[CONTRIBUTION FROM THE NOYES CHEMICAL LABORATORY, UNIVERSITY OF ILLINOIS]

Polyphosphoric Acid as a Dehydrating Agent. III. Identification of the Hydrocarbons from Mesitylene and Aliphatic Acids[1]

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The hydrocarbons obtained from mesitylene and aliphatic acids in the presence of polyphosphoric acid have been shown to be 1,1-dimesitylalkenes. 1,1-Dimesitylethylene has been hydrogenated to 1,1-dimesitylethane and oxidized to dimesityl ketone. Oxidation of 1,1-dimesitylpropene gave α,α-dimesitylacetone. Molecular weight determinations, analyses of the hydrocarbons and their derivatives, and ultraviolet spectra support the structures assigned to the compounds.

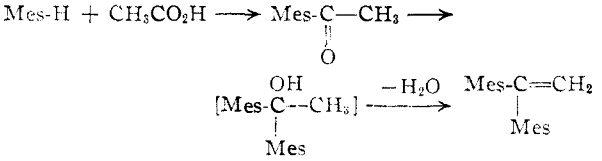
In the preceding paper of this series[1] it was reported that certain aromatic hydrocarbons react with simple carboxylic acids in the presence of polyphosphoric acid to give hydrocarbons. The identification of these white, crystalline hydrocarbons is the subject of the present communication. They were obtained in attempts to acylate mesitylene with aliphatic acids in the presence of polyphosphoric acid. The reactions were conducted with vigorous stirring for three to five hours at about 140°, and the reaction mixtures were decomposed by adding them to an excess of water or ice. Vacuum distillation of the resulting organic phase gave the hydrocarbons and left a relatively large residue of undistillable material. The yields of the hydrocarbons increase with increasing chain length of the aliphatic acid, being 9, 39 and 48% from acetic, propionic and butyric acids, respectively. The yields are calculated on the basis of the amount of mesitylene put into the reaction vessel; usually about 20% of it was recovered. Even in the experiments in which a threefold excess of the aliphatic acid was used, little of the acid was recovered

The minimum amount of polyphosphoric acid necessary for an effective reaction is about equal to the combined weight of mesitylene and aliphatic acid. When less polyphosphoric acid was used, or when the temperature of the reaction did not exceed 110°, none of the hydrocarbon was isolated, and the acylmesitylene was obtained in low yield.

Since some of the acylmesitylene was obtained under mild reaction conditions, and since chloroacetic acid gave only ω-chloroacetomesitylene and di-(ω-chloroaceto)-mesitylene under the more strenuous conditions, it seemed probable that acylation was the first step in the formation of the hydrocarbons. Treatment of acetomesitylene with polyphosphoric acid at 140° gave the same hydrocarbon that was obtained from acetic acid, mesitylene and polyphosphoric acid, in 17% yield. Some mesitylene was also formed in the reaction of acetomesitylene.

Molecular weight determinations showed that the hydrocarbons were members of an homologous series and that they might have been formed from two molecules of mesitylene and one of the aliphatic acid, with loss of two molecules of water.

Oxidation of the hydrocarbon from acetic acid and mesitylene with chromium trioxide in glacial acetic acid at room temperature converted it to dimesityl ketone, which was identified by a mixed melting point and comparison of the infrared spectrum with that of a known sample. Catalytic hydrogenation of the same hydrocarbon converted it to 1,1-dimesitylethane. A mononitro derivative was prepared which has the composition calculated for $C_{20}H_{23}O_2N$. Thus it is shown that the hydrocarbon from acetic acid and mesitylene is 1,1-dimesitylethylene (I), which must be formed as outlined below.

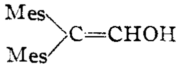


$$\text{Mes-H} + CH_3CO_2H \longrightarrow \text{Mes-}\underset{\underset{O}{\|}}{C}\text{—}CH_3 \longrightarrow$$

$$[\text{Mes-}\underset{\underset{\text{Mes}}{|}}{\overset{OH}{C}}\text{—}CH_3] \xrightarrow{-H_2O} \text{Mes-}\underset{\underset{\text{Mes}}{|}}{C}{=}CH_2$$

I

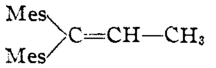
The ultraviolet absorption spectra of the different hydrocarbons are almost identical, and they are quite similar to the spectrum of β,β-dimesitylvinyl alcohol (II).[2] The infrared spectra also show that the various hydrocarbons are quite similar.



$$(\text{Mes})_2C{=}CHOH$$

II

Oxidation of the hydrocarbon from propionic acid and mesitylene yielded α,α-dimesitylacetone, again identified by mixed melting point and comparison of the infrared spectrum with that of an authentic sample. Since the infrared spectrum of this hydrocarbon indicates no terminal methylene group, the compound is shown to be 1,1-dimesitylpropene (III).



$$(\text{Mes})_2C{=}CH\text{—}CH_3$$

III

The double bond in these hydrocarbons is quite unreactive, because of the steric effect of the mesityl groups. None of the compounds decolorized bromine or potassium permanganate under the conditions of the usual qualitative tests. Hydrogenation of 1,1-dimesitylethylene was accomplished in three hours at 200° under a pressure of 2000 p.s.i., but the other hydrocarbons survived all hydrogenation attempts.

Hydrocarbons were also obtained from the action of propionic and butyric acid on durene in the presence of polyphosphoric acid. The mode of formation, the molecular weights and the analytical data indicate that the compounds are analogous to those from mesitylene. Propionic acid and triethylben-

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[1] For the preceding paper in this series, see H. R. Snyder and F. X. Werber, THIS JOURNAL, 72, 2965 (1950).

[2] W. H. Rodebush and I. Feldman, *ibid.*, 68, 896 (1946).

zene reacted only slightly, and the small amount of viscous liquid obtained was insufficient for purification.

Experimental[3,4]

Reaction of Propionic Acid with Mesitylene.—A mixture of 37 g. of propionic acid, 30 g. of mesitylene and 60 g. of polyphosphoric acid[5] was gently refluxed (145°) with vigorous stirring for 5 hours. The black reaction mixture was poured immediately into 200 ml. of water. After the mixture had cooled, the layers were separated and the organic liquid was washed with 5% sodium hydroxide and with water before it was distilled. Propionic acid and mesitylene were present in the foreruns and 13.5 g. (39%) of a yellow liquid distilled at 148–150° (0.7 mm.). It solidified when cooled and was recrystallized from 95% ethanol as white crystals of m.p. 95–96°.

Anal. Calcd. for $C_{21}H_{26}$: C, 90.58; H, 9.42; mol. wt., 278. Found: C, 90.40; H, 9.38; mol. wt., 284, 280, 266; av. 277 (ebullioscopic in benzene).

The above conditions were the most satisfactory of a number tested; if the temperature remained below 125°, or if less polyphosphoric acid was used, the yield decreased sharply.

Reaction of Butyric Acid with Mesitylene.—In a 1-l. three-necked flask were placed 240 g. of mesitylene, 100 g. of butyric acid and 350 g. of polyphosphoric acid. The mixture was stirred with a Hershberg stirrer and the temperature was maintained at 140° for 2.5 hours. The reaction mixture was poured into 800 ml. of water. The organic layer solidified after a short time; 200 ml. of ether was added and the two layers were separated. After removal of the ether, the organic layer was distilled. One hundred and forty grams (48%) of a yellow liquid distilled at 163–170° (0.6 mm.). The liquid solidified in the receiver and was recrystallized from 95% ethanol, m.p. 107–109°. A small sample purified for analysis melted at 109–110°.

Anal. Calcd. for $C_{22}H_{28}$: C, 90.35; H, 9.65; mol. wt., 292. Found: C, 90.41; H, 9.99; mol. wt., 278, 286, 297; av. 287 (ebullioscopic in benzene).

A mixture of mesitylene, acetic acid and polyphosphoric acid, when subjected to essentially the same conditions as above, gave a 9% yield of a hydrocarbon, but it is best obtained from acetomesitylene, as described below.

Reaction of Acetomesitylene in Polyphosphoric Acid.—Thirty grams of acetomesitylene and 60 g. of polyphosphoric acid were heated at 140–155° with vigorous stirring for two hours. The reaction mixture was decomposed with water and treated as above to yield 4.0 g. (17.1%) of a hydrocarbon which melted at 97–98° after repeated recrystallization from ethanol. It did not depress the melting point of the hydrocarbon obtained from acetic acid and mesitylene.

Anal. Calcd. for $C_{20}H_{24}$: C, 90.85; H, 9.15; mol wt., 264. Found: C, 91.10; H, 9.18; mol. wt., 249, 276, 261, 239, 266; av. 258 (ebullioscopic in benzene).

Reaction of Propionic Acid with Durene.—The reaction was carried out under the conditions described for propionic acid and mesitylene, and the product was isolated in the usual way. Thirty grams (20%) of a viscous yellow liquid which distilled at 160–210° (4 mm.) was dissolved in 150 ml. of boiling ethanol. When the solution cooled, white crystals formed. They weighed 15 g. (10%). Repeated recrystallization of the sample from ethyl acetate–ethanol and low-boiling petroleum ether gave a product melting almost completely from 109–111°, but a small portion of the sample melted up to 118°.

Anal. Calcd. for $C_{23}H_{30}$: C, 90.13; H, 9.87; mol. wt., 306. Found: C, 90.30; H, 9.74; mol. wt., 296, 296, 337; av. 309 (ebullioscopic in benzene).

Reaction of Butyric Acid with Durene.—The procedure for butyric acid and mesitylene was followed. A dark yellow, viscous oil distilled at 180–220° (1.5 mm.). It hardened to a glass in the refrigerator. The amorphous mass was dissolved in 75 ml. of boiling absolute ethanol and the solution was allowed to cool slowly. Yellow crystals of m.p. 120–126° precipitated. After the compound was recrystallized from ethanol and ethyl acetate–ethanol, it melted at 130–131.5°.

Anal. Calcd. for $C_{24}H_{32}$: C, 89.93; H, 10.07; mol. wt., 320. Found: C, 89.94; H, 10.23; mol. wt., 328, 324, 316; av. 323 (ebullioscopic in benzene).

Reaction of Chloroacetic Acid with Mesitylene.—A mixture of 47.3 g. of chloroacetic acid, 30.0 g. of mesitylene and 60 g. of polyphosphoric acid was refluxed for five hours with stirring. The hot reaction mixture was poured into 300 ml. of water and allowed to stand overnight. When the organic layer was distilled, two high-boiling fractions were collected. The first (b.p. 95–130° (0.7 mm.)) crystallized in the receiving flask. After two recrystallizations from an acetic acid–water mixture and two from ethanol, white crystals melting at 67–69.5° were obtained. The compound did not depress the m.p. of an authentic sample of ω-chloroacetomesitylene. The yield was 16%. Fraction two was collected at 140–170° (0.3 mm.). It was a viscous brown liquid which began to crystallize overnight and almost completely crystallized after three days. The melting point was 136–137° after three recrystallizations from ethanol. The yield was 3%. Di-(ω-chloroaceto)-mesitylene is reported to melt at 134–135°.[6]

Nitration of 1,1-Dimesitylethylene.—The procedure of Schultz[7] for the mononitration of mesitylene was followed. Four milliliters of nitric acid (density 1.49) was added dropwise to a solution of 14.5 g. of the hydrocarbon obtained from acetomesitylene in 75 ml. of glacial acetic acid at 50°. The mixture was allowed to stand at 50° for two hours, then poured over 200 g. of cracked ice. After one recrystallization from ethanol, the yellow crystals melted at 100–102° and weighed 15.8 g. A small sample was purified for analysis and melted at 106–107°.

Anal. Calcd. for $C_{20}H_{23}O_2N$: C, 77.64; H, 7.49; N, 4.53; mol. wt., 309. Found: C, 77.50; H, 7.32; N, 4.64; mol. wt., 330, 296, 316; av. 314 (ebullioscopic in benzene).

Reduction of 1,1-Dimesitylethylene.—A solution of 5.28 g. of 1,1-dimesitylethylene in 150 ml. of 95% ethanol was hydrogenated at a pressure of 2000 p.s.i. at 200° for three hours in the presence of a Raney nickel catalyst. The catalyst was removed by filtration and solution evaporated to 50 ml. on the steam-bath. The white crystals which separated on standing overnight weighed 3.1 g. and melted at 88–90°. The melting point was raised to 93–95° by four recrystallizations from ethanol, methanol, petroleum ether and ethyl acetate–ethanol. A mixture of this compound and the unreduced material melted from 82–92°. The compound did not depress the melting point of a sample of 1,1-dimesitylethane prepared by another method.[8]

Anal. Calcd. for $C_{20}H_{26}$: C, 90.16; H, 9.84. Found: C, 89.97; H, 9.79.

1,1-Dimesitylpropene was recovered unchanged after shaking for 5.5 hours with hydrogen under a pressure of 3000 p.s.i. in the presence of a Raney nickel catalyst. The attempted hydrogenation also failed in the presence of copper chromite.

Oxidation of 1,1-Dimesitylethylene.—A procedure[9] for the oxidation of β,β-dimesitylvinyl alcohol was used. Five grams of chromium trioxide was added to a solution of 2 g. of 1,1-dimesitylethylene in 160 ml. of glacial acetic acid at 35°. The mixture warmed to about 90° spontaneously and was cooled immediately to 35°. After the mixture had been allowed to stand overnight, it was diluted with 500 ml. of water. The solid which settled was recrystallized from ethanol and from high-boiling petroleum ether. Its melting point was 137–138°. The compound did not depress the melting point of a known sample of dimesityl ketone, and its infrared spectrum was identical with that of dimesityl ketone.

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[3] All melting points are corrected.

[4] The authors are indebted to Miss Elizabeth Petersen for the infrared spectra and to Miss Rachel Kopel, Miss Emily Davis, Mrs. Katherine Pih and Mr. Howard Clark for the microanalyses.

[5] The authors are indebted to the Victor Chemical Works for samples of this material.

[6] F. Kunckell, K. Eras, E. Muller and A. Hildebrandt, *Chem. Zentr.*, **84**, I, 1770 (1913).

[7] G. Schultz, *Ber.*, **17**, 1477 (1884).

[8] R. C. Fuson, H. L. Jackson, J. A. Fuller and D. E. Brasure, This Journal, unpublished; these authors kindly furnished the sample for comparison.

[9] R. C. Fuson, P. I. Southwick and S. P. Rowland, *ibid.*, **66**, 1109 (1944).

Oxidation of 1,1-Dimesitylpropene.—To a solution of 13.6 g. of 1,1-dimesitylpropene in 500 ml. of glacial acetic acid was added 16.5 g. of chromium trioxide. The mixture warmed spontaneously and was cooled in an ice-bath to 35°. After the mixture had been allowed to stand overnight, it was diluted with 2 l. of water. The resulting suspension stood for 24 hours, during which time most of the oxidation product precipitated as a sticky solid. The water–acetic acid mixture was extracted with three 300-ml. portions of ether; the ether solution was washed with 10% sodium hydroxide and then with a 10% sodium carbonate solution until no more carbon dioxide was evolved, and finally was dried over sodium carbonate. After the ether was removed the residue (about 8 g.) partially crystallized when it was allowed to stand overnight in the refrigerator. It was triturated with 10 ml. of absolute ethanol and filtered. The yield of light brown crystals of m.p. 138–141° was 2.0 g. After repeated crystallization, the crystals melted at 144–146° and did not depress the melting point of a known sample of α,α-dimesitylacetone. Infrared analysis also showed the two to be identical.

Oxidation of 1,1-Dimesitylbutene.—The oxidation was carried out with 14.2 g. of 1,1-dimesitylbutene and 16.5 g. of chromium trioxide, and the product extracted as described above. Evaporation of the ether left 10 to 15 ml. of a yellow oil which partially crystallized overnight. After three recrystallizations from ethanol, the product melted at 133–135.5°. This oxidation product probably is 1,1-dimesityl-1-butene-3-one.

Anal. Calcd. for $C_{22}H_{26}O$: C, 86.23; H, 8.55. Found: C, 86.07; H, 8.51.

The infrared spectrum of this substance indicates the presence of a conjugated carbonyl group; a positive test with the dinitrophenylhydrazine reagent was observed.

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[CONTRIBUTION FROM THE GEORGE HERBERT JONES LABORATORY OF THE UNIVERSITY OF CHICAGO]

Photochemical Reactions of Diazomethane with Polyhalomethanes and α-Haloesters[1]

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The novel light-induced reaction of diazomethane with carbon tetrachloride gives 1,3-dichloro-2,2-bis-(chloromethyl)-propane and nitrogen. Analogous reactions with bromotrichloromethane and chloroform yield 1,3-dichloro-2-bromomethyl-2-chloromethylpropane and 1,3-dichloro-2-chloromethyl-2-methylpropane, respectively. α-Haloesters undergo similar reactions: methyl trichloroacetate to give methyl tris-(chloromethyl)-acetate, and ethyl bromoacetate and methyl α-bromopropionate to give ethyl β-bromopropionate and methyl β-bromoisobutyrate, respectively. A free-radical, chain mechanism is proposed since these reactions exhibit the following characteristics: (1) light initiation, (2) inhibition by antioxidants and (3) zero order kinetics at constant temperature and light intensity.

In the light-induced reactions of diazomethane with polyhalomethanes to yield polyhaloneopentane derivatives and with α-haloesters to give β-haloesters, a methylene group is interposed between each halogen atom in the organic halide and the carbon atom to which it is attached ($CCl_4 \rightarrow C(CH_2Cl)_4$; $Cl_3CCOOCH_3 \rightarrow (ClCH_2)_3COOCH_3$). This paper records the results of an investigation of the scope and mechanism in this reaction.

In this study, solutions of diazomethane in many organic halides have been irradiated, but this reaction has been observed only with some of those which undergo the free radical chain reaction addition to olefins.[2-4] The following reactions have been effected (yields in parentheses).

$$CCl_4 + 4CH_2N_2 \longrightarrow C(CH_2Cl)_4\ (60\%) \quad (1)$$

$$BrCCl_3 + 4CH_2N_2 \longrightarrow BrCH_2C(CH_2Cl)_3\ (40\%) \quad (2)$$

$$HCCl_3 + 4CH_2N_2 \longrightarrow CH_3C(CH_2Cl)_3\ (45\%) \quad (3)$$

$$Cl_3CCOOCH_3 + 3CH_2N_2 \longrightarrow (ClCH_2)_3CCOOCH_3\ (60\%) \quad (4)$$

$$CH_3CHBrCOOCH_3 + CH_2N_2 \longrightarrow CH_3CH(CH_2Br)COOCH_3\ (20\%) \quad (5)$$

$$BrCH_2COOCH_3 + CH_2N_2 \longrightarrow BrCH_2CH_2COOCH_3 \quad (6)$$

In each of these reactions the expected amount of nitrogen was evolved, and two products of side reactions were obtained in small amount: polymethylene and the methyl ether (methyl ether and methyl ether ether) derived from the alcohol used as solvent in the preparation of the diazomethane.

The required analytical results and the following evidence for the assigned structures of the products in these reactions (1 to 6) were obtained: (1) The 1,3-dichloro-2,2-bis-(chloromethyl)-propane was identical with a synthetic sample prepared by the reaction of thionyl chloride with pentaerythritol in pyridine.[5] (2) The structure of the 1,3-dichloro-2-bromomethyl-2-chloromethylpropane was confirmed by its identity with an authentic sample prepared by the reaction of 1,3-dichloro-2-chloromethyl-2-hydroxymethylpropane (prepared by the method of Mooradian and Cloke[5]) with phosphorus tribromide. It was converted to 1,3-diiodo-2,2-bis-(iodomethyl)-propane by reaction with sodium iodide in acetone (72 hr. in a bomb tube at 120°). (3) The 1,3-dichloro-2-chloromethyl-2-methylpropane was shown to be identical in index of refraction, specific gravity, boiling point and infrared spectrum (Fig. 1) with the substance prepared by the reaction of 2-hydroxymethyl-2-methyl-1,3-propanediol (prepared by the base-catalyzed reaction of propionaldehyde with formaldehyde) with thionyl chloride in pyridine. (4) The structure of methyl tris-(chloromethyl)-acetate was identified by its two step conversion (reactions 7 and 8) to 1,3-dichloro-2,2-bis-(chloromethyl)-propane. (5) The refractive index and boiling point of the methyl β-

$$(ClCH_2)_3CCOOCH_3 \xrightarrow{LiAlH_4} (ClCH_2)_3CCH_2OH \quad (7)$$

$$(ClCH_2)_3CCH_2OH + SOCl_2 \xrightarrow{pyridine} C(CH_2Cl)_4 \quad (8)$$

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[1] Previous communications; W. H. Urry and J. R. Eiszner, THIS JOURNAL, **73**, 2977 (1951). A part of this work was presented in summary at the Twelfth Annual Organic Symposium in Denver, Colorado, June, 1951.

[2] M. S. Kharasch, W. H. Urry and E. V. Jensen, THIS JOURNAL, **67**, 1626 (1945).

[3] M. S. Kharasch, E. V. Jensen and W. H. Urry, *ibid.*, **69**, 1100 (1947).

[4] M. S. Kharasch, O. Reinmuth and W. H. Urry, *ibid.*, **69**, 1105 (1947).

[5] A. Mooradian and J. B. Cloke, *ibid.*, **67**, 942 (1945).