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The Jacobsen Reaction. IV[1]

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In a previous paper[2] it has been shown that the monobromo derivatives of durene, isodurene, and prehnitene undergo the Jacobsen rearrangement. The principal reaction involved the conversion of each of the monobromo compounds into the corresponding dibromo compound and prehnitene sulfonic acid. In each case the migration of a *bromine atom* from one molecule to another constituted the initial phase of the rearrangement.

In the present study, the work reported in the previous paper[2] has been extended by an investigation of the action of sulfuric acid upon several other derivatives of polymethylbenzenes.

Monochlorotetramethylbenzenes. — Chlorodurene (I), chloroisodurene (II) and chloroprehnitene (III) rearranged in contact with sulfuric acid to give the same products, chloropentamethylbenzene (IV) and 3-chloropseudocumene-5-sulfonic acid (V).[3] In each case a *methyl group* migrated in such a manner that the same chlorotrimethylbenzene derivative resulted. The rearrangement of chloroisodurene gave, in addition to the two chief products, a very small amount of a white crystalline substance (m. p. 209.5°) which had the composition $C_{20}H_{24}Cl_2$. Because of lack of material the structure could not be settled definitely. This was the only crystalline by-product obtained from the rearrangement of any of the chlorotetramethylbenzenes.

Monochlorotrimethylbenzenes.—5-Chloropseudocumene (VI), and 6-chloropseudocumene (VII) in contact with sulfuric acid rearranged into 3-chloropseudocumene-5-sulfonic acid (V). In the case of these two compounds, the *chlorine atom* migrated in such a way that the same chlorotrimethylbenzene resulted.[4] Chloromesitylene and 4-chlorohemimellithene were both stable toward sulfuric acid and did not rearrange into other products.

Monobromotrimethylbenzenes.—The action of sulfuric acid upon bromomesitylene (XI) gave mesitylenesulfonic acid (XIII) and di- or tribromomesitylene (XII, XIV) depending upon the temperature. The formation of dibromomesitylene had been observed previously by Töhl and Eckel.[5] 5-Bromopseudocumene (VIII) also rearranged, giving largely 3-bromopseudocumene-5-sulfonic acid (IX), together with a small amount of tribromopseudocumene (X). No pseudocumene-5-sulfonic acid was found, although Jacobsen[6] reported it as one of the products when

(1) Abstracted from a thesis by Clarence L. Moyle, presented to the Graduate Faculty of the University of Minnesota, in partial fulfilment of the requirements for the Ph.D. degree, June, 1935. Presented at the 90th meeting of the American Chemical Society, San Francisco, Calif., August, 1935. Paper XV on the Polymethylbenzenes; XIV, THIS JOURNAL, **57**, 2460 (1935).

(2) Smith and Moyle, THIS JOURNAL, **55**, 2460 (1933).

(3) Töhl [*Ber.*, **25**, 1527 (1892)] had reported previously that chlorodurene in contact with sulfuric acid rearranged to give mainly chloropentamethylbenzene and 3-chloropseudocumene-5-sulfonic acid.

(4) Töhl and Müller [*Ber.*, **26**, 1108 (1893)] had observed that solid 5-chloropseudocumene, in contact with fuming sulfuric acid for one week, was converted into a sulfonic acid which after removal of the sulfonic acid group gave a liquid chlorotrimethylbenzene, but they did not determine the structure of the product.

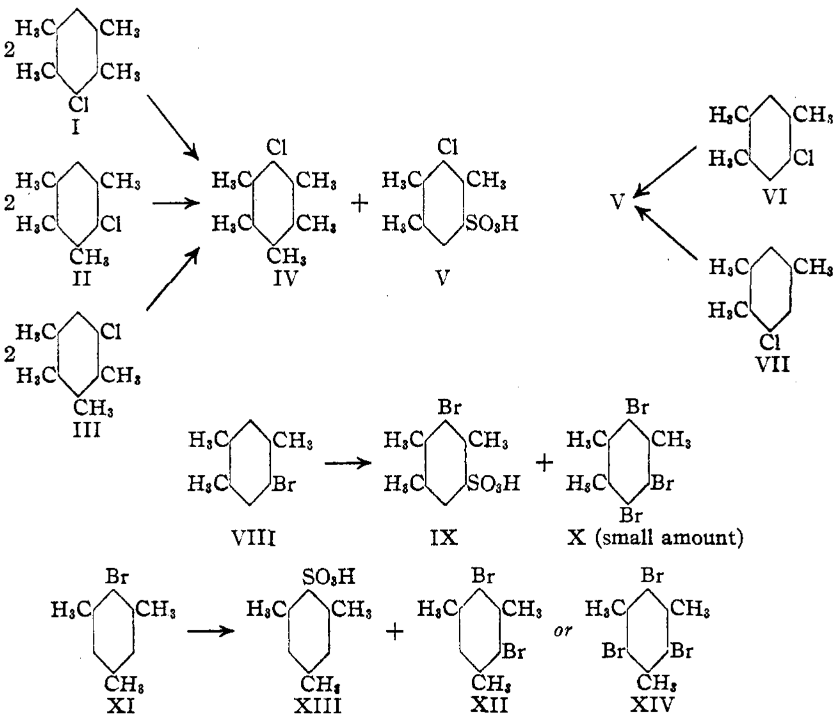
(5) Töhl and Eckel, *ibid.*, **26**, 1099 (1893); see also Rose, *Ann.*, **164**, 63 (1872); *Ber.*, **26**, 1102 (1893).

(6) Jacobsen, *ibid.*, **22**, 1580 (1889).

a large amount (420 g.) of 5-bromopseudocumene was subjected to the action of sulfuric acid.

Stable Compounds.—In order to determine the effect of various substituents upon the ease, course, and limits of the rearrangement, the action of sulfuric acid upon a number of compounds related to the polymethylbenzenes was studied. The compounds investigated were hemimellithene, 5-nitropseudocumene, pseudocumidine-5, pentamethylbenzene-methylsulfonate, pentamethylcyclohexane, 2,3-dimethylnaphthalene, and *p*-bromodiphenyl. None of these compounds showed any rearrangement whatever in the presence of sulfuric acid.

CHART I
REARRANGEMENTS STUDIED



Discussion of the Results.—The results of this work upon the chloropolymethylbenzenes, together with the results of the previous work[2] upon the bromotetramethylbenzenes, show that all the monochloro- and monobromotetramethyl benzenes rearrange in contact with sulfuric acid, and that the ease of migration in the case of these derivatives is in the order Br > CH_3 > Cl. In the case of the bromotetramethylbenzenes, a bromine atom was transferred from one molecule to another, producing the dibromo derivative and a tetramethylbenzene sulfonic acid corresponding to the original hydrocarbon. The sulfonic acids of durene and isodurene then rearranged into prehnitene sulfonic acid by a shift of a methyl group within the molecule. It is certain that the transformations of the chlorotetramethylbenzenes also involve at least two rearrangements. Thus it is possible to remove a methyl group from chlorodurene (I) or chloroisodurene (II) and obtain 3-chloropseudocumene directly, although in the first case the migrating methyl group is meta, and in the second case it is para to the chlorine atom. But in the case of chloroprehnitene (III) it is not possible to obtain 3-chloropseudocumene directly by removal of any one of the methyl groups. Moreover, the removal of the methyl group in position 1 cannot be the first stage in the rearrangement, for removal of this methyl group would lead to 4-chlorohemimellithene, which is stable in the presence of sulfuric acid. Removal of a methyl group in position 2 or 3 would lead to 6-chloro- or 5-chloropseudocumene, respectively, both of which would then rearrange into 3-chloropseudocumene by migration of the chlorine atom. Removal of the methyl group in position 4 would lead to 5-chlorohemimellithene but, unfortunately, the behavior of this compound toward sulfuric acid could not be investigated as the substance was not available.

In the case of the monohalogen derivatives of the trimethylbenzenes, chloromesitylene and 4-chlorohemimellithene did not rearrange at all, while 5-chloro- and 6-chloropseudocumene rearranged into 3-chloropseudocumene. Here the chlorine atom migrated, but the shift was entirely intramolecular, no polychloro derivatives resulting. On the other hand, both bromomesitylene and 5 bromopseudocumene rearranged, and the halogen atom was again the mobile group. The rearrangement of 5-bromopseudocumene closely paralleled that of 5-chloropseudocumene in that the chief product was 3-bromopseudocumene, but there was formed also a small amount of tribromopseudocumene resulting from the transfer of bromine atoms from one molecule to another. The rearrangement of bromomesitylene was entirely of the latter type and the only products were mesitylene sulfonic acid and polybromomesitylenes. Thus it appears that the halogen always migrates in the monohalotrimethylbenzenes if any rearrangement occurs at all, and the available evidence indicates that the ease of migration in the case of these derivatives is in the order of $Br > Cl > CH_3$.

The investigation of the behavior of hemimellithene toward sulfuric acid completes the series of the trimethylbenzenes. All of these substances are stable toward sulfuric acid, and no rearrangements are shown.[7]

The negative results obtained in this work from a variety of compounds indicate that the Jacobsen rearrangement is not a very general or extensive reaction. With few exceptions[8] it is limited to halogen derivatives of benzene itself, the halogenated methylbenzenes, tetramethylbenzenes, pentamethylbenzene and pentaethylbenzene, and the substituents which have been found to be labile in the presence of sulfuric acid are I, Br, Cl, CH_3, C_2H_5, and SO_3H. No Jacobsen reactions are known in which a nitro-, acetyl-, methoxyl-, or carboxyl- group is present in the molecule. In general, except when halogen alone is present, at least four substituents must be attached to the benzene ring in order to obtain the rearrangement, but the nature as well as the number of all the substituents present in the ring determines the course of the rearrangement and the ease with which it takes place. Slight changes may make great differences. Thus pentamethylbenzene sulfonic acid rearranges rapidly and fairly smoothly, while the methyl ester of the sulfonic acid is completely inert toward sulfuric acid.

With regard to the mechanism of the reaction, little can be said. The mechanisms proposed by Jacobsen[9] and recently by Schroeter and Götzky[10] are entirely hypothetical and are, in fact, simply restatements in different terms of the course of known rearrangements. Nothing can be predicted by means of either of these mechanisms. It has not been possible, so far, to isolate any intermediate products, nor is it known whether or not all Jacobsen reactions occur through the same mechanism. There is apparently some correlation between the ability of a sulfonated compound to undergo the Jacobsen rearrangement and the ease with which the sulfonic acid can be hydrolyzed. Thus the sulfonic acids of durene, isodurene and pentamethylbenzene, which rearrange, can be hydrolyzed by boiling hydrochloric acid under atmospheric pressure, while the sulfonic acids of prehnitene, chloromesitylene and 3-chloropseudocumene, which do not rearrange, require higher temperatures for hydrolysis and are stable toward boiling hydrochloric acid in open vessels. This is the only relationship so far discovered which connects the ease of rearrangement with any other property, but it remains a problem for future investigation to determine just how far this parallel holds good, and what bearing, if any, it has upon the mechanism of the reaction. Whenever the Jacobsen rearrangement occurs, it is always accompanied by a side reaction which leads to a tarry, amorphous solid and sulfur dioxide. In the case of halogenated compounds, some hydrogen halide is also evolved. Many experiments were tried, chiefly upon pentamethylbenzene sulfonic acid, in the hope of finding reagents or reaction conditions which would avoid the formation of the amorphous material, but all the experiments failed. Dilution of the sulfuric acid with 10% of water, or with phosphoric acid or glacial acetic acid inhibited the rearrangement and the side reaction as well. Various other reagents were tried in place of sulfuric acid. These included calcium chloride, magnesium perchlorate, benzene sulfonic acid, acetic acid and phosphoric acid. Most of these reagents merely hydrolyzed the sulfonic acid to the hydrocarbon, or else had no action at all, and no reagents or conditions were found, other than those already known, which would cause any rearrangements to take place.

Experimental Part

A. The Jacobsen Reactions.—The results are given in Table I. The chief variations were: (a) the sulfuric acid used, which was concentrated or fuming acid of such a strength that sulfonation occurred rather rapidly (one hour or less); (b) the temperature; (c) the time. The reactions were carried out in an Erlenmeyer flask closed with a rubber stopper carrying a stopcock. The reaction mixture was shaken vigorously until sulfonation occurred, then set aside with occasional shaking until the reaction was complete. Depending upon the solubilities of the reaction products, one of three procedures was used for

(7) Smith and Cass, THIS JOURNAL, **54**, 1614 (1932).

(8) Schroeter and Götzky, *Ber.*, **60**, 2035 (1927); Moody, *Chem. News.*, **58**, 21 (1888); *ibid.*, **67**, 34 (1893); Armstrong and Wynne, *ibid.*, **76**, 69 (1897); Friedländer, *Fortschr. der Teerfarbenfabrikation*, **11**, 554–557 (German Patents 253,683, 263,395, 265,727, 266,563).

(9) Jacobsen, *Ber.*, **19**, 1215 (1886).

(10) Schroeter and Götzky, *ibid.*, **60**, 2035 (1927).

TABLE I

PRODUCTS OF THE JACOBSEN REACTIONS

Substance	Amt., g.	Sulfuric acid used	Time	T, °C.	Procedure	Products
Chlorodurene (I)	24	87 cc. concd.	4 hrs.	65	1	A, 12.8 g. (99.2%) of IV; B, 14.8 g. (81%) of Na salt of V; C, trace of oil
Chloroisodurene (II)	25	87 cc. concd.	4 hrs.	65	1	A, 13.1 g. (96.4%) of IV + 0.5 g. $C_{20}H_{24}Cl_2$; B, 13.3 g. (70%) of Na salt of V; C-
Chloroprehnitene (III)	13.5	45 cc. 20% fum. + 30 cc. concd.	5 hrs.	25–30	3	D, 7.2 g. (97.8%) of IV; F, 3.4 g. (55%) of 3 chloropseudocumene, 0.8 g. prehnitene; 1.3 g. tarry residue
Chloroprehnitene (III)	15	45 cc. 20% fum. + 30 cc. concd.	5 hrs.	25–30	2 & 3	D, 8 g. (98%) of IV; E, (from 10 cc. of filtrate) 1.7 g. of Na salt of V; F (from the rest of the filtrate) 4.1 g. 3 chloropseudocumene; 1.5 g. tarry residue
5-Chloropseudocumene (VI)	30	100 cc. 20% fum.	4 hrs.	65–70	2	D, 4.5 g. tar; E, 35.4 g. (71%) of Na salt of V
6-Chloropseudocumene (VII)	4	20 cc. 20% fum. + 15 cc. concd.	3 days	25–30	2 (poured onto 20 g. ice + 20 g. concd. HCl)	D, 0.4 g. white needles, m. p. 148–153°, not identified; E (from filtrate and washings of D) 2.9 g. (44%) of Na salt of V
Chloromesitylene	11	90 g. 20% fum.	6 wks.	60 (sulfonation) 25–30 (standing)	3	D, 0.1 g. dichloromesitylene, m. p. 58–59°; F, 8.4 g. (76.3%) of chloromesitylene
Chloromesitylene	10	90 g. 20% fum.	6 hrs.	70	3	D, 0.3 g. tar; F, 7.7 g. (77%) of chloromesitylene
4-Chlorohemimellithene	2	10 g. 20% fum.	15 hrs.	75	2	D, nothing; E, 1.5 g. (46%) of 4-chlorohemimellithene-5-Na sulfonate
5-Bromopseudocumene (VIII)	19.9	120 g. 20% fum.	6 wks.	70 (sulfonation) 25–30 (standing)	2	D, 1.5 g. tribromopseudocumene (X) m. p. 232°; E (from filtrate and washings of D) 27.1 g. (90%) of Na salt of IX
Bromomesitylene (XI)	16	100 g. 20% fum.	30 days	25–30	3	D, 8.4 g. dibromomesitylene (XII) m. p. 65.5°; F, 3.8 g. of mesitylene + 1.3 g. unchanged bromomesitylene
Bromomesitylene (XI)	10	50 g. 20% fum.	6 hrs.	70	3	D, 4.1 g. (68.5%) tribromomesitylene (XIV) m. p. 224°; F, 1 g. of mesitylene
Hemimellithene-4-sulfonic acid	2	20 g. concd.	20 hrs.	80	Reaction mixture cooled and nitrated directly by adding HNO_3 (d. 1.5). Product, 1.2 g. of trinitrohemimellithene, m. p. 207–208°	
Pentamethylbenzenemethylsulfonate	3	10 cc. concd.	28 hrs.	25–30	2	D, 1.5 g. brown solid, impure ester; E, nothing
Pentamethylcyclohexane	5	40 g. 20% fum.	8 hrs.	75	2	D, 0.9 g. tar + 3.1 g. oil, unchanged material
5-Aminopseudocumene	2	15 g. concd.	100 hrs.	60	Poured into excess alkali, steam distilled. Product, 1.1 g. unchanged amine	
5-Nitropseudocumene	4	15 cc. 20% fum.	45 hrs.	70	2	D, 2.8 g. unchanged material; E, nothing
2,3-Dimethylnaphthalene	10	80 g. 20% fum.	3 wks.	60	Poured into cold 20% HCl; ppt., 10.3 g. sulfonic acid. Hydrolyzed with 50% H_2SO_4 at 225° this gave 2,3-dimethylnaphthalene	
p-Bromodiphenyl	5	60 g. 50% fum.	2 months	60	Poured onto 1:1 HCl-ice (80 g.). Ppt., 3.6 g. sulfonic acid. Hydrolyzed with 50% H_2SO_4 at 260° this gave *p*-bromodiphenyl	

separating the reaction mixture into its components. These are designated in Table I as procedures 1, 2 and 3, and the letters A to F indicate the components isolated by these procedures.

In procedure 1, any solid was removed by filtration of the reaction mixture through a sintered glass crucible. The solid was washed thoroughly with water, and dried at 110° (A). The sulfuric acid filtrate was poured onto about 80% of its weight of ice, which precipitated the crude sulfonic acid. The mixture was filtered (filtrate C). The sulfonic acid was dissolved in water (75–100 cc.), the solution was filtered, and excess 20% sodium hydroxide was added to the ice-cold filtrate to precipitate the sodium sulfonate. The salt was filtered and the filtrate evaporated to one-third of its volume to obtain a second crop. The combined solid was dried at 110° (Solid B). The filtrate C was heated to 190° while steam was passed through it, in order to hydrolyze any sulfonic acids remaining in the solution. Usually only a negligible amount of oil was found in the distillate.

In procedure 2, the whole reaction mixture was poured onto ice (about 300 g.) and filtered. The precipitate (D) was washed with water and dried at 110°. The sulfonic acid (E) was obtained from the filtrate by the same method as that used for isolation of (B).

Procedure 3 was the same as 2 except for the method of handling the filtrate. The sulfonic acid was hydrolyzed by passing steam through the filtrate at about 150°. The organic material (F) in the distillate was then fractionated.

B. Identification of the Products of the Jacobsen Reactions

Chloropentamethylbenzene (IV).—The crude substance, treated with chloroform, and the solution subsequently mixed with alcohol, yielded IV, m. p. and mixed m. p. 154.5–155°. The product from the rearrangement of chloroisodurene contained a small amount of a substance which formed white plates, m. p. 209.5°.

Anal. Calcd. for $C_{20}H_{24}Cl_2$: C, 71.6; H, 7.22; mol. wt., 334. Found: C, 71.5; H, 7.21; mol. wt. (Rast), 338.

This composition corresponds to a dichloro derivative of octamethyldiphenyl, heptamethyldiphenylmethane, or hexamethyldiphenylethane, but sufficient material was not available to establish the structure.

Since mixed melting points of halogen derivatives of polymethylbenzenes are known to be unreliable as tests of identity in certain cases[2] (p. 1680), one specimen of chloropentamethylbenzene was analyzed, and all specimens obtained from the Jacobsen reactions were identified by the quantitative conversion to pentamethylbenzene by removal of the chlorine.

Anal. Calcd. for $C_{11}H_{15}Cl$: C, 72.3; H, 8.28; Cl, 19.4. Found: C, 72.1; H, 8.31; Cl, 19.1.

One gram of the substance was heated at 220° for ten hours with red phosphorus (0.5 g.) and hydriodic acid (5 cc., concd., 45%). Pentamethylbenzene (0.8 g., 98.7%) was obtained; one crystallization from alcohol gave a pure product, m. p. and mixed m. p. 51–52°.

3-Chloropseudocumene-5-sulfonic Acid (V).—3-Chloropseudocumene (30 g.) (impure; see page 8) was sulfonated by shaking it for ten minutes with a mixture of concd. sulfuric acid (60 g.) and 60% fuming sulfuric acid (30 g.). The bright red solution was poured onto ice (150 g.), precipitating sulfonic acid as a gel. The sodium salt was obtained by the addition of excess 20% sodium hydroxide to the water solution of the acid. It crystallized in small white plates; the yield was 40 g. (80%). It was not analyzed. A portion of the sodium salt was converted into the sulfonamide, m. p. 182°.[11] A portion of each specimen of V obtained from the Jacobsen reactions was converted into the amide; all samples of the amide had the same melting point and mixed melting point of 182°. The analysis of the substance showed it to be the amide of a chlorotrimethylbenzene sulfonic acid.

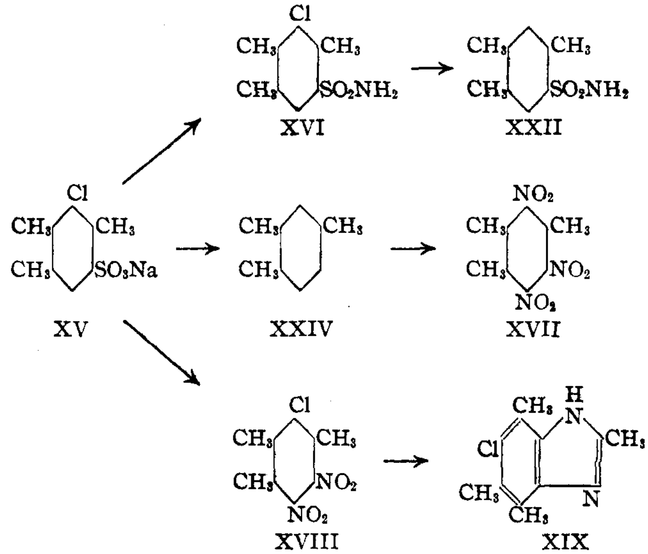
Anal. Calcd. for $C_9H_{12}O_2NClS$: C, 46.3; H, 5.18; Cl, 15.2. Found: C, 46.2; H, 5.09; Cl, 15.0.

It was necessary to prove rigorously the structure of the sulfonic acid corresponding to this amide in order to exclude the possibility of a Jacobsen rearrangement during the sulfonation of 3-chloropseudocumene. The structure proof, by means of which all the groups attached to the ring were definitely located, is outlined in chart II.

(11) Rosengren, *Acta Univ. Lund.*, **30**, II, No. V, p. 9–11; from Beilstein's "Handbuch," Vol. XI, p. 133.

CHART II

PROOF OF THE STRUCTURE OF 3-CHLOROPSEUDOCUMENE-5-SULFONIC ACID



The sulfonamide XVI was refluxed with zinc and dilute acetic acid for twenty-four hours. The product was pseudocumene-5-sulfonamide (XXII), m. p. and mixed m. p. 180°.

The sodium salt XV (1.5 g.) was reduced in aqueous solution by 3% sodium amalgam. The product, which was white and free from chlorine, was pseudocumene-5-sodium sulfonate (XXIII). Nitration of this material gave trinitropseudocumene (XVII), m. p. and mixed m. p. 183.5°.

The sodium salt XV (1 g.) was heated in a sealed tube for fifteen hours with red phosphorus (0.5 g.) and hydriodic acid (6 cc., concd., 45%). The product was a liquid (XXIV), which when nitrated (as above) gave trinitropseudocumene (XVII).

These transformations of XV and XVI located the methyl groups in positions 1, 2 and 4, and the sulfonic acid group in position 5. The chlorine atom was located in position 3 by converting XV to a chlorodinitropseudocumene and proving that the two nitro groups were ortho to each other, that is, in the 5,6-positions, the only vacant adjacent positions in pseudocumene.

The sodium salt XV (4 g.) was hydrolyzed with dilute sulfuric acid at 135–155°. The product was a liquid chloropseudocumene (1.9 g., 79% yield) which boiled at 127° under 61 mm. Nitration of this oil gave 3-chloro-5,6-dinitropseudocumene (XVIII), m. p. 173.5–174°. Direct nitration of XV at 0° also gave XVIII.

3-Chloro-5,6-diaminopseudocumene (XX).—The chloro dinitro compound XVIII (5 g.) was dissolved in hot ethyl alcohol (50 cc.), and a hot solution of stannous chloride (20 g.), in concd. hydrochloric acid (50 cc.) was added. The product, isolated in the usual way, melted at 136.5°.

When very pure, the amine was stable in air for some time, but impure specimens deteriorated rapidly.

12 - Chloro - 10,11,13 - trimethylphenanthrophenazine (XXI).—A hot dilute solution of phenanthraquinone (0.37 g.) in acetic acid (15 cc.) was added to a warm solution of the diamine (0.285 g.) in alcohol (10 cc.). The phenazine precipitated quantitatively. It was crystallized from nitrobenzene, washed with alcohol and ether and dried at 115°. It formed yellow, lustrous plates, m. p. 330.5–331°.

Anal. Calcd. for $C_{23}H_{17}N_2Cl$: C, 77.4; H, 4.81; Cl, 9.96. Found: C, 77.2; H, 4.75; Cl, 9.78.

The melting point of 330–331° was obtained only after repeated recrystallization. Most specimens melted between 310 and 320° after one or two crystallizations.

6-Chloro-2,4,5,7-tetramethylbenzimidazole (XIX).—The nitro compound XVIII (3 g.) was dissolved in hot acetic acid (35 cc.) and a hot solution of stannous chloride (15 g.) in hydrochloric acid (30 cc.) was added. The reaction mixture was refluxed for two hours then cooled and poured into sufficient excess 20% alkali to keep the tin in solution. The white solid was removed and crystallized from dilute alcohol. It melted at 250–251°.

Anal. Calcd. for $C_{11}H_{13}N_2Cl$: C, 63.3; H, 6.28; Cl, 17.0. Found: C, 63.11; H, 6.47; Cl, 17.0.

Chloromesitylene was identified by the formation of chlorodinitromesitylene, m. p. and mixed m. p. 178–179°.[12] Reduction of chlorodinitromesitylene with stannous chloride gave *5-chloro-1,3-diaminomesitylene*, m. p. 137–138°, which gave no phenanthrophenazine when treated with phenanthraquinone, nor any benzimidazole when treated with acetic acid.

Anal. Calcd. for $C_9H_{13}N_2Cl$: Cl, 19.25. Found: Cl, 18.9.

The chloromesitylene yielded mesitylene when reduced by red phosphorus and hydriodic acid. The hydrocarbon was nitrated, giving *trinitromesitylene*, m. p. and mixed m. p. 233–233.5°.

4-Chlorohemimellithene-sodium sulfonate was identified by the formation of **4-chloro-5,6-dinitrohemimellithene**, m. p. 182–182.5°, on nitration. The chlorodinitro compound when reduced by stannous chloride in acetic acid, gave **7-chloro-2,4,5,6-tetramethylbenzimidazole**, m. p. 286.5–287.5°.

Anal. Calcd. for $C_{11}H_{13}N_2Cl$: C, 63.3; H, 6.28. Found: C, 63.0; H, 6.04.

Reduction of 4-chlorohemimellithene-sodium sulfonate by red phosphorus and hydriodic acid gave hemimellithene, identified by conversion to trinitrohemimellithene, m. p. and mixed m. p. 209°.

Tribromopseudocumene (X) was identified by its m. p. 232°, and by analysis.

Anal. Calcd. for $C_9H_9Br_3$: C, 30.3; H, 2.54. Found: C, 30.0; H, 2.52.

3-Bromopseudocumene-5-sodium Sulfonate (IXA).—Dry, powdered pseudocumene-5-sodium sulfonate (25 g.) was suspended in absolute ethyl alcohol (200 cc.). A solution of bromine (25 g.) in chloroform (100 cc.) was added slowly (one hour) with stirring. Stirring was continued for two hours longer, and then the reaction mixture was left overnight. Water (75 cc.) was added, and the solvents were boiled off until the residual volume was 150 cc. The cooled solution deposited 19.1 g. (57.6%) of white needles, which were recrystallized from water.

As in the case of the corresponding chloro compound, it was necessary to prove rigorously the structure of this sodium salt of IX. The proof follows.

Hydrolysis of IXA (5 g.) by dilute sulfuric acid at 145° gave **3-bromopseudocumene** (XXVII) (2.5 g.), identified as tribromopseudocumene (XXVIII), m. p. 231.5°. The action of phosphorus and hydriodic acid upon the sodium sulfonate (IXA) or upon 3-bromopseudocumene (XXVII) obtained from IXA gave **pseudocumene** (XXIV) which was identified as **trinitropseudocumene** (XXIX), m. p. and mixed m. p. 184–185°.

The amide (XXV) was prepared, m. p. 188.5°.[13]

3-Bromo-5,6-dinitropseudocumene (XXVI) was obtained by nitration of the sodium salt (IXA) at 0°. The substance crystallized in white needles, m. p. 181–181.5°.[13,14]

5,6-Diaminopseudocumene (XXX).—The bromodinitro compound (XXVI) (2.6 g.) was dissolved in alcohol and refluxed for thirty minutes with stannous chloride and hydrochloric acid. The amine formed white plates of m. p. 90–91°.[15] The bromine was removed completely by the reduction of the nitro compound.

10,11,13-Trimethylphenanthrophenazine (XXXII) prepared by the method used in the case of XXI, crystallized from chloroform–alcohol in yellow plates of m. p. 253°.

Anal. Calcd. for $C_{23}H_{18}N_2$: C, 85.70; H, 5.63. Found: C, 85.24; H, 5.61.

2,4,5,7-Tetramethylbenzimidazole (XXXI).—Preparation of this substance by the method used for XIX removed the bromine completely. The product melted at 233°.[16]

Dibromomesitylene (XII) was purified by steam distillation followed by recrystallization from alcohol. It was identified by the m. p. (65.5°) and the analysis.

Anal. Calcd. for $C_9H_{10}Br_2$: Br, 57.6. Found: Br, 57.2.

The action of phosphorus and hydriodic acid upon XII gave mesitylene, which was identified as trinitromesitylene, m. p. and mixed m. p. 233.5–234°.

Tribromomesitylene (XIV) was purified in the same manner as XII. It was identified by the m. p. (223.5–224°) and the analysis.

Anal. Calcd. for $C_9H_9Br_3$: Br, 67.3. Found: Br, 67.05.

Mesitylene sulfonic acid (XIII) was not isolated as such. The solution of it was hydrolyzed and steam distilled at 145° and the oil in the distillate was identified as mesitylene by conversion to trinitromesitylene, m. p. and mixed m. p. 232–233°.

Bromomesitylene (XI).—Unchanged XI from the Jacobsen reactions was identified by conversion to bromodinitromesitylene (m. p. 192.5–193.5°) and to tribromomesitylene, m. p. 224°.

(12) Fittig and Hoogewerff, *Ann.*, **150**, 325 (1869).

(13) W. Kelbe and K. Pathe, *Ber.*, **19**, 1551 (1886); Jacobsen, *ibid.*, **22**, 1585 (1889).

(14) Huender, *Rec. Trav. Chim.*, **34**, 22 (1915).

(15) Edler, *Ber.*, **18**, 630 (1885); Noelting and Baumann, *ibid.*, **18**, 1148 (1885).

(16) Bogert and Bender, THIS JOURNAL, **36**, 571 (1914).

TABLE II

JACOBSEN REACTIONS OF PENTAMETHYLBENZENE SULFONIC ACID. VARIATIONS IN REAGENTS AND REACTION CONDITIONS

Pentamethylbenzenesulfonic acid, g.	Reagent	T, °C.	Time	SO_2	Products. (A, recovered pentamethylbenzene sulfonic acid; B, pentamethylbenzene obtained by hydrolyzing the reaction mixture; C, hexamethylbenzene; D, prehnitene sulfonic acid; E, tarry, amorphous by-product.
5	Concd. H_2SO_4, 30 g.	26	48 hrs.	+	D, 1.2 g. (52%);[c] C, 1.5 g. (84.3%); E, 0.8 g.
5	Concd. H_2SO_4, 30 g.; $HgSO_4$, 0.1 g.	26	48 hrs.	+	D, 0.6 g.; C, 0.8 g.; E, 2.8 g.
6	Heat alone	120	3 hrs.	+	B, 3.1 g. (95%); E, 0.6 g.
5	$CaCl_2$, 1.5 g.	25–30	60 days	−	B, 2.5 g. (92%)
5	$Mg(ClO_4)_2$, 10 g.	25–30	60 days	+	Small amount of solid m. p. 155–156°, insoluble in water, contained Cl but no S
5	Acetic acid, 30 g.	26	148 hrs.	−	A, 2.8 g. (56%)[c]
5	Acetic acid, 15 g.; H_2SO_4, 15 g.	65	2 hrs.	−	B, 2.5 g. (92%)
6	100% H_2PO_4, 20 cc.	25–30	30 days	−	A, 4.9 g. (82%)[c]
6	100% H_3PO_4, 20 cc.	80	3 hrs.	−	B, 3.1 g. (95%)
5	100% H_3PO_4, 30 g.; P_2O_5, 8 g.	65	24 hrs.	+	B, 1.5 g. (55%); E, 0.1 g.
5	15 cc. of 1:1 H_3PO_4-H_2SO_4	25–30	30 days	−	A, 3.3 g. (66%)[c]
4	$C_6H_5SO_3H$, 16 g.	65	3 hrs.	−	B, 2.1 g. (97%)
5[a]	H_2SO_4, 20 g.	25–30	7 days	−	A, 3.0 g.;[d] C 0.7 g.; E, 0.1 g.
5[b]	C_2H_5OH, 50 cc. SO_2 passed in	26	10.5 hrs.		A, 4.6 g. (92%)

[a] Anhydrous potassium salt. [b] Pentamethylbenzene. [c] Yield low because the product was too soluble to isolate quantitatively. [d] Mixture of A and D.

C. Studies on Reagents and Reaction Conditions.—These experiments were performed in order to find reagents and/or reaction conditions which would avoid the formation of the tarry, amorphous by-products obtained in the Jacobsen reactions when sulfuric acid was used. The results are given in Table II and they show clearly that none of the reagents tried, except sulfuric acid, caused any Jacobsen rearrangement to occur.

D. Preparation of Materials

Chlorodurene (I).—Durene (60 g., 0.45 mole) was chlorinated at 0° in chloroform (175 g.) by adding a solution of chlorine (35.5 g., 0.5 mole) in chloroform (200 g.). The product was steam distilled and the oil in the distillate was dried and fractionated under 20 mm. pressure. A small amount of durene (5.5 g., 9.2%) came over first, followed by the main fraction, b. p. 120–128° (46.5 g., 61.5%). The residue (mostly dichlorodurene) weighed 4.5 g. The crude product was recrystallized twice from 95% alcohol and yielded 38.7 g. (56.7% corrected for recovered durene) of white plates of pure monochlorodurene, m. p. 47.5–48°. Töhl and Eberhard[17] reported that chlorodurene melted at 48° and boiled at 237°.

Dichlorodurene (8.8 g.), white needles, m. p. 189–189.5°, was obtained from the residue from the steam distillation and vacuum distillation by crystallization from chloroform–alcohol.

Chloroisodurene (II).—Isodurene (30 g.) was chlorinated using the same procedure and molar ratios of reagents as above. The steam distillate was fractionated under 20 mm. pressure. The products were (a) b. p. up to 112°, 8 g. (unchanged isodurene); (b) b. p. 112–120°, 18.3 g. (48.7%), chloroisodurene; (c) residue 1.5 g. The main product was redistilled, giving 13.9 g. (37%, corrected for recovered isodurene) of monochloroisodurene, b. p. 139° under 41 mm., m. p. −1 to +1, n^{28}_D 1.5382.

Recrystallization of the residue from chloroform–alcohol gave dichloroisodurene in the form of long, white needles, m. p. 188°.

Anal. Calcd. for $C_{10}H_{12}Cl_2$: Cl, 34.9. Found: Cl, 34.65.

(17) Töhl and Eberhard, *Ber.*, **26**, 2944 (1893).

Chloroprehnitene (III).—Prehnitene (67 g.) was chlorinated as above. The crude product was fractionated *in vacuo* and the main fraction then steam distilled, followed by fractionation of the oil in the distillate. The fractions were (24 mm.): (a) b. p. up to 108°, prehnitene (9.6 g., 14.3%); (b) b. p. 108–128°, 2.1 g.; (c) b. p. 128–136°, chloroprehnitene (54.2 g., 64.5%); (d) residue, 19.6 g. The main fraction was again steam distilled and the oil in the distillate (46.8 g.) fractionated. There resulted 42.3 g. (58.8% corrected for recovered prehnitene) of chloroprehnitene, b. p. 131–132° under 24 mm., m. p. 24°; n^{28}_D 1.5422. The recorded boiling point is 240°[3] (p. 1524).

Chloromesitylene.—A similar chlorination of mesitylene (36.5 g.) gave chloromesitylene (35 g., 74.6%) b. p. 90–91° at 20 mm., and a by-product of trichloromesitylene, m. p. 207°.[18]

Chloromesitylene Sodium Sulfonate.—Chloromesitylene (3 g.) was sulfonated by shaking with 20% fuming sulfuric acid (15 g.) for fifteen minutes. The sodium salt was prepared and analyzed.

Anal. Calcd. for $C_9H_{10}O_3SClNa \cdot {}^1/_2H_2O$: Cl, 13.37; H_2O, 3.40. Found: Cl, 13.42; H_2O (loss at 110°), 3.45.

The **sulfonyl chloride**, prepared by the action of phosphorus pentachloride upon the salt, was an oil. The **sulfonamide** crystallized from alcohol in small white plates, m. p. 165.5–166°.

Bromomesitylene (XI) was prepared by the method described in the literature.[19]

Bromomesitylene Sodium Sulfonate.—Bromomesitylene (3 g.) was sulfonated by shaking with concd. sulfuric acid (25 cc.). The sodium salt was prepared and recrystallized from water. It formed plates when crystallized slowly, and needles when crystallized rapidly. The plates were analyzed for water of crystallization.

Anal. Calcd. for $C_9H_{10}O_3SBrNa \cdot {}^1/_2H_2O$: H_2O, 2.90. Found: H_2O (loss at 110°), 3.12.

The **sulfonamide** crystallized from alcohol in the form of white needles, m. p. 160–160.5°.

(18) Fittig and Hoogewerff[12] reported the melting point as 204–205°.

(19) Smith and MacDougall, THIS JOURNAL, **51**, 3002 (1929).

Anal. Calcd. for $C_9H_{12}O_2NSBr$: Br, 28.8. Found: Br, 28.6.

5-Chloropseudocumene (VI).—A solution of pseudocumene (80 g., 0.66 mole) in chloroform (100 cc.) was chlorinated at 0° with chlorine (58 g., 0.817 mole) in chloroform (300 g.). The product was fractionated. The main fraction weighed 85 g. and 90% of it boiled at 129–131° under 60 mm. This material was cooled to −15° and the solid filtered off. Recrystallization of the crude solid from alcohol gave 33 g. (34%) of white plates, m. p. 70.5–71°.[3]

3-Chloropseudocumene.—The filtrate from the solid 5-chloropseudocumene was largely 3-chloropseudocumene, and was used directly for the preparation of most of the derivatives of 3-chloropseudocumene. This filtrate was converted into 3-chloropseudocumene sodium sulfonate in 80% yield (page 5) and the sulfonic acid was readily hydrolyzed by dilute sulfuric acid at 135–155° to give 3-chloropseudocumene (b. p. 127° at 61 mm.) in 79% yield. This was the best synthesis of 3-chloropseudocumene of all those tried. Chlorination of pseudocumene-5-sodium sulfonate also gave 3-chloropseudocumene-5-sulfonic acid. Pseudocumene-5-sodium sulfonate (10 g.) was dissolved in a mixture of alcohol (100 cc.) and carbon tetrachloride (100 cc.). The cold (0°) solution was chlorinated by adding a solution of chlorine (5 g.) in carbon tetrachloride (50 cc.). Water (50 cc.) was added, the solution evaporated to 80 cc. on the steam-bath and cooled. It deposited 6.8 g. (56.7%) of white needles. The acid gave an amide m. p. 180–181.5° identical with specimens prepared in other ways. Nitration of the sulfonic acid gave 3-chloro-5,6-dinitropseudocumene, m. p. 173.5–174°.

3-Chloro-5,6-dibromopseudocumene.—Acetic acid (20 cc.) was poured over 3-chloropseudocumene-5-sodium sulfonate (1 g.), the mixture heated to 70° and excess bromine added. The product formed white needles, m. p. 224°.

Anal. Calcd. for $C_9H_9ClBr_2$: halogen, 59.35. Found: halogen, 59.2.

3-Chloro-5,6-dinitropseudocumene (XVIII).—Direct nitration of the above filtrate (crude 3-chloropseudocumene) (10 g.) with fuming nitric acid (50 cc., d. 1.5) and sulfuric acid (50 cc.) at 0° gave 16 g. crude XVIII, white needles. Nitration of 3-chloropseudocumene-5-sodium sulfonate (10 g.) with fuming nitric acid (50 cc., d., 1.5) at 0° also gave XVIII in good yield, m. p. 172–173°.[3]

6-Chloropseudocumene (VII).—Pseudocumidine-5 (47.2 g., 0.35 mole, m. p. 62°) and a few crystals of iodine were dissolved in alcohol (300 cc.). A solution of chlorine (29.8 g., 0.42 mole) in chloroform (200 g.) was added slowly and with stirring. Hydrochloric acid (50 cc.) was added and the chloroform and most of the alcohol were removed by steam distillation. The residual solution was made alkaline and the steam distillation continued for five hours. The distillate contained 37 g. (62%) of crude 6-chloropseudocumidine-5. After crystallization from alcohol the amine was white and melted at 57°.[20]

The crude amine (34 g., 0.2 mole) was dissolved in a mixture of concd. sulfuric acid (200 cc.) and phosphoric acid (50 cc.). The solution was cooled (0°) and stirred, while a solution of sodium nitrite (27.6 g., 0.4 mole) in water (40 cc.) was slowly added (ninety minutes). After stirring for thirty minutes longer, ethyl alcohol (100 cc.) and copper bronze (4 g.) were added and the mixture warmed on the steam-bath for one hour. After standing overnight, water (200 cc.) was added and the mixture was steam distilled. The distillate contained 17 g. (55%) of oil, which was dried and fractionated. The main product distilled at 127–128° under 20 mm. (217° under 722 mm.) and weighed 12.5 g. The recorded boiling point of VII is 210° under 760 mm.[21] Half a gram of the substance was nitrated at 0° with fuming nitric acid *alone* (20 cc., d. 1.5). The product was 6-chloro-3,5-dinitropseudocumene, white needles, m. p. 162°.

Anal. Calcd. for $C_9H_9O_4N_2Cl$: C, 44.2; H, 3.74. Found: C, 44.1; H, 3.70.

Sulfuric acid should be avoided in the nitrating mixture for preparation of this compound, for if the reaction mixture becomes at all warm when sulfuric acid is present, the product is not *6-chloro-3,5-dinitropseudocumene*.[22]

Trichloropseudocumene was prepared by adding excess chlorine to a solution of pseudocumene in chloroform. It formed white needles, m. p. 210°.[23]

Anal. Calcd. for $C_9H_9Cl_3$: C, 48.3; H, 4.05; Cl, 47.65. Found: C, 48.4; H, 4.03; Cl, 47.88.

5-Bromopseudocumene (VIII).—The procedure for the bromination of pseudocumene was essentially the same as that used for the chlorination. After the solvent was removed, the residue was steam distilled and the crude product in the distillate was recrystallized from alcohol. The yield was 27 g. (68%) from 24 g. of pseudocumene, and the product melted at 71–72°.[24] An alternative method, which avoided the formation of any 3-bromopseudocumene, was as follows: pseudocumene-5-sulfonic acid[7] (p. 1606) (25 g., 0.11 mole) was dissolved in water (300 cc.) and brominated at 30° by addition of bromine (20 g., 0.125 mole) in absolute alcohol (50 cc.). The bromine solution was added very slowly (20 drops per minute) and with stirring. On standing overnight, the solution deposited 10.2 g. of white solid. Addition of bromine to the filtrate produced more solid. The total solid obtained after three such treatments of the filtrate weighed 17 g. (77.4%). One crystallization from alcohol brought the melting point up to 71.5–72.5°.

5-Bromo-3,6-dinitropseudocumene was formed when VIII (1 g.) was dropped into concd. sulfuric acid (2 vols.) and fuming nitric acid (d. 1.5, 1 vol.) at 0°. The recrystallized product melted at 216.5–217°.[25]

3-Bromopseudocumene-5-sulfonic Acid (IX).—The preparation of the sodium salt of IX from pseudocumene-5-sodium sulfonate has already been described (page 6). It is to be noted that bromination of the sulfonic acid in water solution by alcoholic bromine replaced the

(20) Orton and King, *J. Chem. Soc.*, **99**, 1189 (1911).

(21) Huender, *Rec. Trav. Chim.*, **34**, 22 (1915).

(22) See Huender, ref. 21, p. 25. The m. p. of 6-chloro-3,5-dinitropseudocumene is given in the literature as 162° (Huender) and 169–170° [Michaelis, *Ann.*, **294**, 15 (1897)].

(23) Schultz, *Ber.*, **42**, 3604 (1909).

(24) Beilstein and Kogler, *Ann.*, **137**, 323 (1866); Fittig and Ernst, *ibid.*, **139**, 187 (1866).

(25) Kelbe and Pathe, ref. 13, p. 1548 reported the m. p. as 213–214°; Fittig, [*Ann.*, **147**, 14 (1868)] reported 214–215°; Huender[21] reported 218°.

sulfonic acid group by bromine and gave VIII, while bromination of a suspension of the sodium sulfonate in alcohol by bromine in chloroform did not replace the sulfonic acid group, but brominated the ring and gave the sodium salt of IX. Derivatives of 3-bromopseudocumene have been described on page 6, Col. 2.

6-Bromopseudocumene.—Pseudocumidine-5 (40.5 g., 0.3 mole, m. p. 62°), dissolved in hydrochloric acid (100 cc.) and water (250 cc.) was brominated by addition of a solution of bromine (51 g., 0.32 mole) in acetic acid (50 cc.). Steam distillation removed 3 g. of a red impurity. The solution was made basic and the amine removed by steam distillation (five hours) and recrystallized from alcohol.

6-Bromopseudocumidine-5 formed white needles, m. p. 69°. The yield was 38.2 g. (56.8%).

Anal. Calcd. for $C_9H_{12}NBr$: Br, 37.4. Found: Br, 37.5.

The amine (33.6 g., 0.15 mole) was diazotized and the solution treated in the manner described for the corresponding chloro-compound. The product was an orange oil (15.5 g., 63.5%) which was dried and fractionated. The main fraction was 11.3 g. of 6-bromopseudocumene, b. p. 117° under 17 mm., 233° (corr.) under 724 mm., n^{26}_D 1.5516. The substance did not solidify at −10°[21] (p. 12).

Nitration of 6-bromopseudomene with fuming nitric acid gave 6-bromo-3,5-dinitropseudocumene, white needles (from alcohol), m. p. 179°[21] (p. 22).

4-Chlorohemimellithene.—Hemimellithene (12 g., 0.1 mole) and a crystal of iodine were dissolved in chloroform (20 cc.) and chlorinated at 0° by addition of a solution of chlorine (9 g., 0.127 mole) in chloroform (40 g.). The solvent was removed by distillation through a column, and the residual oil was fractionated at 16 mm. The fractions were: (a) b. p. up to 86°, 2.4 g.; (b) b. p. 86–87°, 7.7 g.; (c) residue 3.3 g. Fraction b was 4-chlorohemimellithene; yield, 50%.

4-Chloro-5,6-dibromohemimellithene was obtained by bromination of 4-chlorohemimellithene in acetic acid solution. The product, recrystallized from alcohol, formed long white needles, m. p. 229–230°.

Anal. Calcd. for $C_9H_9ClBr_2$: halogen, 59.35. Found: halogen, 59.0.

4-Chloro-5,6-dinitrohemimillithene was obtained by nitration at 0° of 4-chlorohemimellithene with 1:1 concd. sulfuric acid and fuming nitric acid (d. 1.5). The product formed white needles of m. p. 183°.

4-Chloro-5,6-diaminohemimellithene.—The dinitro compound was reduced in the same manner as that used for preparation of XX. The diamine crystallized from dilute alcohol in long needles, m. p. 137–137.5°.

The diamine reacted with diacetyl to give **8-chloro-2,3,5,6,7-pentamethylquinoxaline**, pale yellow needles from alcohol, m. p. 160.5°.

13 - Chloro - 10,11,12 - trimethylphenanthrophenazine, prepared from the diamine and phenanthraquinone, crystallized from nitrobenzene in yellow plates, m. p. 346.5–347°.

Anal. Calcd. for $C_{23}H_{17}N_2Cl$: C, 77.4; H, 4.81. Found: C, 77.0; H, 4.65.

7-Chloro-2,4,5,6-tetramethylbenzimidazole, prepared from the nitro compound by the method used for preparation of XIX, formed small white plates (and needles) m. p. 288.5°.

Anal. Calcd. for $C_{11}H_{13}N_2Cl$: C, 63.3; H, 6.28. Found: C, 63.15; H, 6.21.

4-Bromohemimellithene.—Hemimellithene (9 g., 0.075 mole) was dissolved in chloroform (20 cc.) and brominated at 0° with a solution of bromine (13 g., 0.0185 mole) in chloroform (30 cc.). The solvent was removed by distillation, and the residue fractionated under 12 mm. The main fraction weighed 7 g. (47%) and had the following constants: b. p. 103–103.5° under 12 mm.; 229.5° under 750 mm.; m. p. +1°; n^{21}_D 1.5618.

4-Bromo-5,6-dinitrohemimellithene was obtained by nitration of 4-bromohemimellithene with 2:1 (by vol.) concd. sulfuric acid and fuming nitric acid (d. 1.5). It was recrystallized from alcohol, and formed white needles, m. p. 196.5°.

10,11,12-Trimethylphenanthrophenazine.—An alcoholic solution of 4-bromo-5,6-dinitrohemimellithene was reduced by stannous chloride in hydrochloric acid in the same manner as that described for the reduction of 3-chloro-5,6-dinitropseudocumene (XVIII). The diamine was not characterized, but was converted directly into the phenazine by the action of phenanthraquinone. The phenazine formed orange plates, m. p. 311°, when crystallized from nitrobenzene, and contained no halogen.

Anal. Calcd. for $C_{23}H_{18}N_2$: C, 85.70; H, 5.63. Found: C, 85.42; H, 5.74.

Pentamethylcyclohexane.—Pentamethylbenzene (35 g., 0.236 mole) was dissolved in methylcyclohexane to make a solution having a volume of 125 cc. Reduction was carried out in a bomb (Adkins type) at 225°, using 3 g. of a nickel catalyst (ammonium carbonate type), deposited on kieselguhr. The reduction required five hours. The product was filtered and fractionated. Pentamethylcyclohexane was a colorless liquid with an odor similar to that of camphor. It did not solidify at −50°, and had the constants: b. p. 98–98.5° under 38 mm., 188° under 730 mm., n^{31}_D 1.4484.

Pentamethylbenzene Sulfonic Acid.—Pentamethylbenzene (40 g.) was added quickly (fifteen minutes) in small portions to 20% fuming sulfuric acid (120 cc.), with cooling and vigorous stirring. The reaction mixture was poured onto ice (375 g.) and the white sulfonic acid collected on a cloth filter and washed with cold 20% hydrochloric acid (50 cc.). The acid was dissolved in water (450 cc.) at 75°, the undissolved material was separated, and the product was precipitated by addition of concd. hydrochloric acid (250 cc.) at 0°. The solid was filtered, pressed as dry as possible on the filter and spread on a porous plate. The last traces of hydrochloric acid were removed by keeping the material for four days in a vacuum desiccator over potassium hydroxide. The sulfonic acid was white and weighed 41 g. (66%); m. p. 113°.

Pentamethylbenzenesulfonylchloride was prepared from the sodium sulfonate in the usual manner. It crystallized from ether in white, rectangular prisms of m. p. 81°.

Pentamethylbenzenesulfonamide was prepared from the chloride and ammonia. It crystallized from dilute alcohol in fine white needles of m. p. 186°.[26]

(26) Jacobsen, *Ber.*, **20**, 900 (1887).

Pentamethylbenzene Methyl Sulfonate.—The sulfonyl chloride (8 g.) was refluxed for one hour with a solution of sodium methoxide prepared from sodium (3 g.) and methanol (50 cc.). The reaction mixture, poured into water, deposited a solid which was removed and crystallized twice from methanol. The ester (6.0 g.) was white and melted at 91–91.5°. It was readily soluble in ether, benzene, chloroform and warm methanol, and insoluble in water.

Anal. Calcd. for $C_{12}H_{18}O_3S$: C, 59.5; H, 7.49. Found: C, 59.4; H, 7.32.

Summary

1. Subjected to the reagents and conditions which cause the Jacobsen rearrangement to occur, chlorodurene, chloroisodurene, chloroprehnitene, 5-chloropseudocumene, 6-chloropseudocumene, 5-bromopseudocumene, and bromomesitylene rearranged. Chloromesitylene, 4-chlorohemimellithene, hemimellithene, 5-nitropseudocumene, pseudocumidine-5, pentamethylbenzene-methylsulfonate, pentamethylcyclohexane, 2,3-dimethylnaphthalene, and *p*-bromodiphenyl did not rearrange.

2. The ease of migration of groups present in the chloro- and bromotetramethylbenzenes is in the order Br > CH_3 > Cl; in case of the corresponding derivatives of the trimethylbenzenes, the order is Br > Cl > CH_3.

3. Attempts to find mild conditions which would cause Jacobsen rearrangements without producing amorphous by-products were unsuccessful.

4. The limits and mechanism of the Jacobsen rearrangement have been discussed.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, YALE UNIVERSITY]

The Chemistry of the Lipids of Tubercle Bacilli. XLI. Part 1. The Composition of the Timothy Bacillus Wax. Part 2. The Isolation of *d*-Eicosanol-2 and *d*-Octadecanol-2 from the Unsaponifiable Matter of the Timothy Bacillus Wax[1]

BY MARY C. PANGBORN[2] AND R. J. ANDERSON

Part 1. The Composition of the Timothy Bacillus Wax

Introduction

All of the acid-fast bacteria contain relatively large quantities of wax-like material; in fact the wax is quantitatively the most important part of the ether-soluble constituents. The bacterial waxes are easily soluble in ether, chloroform or benzene but they are practically insoluble in alcohol or acetone. The method used in this Laboratory of first extracting the bacteria with a mixture of alcohol and ether removes very little of the wax fractions owing to the insolubility of the waxes in alcohol, while the subsequent extraction with chloroform removes the waxes almost completely. The bacterial residues after extraction with alcohol–ether and chloroform are practically free from lipids soluble in neutral solvents.

Since very little information is available concerning either the chemical composition or the biological effects of the bacterial waxes, we have devoted some study to these interesting compounds. Previously the waxes from the human tubercle bacillus have been examined by Anderson[3] and the wax from the BCG has been analyzed by Chargaff.[4] As a further contribution on this subject we wish to report some experiments dealing with the chemical composition of the timothy bacillus wax.

The chief constituents of the wax were found to be optically active fatty acids of high molecular weight, two higher secondary alcohols, a carbohydrate which was identified as trehalose, and glycerol. The wax is therefore a complex compound or mixture containing solid glycerides, esters of fatty acids with trehalose, and esters of fatty acids with higher alcohols. None of the ordinary fatty acids could be found. Only one of the fatty acids could be isolated in a state approaching purity. The composition of this acid corresponded approximately to the formula $C_{70}H_{138}O_6$ and it contained one hydroxyl, one double bond, and apparently two carboxyl groups.

The isolation of the ether-soluble neutral ma-

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(2) Holder of a National Tuberculosis Association Fellowship at Yale University, 1933–1934.

(3) R. J. Anderson, *J. Biol. Chem.*, **83**, 505; **85**, 327 (1929).

(4) E. Chargaff, *Z. physiol. Chem.*, **217**, 115 (1933).