measure of the rate of carbonium ion formation. On a purely chance basis, therefore, isomerization might be expected to be greater in 19 than in 17. Actually, isomerization in 17 is about twice as great as in 19. Thus, the behavior of the postulated carbonium ion intermediate shows some environment dependence.

The very low degree of cracking occurring in these reaction mixtures attained through extreme purification of the materials used suggests that the cracking activity attributed to aluminum bromide in reactions with hydrocarbons of chain length greater than four[25] may more reasonably be attributed, at least in part, to the presence of trace impurities which operate as catalyst promoters in much the same way as in the isomerization reactions studied by Pines and Wackher.[15]

The purity of the 3-methylhexane requires comment. If natural 2-methyl-1-butanol is assumed to be optically pure, then, from its low rotation,[17] the sample employed here contained 1–2% of isoamyl alcohol. While this would lead to about the same proportion of 2-methylhexane in the final hydrocarbon, such quantity could not be detected by boiling point, refractive index, or density determinations, and probably not by the infrared technique used here. Further impurities entered

(25) Discussion with Dr. D. P. Stevenson.

during the conversion of active amyl alcohol to the bromide since the rotation of the bromide was about 25% low.[17] Presumably racemization and formation of t-amyl bromide and possibly 2-methyl-3-bromobutane were involved as reported by Brokaw and Brode.[26] Hydrocarbons derived from the isomeric bromides must have been largely removed by the preparative and purification procedures, since a maximum of about 2% impurities in the final product was indicated by infrared analysis.

The impurity shown by the ultraviolet absorption spectrum to persist through the purification processes probably was partly responsible for the inability of this worker to produce 3-methylhexane which was stable in the presence of aluminum bromide. However, its effect should have been more or less constant from reaction to reaction in contrast to the erratic behavior observed. As affairs stand, the writer would not care to attempt to evaluate its effect quantitatively.

(26) G. Y. Brokaw and W. R. Brode, J. Org. Chem., 13, 194 (1948).

The Acyloin Condensation of Aralkyl Esters

BY EARLE VAN HEYNINGEN

The acyloin condensation was carried out on several aralkyl esters and the products of the reaction indicate that it proceeds by a free radical mechanism.

It has been proposed by several authors that the acyloin condensation proceeds by a free radical mechanism.[1,2] Kharasch and co-workers, by studying the reaction of esters with sodium in liquid ammonia, have substantiated the initial formation of a sodium ketyl under these conditions and have postulated that the acyloin condensation in an inert solvent goes in a like manner. The work of Lynn and English on the reaction of dialkylamides of aromatic acids with sodium in inert solvent, further corroborates the free radical mechanism.[3] An investigation of the acyloin condensation of aralkyl esters has yielded additional evidence that a sodium ketyl is first formed in this reaction.

The acyloin condensation of 1-phenyl-1-carbethoxycyclopentane yields a solid, bi-(1-phenylcyclopentyl) (V). which is not the expected acyloin.

To account for the formation of this hydrocarbon (V), the following mechanism has been assumed (Fig. 1). Sodium adds to the carbonyl of

(1) F. F. Blicke, THIS JOURNAL, 47, 229 (1925).
(2) M. Kharasch, E. Sternfeld and F. R. Mayo. J. Org. Chem., 5, 362 (1940).
(3) J. Lynn and J. English, ibid., 16, 1546 (1951).

the ester to form the sodium ketyl, which splits to the phenylcyclopentyl free radical (III), and the elements of sodium ethyl formate (IV). The free radical (III) then dimerizes to bi-(1-phenylcyclopentyl) (V).

Should the foregoing explanation be correct, one would also expect as a result of the production of the radicals II and III, the formation of the products of their reduction (VI, XI), disproportionation (VI, VII), and interaction with themselves (IX, X) and each other (VIII). Since the isolation of such compounds would substantiate the postulated mechanism, a thorough investigation of the reaction product was undertaken.

The oily residue from the separation of V was separated into three main fractions by distillation. The lowest boiling fraction proved to be mainly phenylcyclopentane (VI) containing some phenylcyclopentene (VII). The second fraction consisted of the starting ester. The highest boiling fraction yielded the monoketone (VIII) whose structure was established by analysis and by its infrared spectrum, and the colorless acyloin (IX) whose identity was established by analysis and the presence of hydroxyl and carbonyl absorption in its
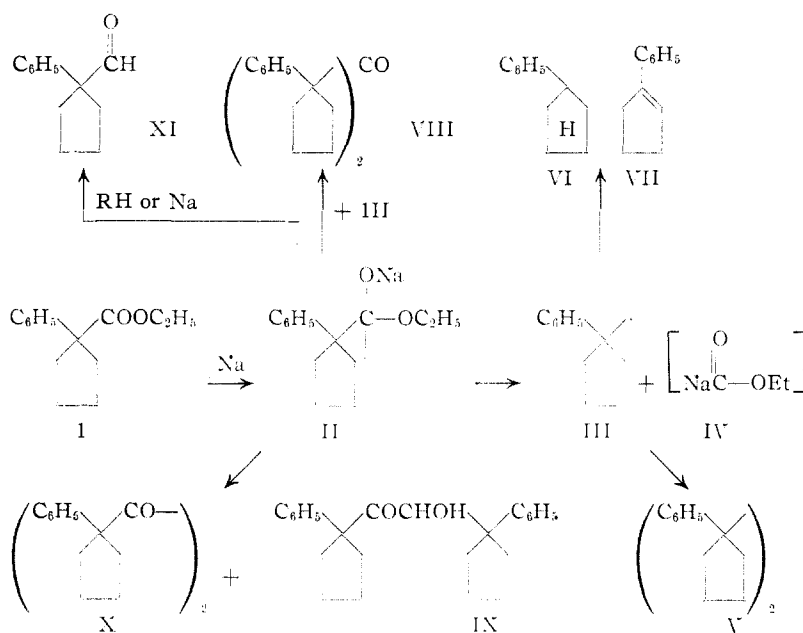
Fig. 1.

infrared spectrum. Although the presence of a diketone (X) was indicated by the yellow color of the solutions, no pure compound could be isolated. No indication of the presence of XI or its reduction products in any of the fractions was obtained.

The general applicability of this reaction to aryldialkyl acetic esters was demonstrated by subjecting ethyl dimethylphenylacetate (XII), ethyl dimethyl-*p*-methoxyphenylacetate (XIII). and ethyl 1-phenylcyclohexanecarboxylate (XIV) to acyloin condensations with similar results to those obtained with ethyl 1-phenylcyclopentanecarboxylate, above. Thus, a liquid hydrocarbon, a dimeric hydrocarbon and an acyloin were isolated in every instance. An impure monoketone was isolated only from the reaction product of XIV: there were no indications of corresponding compounds in the products of XII and XIII. In no case was a pure diketone isolated, although the characteristic yellow color furnished a strong indication for its presence.

Because the products are those which would be expected only from a free radical decomposition, it follows that the acyloin condensation of aralkyl esters in inert solvent proceeds through the initial formation of a sodium ketyl free radical.

Acknowledgments.—The author is indebted to Howard L. Hunter for the microanalyses and to Donald Woolf for the infrared spectra.

Experimental[4]

Preparation of Ethyl 1-Phenylcyclopentanecarboxylate.—1-Phenylcyclopentyl cyanide was prepared by the method of Tilford.[5] The nitrile (54.5 g., 0.288 mole) was dissolved in 50 ml. of methanol containing 50.0 g. (0.89 mole) of potassium hydroxide and 12 ml. of water. The mixture was heated in a sealed bomb at 140° for 57 hours. The bomb was cooled, the contents were removed and dissolved in water. Dilute hydrochloric acid was added to precipitate the acid, which was filtered and dried. The acid, which melted at

(4) All melting points and boiling points are uncorrected.
(5) C. H. Tilford, M. C. Van Campen and R. S. Shelton, THIS JOURNAL, **69**, 2903 (1947).

154–156°, was not purified. It was converted directly to the ester by solution in 150 ml. of absolute ethanol, 75 ml. of toluene and 0.4 ml. of concentrated sulfuric acid and slowly distilling this mixture. The distillation was repeated with added quantities of ethanol–benzene in the ratio of two to one. until the temperature of the distillate reached 80° at the end of a distillation. The product was dissolved in benzene and washed with a sodium bicarbonate solution. There was obtained 1.5 g. of starting acid, m.p. 154–156°. on acidification of the sodium bicarbonate extract.

The benzene was evaporated and the product distilled at 9 mm. The boiling point was 121°, n^{25}D 1.5104. There was obtained 54.0 g. (0.249 mole) of the ester (86.5%).

Anal. Calcd. for $C_{14}H_{18}O_2$: C, 77.04: H, 8.31. Found: C, 77.35; H, 8.68.

Preparation of Ethyl 1-Phenylcyclohexanecarboxylate.—1 - Phenylcyclohexyl cyanide was also prepared by the method of Tilford and converted to the ester in the same manner as was the cyclopentane analog. From 46.4 g. (0.257 mole) of the nitrile, there was formed 20.5 g. (0.0882 mole) of the ester, b.p. 130–133° at 3.2 to 3.9 mm., n^{25}D 1.5145.

Anal. Calcd. for $C_{15}H_{20}O_2$: C, 77.55: H, 8.68. Found: C, 77.75: H. 8.66.

Preparation of *p*-Methoxybenzylcyanide.—Two hundred grams (1.45 moles) of *p*-methoxybenzyl alcohol was dissolved in 1500 ml. of dry benzene and 500 ml. of dry petroleum ether. The solution was cooled in a Dry Ice–acetone-bath while gaseous hydrogen chloride was passed in. The temperature was kept below 0°. When the solution was saturated. the reaction was complete. Excess hydrogen chloride and the petroleum ether were removed at water-pump pressure. The benzene layer was washed with water twice. followed by dilute sodium bicarbonate, water and dried with magnesium sulfate. Removal of the benzene gave the crude *p*-methoxybenzyl chloride. It was mixed with 5 l. of acetone, and 195.3 g. (3.0 moles) of potassium cyanide in 3 l. of water was added, and the solution was allowed to stand for 48 hours. The acetone was removed at atm. pressure. The residue was extracted with ether, the ether solution dried with magnesium sulfate (anhyd.). After removing the ether at reduced pressure, the product was distilled, b.p. 106–108° (8 mm.), n^{25}D 1.4330. The yield was 150.1 g. (1.02 moles, 70.5%).[6]

Preparation of *p*-Anisyldimethylacetonitrile.—Sodamide was prepared from 53.0 g. (2.3 atoms) of sodium in 1.5 l. of liquid ammonia. Benzene (1 l.) was added and the ammonia evaporated. Then 150.1 g. (1.02 moles) of *p*-methoxybenzyl cyanide was added, the ammonia removed by heating, and 330 g. (2.33 moles) of methyl iodide was added dropwise while stirring and heating. The reaction mixture was poured on ice and water. and the benzene layer was separated. The benzene was evaporated in vacuum, and the product was distilled at 8 mm. After a forerun of *p*-isopropylanisole,[7] b.p. 73–76°, n^{25}D 1.5100. weight 75.8 g., the desired nitrile, b.p. 111–113°, n^{25}D 1.5135, weight 44.0 g. was obtained.

Anal. Calcd. for $C_{11}H_{13}NO$: C, 75.40: H, 7.48; N, 7.99. Found: C, 74.90: H, 8.15; N, 8.19.

The large amount of by-product presumably resulted from the fission of the *p*-anisyldimethylacetonitrile by the sodamide at the temperatures employed.

Preparation of Ethyl *p*-Anisyldimethylacetate.—The saponification and esterification procedure used for the phenylcycloalkyl cyanides was employed. There was obtained from 44.0 g. (0.251 mole) of *p*-anisyldimethylacetonitrile 23.4 g. (0.104 mole) of the ethyl ester, b.p. 120° (10 mm.), n^{25}D 1.4976.

(6) S. Cannizarro, *Ann.*, **117**, 246 (1861).
(7) A. Behal and M. Tiffeneau, *Compt. rend.*, **141**, 596 (1907).

Anal. Calcd. for $C_{13}H_{18}O_3$: C, 70.22: H. 8.16   Found: C. 70.43: H, 8.25.

Preparation of Ethyl Phenyldimethylacetate.—Phenyldimethylacetonitrile was prepared. in 65% yield. from benzyl cyanide using the above alkylation procedure for the p-methoxy analog (b.p. 73.5–78° (8 mm.). n^{25}D 1.5027).[8] It was converted to the ethyl ester[9] as were the other nitriles; yield 72%, b.p. 68–71° (0.5 to 0.6 mm.), n^{25}D 1.4893.

The Acyloin Condensation with Ethyl 1-Phenylcyclopentanecarboxylate.—In a 1000-ml., 3-necked flask, equipped to exclude moisture and also air by use of nitrogen, 10.3 g. (0.442 atom) of sodium was finely dispersed under 600 ml. of dry toluene. Then, with rapid stirring and refluxing. 48.0 g. (0.221 mole) of ethyl 1-phenylcyclopentanecarboxylate was added dropwise during 1.75 hours, followed by one-half hour of refluxing. The reaction was cooled and 70 ml. of methanol was added and finally 100 g. of ice. The benzene extract of this mixture was water washed, dried with magnesium sulfate, and then evaporated in vacuum. The residue partially solidified on cooling and the solid, bi-(1-phenylcyclopentyl). was purified by repeated recrystallizations from alcohol–water until it melted at 137–138°. softening at 134°.

Anal. Calcd. for $C_{22}H_{26}$: C, 90.97: H, 9.03.   Found: C. 90.75: H, 9.25.

By reworking the filtrates 4.0 g. (0.147 mole), 13.3%. of this compound was obtained.   It proved to be identical with the product of the Kolbe electrolysis of potassium 1-phenylcyclopentanecarboxylate (see below).

The filtrates from the recrystallizations were concentrated and distilled to give three main fractions. The first two were redistilled. The first yielded 2.4 g. of phenylcyclopentane, b.p. 62° (1.7 mm.), n^{25}D 1.5288,[10] contaminated with a trace of material, probably 1-phenylcyclopentene, as shown by absorption of bromine in carbon tetrachloride.

Anal. Calcd. for $C_{11}H_{14}$: C, 90.35; H, 9.65.   Found: C. 90.20: H, 9.45.

The second fraction was redistilled to give 9.0 g. of starting ester, b.p. 111° (2.5 mm.), n^{25}D 1.5225. Saponification gave 1-phenyl-1-carboxycyclohexane, m.p. 154–157°.

A 4.0 g.-portion of the third fraction (9.5 g.) was separated by chromatography on alumina through successive petroleum ether elutions into the hydrocarbon (V). and the monoketone (VIII), m.p. 93–95°, from dilute acetic acid. then dilute ethanol, IR_{max} 5.94, 9.26 and 9.67 μ.

Anal. Calcd. for $C_{23}H_{26}O$: C, 86.74: H, 8.23.   Found: C, 86.93; H, 8.56.

A final benzene elution yielded the acyloin (IX), m.p. 69–71° from ethanol, IR_{max} 2.76, 5.86 μ (mineral oil mull).

Anal. Calcd. for $C_{24}H_{28}O_2$: C. 82.72: H, 8.10.   Found: C, 83.01: H, 8.11.

An attempt to isolate the yellow diketone from the filtrates of the monoketone purification was made by concentration, removal of acetic acid by washing with bicarbonate, drying, and rechromatographing on alumina. The solids from the initial yellow fraction could not be purified by recrystallization from alcohol–water. An obviously impure sample was analyzed, m.p. 56–66°.

Anal. Calcd. for $C_{24}H_{26}O_2$: C. 83.20: H, 7.56.   Found: C, 84.60: H, 8.43.

Its infrared spectrum showed strong carbonyl absorption at 5.84 μ and weaker absorption at 5.96 μ. The latter may be due to monoketone (5.94 μ) present as an impurity.

The Acyloin Condensation with Ethyl Dimethylphenylacetate.—To 9.2 g. (0.4 atom) of finely dispersed sodium under 250 ml. of dry, refluxing toluene in a 500-ml. flask, 38.2 g. (0.2 mole) of ethyl dimethylphenylacetate was added dropwise over a period of 30 minutes. Refluxing was continued for one hour. After standing overnight, the reaction was decomposed by the slow addition of 30 ml. of methanol followed by 50 ml. of water. The organic layer was separated and washed with water. The combined water layers were extracted once with ether, and the combined ether toluene solution was dried and solvent removed through a Widmer column at atm. pressure. When the still-pot temperature was 150°, the distilland was transferred to a small

distilling flask and distillation was resumed at 3.5 mm. At 32° (3.5 mm.) 2.1 g. of cumene was collected. n^{25}D 1.4859 (Eastman Kodak Co. cumene, n^{25}D 1.4880).

Anal. Calcd. for C_9H_{12}: C. 89.93: H, 10.07.   Found: C. 89.80; H, 10.25.

The still residue (18.5 g.) was twice recrystallized from ethanol to give 2.3-dimethyl-2,3-diphenylbutane, m.p. 114–115°.[11]

Anal. Calcd. for $C_{18}H_{24}$: C, 89.94; H, 10.06.   Found: C, 90.20: H, 9.72.

Reworking the filtrates gave 2.4 g. more of the hydrocarbon. Finally, they were concentrated to dryness with benzene and distilled at 2.6 mm. to give three fractions. One yielded an additional 1.3 g. of the hydrocarbon and the next 2.7 g. of crude acyloin which crystallized on standing. It was recrystallized from alcohol–water, m.p. 55–57°.

Anal. Calcd. for $C_{20}H_{24}O_2$: C, 81.04: H. 8.16.   Found: C. 80.91: H, 8.14.

An attempt to isolate the yellow diketone by chromatographing a portion of the highest boiling fraction was unsuccessful: only the acyloin was isolated, and there were no indications that the monoketone was present.

The Acyloin Condensation with Ethyl Dimethyl-p-anisylacetate.—The ester (23.4 g.. 0.104 mole) was added dropwise to a rapidly stirred suspension of sodium (4.8 g., 0.208 mole) in 500 ml. of toluene at 105–110°. After complete addition, heating was continued for one hour. The cooled reaction mixture was decomposed with 30 ml. of methanol followed by 100 ml. of water. The organic layer was washed with water and concentrated. The yellow semi-solid residue was recrystallized three times from methanol to give 2,3-dimethyl-2,3-di-p-anisylbutane, m.p. 182–184°. Reworking the filtrates gave a total yield of 2.9 g.

Anal. Calcd. for $C_{20}H_{26}O_2$: C, 80.49; H, 8.78.   Found: C, 80.66: H. 9.10.

The filtrates from above were concentrated and then distilled at 1.5–1.6 mm. to give three fractions. The first was p-methoxycumene. 0.3 g., b.p. 59°. n^{25}D 1.5035.

Anal. Calcd. for $C_{10}H_{14}O$: C, 79.95: H, 9.39.   Found: C, 79.86: H. 9.64.

The second (0.5 g.) was mainly the hydrocarbon isolated above. The third (b.p. 120–220°. 8.5 g.) by chromatography on alumina yielded a yellow solid from the initial petroleum ether eluate which could not be purified. Its infrared spectra showed no hydroxyl absorption but did have two bands in the carbonyl region, 5.82 and 5.92 μ, indicating the presence of the diketone. The final benzene eluate gave the colorless acyloin, m.p. 83–85° from ethanol–water.

Anal. Calcd. for $C_{22}H_{28}O_4$: C, 74.13: H, 7.92.   Found: C, 73.80: H, 8.35.

The Acyloin Condensation with Ethyl 1-Phenylcyclohexanecarboxylate.—In a 500-ml. flask 4.06 g. (0.176 atom) of sodium was dispersed under 150 ml. of refluxing dry toluene and an atmosphere of nitrogen, and then, 20.5 g. (0.088 mole) of the ester was added during one-half hour. After 1.5 hours of refluxing, 25 ml. of methanol, followed by 50 ml. of water, was added while cooling. The organic layer was washed with water, dried, and concentrated. The residue was distilled to give 2.6 g. of phenylcyclohexane,[12] b.p. 83–85° (4.5 mm.), n^{25}D 1.5270. Absorption of bromine from carbon tetrachloride indicated that a trace of phenylcyclohexene was present.

Anal. Calcd. for $C_{12}H_{16}$: C, 89.93: H, 10.07.   Found: C, 89.67; H, 9.81.

The residue from the distillation was repeatedly recrystallized from ethanol to give bi-(1-phenylcyclohexyl), m.p. 178–178.5° (needles).

Anal. Calcd. for $C_{24}H_{30}$: C, 90.50: H, 9.50.   Found: C, 90.15; H, 8.89.

Repeated reworking of the filtrates yielded more of the hydrocarbon until, finally, a sample was obtained that melted constantly at 127–129°. It had an infrared spectrum practically identical to di-(1-phenylcyclopentyl) ketone, IR_{max} 5.94, 9.16 and 9.64 μ. but did not analyze for the monoketone. The diketone whose presence was in-

(8) A. Haller and E. Bauer, *ibid.*, **155**, 1582 (1912).

(9) O. Wallach, *Chem. Centr.*, II, 1048 (1899).

(10) E. Bauer, *Compt. rend.*, **156**, 1686 (1913), gives n^{25}D 1.5287 for phenylcyclopentane.

(11) M. Kharasch, E. Jensen and W. Urry, *J. Org. Chem.*, **10**, 401 (1945).

(12) H. Gelissen and P. H. Hermans, *Ber.*, **59**, 664 (1926), give n^{25}D 1.5274 for phenylcyclohexane. m.p. 7°. The above material did not solidify after long chilling in the ice-bath.

dicated by the yellow color of the filtrates likewise could not be isolated pure.

The filtrates were concentrated to dryness and chromatographed on alumina. The benzene eluate yielded the acyloin, m.p. 123–124° from ethanol.

Anal. Calcd. for $C_{26}H_{32}O_2$: C. 82.94: H, 8.57. Found: C, 82.91: H, 8.75.

The Kolbe Electrolysis of Potassium 1-Phenylcyclopentanecarboxylate.—The method of Fichter and Stenzl[13]

(13) F. R. Fichter and H. Stenzl, *Helv. Chim. Acta,* **22,** 970 (1939).

was used. In a 50-ml. beaker 1.5 g. of acid was dissolved in 30 ml. of anhydrous methanol containing 0.3 g. of potassium hydroxide and 10 ml. of dry pyridine. The solution was electrolyzed at 0.3 amp. and 6 volts for four hours. The resulting dark brown solution was evaporated to dryness. dissolved in water and extracted with ether. The ether layer was washed with dilute hydrochloric acid, then water, and finally evaporated to dryness. The residue was recrystallized several times from ethanol–water, m.p. 137–138°. The mixed melting point with V was 136–138°.

INDIANAPOLIS, INDIANA

Cleavage of Sulfonamides with Aqueous Hydrobromic Acid and Phenol. II

BY H. R. SNYDER AND HENRY C. GELLER[1]

The cleavage of sulfonamides by aqueous hydrobromic acid is an oxidation–reduction process in which disulfides are produced. When phenol is present in the reaction mixture disulfides are not formed. β-Naphthalenesulfonanilide reacts with phenol and hydrobromic acid to yield a hydroxyphenyl β-naphthyl sulfide as the principal sulfur-containing product. A mechanism for the process is discussed.

In the previous communication[2] a rapid cleavage of sulfonamides by hydrobromic acid and phenol was described. It was shown that the presence of phenol protected aromatic amines. when these were liberated in the cleavage, from bromination. presumably by reacting with a brominating agent formed in an oxidation–reduction process involving the sulfonyl function and the hydrobromic acid. The fate of the sulfur atom was not determined. In a somewhat similar cleavage of *p*-toluenesulfonamides by anhydrous hydrogen bromide and acetic acid Ohle and his associates[3] found di-*p*-tolyl disulfide as the reduction product. However in their studies bromine acceptors were not added, and the aromatic amines liberated in the cleavage were brominated. The present study was undertaken to determine the fate of the sulfur atom in cleavage by aqueous hydrobromic acid in the presence of phenol.

In the first experiments benzenesulfonanilide and *p*-toluenesulfonanilide were cleaved with 48% aqueous hydrobromic acid alone. Diphenyl disulfide and di-*p*-tolyl disulfide, respectively, were found among the reaction products; pure aniline was not isolated, but instead a mixture of aniline and its bromination products was obtained. There was no indication of the presence of a thiophenol in any of these reaction mixtures. Cleavages of benzenesulfonanilide were carried out in the presence of phenol, added in successive experiments in successively greater concentrations, up to a weight amount equal to that of the sulfonanilide. It was found that the amount of disulfide formed decreased with increasing phenol concentration; no disulfide was detected at the highest concentration of phenol. In these experiments it was noted that the purity of the aniline formed increased with

(1) Minnesota Mining and Manufacturing Co. Fellow, 1950–1951.

(2) H. R. Snyder and R. E. Heckert, THIS JOURNAL, **74,** 2006 (1952). See also D. I. Weisblat. B. J. Magerlein and D. R. Myers, U. S. Patent 2,562,222 (July 31, 1951), and D. I. Weisblat, Abstracts of the Twelfth International Congress of Pure and Applied Chemistry (Sept., 1951), p. 76.

(3) H. Ohle, H. Friedeberg and G. Haeseler, *Ber.,* **69,** 2311 (1936).

the concentration of the phenol. Examination of the alkali-soluble fraction in the reaction mixture in which the largest amount of phenol was employed revealed that *p*-bromophenol was a major product.

None of the above reaction mixtures had the characteristic odor of thiophenols. Nevertheless, chemical tests for thiophenols were conducted. When they proved to be negative a cleavage of methanesulfonanilide in the presence of phenol was carried out. If methyl mercaptan (b.p. 6°) were an intermediate it should have been evolved during the cleavage. No liquid condensed in a Dry Ice trap connected to the apparatus used, and only a very faint odor, which might have been due to traces of this mercaptan, could be detected.

The results of the above experiments indicated that the reduction products containing sulfur were removed from the reaction mixtures along with the phenol. It was observed in the distillation of samples of recovered phenol that high-boiling residues were present; decomposition occurred near the end of such distillations, and the odors of the decomposition products suggested the presence of sulfur-containing compounds. In cleavages of β-naphthalenesulfonanilide with hydrobromic acid the phenolic fraction was found to contain a crystalline material which could be separated easily from phenol and bromophenols. This substance had the composition of a hydroxyphenyl β-naphthyl sulfide; it is probably the *p*-hydroxy compound. The yield of the pure compound was as high as 63%, based on the sulfonanilide cleaved. Thus it appears that in the cleavage in the presence of phenol the major. and perhaps the only, sulfur-containing reduction product is a sulfide containing one group derived from the sulfonamide and one derived from phenol.

Ohle[3] proposed that the first step in the hydrogen bromide–acetic acid cleavage is the formation of the amine hydrobromide and the sulfonyl bromide, and that the sulfonyl bromide is reduced to the disulfide by further action of hydrogen bromide. This view is supported by the fact that sulfonyl