenation before distillation, for it was shown that hydrogenation of the methoxycrotylresorcinol occurred readily.

Considerable study was directed to the synthesis of alkoxyacetylresorcinols (ω-alkoxyresacetophenone), $ROCH_2COC_6H_3(OH)_2$, and their reduction to alkoxyethylresorcinols, $ROCH_2CH_2$-$C_6H_3(OH)_2$, since this is the customary approach to the simpler 4-alkylresorcinols. Because of the known destructive action of aluminum chloride on ether linkages, the Fries rearrangement of a *m*-hydroxyphenyl alkoxyacetate was omitted. Neither Nencki's condensation (resorcinol, ethoxyacetic acid, zinc chloride) nor Cox's modification[6] (resorcinol and ethoxyacetyl chloride, heated) gave rise to any ω-ethoxyresacetophenone.

ω-Propoxy- and ω-butoxyresacetophenone, RO-$CH_2COC_6H_3(OH)_2$, were prepared by the Hoesch reaction. Butoxyacetonitrile, required for the latter, was made by heating butoxymethyl chloride and cuprous cyanide for fifteen minutes which is one-twentieth the time specified for lower homologs.[7] ω-Methoxy- and ω-ethoxyresacetophenone were prepared by described methods.[8] A Hoesch condensation of β-ethoxypropionitrile, $C_2H_5OCH_2CH_2CN$, with resorcinol and zinc chloride gave rise to β-(2,4-dihydroxyphenyl)-propionic acid, $1,3,4-(HO)_2C_6H_3CH_2$-CH_2COOH, instead of ω-ethoxyresopropiophenone. The same acid was isolated by Langley and Adams[9] as a condensation product of β-chloropropionitrile and resorcinol under similar conditions.

Two methods were studied for the conversion of alkoxyresacetophenones into alkoxyalkylresorcinols, namely, direct hydrogenation and the Clemmensen method. Only a slight yield of 4-ethylresorcinol was obtainable from resaceto-

(5) Claisen and co-workers, *Ann.*, 442, 210 (1925); *Ber.*, 59, 2344 (1926); Hurd and McNamee, This Journal, 59, 104 (1937).

(6) Cox, *Rec. trav. chim.*, 50, 848 (1931).

(7) (a) Gauthier, *Compt. rend.*, 143, 831 (1906); (b) Henze and Rigler, This Journal, 56, 1350 (1934).

(8) Sonn, *Ber.*, 52, 923 (1919); Slater and Stephen. *J. Chem. Soc.*, 117, 309 (1920).

(9) Langley and Adams, This Journal, 44, 2320 (1922).

| Alcohol | | PBr₃, | Pyridine, | Alkoxyalkyl bromides | | | |
| Name | G. | g. | g. | Yield | | B. p. | |
				G.	%	°C.	Mm.
β-Ethoxyethyl	72.5	87.3	17.0	61.0	49.5	126–128	750
β-Butoxyethyl	59.0	54.5	10.5	44.3	49.0	58–63	11
γ-Ethoxypropyl	74.5	77.7	12.6	85.5	71.5	148–150	750
γ-Butoxypropyl	64.0	61.0	10.0	42.8	45.3	80–83	21

phenone by the first method with a palladium catalyst, so it was not extended. The second procedure[10] was too powerful, for it brought about cleavage of the ether as well as reduction of the carbonyl

$$ROCH_2COC_6H_3(OH)_2 + 6H \longrightarrow$$
$$CH_3CH_2C_6H_3(OH)_2 + H_2O + ROH$$
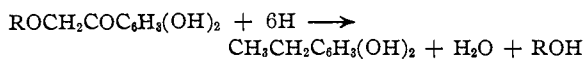
4-Ethylresorcinol, which was formed, was characterized as 4-ethylresorcinoldiacetic acid, C_2H_5-$C_6H_3(OCH_2COOH)_2$.

Experimental Part

β-Ethoxyethyl Sulfite.—Forty grams of thionyl chloride was added slowly at 20° to 74.5 g. of β-ethoxyethyl alcohol ("cellosolve") while a rapid stream of carbon dioxide bubbled through the latter. The last traces of hydrogen chloride were removed by heating to 40–50° for several hours, finally under diminished pressure. Two fractionations of the product were made. The second, through a 20-cm. column, resulted in a 36-g. fraction (48% yield) which boiled at 96–100° and 1–2 mm. Other observed properties were: b. p. 120° (5 mm.); $n^{20}D$ 1.4382; d^{20}_4 1.1015. It was a water-clear liquid, almost colorless.

Anal. Calcd. for $C_8H_{18}O_5S$: S, 14.17. Found: S, 14.04.

Phenyl β-Ethoxyethyl Ether from β-Ethoxyethyl Sulfite.—To the dry sodium phenoxide, prepared in a hydrogen atmosphere from 10 g. of phenol and sodium methoxide, was added 60 cc. of dry toluene and 26.4 g. of β-ethoxyethyl sulfite. During an hour of refluxing the sodium phenoxide dissolved, after which aqueous sodium hydroxide was added and the mixture steam distilled. The toluene layer was separated, dried and distilled. At 225–230°, 8.6 g. (50% yield) of phenyl β-ethoxyethyl ether was collected. The b. p. of the pure ether[11] is 230–232°.

β-Ethoxyethyl Chloride.—Into a mixture of 75.5 g. of β-ethoxyethyl alcohol and 66.4 g. of dry pyridine at 0° was added slowly and with stirring a mixture of 100 g. of thionyl chloride and 80 cc. of chloroform. With gradual warming a vigorous evolution of sulfur dioxide ensued, which process continued for several hours at 100°. The residual product was washed with dilute acid, sodium carbonate solution and water. After drying it over potassium carbonate, the product was distilled (b. p. 105–110°). The yield was 53.0 g., or 58.3%. Its b. p. is listed[3] as 108–109°.

Alkoxyalkyl Bromides

Alkoxyethanols and alkoxypropanols were used as alcohols in these syntheses. The latter, not commercially

available, were prepared by the method of Noyes.[12] From 200 g. of trimethylene glycol, 80.0 g. of ethyl bromide and 18.4 g. of sodium there resulted 49.7 g. (65.4% yield) of γ-ethoxypropyl alcohol, b. p. 158–164°. From 63.0 g. of trimethylene glycol, 41.2 g. of *n*-butyl bromide and 8.5 g. of sodium the yield was 33.0 g. (83.3%) of γ-butoxypropyl alcohol, b. p. 78–85° at 10 mm.

γ-Butoxypropyl Bromide.—In the preparation of this and other alkoxyalkyl bromides the general procedure of Palomaa and Kenetti[13] was modified to include removal of the product from the reaction mixture by distillation at reduced pressure. The data are assembled in Table II. These properties were observed for γ-butoxypropyl bromide: $n^{20}D$ 1.4480, d^{20}_4 1.187, MR. calcd. 43.93, MR. found 43.98.

Anal. Calcd. for $C_7H_{15}OBr$: Br, 40.98. Found: Br (Volhard), 41.08.

Resorcinol Ethers

Equimolar amounts of the alkoxyalkyl bromide, resorcinol, and sodium hydroxide were dissolved in water and acetone and the whole was refluxed for twelve hours. The two solvents were added in such proportions as to equalize the density of the two phases so that intimate mixing was accomplished by boiling. As the reaction progressed, the aqueous layer became the more dense.

At the completion of the refluxing period, acetone was distilled off at reduced pressure. An excess of dilute acid was added, after which the water-insoluble oil was extracted with 50 cc. of carbon tetrachloride. The extract was washed with two 100-cc. portions of water to remove resorcinol and then with an excess of dilute alkali. The alkali-insoluble material contained the diether, which was purified by vacuum distillation.

To the alkali-soluble portion was added an excess of dilute acid. The monoethers which separated were red, viscous oils. These were purified by vacuum distillation. The results are assembled in Tables III and IV.

Nuclear-substituted Resorcinols

ω-Methoxyresacetophenone Oxime.—ω-Methoxyresacetophenone,[14] prepared from methoxyacetonitrile and resorcinol, did not react satisfactorily with phenylhydrazine or 2,4-dinitrophenylhydrazine. The oxime was found to be a more suitable derivative.

Half gram portions each of the ketone and hydroxylamine hydrochloride were warmed with 5 cc. of water and 0.7 g. of sodium acetate. From the resultant clear solution, the oxime separated readily on cooling. After recrystallization from hot water it melted at 158°.

(10) Clemmensen, *Ber.*, **46**, 1837 (1913).
(11) Swallen and Boord, THIS JOURNAL, **52**, 659 (1930).
(12) Noyes, *Am. Chem. J.*, **19**, 766 (1897).
(13) Palomaa and Kenetti, *Ber.*, **64**, 797 (1931).
(14) Slater and Stephen, *J. Chem. Soc.*, **117**, 309 (1920).

TABLE III

RESORCINOL ALKOXYALKYL ETHERS

———Alkoxyalkyl——— Bromide	G.	Resorcinol, g.	NaOH, g.	Water, cc.	Acetone, cc.	Yield of monoether, g.	Yield of diether, g.
β-Ethoxyethyl	30.8	22.0	8.0	175	60	18.1	4.8
β-Butoxyethyl	44.0	26.8	9.7	105	22	24.8	4.6
γ-Ethoxypropyl	51.8	34.1	12.4	180	30	37.6	9.9
γ-Butoxypropyl	37.1	20.9	7.6	90	25	23.0	1.7

TABLE IV

PROPERTIES AND ANALYSES OF THE RESORCINOL ALKOXYALKYL ETHERS

Resorcinol	B. p. °C.	Mm.	$n^{20}D$	d^{20}_4	Formula	Calcd. C	Calcd. H	Calcd. OH	Found C	Found H	Found OH
β-Ethoxyethyl monoether	146–152	3	1.5294	1.118	$C_{10}H_{14}O_3$	65.84	7.75	1.00	65.56	7.94	0.98
β-Ethoxyethyl diether	170–175	4	1.5001	1.052	$C_{14}H_{22}O_4$	66.09	8.72	..	{ 64.60 { 64.64	{ 8.35 { 8.57	..
β-Butoxyethyl monoether	153–160	2	1.5193	1.073	$C_{12}H_{18}O_3$	68.53	8.63	1.00	68.24	8.56	1.04
β-Butoxyethyl diether	181–185	2	1.4930	1.007	$C_{18}H_{30}O_4$	69.62	9.75	..	69.24	9.66	..
γ-Ethoxypropyl monoether[a]	165–170	4	(Solid)	...	$C_{11}H_{16}O_3$	67.30	8.22	..	67.35[b]	8.21[b]	..
γ-Ethoxypropyl diether	171–180	4	1.4979	1.032	$C_{16}H_{26}O_4$	68.04	9.29	..	67.94[b]	9.36[b]	..
γ-Butoxypropyl monoether	170–172	2	1.5143	1.050	$C_{13}H_{20}O_3$	69.59	8.99	1.00	69.29	8.83	1.08
γ-Butoxypropyl diether	181–189	2	1.4865	0.987	$C_{20}H_{34}O_4$	70.95	10.13	..	70.51	9.98	..

[a] The m. p. after crystallization from butyl chloride was 38–39°.   [b] Analyses by Stanley Cristol.

Anal. Calcd. for $C_9H_{11}O_4N$: C, 54.8; H, 5.63. Found: C, 55.2; H, 5.73.

Butoxyacetonitrile.—The method of Gauthier[7a] was modified. In a flask equipped with a stirrer and reflux condenser was placed 74.5 g. (0.830 mole) of anhydrous cuprous cyanide. The flask was heated to 100° and the contents stirred vigorously while 92.5 g. (0.754 mole) of butoxymethyl chloride[15] was added slowly. An exothermic reaction took place continuously. At the end of fifteen minutes of additonal heating the stirrer and reflux condenser were replaced by a Kjeldahl trap and distillation condensation. The product was vacuum distilled from the solid residue and fractionated at atmospheric pressure. There was produced 65.9 g. (77.3%) of butoxyacetonitrile; b. p. 167–171° (738 mm.); $n^{20}D$ 1.4078; d^{20}_4 0.883; MR. calcd.[16] 31.24; MR. found, 31.57.

Anal. (by Mr. S. Cristol). Calcd. for $C_6H_{11}NO$: C, 63.67; H, 9.80. Found: C, 63.66; H, 9.94.

ω-Butoxyresacetophenone.—A solution of 37.7 g. (0.33 mole) of butoxyacetonitrile and 40.3 g. (0.36 mole) of resorcinol in 300 cc. of dry ether was saturated with anhydrous hydrogen chloride at 0°. Then 5.3 g. (0.39 mole) of anhydrous zinc chloride was added and the tightly-stoppered flask allowed to remain near 0° for one week. The salt which had precipitated was then removed and hydrolyzed in water on a steam-bath. A resulting red oil was ether extracted and found to weigh 21.2 g. Calculation of yield on the basis of the crude product shows that the condensation was not more than 28% efficient.

Distillation at 170° (1–2 mm.) was the procedure used in purifying the crude ω-butoxyresacetophenone. Fractions which solidified were recrystallized from a toluene-petroleum ether mixture. The melting point was 64–65°.

ω-Propoxyresacetophenone.—A solution of 18.4 g. (0.167 mole) of resorcinol and 15.1 g. (0.153 mole) of propoxyacetonitrile[17] in 150 cc. of dry ether was saturated with dry hydrogen chloride at 0°. After standing at this temperature for one day there was no precipitate, so 2 g. of anhydrous zinc chloride was added. After eleven days a solid was removed, hydrolyzed in warm water and the insoluble oil separated. After distillation at 150–160° (2 mm.) the material (2 g.) solidified and was recrystallized from hot water; m. p., 106–107°.

Anal. Calcd. for $C_{11}H_{14}O_4$: C, 62.82; H, 6.71. Found: C, 62.80; H, 6.77.

Clemmensen Reduction of ω-Butoxyresacetophenone.—A solution of 1.93 g. of ω-butoxyresacetophenone in 40 cc. of approximately 4 N hydrochloric acid was warmed for four hours on a steam-bath with 7 g. of amalgamated[10] mossy zinc. The test for completion of reduction was the absence of a red color when a sample was treated with ferric chloride solution, the red being characteristic of o-hydroxyaryl ketones. About 1.5 g. of a red oil, isolated by ether extraction, solidified on standing. By extraction with hot carbon tetrachloride yellow crystals were obtained which melted at 92°. Remaining impurities were not removed easily but its identity was established as 4-ethylresorcinol,[18] m. p. 97–98°.

4-Ethyl-1,3-resorcinoldiacetic Acid, $C_2H_5C_6H_3(OCH_2COOH)_2$.—When the above material was treated with chloroacetic acid in alkaline solution the aryloxyacetic acid derivative obtained was identical with that obtained from a known sample of 4-ethylresorcinol. This derivative was recrystallized from hot water several times, m. p. 180–181°.

(15) Farren, Fife, Clark and Garland, THIS JOURNAL, **47**, 2419 (1925); Hill and Keach, *ibid.*, **48**, 257 (1926).

(16) An average value 5.41 for —CN was derived from calculations on accepted constants for acetonitrile and propionitrile.

(17) Karvonen, *Ann. Acad. Sci. Fennicae*, **20**, No. 14 (1923); *C. A.*, **18**, 1980 (1924).

(18) Johnson and Lane, THIS JOURNAL, **43**, 348 (1921).

Neutral Equiv. Calcd. for $C_2H_5C_6H_3(OCH_2COOH)_2$: 127.1. Found: 127.5. *Anal.* Calcd. for $C_{12}H_{14}O_6$: C, 56.67; H, 5.55. Found: C, 56.56; H, 5.51.

Condensation of β-Ethoxypropionitrile with Resorcinol —Under the conditions of the Hoesch reaction 10.0 g. (0.101 mole) of β-ethoxypropionitrile,[19] 12.2 g. (0.111 mole) of resorcinol, 4.8 g. of zinc chloride and an excess of dry hydrogen chloride were allowed to react in 70 cc. of dry ether. At the end of three days a white precipitate of 8 g. was removed. The material dissolved on warming with 30 cc. of water, and on cooling 3.3 g. of a light yellow solid separated. The material could be recrystallized from hot water without improvement of color or melting point. This melting point was near 150° when heated slowly but 164–165° when heated to 160° rapidly. The compound was observed to be an acid and gave an indigo-blue color with ferric chloride solution. A white solid which melted at 134–135° when recrystallized from benzene was obtained from the acid by distillation at reduced pressure or by heating it at 120° for several hours.

This information served to identify the acid as β-(2,4-dihydroxyphenyl)-propionic acid, which had been prepared by Langley and Adams.[9] The properties correlated well. The acid formed a lactone, m. p. 132–134°.

1,4-Dibromo-2-butene, $BrCH_2CH{=}CHCH_2Br$.—1,3-Butadiene was prepared in 77% yield by pyrolysis of cyclohexene[20] as it refluxed around 1.5 meters of glowing platinum wire. Although the addition of bromine to butadiene has been the subject of considerable study, no procedure for the preparation of 1,4-dibromo-2-butene from butadiene could be found. The following directions furnished a satisfactory synthesis.

To a mixture of 52.5 g. of butadiene in 175 cc. of chloroform was added 155 g. of bromine during one-half hour. Mechanical stirring was maintained. A reflux condenser cooled by solid carbon dioxide and acetone prevented loss of butadiene. No tetrabromide separated, but in experiments with slower addition of bromine some was formed. The solvent was removed under diminished pressure and the residue crystallized from petroleum ether. The yield of lachrymatory dibromide, m. p. 50–52°, was 145 g. or 70%.

δ-Methoxycrotyl Bromide.—Into a stirred mixture of 60 g. of 1,4-dibromo-2-butene and 100 cc. of dry ether was added 70 cc. of a solution of sodium methoxide (6.45 g. of sodium) during fifteen minutes. Sodium bromide separated and the ether refluxed. After half an hour, 50 cc. of water was added. The layers were separated and the aqueous layer extracted with ether. The combined ether solutions were dried over magnesium sulfate and distilled. After several fractionations through an efficient column, 15.5 g. of δ-methoxycrotyl bromide was collected at 54.5–56.5° (10 mm.); $n^{20}D$ 1.4882, d^{20}_4 1.370. There was 11.8 g. of higher boiling 1,4-dibromo-2-butene.

Anal. Calcd. for C_5H_9OBr: Br, 48.44. Found: Br, 48.15.

C-Alkylation of Resorcinol by δ-Methoxycrotyl Bromide.—A slush was made by shaking together in a nitrogen atmosphere 100 cc. of dry benzene, some glass beads, and the dry sodium resorcinolate from 9.2 g. of sodium,

40 cc. of methanol, and 22 g. of resorcinol. Into this was stirred rapidly a solution of 24.6 g. of δ-methoxycrotyl bromide in 25 cc. of dry benzene. The reaction was exothermic, but reflux was maintained for eight hours. An excess of dilute acid was added and the insoluble portion was extracted with 30 cc. of ether, washed thrice with 30-cc. portions of water to remove resorcinol, and then concentrated at reduced pressure and 100° to 20.8 g. of a very viscous red oil. This alkali-soluble product was transferred to a Hickman molecular still.[21] The first material to be removed was resorcinol, which sublimed on cooler parts of the apparatus. Then a yellow oil came over, but very slowly, according to the following data. All of the fractions were soluble in sodium hydroxide solution.

Fraction	Time, hrs.	Bath temp., °C.	Pressure, mm. $\times 10^{-3}$	Wt., g.	$n^{20}D$
1	17.5	100	6–8	0.75	1.5575
2	11.5	100–125	3–8	.70	1.5583
3	5.5	123–130	8–10	1.80	1.5602
4	10.5	122–130	8–9	1.80	1.5600
5	12.5	125–140	8–30	1.25	1.5590
6	14	135–140	10–20	0.75	1.5555

The residue in the still was a red glass, of which 4.6 g. was insoluble in ether. The molecular weight of the insoluble portion, taken cryoscopically in camphor, was 722. It softened at 90–100° and was soluble in alkali. There was an equal weight (4.6 g.) of ether-soluble material. It was an alkali-soluble, red oil which was much more viscous than the original material or the distillates. Its mol. wt. (in camphor) was 284. An attempt to form an aryloxyacetic acid from it was unsuccessful.

4-(δ-Methoxycrotyl)-resorcinol.—Fractions 3, 4 and 5 appeared to be uniform. They possessed the same index of refraction and gave a bright green coloration with ferric chloride. Hydrogenation with a palladium catalyst yielded an oil which was probably impure 4-(δ-methoxybutyl)-resorcinol. Two fractions were obtained by distillation of it in the molecular still at 150–190°: (g., $n^{20}D$) 1.0, 1.5427; 1.3, 1.5390. Analysis of the last fraction for methoxybutylresorcinol gave these results: C, 68.5; H, 8.50 (calcd.: C, 67.3; H, 8.22). The small quantity at hand prevented further purification.

Fraction 3 was analyzed for methoxycrotylresorcinol.

Anal. Calcd. for $C_{11}H_{14}O_3$: C, 68.0; H, 7.27; mol. wt., 194. Found: C, 66.9; H, 7.34; mol. wt. (in camphor), 191.

4-δ-Methoxycrotyl-1,3-resorcinoldiacetic Acid.—A 0.35-g. sample of the third fraction of distillate was kept at 100° for an hour with 3 cc. of 50% chloroacetic acid solution and a slight excess of dilute alkali. The sticky solid obtained on acidification was crystallized from hot water. The light, cream-colored crystals melted at 148–150°.

Anal. Calcd. for $CH_3OCH_2CH{=}CHCH_2C_6H_3(OCH_2COOH)_2$: neut. equiv., 155; mol. wt., 310. Found: neut. equiv., 162; mol. wt. (in camphor), 295.

Summary

Eight resorcinol alkoxyalkyl ethers have been prepared and characterized. They are mono-

(19) Henry, *Bull. soc. chim.*, [2] **44**, 458 (1885).

(20) Kistiakowsky, Ruhoff, Smith and Vaughan, THIS JOURNAL, **58**, 146 (1936).

(21) Hurd and Parrish, THIS JOURNAL, **57**, 1732 (1935).

and diethers in which the alkoxyalkyl groups are: β-ethoxyethyl, β-butoxyethyl, γ-ethoxypropyl and γ-butoxypropyl. As germicides, the monoethers are less efficient than the alkyl monoethers of analogous size.

ω-Propoxy- and ω-butoxyresacetophenones have been prepared. The reduction of ω-alkoxyresacetophenone to ethylresorcinol was observed to take place under the conditions of the Clemmensen reduction.

A condensation of β-ethoxypropionitrile with resorcinol has been found to produce β-(2,4-dihydroxyphenyl)-propionic acid. The reaction does not follow the course of a typical Hoesch condensation.

δ-Methoxycrotyl bromide, synthesized from butadiene, was condensed with resorcinol to produce 4-(δ-methoxycrotyl)-resorcinol. These additional new compounds also were prepared: β-ethoxyethyl sulfite, butoxyacetonitrile, γ-butoxypropyl bromide, ω-methoxyresacetophenone oxime, 4-ethyl-1,3-resorcinoldiacetic acid, 4-δ-methoxycrotyl-1,3-resorcinoldiacetic acid. Also, new syntheses of β-ethoxyethyl chloride and phenyl β-ethoxyethyl ether were developed.

Kinetics of the Catalyzed Esterification of Normal Aliphatic Acids in Methyl Alcohol

BY HILTON A. SMITH

During the period from 1895–1928, Goldschmidt[1] published a number of papers on the subject of esterification reactions catalyzed by acids. He demonstrated the fact that, under these conditions, the H^+ ions from the catalyst form complexes with the alcohol molecules, and that esterification proceeds through interaction of the molecules of complex with the molecules of organic acid. Goldschmidt's work may be summarized briefly thus. The reaction representing the acid-catalyzed esterification of an organic acid with an alcohol is

$$RCOOH + R^1OH_2^+ \longrightarrow RCOOR^1 + H_3O^+$$

and the rate of formation of ester is expressed by the equation

$$\frac{d(RCOOR^1)}{dt} = k(RCOOH)(R^1OH_2^+) \qquad (1)$$

In dry alcohol, the concentration of alcohol complex may be considered to be equal to the total H^+ concentration, or when a strong mineral acid is used as a catalyzer, equal to the concentration of such acid. The rate of formation of ester in any particular case is thus proportional to the momentary concentration of the organic acid.

However, as water is formed, it competes with the alcohol for the hydrogen ion, cutting down the concentration of alcohol complexes, and hence slowing up the esterification. An equilibrium

(1) See especially Goldschmidt and Udby, Z. physik. Chem., **60**, 728 (1907); Goldschmidt and Theusen, ibid., **81**, 30 (1912); Goldschmidt and Melbye, ibid., **143**, 139 (1929); Goldschmidt, Haaland and Melbye, ibid., **143**, 278 (1929).

is set up between alcohol and water complexes, thus
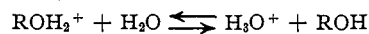
$$ROH_2^+ + H_2O \rightleftharpoons H_3O^+ + ROH$$

and the equilibrium constant, K, for this reaction is given by the equation

$$K = \frac{(H_3O^+)(ROH)}{(ROH_2^+)(H_2O)}$$

Since in an alcohol, (ROH) may be considered constant, a new constant, r, may be defined by the equation

$$r = \frac{(ROH)}{K} = \frac{(ROH_2^+)(H_2O)}{(H_3O^+)} \qquad (2)$$

Essentially all the hydrogen ions present will be tied up as complexes with either water or alcohol molecules so that

$$(H_3O^+) = (\text{total } H^+) - (ROH_2^+) \qquad (3)$$

Combining equations (2) and (3), one obtains for r the expression

$$r = \frac{(ROH_2^+)(H_2O)}{(\text{total } H^+) - (ROH_2^+)}$$

whence

$$(ROH_2^+) = \frac{r(\text{total } H^+)}{r + (H_2O)} \qquad (4)$$

Substituting this value in equation (1), the rate of formation of ester is given by

$$\frac{d(RCOOR^1)}{dt} = \frac{k(RCOOH)\, r(\text{total } H^+)}{r + (H_2O)}, \text{ or}$$

$$\frac{dx}{dt} = \frac{kr\,(\text{catalyst})\,(a - x)}{r + x} \qquad (5)$$

where a is the original concentration of organic acid, x is the concentration of ester formed after time t, and the catalyst is a strong mineral acid.