2. The derivative obtained by the action of ammonia upon the symmetrical acid chloride was the ammonium salt of the imide. From this the imide itself was prepared by the action of dilute hydrochloric acid. The silver salt and the potassium salt of the imide also were made and analyzed.

3. The derivative obtained by the action of ammonia on the unsymmetrical acid chloride was the ammonium salt of the cyan acid; no imide was found. The silver and potassium salts of the cyan acid also were made and analyzed.

4. The derivatives obtained by the action of aniline on the symmetrical acid chloride were the symmetrical dianilide and the anil.

5. The derivatives obtained by the action of aniline on the unsymmetrical acid chloride were the symmetrical dianilide and the unsymmetrical dianilide.

6. By the action of phosphorus oxychloride, each of the two dianilides was transformed into the dianil. This in turn when heated with concentrated hydrochloric acid gave the anil or, heated with glacial acetic acid it gave the unsymmetrical dianilide.

7. The derivative obtained by the action of the alcohols on the symmetrical acid chloride was the benzoic ester of the sulfonic acid.

8. The derivatives obtained by the action of alcohols on the unsymmetrical acid chloride were the benzoic ester of the sulfone chloride, and the benzoic ester of the sulfonic acid.

9. The derivative obtained by the action of phenol upon either of the acid chlorides was always the diphenyl ester. No particular effort was made to prepare the phenyl sulfone chloride. When pyridine was used in the reaction, a second substance was formed which may be the pyridine salt of the phenyl benzoic ester acid. Its constitution was not established.

10. By the action of methyl iodide on the silver salt of the methyl benzoic ester acid, the dimethyl ester was formed.

IOWA CITY, IOWA.

[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF COLUMBIA UNIVERSITY.]

THE SYNTHESIS OF *p*-CYMENE 2-MONOCARBOXYLIC ACID AND OF *p*-CYMENE 3-MONOCARBOXYLIC ACID, TOGETHER WITH CERTAIN OF THEIR DERIVATIVES.

BY MARSTON TAYLOR BOGERT AND JOHN ROSS TUTTLE.[1]

Received May 12, 1916.

The acids which are the subject of the present article are depicted by the following structural formulas:

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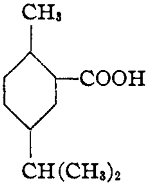
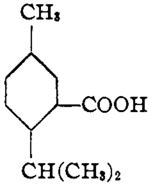
[1] The experimental work upon which this paper is based was carried out by Mr. Tuttle in partial fulfilment of the requirements for the degree of Doctor of Philosophy under the Faculty of Pure Science of Columbia University.



p-Cymene 2-Monocarboxylic Acid.



p-Cymene 3-Monocarboxylic Acid.

I. p-Cymene 2-Monocarboxylic Acid.—Paterno and Fileti,[1] in 1875, fused cymene sodium sulfonate with potassium cyanide and saponified the dark colored crude product with alcoholic potassium hydroxide solution, obtaining what was apparently the amide (m. 138–9°, corr.) of the cymene 2-carboxylic acid.

Four years later, Paterno and Spica,[2] by hydrolysis of this amide, secured what they believed to be the cymene carboxylic acid itself as a solid crystallizing from water in fine needles, m. 63°, but failed to get enough pure material for an analysis. They also endeavored to prepare this acid by the fusion of the corresponding cymene sodium sulfonate with sodium formate, and by the action of CO_2 and metallic sodium upon bromocymene, but were unsuccessful in both cases.

Kreysler[3] heated tricarvacryl phosphate with potassium cyanide and obtained, in an impure form, the nitrile of the desired acid. By heating this nitrile with alcoholic potassium hydroxide solution under pressure and purifying the product, an acid was isolated which on analysis gave figures agreeing with those calculated for cymene carboxylic acid. He described his product as forming colorless needles, m. 75°, and also prepared a silver salt.

In 1886, Cropp[4] described as a cymene monocarboxylic acid a substance m. 272° resulting from the oxidation of methyl p-cymyl ketone. Murtfeld,[5] in the following year, obtained an acid, m. 272°, by oxidation of di-p-cymyl ethylene diketone with dilute nitric acid at 150°, which he regarded as a cymene monocarboxylic acid and as probably identical with the acid mentioned by Cropp. Claus,[6] however, later showed that the supposititious cymene carboxylic acid of Cropp and Murtfeld was in all probability a mixture consisting mainly of methyl isophthalic acid (m. 320–330°).

Claus,[7] and Neukranz[8] by careful oxidation of methyl p-cymyl ketone

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[1] *Gazz. chim. ital.*, **5**, 30 (1875).

[2] *Ibid.*, **9**, 400 (1879).

[3] *Ber.*, **18**, 1714 (1885).

[4] *Inaug. Diss.*, Freiburg, **1886**; *Ber.*, **19**, 233 (1886).

[5] *Inaug. Diss.*, Freiburg, **1887**.

[6] *J. prakt. Chem.*, [2] **43**, 138 (1891).

[7] *Loc. cit.*

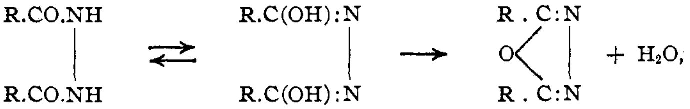
[8] *Inaug. Diss.*, Freiburg, **1891**.

with potassium permanganate, obtained a small amount of the cymene 2-carboxylic acid in small, colorless needles, m. 69° (uncorr.), which they stated sublimed in crystals when heated. In addition to the free acid, Neukranz prepared also the K, Ba, Ca, Cu and Ag salts, as well as an impure sodium salt. So far as we have been able to discover, these salts have never been described in any of the chemical journals and appear only in the above dissertation.

To sum up: small amounts of the free acid have been obtained hitherto and its m. p. has been given by these investigators as 63°, 69° or 75°; K, Ba, Ca, Cu, Ag and an impure Na salt have been described; also an amide and an impure nitrile.

The original work reported in the Experimental Part includes a method for preparing this acid in any desired amount from 2-bromocymene by the Barbier-Grignard reaction, a study of various salts and of the amide, the preparation and characterization of the hitherto unknown methyl and ethyl esters, the acid chloride, anilide, diacyl hydrazine, α,α'-dicymyl-[bb_1]-furodiazole, 2-methyl-5-isopropylhippuric acid and its ethyl ester. Preliminary studies have also been made upon the bromination of the free acid.

The furodiazole was easily obtained by the dehydration of the di-acyl hydrazine, as follows:



and the hippuric acid derivative by condensing the acid chloride with glycine ester,

$$R.CO.Cl + H_2N.CH_2.COOR \longrightarrow R.CO.NH.CH_2.COOR + HCl.$$

Incidentally, the experiments showed that the bromocymene produced by direct bromination of the hydrocarbon is not, as has been supposed hitherto, pure 2-bromocymene, but generally contains some of the 3-bromo isomer also, which cannot be separated by any ordinary fractional distillation.

The process of Paterno and Fileti, and of Paterno and Spica, has been repeated, and it has been found that the acid so obtained was an impure cymene 2-monocarboxylic acid.

II. *p*-Cymene 3-Monocarboxylic Acid.—Our search of the literature has so far failed to disclose any record of this acid or of any of its derivatives. The only reference to attempts to prepare it, appears to be the statement of Kreysler[1] that he endeavored unsuccessfully to obtain it by distilling tri-thymyl phosphate with potassium cyanide and saponi-

[1] *Loc. cit.*

fying the product; but he failed to get either the pure nitrile or sufficient of the acid to analyze or identify.

In the Experimental Part is recorded the synthesis of this acid from 3-bromocymene by the Barbier-Grignard reaction; also the preparation of its Na, K, Ba, Ca, Cu and Ag salts; its methyl, ethyl and phenyl esters, acid chloride, amide, anilide, and diacyl hydrazine; and, from the latter, the α,α'-dicymyl-[bb_1]-furodiazole and N-phenyl-α,α'-dicymyl-[bb_1]-pyrrodiazole; and the 3-methyl-6-isopropylhippuric acid from the acid chloride and glycine.

The yield of both cymene carboxylic acids was greatly increased by employing CO_2 under pressure, and a "Prana" carbonating siphon proved most convenient for the purpose.

EXPERIMENTAL PART.

I. *p*-Cymene 2-Monocarboxylic Acid.

Cymene.—The cymene used in these experiments was purified by the following process: (1) fractional distillation at ordinary pressure, (2) digestion with metallic sodium or phosphoric anhydride, (3) fractional distillation under reduced pressure, and (4) finally repeated rectification over metallic sodium at ordinary pressure. In spite of this, we failed to get a constant and unvarying boiling point, the purified hydrocarbon generally showing a corrected b. p. varying between the limits 176.5° and 178° at ordinary pressure. Density and refractive index determined on different lots showed the following range: D_{15} 0.8615 to 0.8622; $N_D^{20°}$ 1.4883 to 1.4897. This refractive index agrees with that calculated for the sodium line from the figures given by Perkin[1] for pure cymene at 4°, namely μ 7.9°/4° = 1.49664. Assuming that the difference for 1° is approximately that for benzene, namely 0.00066, then N at 20° would be 1.49664—0.00799 = 1.48865. Examined in a 200 mm. tube, the hydrocarbon showed no trace of rotation.

2-Bromocymene has been prepared by the direct bromination of cymene, in presence of small amounts of iodine as catalyst, by Landolph,[2] Fittica,[3] and by Remsen and Day;[4] by Kelbe and Koschnitzky,[5] by warming cymene sulfo acid with bromine water; and by Klages and Kraith[6] by the action of PBr_5 upon carvone. The b. p. is variously stated by these investigators as 228–9° (Fittica), 233° (Klages and Kraith) 233–5°, (in vapor) (Landolph), and 237° (corr.) (or 228–9°, uncorr.) (Remsen and Day).

According to our experiments, the most convenient method of prepara-

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[1] *J. Chem. Soc.*, **77**, 279 (1900).

[2] *Ber.*, **5**, 267 (1872).

[3] *Ann.*, **172**, 311 (1874).

[4] *Am. Chem. J.*, **5**, 150 (1883).

[5] *Ber.*, **19**, 1732 (1886).

[6] *Ibid.*, **32**, 2557 (1899).

tion proved to be the following: Bromine (about 10% excess) was added very gradually to pure cymene containing a small amount of iron powder as catalyst, the reaction being carried out in a flask protected from strong daylight, and cooling when necessary to moderate the reaction. The mixture was then warmed on the water bath, the HBr and excess of bromine blown out by a current of dry air, the crude product washed with water, digested with warm sodium carbonate solution, washed again with water, distilled with steam, the oily layer separated from the distillate, dried over calcium chloride, and fractioned under reduced pressure. The fraction b. 116.5–118.5° at 14.7 mm. (corr.) was employed in the subsequent experimental work. The yield of this purified material from 915 g. cymene amounted to 630 g. and its uncorrected b. p. at ordinary pressure was 231–3°.

The use of an excess of bromine was found to increase the yield of bromocymene, whereas the length of time the reaction mixture was allowed to stand after the addition of the bromine did not appear to influence the yield materially. Iron powder proved a much more active catalyst than iodine for this reaction. Fractionation under diminished pressure was necessary, as some decomposition occurred at the ordinary pressure. No unchanged cymene was found in the product, and the purified substance was colorless with a pleasant odor somewhat recalling that of cymene itself. The subsequent work with this product, however, proved conclusively that it was contaminated with the 3-bromo isomer, and the boiling points of the two lie so close together that it was impossible to separate them by fractional distillation.

Some 2-bromocymene was, therefore, prepared also by the action of PBr_5 upon purified carvacrol, in practically the same way as Fileti and Crosa[1] made the 3-bromo isomer from thymol. The yield was not very good, as considerable of the phenol remains behind as a phosphoric ester (from which it can be recovered if desired). 57 g. carvacrol gave 8.6 g. of the 2-bromocymene, b. 232–5° (uncorr.).

Large amounts of bromocymene can be prepared easily by the direct bromination of the hydrocarbon, as described above, but the product is a mixture of the two isomers. On the other hand, it is not very convenient to prepare large amounts of 2-bromocymene from carvacrol, but the product so obtained is free from the 3-bromo isomer.

Cymene 2-Carboxylic Acid.—In view of Landolph's observation[2] that the bromine in 2-bromocymene does not react with metallic sodium, alone or in the presence of methyl iodide or CO_2, it was to be expected that it would prove somewhat unreactive even with magnesium, and this was found to be the case not only with this particular bromocymene

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[1] *Gazz. chim. ital.*, 16, 292 (1886).

[2] *Loc. cit.*

but also with the isomeric 3-bromo compound. An anhydrous ethereal solution of either compound showed no evidence of any reaction upon boiling with metallic magnesium for about an hour, even after the addition of small amounts of iodine. To activate the magnesium, it was found advantageous to add a few drops of ethyl iodide. If, then, after a few minutes' standing, the anhydrous ether solution of bromocymene was added, the mixture being warmed, the reaction began immediately and proceeded to completion without further external heating, the bromocymene solution being added gradually from time to time. When the latter had all been added, the solution was heated for a short time on the water bath, when the magnesium almost wholly dissolved. The solution was cooled, and siphoned carefully into a "Prana" carbonating flask in such a way as to avoid contact with the moisture of the air, both containers being protected by calcium chloride guard tubes. The Prana flask was kept in a freezing mixture, and the solution therein treated with CO_2 under pressure for several hours, using capsules of the liquid gas. This caused the mixture to separate into a clear upper ethereal layer and a lower darker one. The contents of the flask were decomposed with ice and dilute hydrochloric acid in the usual way, extracted with ether, the ether solution extracted in turn with sodium carbonate or potassium hydroxide solution, the alkaline solution concentrated somewhat, acidified with dilute hydrochloric acid, the white precipitate filtered out, washed, dried, and recrystallized. The yield of pure acid amounted to about 35%, when a pure 2-bromocymene was used. If the CO_2 was not used under pressure, the yield was much less.

The 2-bromocymene used in the early experiments was made from carvacrol, so as to avoid complications due to the presence of the isomer. In a sample experiment, 8.6 g. of the bromocymene and 1 g. magnesium, yielded 2.7 g. of the crude acid, or about 40% of the theoretical. A small amount of cymene was usually formed in the reaction.

The crude acid was purified by dissolving it in about its own weight of glacial acetic acid, adding water until the solution clouded, warming until it cleared, and then allowing the solution to cool slowly, finally in the ice box. It can be crystallized also from dilute alcohol, but the crystals are not usually so fine as those secured by the above method.

The pure acid forms large, colorless, brittle, glassy prisms, m. 71.7° (corr.), difficultly soluble in cold water, slightly in hot; soluble in methyl or ethyl alcohol, ether, ligroin, benzene, xylene, chloroform, carbon tetrachloride, acetone, carbon disulfide, glacial acetic acid or ethyl acetate. It volatilizes slowly with steam, but does not sublime, contrary to the statement of Claus and Neukranz.[1] It can be distilled under reduced

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[1] *Loc. cit.*

pressure, and boils at about 171–2° at 20 mm. Distilled with excess of soda lime, it gives cymene again.

The following analysis was made of a sample of purified acid prepared from cymene:

Subs. 0.1662: CO_2, 0.4515; H_2O, 0.1137. Calc. for $C_{11}H_{14}O_2$: C, 74.16; H, 7.87. Found: C, 74.09; H, 7.60.

Cryoscopic molecular weight determinations in acetic acid gave the figures 171 and 176, while the calculated molecular weight is 178.

The preparation of pure 2-acid from the bromocymene obtained from cymene proved very troublesome, on account of the presence of the 3-isomer. In one experiment, for example, a mixture of 200 g. bromocymene, 23 g. magnesium and 400 cc. anhydrous ether, was treated for about $10^1/_2$ hours with CO_2 under pressure, supplying the latter as fast as it was absorbed. In all, a total of 68 g. liquid CO_2 was used, the amount theoretically required being about 40 g. The reaction was conducted at a temperature of —13° to —3°. 60 g. of crude acid were obtained, as a yellowish semi-solid mass, which proved very difficult to purify. By fractional crystallization, only 30 g. of pure 2-acid could be recovered. The mother-liquors were united, the acid neutralized with sodium carbonate, the solution filtered, washed with ether, warmed to eliminate any dissolved ether, and then fractionally precipitated with dilute hydrochloric acid. The 2-acid was found in the first fractions, the 3-acid in the later ones, the intermediate fractions being mixtures of the two.

In another experiment, 230 g. bromocymene and 27 g. magnesium were used, and the crude acid was distilled under reduced pressure. 105 g. of impure 2-acid resulted, from which by filtering and pressing 79 g. solid acid were obtained. When these 79 g. were converted into the sodium salt and the solution of the latter precipitated fractionally by dilute hydrochloric acid, 36 g. pure 2-acid and 9 g. pure 3-acid were recovered.

Sodium Salt, NaA.—This was prepared in the same way as described below for the potassium salt. It does not crystallize well, but forms a white powder, without water of crystallization, and is not hygroscopic.

Subs. 0.3190: Na_2SO_4, 0.1105. Calc. for $C_{11}H_{13}O_2Na$: Na, 11.50. Found: Na, 11.23.

Neukranz[1] prepared a sodium salt, which on analysis was found to contain 23.22% sodium, and which must, therefore, have been very impure. Apparently, his calculations misled him, as he puts down for the calculated percentage of sodium in this salt 23.5, whereas as a matter of fact it is 11.5, as stated above.

Potassium Salt, KA.H_2O.—A 5% aqueous solution of potassium hydroxide was treated with a slight excess of the 2-acid, the mixture allowed to stand for a few hours and the excess of free acid (which is prac-

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[1] *Loc. cit.*

tically insoluble in cold water) then filtered off. The filtrate was concentrated on the water bath to a paste and then placed in a desiccator where it gradually became crystalline. It carries one molecule of water of crystallization, but is not appreciably hygroscopic.

0.2550 g. salt dried to constant weight in desiccator over H_2SO_4, and then heated to constant weight at 115°, lost 0.0194 g. Calc. for $C_{11}H_{13}O_2K.H_2O$: H_2O, 7.69. Found: H_2O, 7.61.

Anhydrous salt, 0.2845: K_2SO_4, 0.1142. Calc. for $C_{11}H_{13}O_2K$: K, 18.09. Found: K, 18.03.

It forms small, colorless, glassy crystals. Neukranz makes no mention of any water of crystallization in the potassium salt he prepared.

Calcium Salt, $CaA_2.2H_2O$.—This was made in the same manner as the barium salt below. In water, it is much less soluble than the latter, and but little more soluble in hot water than in cold. Upon evaporation of the aqueous solution, the salt separates gradually in fine colorless crystals, which were dried in a desiccator.

Heated to const. wt. at 105–10°, the salt lost 8.32%. Calc. for 2 H_2O: 8.37%.

Anhydrous salt, 0.2765: $CaSO_4$, 0.0952. Calc. for $(C_{11}H_{13}O_2)_2Ca$: Ca, 10.15. Found: Ca, 10.12.

Neukranz also reports the calcium salt as containing two molecules of water of crystallization.

Barium Salt, BaA_2.—The acid was suspended in water and digested with excess of $BaCO_3$ at 100° for three or four hours. It was then filtered, the filtrate again digested with $BaCO_3$, to make sure that all acid was converted into the salt, and once more filtered. The filtrate was concentrated until the salt began to separate and was then left in a desiccator over H_2SO_4 for several days, where it slowly solidified. Dried at 105–110°, and then for two hours at 120–5°, it lost 1.5% in weight, whereas the loss calculated for one molecule water is 3.42. Evidently the salt either crystallizes without water of crystallization, or else this water is lost partly when the salt is left for a few days over H_2SO_4.

Anhydrous salt, 0.3584: $BaSO_4$, 0.1687. Calc. for $(C_{11}H_{13}O_2)_2Ba$: Ba, 27.90. Found: Ba, 27.70.

The barium salt isolated by Neukranz carried two molecules of water.

The **Copper Salt,** CuA_2, was prepared by warming a solution of the calcium salt with an excess of copper acetate solution. A voluminous blue precipitate resulted. It was filtered out, washed and dried over H_2SO_4. As no loss of weight occurred at 120°, the salt carries no water of crystallization.

Calc. for $(C_{11}H_{13}O_2)_2Cu$: Cu, 15.23. Found: Cu, 15.62.

This high figure for the copper is probably due to the presence of a little adsorbed copper acetate, as the voluminous precipitate was not easily washed.

Neukranz reports a copper salt carrying one molecule of water of crystallization.

The **Silver Salt,** AgA, was prepared by dissolving the acid in ammonium hydroxide solution, warming to remove all excess of ammonia, and then adding silver nitrate solution. The acid used was obtained from carvacrol, and the salt was, therefore, analyzed completely, as a check upon the accuracy of the work.

Subs. 0.2155, 0.2350: Ag, 0.0814; CO_2, 0.4012; H_2O, 0.0946.

Calc. for $C_{11}H_{13}O_2Ag$: Ag, 37.87; C, 46.33; H, 4.56. Found: Ag, 37.77; C, 46.52; H, 4.47.

It is a colorless, crystalline powder, which darkens on standing in the light, and has been prepared also by Kreysler[1] and by Neukranz.

Methyl Ester, $C_{10}H_{13}COOCH_3$.—Three grams of methyl alcohol were dissolved in 25 cc. pyridine and 9.5 g. of the chloride of cymene 2-carboxylic acid added gradually with cooling and shaking. The reaction liberated considerable heat, but no precipitate separated until the last few drops of the acid chloride were being run in, when it began to form rapidly and in large amount. After standing for five hours, the mixture was poured into well cooled dilute sulfuric acid. A colorless oil separated, which was removed, washed four times with acidulated water to eliminate all pyridine, then with dilute potassium hydroxide solution to remove any free 2-acid (of which there proved to be very little), after which it was collected with ether, the ethereal solution washed, dried, the ether distilled off and the residue fractioned at a pressure of 16.2 mm. (corr.), the ester coming over at 132°, as a colorless oil of pleasant odor.

Subs. 0.1150: CO_2, 0.3157; H_2O, 0.0860. Calc. for $C_{12}H_{16}O_2$: C, 75.00; H, 8.33. Found: C, 74.87; H, 8.31.

The **Ethyl Ester** was obtained by dissolving the acid in a slight excess of potassium hydroxide solution, and then digesting with diethyl sulfate, essentially as described beyond for the ethyl ester of the 3-acid.

It is a colorless heavy oil of pleasant ethereal odor, which can be saponified readily to the acid by alcoholic potassium hydroxide solution.

Acid Chloride, $C_{10}H_{13}.CO.Cl$.—The anhydrous acid was treated, in a flask provided with a calcium chloride guard tube, with slightly more than the calculated amount of PCl_5. Upon shaking the mixture, the reaction began almost immediately and proceeded so vigorously that within two or three minutes, with the exception of a small amount of PCl_5, the whole mass was liquid and quiescent. After standing for three-quarters of an hour, it was warmed for 15 minutes at 100°, when the small amount of undissolved PCl_5 went into solution, and was then transferred to a distilling flask and fractioned under reduced pressure, the acid chloride coming over as a clear colorless liquid of pungent odor, b. 131.5–132°

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[1] *Loc. cit.*

at 17.7 mm., or 135.5–136° at 21.5 mm. The yield was usually better than 90%. In one experiment, for example, 21 g. acid gave 23.5 g. of the chloride.

Acid Amide, $C_{10}H_{13}.CO.NH_2$.—Prepared from the acid chloride, in practically the same way as described beyond for the amide of the 3-acid, this substance crystallizes from ligroin, water or dilute alcohol, in microscopic needles which felt together like shredded asbestos, and m. 147° (corr.). It is soluble in methyl alcohol, ethyl alcohol, or warm benzene; slightly soluble in ether or in cold carbon tetrachloride; insoluble in cold, slightly soluble in hot ligroin. Yield, 95%.

Subs. 0.1878: 12.7 cc. N at 21° and 762 mm. Calc. for $C_{11}H_{15}ON$: N, 7.91. Found: N, 7.69.

An attempt to convert this amide into the phenyl hydrazide by heating it for $2^1/_2$ hours at 150–160° with phenyl hydrazine failed, the amide being recovered practically unchanged.

Acid Anilide, $C_{10}H_{13}.CO.NHC_6H_5$.—This was obtained from the acid chloride and aniline, in anhydrous ether solution, as outlined beyond for the anilide of the 3-acid. Yield, 87%.

The pure substance crystallizes from ligroin or dilute alcohol in small, colorless, glassy prisms, m. 143.5° (corr.); soluble in methyl or ethyl alcohols, in benzene, chloroform, acetone or amyl acetate; but slightly soluble in ether, hot water or cold ligroin; fairly soluble in cold carbon disulfide or carbon tetrachloride, easily soluble in the same hot.

Subs. 0.2521: 12.4 cc. N at 21° and 756 mm. Calc. for $C_{17}H_{19}ON$: N, 5.53. Found: N, 5.54.

Sym.-**2,2′-Dimethyl-5,5′**-diisopropyl **Dibenzoylhydrazine,** $C_{10}H_{13}.CO.NH.NH.CO.C_{10}H_{13}$.—In the production of this diacyl hydrazine, both the ordinary 50% aqueous solution of hydrazine hydrate was employed and also the more concentrated solution obtained by distilling the former until the temperature of the distillate reached 115°, when the residue is stated[1] to contain 55–60% of absolute N_2H_4 or 90% of $N_2H_4.H_2O$. The results secured with the 50% aqueous solution were just as good as those with the more concentrated solution.

In a typical experiment, 13.5 g. acid chloride were dissolved in 4 cc. absolute ether and the solution added very gradually with shaking to an excess (approximately 4 mols) of well cooled hydrazine hydrate solution. A white precipitate began to separate immediately and slowly increased in amount. After all the acid chloride had been added (about an hour), the mixture was a white, pasty mass of strong alkaline reaction, due to the excess of hydrazine hydrate present. After standing for three hours, it was filtered, the precipitate washed thoroughly with cold

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[1] Curtius, *J. prakt. Chem.*, [2] 42, 523 (1890).

water, dried, and crystallized from dilute alcohol.[1] Yield, 91% (11 g.).

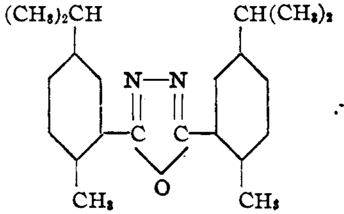
The pure substance crystallizes in minute, colorless, glassy prisms, m. 192° (corr.); insoluble in ligroin or water; moderately soluble in chloroform or acetic acid; little soluble in ether or in cold alcohol, benzene or acetone, but readily soluble in the latter at their b. p. It forms no salts with hydrochloric or nitric acids, even in non-aqueous solvents.

Subs. 0.2341 g.: 16.8 cc. N at 21° and 754 mm. Calc. for $C_{10}H_{13}.CO.NH.NH.CO.C_{10}H_{13}$: N, 7.95; for $C_{10}H_{13}.CO.NH.NH_2$: N, 14.56. Found: N, 8.07.

An attempt was made to secure the monacyl hydrazine by heating the amide with excess of hydrazine hydrate alone, and in alcoholic solution, but the amide was recovered unchanged in both cases.

The diacyl hydrazine is unattacked by nitrous acid in glacial acetic acid solution.

α,α′-2,2′-Di-*p*-cymyl-[*bb*₁]-furodiazole,



.—The diacyl hydrazine was heated for an hour and three-quarters at 260–80° (thermometer in melt), and then cooled. The cold melt was purified by repeated crystallization from methyl alcohol in presence of boneblack.

The pure compound forms small, colorless, glassy prisms, m. 111.5° (corr.), quite soluble in benzene or chloroform, less so in benzine or acetone; slightly soluble in cold methyl alcohol or ethyl alcohol; and practically insoluble in water.

Subs. 0.1579: 11.83 cc. N at 21° and 752 mm. Calc. for $C_{22}H_{26}ON_2$: N, 8.38. Found: N, 8.40.

An effort was made to get the corresponding thiodiazole by the action of P_2S_5 upon the diacyl hydrazine, but the product was a mixture of furo- and thiodiazole, from which we failed to isolate any really pure thiodiazole.[2]

2-Methyl-5-isopropyl Hippuric Acid and its Ethyl Ester, $C_{10}H_{13}.CO.NH.CH_2.COOH$.—35 g. of the acid chloride were added slowly, with cooling and shaking, to an excess of glycine ester in ethereal solution. A white precipitate separated. After standing at laboratory temperature for three hours, the white precipitate of glycine ester hydrochloride was filtered out, and the ethereal filtrate evaporated, leaving an oily residue,

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[1] Compare also Pellizzari, *Atti r. Accad. Lincei Roma* [5] 8, I, 327; *Chem. Zentralbl.*, 1899, I, 1240; Stollé, *J. prakt. Chem.*, [2] 69, 474 (1904).

[2] Compare also Stollé, *J. prakt. Chem.*, [2] 69, 157, 374 (1904); Stevens, *Inaug. Diss.*, Heidelberg, 1899.

which was washed with dilute hydrochloric acid to remove any glycine ester present, taken up again with ether, the ethereal solution washed with dilute potassium hydroxide solution, to remove any free 2-acid, then with water, dried with calcium chloride, and the ether removed by evaporation. The residue was an oil, which did not solidify in an ordinary freezing mixture of ice and salt. As it was deemed unwise to attempt further purification by distillation, on account of the small amount in hand and the likelihood of some decomposition on heating,[1] the ester was saponified to the free acid by careful hydrolysis with alcoholic potassium hydroxide solution.[2]

After warming the ester on the water bath for a few minutes, a drop of the mixture was completely soluble in water, showing the total hydrolysis of the ester, and the solution was then largely diluted with water and acidified cold with dilute hydrochloric acid. A yellowish precipitate appeared, which was filtered out, washed, dried, washed with ligroin, to eliminate any 2-acid, again dried, and finally crystallized from very dilute alcohol.

As thus purified, it forms colorless, glassy scales, m. 183° (corr.); apparently insoluble in water or ligroin; slightly soluble in benzene, ether or chloroform; quite soluble in methyl or ethyl alcohol or in acetone.

Subs. 0.2632 g.: 14.0 cc. N at 21° and 748 mm. Calc. for $C_{10}H_{13}.CO.NH.CH_2.COOH$: N, 5.96. Found: N, 5.93.

Repetition of the Method of Paterno and Fileti,[3] and of Paterno and Spica.[4]—The anhydrous barium sulfonate of cymene was distilled dry with potassium cyanide, and the sodium sulfonate with potassium cyanide and with potassium ferrocyanide. In all cases, the results were most unsatisfactory, on account of the large amount of decomposition. The best results were secured by intimately mixing 10 g. anhydrous sodium sulfonate with an equal weight of potassium cyanide and heating the mixture as uniformly as possible, the temperature being raised gradually (5 minutes) until the thermometer registered 240° for the vapor distilling over, and then raising it to 240–300° for 10 minutes. Washed with sodium hydroxide solution, the crude liquid distillate amounted to 2.5 g.

20 g. of the crude nitrile so obtained were distilled with steam, the yellow, oily distillate collected with ether, dried with calcium chloride, and fractioned. The first fractions (below 200°) were obviously cymene; from 200 to 255°, 5.5 g. of impure nitrile were collected as a pale yellow liquid. Kreysler[5] gives the b. p. of the nitrile as 244–6°. This impure

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[1] *J. prakt. Chem.*, [2] **15**, 247 (1877).

[2] Compare *J. Chem. Soc.*, **79**, 397 (1901); *Ber.*, **31**, 3276 (1898).

[3] *Gazz. chim. ital.*, **5**, 30 (1875).

[4] *Ibid.*, **9**, 400 (1879).

[5] *Ber.*, **18**, 1714 (1885).

nitrile was saponified by boiling it with alcoholic potassium hydroxide solution under a reflux condenser. When the heating was continued for about 24 hours, the product was almost exclusively the amide; longer heating gave increasing amounts of the acid.

The amide so obtained crystallized from water in colorless, glassy needles, m. 138–41° (corr.), and this m. p. could not be altered either by further crystallization or by fractional crystallization. Paterno and Fileti give the m. p. of their amide as 138–9° (corr.). The above amide, m. 138–41°, mixed with some amide of the 2-acid prepared from the chloride of the 2-acid, showed a m. p. of 139–44° (uncorr.); but, when mixed with the amide of the 3-acid, melted at 121–32° (uncorr.).

A small amount of cymene 2-carboxylic acid recovered in the above saponification, when recrystallized from dilute alcohol, showed a m. p. 69–71°, and when mixed with some pure 2-acid, m. 69–72°. The acid obtained by Paterno and Spica, therefore, by fusing the amide with potassium hydroxide, or by heating it with concentrated hydrochloric acid at 180°, was manifestly an impure cymene 2-monocarboxylic acid.

II. *p*-Cymene 3-Carboxylic Acid.

3-Bromocymene has been prepared by Von Gerichten[1] and by Fileti and Crosa[2] by the action of PBr_5 upon thymol. The latter give the b. p. as 232–3° (in the vapor) at 740.9 mm. (reduced to 0°). Kelbe and Koschnitzky[3] claimed to have obtained this bromocymene from what they believed to be the 3-bromocymene-6-sulfo acid; but Claus and Christ[4] were of opinion that the product obtained by these investigators was in reality the 2-bromocymene.

The 3-bromocymene used in the following experiments was made by the method of Fileti and Crosa from thymol and PBr_5, and our yields checked those of these investigators (60%). The purified material showed a b. p. 231.2–233.2° (corr.). It was found, further, that any increase in the amount of PBr_5 above that given by Fileti and Crosa resulted in a decreased yield.

An effort was made to help the yield by the addition of fused zinc bromide to the reaction mixture, since Dehn and Davis[5] have shown that the presence of zinc chloride materially increases the amount of alkyl halide obtainable from the alcohol and phosphorus halide, but the results were unsatisfactory. The effect of fused zinc bromide upon tri-thymyl phosphate was also studied, in the hope that thereby the bromocymene might be secured directly from the phosphate which is a by-product in

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[1] *Ber.*, 11, 1719 (1878).

[2] *Gazz. chim. ital.*, 16, 292 (1886).

[3] *Ber.*, 19, 1731 (1886).

[4] *Ibid.*, 19, 2165 (1886).

[5] THIS JOURNAL, 29, 1328 (1907).

the preparation of the bromocymene from thymol and PBr_5. It was expected that reaction might occur in the following sense:

$$2(C_{10}H_{13})_3PO_4 + 3ZnBr_2 = 6C_{10}H_{13}Br + Zn_3(PO_4)_2$$

The results were disappointing, for on distilling 60 g. of the tri-thymyl phosphate and 40 g. anhydrous zinc bromide (in intimate mixture) from a retort, but small amounts of the bromocymene were formed.

As has been pointed out already, in the foregoing, 3-bromocymene is also produced in the direct bromination of cymene.

***p*-Cymene 3-Carboxylic Acid,** $C_{10}H_{13}.COOH$, was prepared from 3-bromocymene, magnesium and CO_2, practically as described already for the isomeric 2-acid. In a typical experiment, 119 g. 3-bromocymene, 13.6 g. magnesium, and 300 cc. absolute ether, were treated for 16 hours with excess of CO_2 under pressure, at a temperature below —5°. The yield of crude acid was 55 g., or approximately 55% of the theoretical.

Purified by crystallization from dilute alcohol, this acid forms colorless, glassy needles, m. 84° (corr.); practically insoluble in cold water; difficultly soluble in hot water; more or less soluble in ligroin, benzene, xylene, methyl or ethyl alcohols, chloroform, carbon tetrachloride, acetone, carbon disulfide, dilute acetic acid or in ethyl acetate. It does not sublime, but distils at ordinary pressure with but little decomposition, b. 285° (corr.), and the distillate immediately solidifies. It volatilizes quite easily with steam, and when distilled with excess of soda lime gives cymene again. The unsatisfactory m. p. often found for this acid is due in most cases to moisture, rather than to the presence of other contaminants. For a sharp m. p., the acid must be dried for several days in a vacuum desiccator over calcium chloride, or heated for a short time at 65–70°.

Subs. 0.1800, 0.2034: CO_2, 0.4891, 0.5531; H_2O, 0.1264, 0.1455. Calc. for $C_{11}H_{14}O_2$: C, 74.16; H, 7.87. Found: C, 74.11, 74.16; H, 7.80, 7.95.

A cryoscopic molcular-weight determination in acetic acid gave the figures 172 and 175, the calculated figure being 178.

Sodium Salt, NaA.—The barium salt was dissolved in hot water, and a dilute solution of sodium carbonate added carefully as long as it caused a precipitate. The precipitated barium carbonate was then filtered out and the filtrate concentrated. As the salt is very soluble in water, this concentration must be carried practically to dryness. The salt is thus obtained as a white, pulverulent solid, which appears to deliquesce at 10°, but loses this water again at room temperature. It crystallizes without water of crystallization.

Anhydrous salt, 0.3100: Na_2SO_4, 0.1147. Calc. for $C_{11}H_{13}O_2Na$: Na, 11.50. Found: Na, 11.99.

Potassium Salt, KA.—A dilute solution of potassium hydroxide was treated with excess of the pure 3-acid, the excess of acid filtered out of the cold solution, and the filtrate evaporated. The salt is very easily soluble in water, but carries no water of crystallization. It is a white powder.

Anhydrous salt, 0.3226: K_2SO_4, 0.1280. Calc. for $C_{11}H_{13}O_2K$: K, 18.09. Found: K, 17.82.

Barium Salt, $BaA_2.2H_2O$.—Some of the free acid was suspended in hot water and digested for four or five hours with excess of barium carbonate at 100°. The acid dissolved gradually. The excess of barium carbonate was removed, and the filtrate concentrated to small volume, the salt then separating as a colorless solid, quite easily soluble in hot water.

Subs. 0.3412, heated to constant weight at 110°: H_2O, 0.0237. Calc. for $(C_{11}H_{13}O_2)_2Ba.2H_2O$: H_2O, 6.83. Found: H_2O, 6.94.

Anhydrous salt, 0.3146: $BaSO_4$, 0.1476. Calc. for $(C_{11}H_{13}O_2)_2Ba$: Ba, 27.9. Found: Ba, 27.6.

Calcium Salt, $CaA_2.2H_2O$.—This salt was prepared in the same manner as the above Ba salt. It is much less soluble in water than the latter, and only slightly more soluble in hot than in cold water, separating in imperfect crystals.

Subs. 0.2882, dried to constant weight at 110°: H_2O, 0.0238. Calc. for $(C_{11}H_{13}O_2)_2Ca.2H_2O$: H_2O, 8.37. Found: H_2O, 8.26.

Anhydrous salt, 0.2644: $CaSO_4$, 0.0892. Calc. for $(C_{11}H_{13}O_2)_2Ca$: Ca, 10.15. Found: Ca, 9.96.

Copper Salt, CuA_2.—A copper acetate solution was added carefully to a hot aqueous solution of the calcium salt of the acid. The copper salt separated as an amorphous, light blue precipitate, which was filtered out, washed and dried. It is practically insoluble in water, but quite soluble in hot alcohol or in hot benzene, and crystallizes from alcohol in greenish blue microscopic needles, without water of crystallization.

Silver Salt, AgA.—This was prepared in the same manner as the silver salt of the 2-acid. It is colorless, apparently fairly stable in the light, and is somewhat soluble in water.

Subs. 0.2595, 0.2033: Ag, 0.0982; CO_2, 0.3487; H_2O, 0.0851. Calc. for $C_{11}H_{13}O_2Ag$: Ag, 37.87; C, 46.33; H, 4.56. Found: Ag, 37.84; C, 46.77; H, 4.65.

Methyl Ester, $C_{10}H_{13}.COOCH_3$.—17 g. of the 3-acid were dissolved in a small excess of 10% potassium hydroxide solution, 23 g. of dimethyl sulfate added, and the mixture shaken vigorously for three hours. It was then heated for an hour on the water bath, to decompose any unchanged dimethyl sulfate, cooled, made slightly alkaline with potassium hydroxide and distilled with steam. The ester came over slowly as a colorless, heavy oil. It was collected with ether, the ethereal solution dried with calcium chloride, the ether distilled off and the residue fractioned at 13.5 mm. (reduced to 0°), most of the ester (6.3 g.) then coming over at 128–9°, as a colorless liquid, with a characteristic pleasant odor.

Upon acidifying the residue from the steam distillation, 3.2 g. of the acid were recovered, its formation being probably referable to hydrolysis during the distillation with steam.

Subs. 0.1938: CO_2, 0.5324; H_2O, 0.1436. Calc. for $C_{12}H_{16}O_2$: C, 75.00; H, 8.33. Found: C, 74.92; H, 8.23.

Ethyl Ester.—15 g. of the acid were dissolved in a slight excess of potassium hydroxide solution, 25 g. (two mols) of diethyl sulfate added, the mixture shaken mechanically for three hours, and finally heated for an hour at 100°, to decompose the excess of diethyl sulfate. The ester separated as a pale yellowish oil. The mixture was made alkaline with KOH, the ester extracted with ether, the ether dried with calcium chloride, the solvent distilled off, and the residue fractioned under reduced pressure, collecting the fraction b. 141–2° at 13.5 mm. (corr.).

The product was a colorless oil, of pleasant odor, similar to that of the methyl ester but rather stronger. By acidifying the aqueous solution, after the ether extraction, some of the original acid was recovered.

Subs. 0.2059, 0.1413: CO_2, 0.5547, 0.3807; H_2O, 0.1596, 0.1100. Calc. for $C_{13}H_{18}O_2$: C, 75.72; H, 8.74. Found: C, 73.47, 73.48; H, 8.61, 8.65.

The product was, therefore, somewhat impure, the source of this contamination being possibly the commercial diethyl sulfate employed.

Phenyl Ester.—2.3 g. phenol (theory 2.1) were dissolved in 15 cc. pyridine, and 4.2 g. acid chloride added gradually with shaking and cooling. The solution soon turned red, and a white precipitate separated of pyridine hydrochloride. After standing overnight in the ice box, the mixture was poured into cold dilute sulfuric acid. An oil collected, which was washed thoroughly with water, to remove all pyridine, then with dilute caustic alkali, to remove any 3-acid, after which it was taken up in ether, the solution dried with calcium chloride, the ether evaporated and the residue fractioned at 22.5–24.5 mm. when it distilled at 199–208°. It remained a liquid, and all attempts to congeal it by freezing, or by leaving it in a desiccator over concentrated H_2SO_4, failed. The inference, therefore, is that this ester is either a liquid at ordinary temperatures or a low-melting solid.

The **Acid Chloride** was prepared in much the same way as the chloride of the 2-acid. The yield was 93% or better.

In the pure state, it is a colorless mobile liquid of penetrating odor, b. 115–6° at 9.2 mm., or 128–9° at 20.1 mm., and is slowly hydrolyzed by cold water.

Acid Amide.—3 g. of the acid chloride were dissolved in a small amount of anhydrous ether and a rapid current of dry ammonia past into the solution, cooling the vessel with a freezing mixture. An abundant white precipitate rapidly separated. The solution, saturated with ammonia, was allowed to stand for a short time and then filtered. Very little amide remained in the ethereal filtrate. The original precipitate was washed thoroughly with water, to eliminate ammonium chloride, dried and crystallized from benzene. Yield before crystallization, 93%.

The pure amide crystallizes from benzene in radiating clusters of minute colorless, silky needles which mat together, and m. 137.5° (corr.). It is but slightly soluble in cold ligroin, benzene, ether or carbon tetrachloride; somewhat soluble in hot water; quite soluble in methyl or ethyl alcohol or in chloroform; and crystallizes well from either ligroin, benzene or carbon tetrachloride.

Subs. 0.2419: N, 16.82 cc. at 21° and 753 mm. Calc. for $C_{11}H_{15}ON$: N, 7.91. Found: N, 7.81.

Acid Anilide.—A dry ether solution of 3 g. of the acid chloride was added gradually, with shaking and cooling, to a dry ether solution of 6 g. aniline (4 mols.). A colorless precipitate appeared, and heat was liberated in the reaction. After standing overnight, the mixture was filtered and anilide was found both in the original precipitate and in the ethereal filtrate. From the latter, it was recovered by simple evaporation of the solvent; from the former, by washing with water, to remove aniline salt. The two lots thus secured were united, washed with a little dilute hydrochloric acid, to eliminate final traces of aniline, then with water, and dried. Yield, 74%.

The anilide is quite soluble in methyl alcohol, ethyl alcohol, ether, benzene, or chloroform, and but slightly soluble in water. It can be crystallized from ligroin, carbon tetrachloride or dilute alcohol. From the latter, it separates in beautiful colorless, silky needles, m. 151° (corr.).

Subs. 0.3350, 0.2722: N, 17.1 cc. at 19° and 751 mm.; 13.1 cc. at 18.5° and 762 mm. Calc. for $C_{17}H_{19}ON$: N, 5.53. Found: N, 5.78, 5.53.

***Sym.*-3,3′-Dimethyl-6,6′-diisopropyl Dibenzoylhydrazine,** $C_{10}H_{13}.CO.NH.NH.CO.C_{10}H_{13}$.—The procedure for the synthesis of this hydrazine was the same as in the case of the analogous derivative of the 2-acid, using 10 g. of the acid chloride and 11 g. of 50% aqueous hydrazine hydrate solution. The crude product was washed with water, to remove hydrazine salt, and then with dilute sodium hydroxide solution, to eliminate any 3-acid. Acidification of the alkaline washings showed that practically none of the acid chloride had been hydrolyzed. Yield of crude diacyl hydrazine, 93%.

The pure compound crystallized in fine, colorless, silky needles, from alcohol, and m. 213.5° (corr.). It is very slightly soluble in ether, slightly soluble in chloroform or acetic acid, and moderately soluble in methyl alcohol, ethyl alcohol, benzene or acetone.

Subs. 0.1645: N, 11.90 cc. at 21° and 753 mm. Calc. for $C_{22}H_{28}O_2N_2$: N, 7.95. Found: N, 8.12.

α,α'-3,3′-Di-*p*-cymyl-[*bb*$_1$]-furodiazole was obtained by heating 2.5

g. of the above diacyl hydrazine at 200° or higher for about two hours, cooling, and extracting with benzene. The insoluble residue, 0.5 g. in amount, proved to be unchanged diacyl hydrazine. The benzene solution was boiled with boneblack, filtered, and the benzene evaporated, leaving behind 1.3 g. of the furodiazole sought.

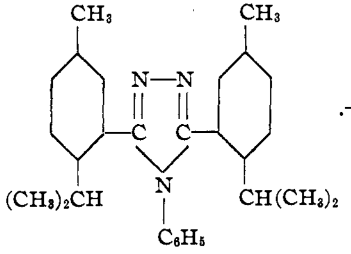
Crystallized from methyl alcohol, this diazole forms long, colorless, silky needles, much like the corresponding derivative of the 2-acid, and m. 132.5° (corr.). It is insoluble in water, slightly soluble in methyl alcohol or ethyl alcohol; quite soluble in benzene, benzine, chloroform, ether or acetone.

Subs. 0.1739: N, 12.9 cc. at 20.5° and 750.7 mm. Calc. for $C_{22}H_{26}ON_2$: N, 8.38. Found: N, 8.32.

An attempt to obtain the hydrazide chloride by the action of PCl_5 upon the diacyl hydrazine, as described by Stollé[1] gave a final product composed of the furodiazole mixed with the hydrazide chloride sought, but the latter is apparently so unstable and reactive that our efforts to separate it in the pure state were fruitless. That it was present in the mixture was demonstrated by the amount of halogen found, the liberation of HCl during the attempted purification, and the production therefrom of the pyrrodiazole noted beyond.

The action of P_2S_5 upon the diacyl hydrazine likewise yielded a mixture composed largely of the furodiazole, and from which no pure thiodiazole could be isolated. The difficulty in all these reactions is the ease with which the diacyl hydrazine loses water and goes over to the furodiazole condition.

α,α′-3,3′-Di-*p*-cymyl-N-phenyl-$[bb_1]$-pyrrodiazole,



.—6 g. of the mixture of hydrazide chloride and furodiazole obtained from the diacyl hydrazine and PCl_5 by the method noted above, were warmed gradually to 170° and kept at that temperature (thermometer in melt) for half an hour. The mass fused slowly and quietly and on cooling formed a bluish green semisolid melt. It was washed thoroughly with dilute hydrochloric acid, to remove aniline, and then with ether, to remove the furodiazole. The residue was crystallized repeatedly from dilute alcohol, and the pyrrodiazole thus obtained in small compact, colorless, glassy crystals, m. 182.5° (corr.).

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[1] *J. prakt. Chem.*, [2] 73, 288 (1906); 74, 1, 13 (1906); see also Thoma, *Inaug. Diss.*, Heidelberg, 1904.

It is practically insoluble in water or benzine, moderately soluble in ether, and quite soluble in benzene, methyl alcohol, ethyl alcohol, chloroform, carbon tetrachloride or acetone.

Subs. 0.1360: N, 12.7 cc. at 22° and 751 mm. Calc. for $C_{28}H_{31}N_3$: N, 10.27. Found: N, 10.45.

From the ether washings of the crude product, there were isolated both the furodiazole (m. 132.5°, corr.) and the above pyrrodiazole (m. 182.5°, corr.).

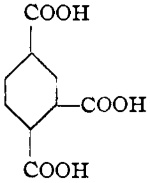
3-Methyl-6-isopropyl Hippuric Acid, $CH_3(C_3H_7)C_6H_3.CO.NH.CH_2$-COOH.—2 g. of the acid chloride were added to a concentrated aqueous solution of 2 g. glycine, then a little dilute sodium hydroxide solution, and the mixture shaken mechanically, testing from time to time and adding more alkali as needed to maintain a feebly alkaline reaction. In two hours the acid chloride had essentially all dissolved and the mixture was acidified cold with dilute hydrochloric acid. The white precipitate which separated was removed, washed with ligroin, to rid it of any 3-acid, and crystallized by dissolving it in a small quantity of alcohol, then pouring in several volumes of boiling water and allowing to stand. The colorless pearly scales resulting were thoroughly washed with cold ligroin, and then m. 205.5° (corr.).

As thus purified, this hippuric acid derivative is soluble in methyl alcohol, ethyl alcohol or acetone; much less soluble in chloroform or ether; still less in benzene or carbon tetrachloride, and practically insoluble in water or ligroin.

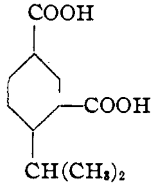
Subs. 0.1743: N, 9.45 cc. at 22° and 746.5 mm. Calc. for $C_{13}H_{17}O_3N$: N, 5.96. Found: N, 6.00.

The use of heat to hasten this reaction is objectionable, as it causes too much hydrolysis of the acid chloride with consequent falling off in the yield of hippuric derivative.

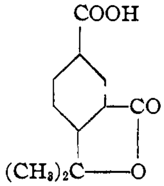
Oxidation of Cymene 3-Carboxylic Acid.—Preliminary experiments indicated the formation of the following acids on oxidation of cymene 3-carboxylic acid:



Trimellitic acid.



Isopropyl *m*-phthalic acid.



Dimethylphthalide *m*-carboxylic acid.

By oxidation with dilute (1 : 1) nitric acid, an acid was obtained, m. 218–24°, believed to be trimellitic acid, the m. p. of which is variously, stated in the literature from 217 to 225°.

With alkaline potassium permanganate, an acid resulted, m. 233–5° (uncorr.), apparently isopropyl *m*-phthalic acid (m. 236°) and, by further oxidation, an acid, m. 195–8°, which gave an impure ethyl ester, m. 102–5°. The latter is, therefore, probably the dimethylphthalide *m*-carboxylic acid, which m. 205–6°, and its ethyl ester at 105–6°.

Unfortunately, the reactions were not carried out with enough material to adequately purify these oxidation products and more definitely establish their identity, but it is hoped to complete this part of the work at a later date.

Reduction of Cymene 3-Carboxylic Acid.—A solution of the acid in glacial acetic acid was mixed with a solution of colloidal platinum, and the resulting homogeneous solution shaken mechanically for 20 hours while it was subjected to treatment with hydrogen at 13 lbs. pressure. No reduction occurred, the original acid being recovered unchanged. Experiments on the reduction of an amyl alcohol solution of the acid by metallic sodium are under way and will be reported later.

Summary of Results.

1. The syntheses of *p*-cymene 2-carboxylic acid and of *p*-cymene 3-carboxylic acid, have been accomplished from the corresponding bromo cymenes, and numerous derivatives of these acids prepared and studied.
2. The statements in the literature concerning cymene 2-carboxylic acid and its salts have been tested and corrected. The following hitherto unknown derivatives have been prepared: methyl ester, ethyl ester, acid chloride, acid anilide, diacyl hydrazine, the furodiazole condensation product from the latter, the cymyl hippuric acid and its ethyl ester.
3. Cymene 3-carboxylic acid is entirely new. In addition to the free acid, the following derivatives have been synthesized and examined: Na, K, Ca, Ba, Cu and Ag salts, methyl ester, ethyl ester, phenyl ester, acid chloride, acid amide, acid anilide, diacyl hydrazine, the furo- and *N*-phenyl pyrrodiazole condensation products from the latter, and the cymyl hippuric acid.
4. The bromination product of cymene has been shown to be a mixture of 2- and 3-bromo derivatives, and not a pure 2-bromo derivative as hitherto assumed.

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[CONTRIBUTION FROM THE MELLON INSTITUTE OF THE UNIVERSITY OF PITTSBURGH.]

THE HYDROLYSIS OF CHLOROPENTANES AS AFFECTED BY HIGH PRESSURE: SYNTHETIC FUSEL OIL.

BY HARRY ESSEX, HAROLD HIBBERT AND BENJAMIN T. BROOKS.

Received May 6, 1916.

The recent work of Meyer and Bergius[1] on the conversion of chlorobenzene and chloronaphthalene into phenol and α-naphthol, respectively,

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[1] *Ber.*, 47, 3155 (1914).