[CONTRIBUTION FROM THE UNIVERSITY OF TORONTO]

SOME PREPARATIONS FROM MALEIC AND FUMARIC ACIDS

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Received June 16, 1923

Pechman[1] and Gabriel and Coleman[2] have prepared β-benzoyl-acrylic acid from maleic anhydride, benzene and aluminum chloride, and Pechman and Kosniewski and Marchlewski[3] prepared β-toluyl-acrylic acid from maleic anhydride, toluene and aluminum chloride. This work has been repeated and the conditions for better yields determined. In the preparation of β-benzoyl-acrylic acid a yield of 95% (crude) was obtained by using 3 g. of maleic anhydride, 25 cc. of benzene, and 9 g. of aluminum chloride. This was kept cool for 20 minutes and then heated to 60° for 1.5 hours. Longer heating reduces the yield. In the preparation of β-toluyl-acrylic acid the same method gave a yield of 77%. Naphthalene, anthracene and diphenyl have been used in this experiment, giving the corresponding unsaturated keto acids, and various addition compounds of these acids have been prepared.

Rubidge and Qua's[4] method of preparing diphenylphthalide from phthalic anhydride, benzene and aluminum chloride by using an acid anhydride on the intermediate compound has been shown to have quite general application. If maleic anhydride were substituted for phthalic anhydride in the reaction the product should be diphenyl-croton lactone but although the conditions were varied considerably the results of an attempt to effect this reaction were negative.

Since Pechmann[5] prepared diphenylphthalide from the mixed anhydride of benzoyl-benzoic acid and acetic acid, the anhydride of β-benzoyl-acrylic acid and acetic acid, m. p. 113–114°, was prepared and treated with benzene and aluminum chloride but no diphenyl-croton lactone was obtained.

Fumaryl chloride, benzene and aluminum chloride have been used to prepare dibenzoyl-ethylene and instead of benzene, other hydrocarbons such as toluene, *m*-xylene and diphenyl have been used and the corresponding 1,4-diketones obtained. Since this work was done, Conant and Lutz[6] have described the preparation of 1,4-diketones by this method using benzene, toluene, chlorobenzene and mesitylene. Paal and Schulze[7] had prepared dibenzoyl-ethylēne (*trans*) from dibenzoyl-malic acid and

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[1] Pechman, *Ber.*, **15**, 885 (1882).

[2] Gabriel and Coleman, *ibid.*, **32**, 393 (1889).

[3] Kosniewski and Marchlewski, *Chem. Centr.*, (2) **77**, 1190 (1906).

[4] Rubidge and Qua, THIS JOURNAL, **36**, 732 (1914).

[5] Pechmann, *Ber.*, **14**, 1865 (1881).

[6] Conant and Lutz, THIS JOURNAL, **45**, 1303 (1923).

[7] Paal and Schulze, *Ber.*, **33**, 3795 (1900).

changed it to the *cis* form by exposure to sunlight. The author found that ditoluyl-ethylene (*trans*) and di-2,4-xylyl-ethylene (*trans*) prepared from fumaryl chloride were changed, on exposure to sunlight, to the colorless *cis* form. Conant and Lutz also changed their *trans* 1,4-diketones to the *cis* forms by this method but my results in the case of ditoluyl-ethylene do not quite agree with theirs.

Paal and Schulze noted that the bromine addition compounds of the *trans* and *cis* forms of dibenzoyl-ethylene were identical. The author found this to be true also for the bromine addition compounds of di-*p*-toluyl-ethylene and di-2,4-xylyl-ethylene.

The melting points given in this paper were taken with a mercury thermometer which was calibrated by Professor J. B. Ferguson against a standard platinum-platinumrhodium thermocouple by means of a precision potentiometer.

Experimental Part

Identification of β-*p*-Toluyl-acrylic Acid.—One g. of the toluyl-acrylic acid was boiled with 10% sodium hydroxide solution for a few minutes; the methyltolyl ketone separated as an oil. This oil was oxidized in a cold alkaline solution of potassium ferricyanide, giving *p*-toluic acid. Previous experimenters had assumed that this acid was the *para* derivative.

Methyl β-*p*-Toluyl-acrylate.—Six g. of the toluyl-acrylic acid was dissolved in methyl alcohol and the solution saturated with hydrogen chloride. The oil remaining on the evaporation of the methyl alcohol was dried and most of it distilled at 240–245° under 115 mm. pressure. After recrystallization from acetic acid it formed long, colorless crystals, m. p., 45.5–46° and was readily soluble in ether, chloroform, benzene or ethyl alcohol.

β-*p*-Toluyl-α-chloropropionic Acid.—One g. of the toluyl-acrylic acid was allowed to stand with 25 cc. of concd. hydrochloric acid in a closed flask for 60 hours. The product, which was colorless, was washed with water, dried and freed from the original acid by warming it with a small amount of toluene. It was then recrystallized from a large volume of toluene; m. p., 144–144.5°. It is quite soluble in acetone or ethyl alcohol and less so in ether or chloroform. Since, in the analogous compound, β-benzoyl-chloropropionic acid, prepared by Bougault,[8] the chlorine was in the α-position, this compound is β-*p*-toluyl-α-chloropropionic acid.

Analysis. Calc. for $C_{11}H_{11}O_3Cl$: Cl, 15.65. Found: 15.45.

β-*p*-Toluyl-β,α-dibromopropionic Acid.—In cold acetic acid solution the toluyl-acrylic acid immediately reacted with bromine. Very pure material was obtained by recrystallizing the product from 75% methyl alcohol. It is soluble in chloroform, benzene, acetone or ethyl alcohol.

Analysis. Calc. for $C_{11}H_{10}O_3Br_2$: Br, 45.67. Found: 45.25.

β,β-Naphthoyl-acrylic Acid.—Five g. of maleic anhydride and 7 g. of naphthalene were dissolved in 35 cc. of benzene, and 15 g. of aluminum chloride was slowly added. After 30 minutes the flask was warmed to 60–70° for 4 hours. After decomposition of the intermediate compound with hydrochloric acid and removal of the benzene and excess naphthalene by distillation with steam the crude product was dissolved in sodium hydroxide solution and the solution gradually acidified, the first precipitate being re-

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[8] Bougault, *Ann. chim. phys.*, [8] **15**, 499 (1909).

jected. A small amount of benzoyl-acrylic acid was removed by washing the crystals with benzene and the material was further purified by recrystallizing it from a large volume of 10% hydrochloric acid; it seemed to be principally one product. By making the methyl ester of this material and hydrolyzing the ester, a pure acid, m. p., 189–190°, was obtained. It is easily soluble in acetone, ether, acetic acid, alcohol or chloroform and slightly soluble in benzene. In one preparation a small amount of a second product, m. p., 158–159°, was obtained which seemed to be more soluble in benzene, and the methyl ester was an oil. The acid, m. p., 189–190°, did not react with bromine in cold acetic acid solution, and in hot acetic acid hydrogen bromide was evolved.

Analysis of silver salt. Calc. for $C_{14}H_9O_3Ag$: Ag, 32.5. Found: 31.9.

Identification of the Acid Melting at 189–190°.—One g. of this acid was dissolved in acetic acid and 6 g. of sodium dichromate added. The flask was kept on the water-bath for 6 hours and after it had then cooled the contents were diluted with thrice their volume of water. A brown precipitate formed that on sublimation gave β-naphthoic acid. The acid is, therefore, β,β-naphthoyl-acrylic acid.

Methyl-β,β-naphthoyl-acrylate.—Five g. of the acid was dissolved in methyl alcohol and the solution saturated with hydrogen chloride. The ester crystallized in plates, m. p., 94–95°, and is soluble in acetic acid, chloroform or benzene.

β-*p*-Phenyl-benzoyl-acrylic Acid.—Five g. of maleic anhydride and 8 g. of diphenyl were dissolved in 50 cc. of benzene and 15 g. of aluminum chloride was added. The temperature was kept at 60–70° for 4 hours. Only a small amount of diphenyl and no benzoyl-acrylic acid were recovered and practically no tar was formed. Recrystallization from acetic acid gave yellow needles; m. p., 167–168°; yield, 80%. The acid is quite soluble in acetone, ether or ethyl alcohol and insoluble in cold benzene or toluene. The sodium salt is only slightly soluble in water.

Analysis of silver salt. Calc. for $C_{16}H_{11}O_3Ag$: Ag, 30.05. Found: 29.75.

Methyl β-*p*-Phenyl-benzoyl-acrylate.—Four g. of the acid was dissolved in methyl alcohol and after treatment with hydrogen chloride the solution was boiled for $^1/_2$ hour. The ester on recrystallization from ethyl alcohol melted at 73.5–74° and is readily soluble in benzene, acetone or ether.

β-*p*-Phenyl-benzoyl-α,β-dibromopropionic Acid.—Five g. of β-*p*-phenyl-benzoyl-acrylic acid was dissolved in hot acetic acid and bromine slowly added. It was immediately absorbed. The powder obtained by evaporating the solution was recrystallized from toluene; m. p., 180–181°. It was readily soluble in alcohol, acetone or ether and difficultly soluble in benzene or toluene.

Analysis. Calc. for $C_{16}H_{12}O_3Br_2$: Br, 38.8. Found: 38.35.

Identification of β-*p*-Phenyl-benzoyl-α,β-dibromopropionic Acid.—One g. of this acid was fused with 2 g. of potassium hydroxide for 10 minutes at 160° and *p*-phenyl-benzoic acid obtained from the product. This gives the formula for the original acid and for the bromine addition compound.

Methyl β-*p*-Phenyl-benzoyl-α,β-dibromopropionate.—Two g. of the acid was boiled for 30 minutes with methyl alcohol and hydrogen chloride. The ester on recrystallization from ethyl alcohol was white, m. p., 120–121°, and soluble in acetone, ether, acetic acid or benzene.

β-*meso*-Anthroyl-acrylic Acid.—Eight g. of maleic anhydride and 16 g. of anthracene were dissolved in 100 cc. of benzene and 24 g. of aluminum chloride was added slowly There was little action in the cold and the flask was warmed for 5 hours at 60–70°. After addition of hydrochloric acid, the solid was separated from the liquid and washed with benzene, yielding 15 g. of a light green product, which after recrystallization from acetic acid gave 10 g. of colorless crystals; m. p., 261°. This acid is soluble in acetone or chloroform and slightly soluble in benzene, toluene or acetic acid. It did not react with bromine in either cold or hot acetic acid solution, and fusion with potassium hydroxide at 250° gave no decomposition. It is assumed to be the *meso*-anthroyl derivative. The sodium salt and the ammonium salt are only slightly soluble in water.

Analysis of ammonium salt. Calc. for $C_{18}H_{15}O_3N$: N, 4.77. Found: 4.82.

Methyl β-*meso*-Anthroyl-acrylate.—Three g. of β-*meso*-anthroyl-acrylic acid was dissolved in 100 cc. of methyl alcohol and hydrogen chloride added. After the solution had stood for 2 days, colorless plates crystallized and these after recrystallization from acetic acid gave needles 2 cm. long; m. p., 149.5–150°. The ester is soluble in acetone, chloroform or benzene and less soluble in acetic acid.

Di-*p*-toluyl-ethylene (*trans*).—To 7 g. of fumaryl chloride and 50 cc. of toluene 20 g. of aluminum chloride was added slowly. The reacting substances were kept at room temperature overnight. After decomposition of the intermediate compound the product was light yellow and after 3 recrystallizations from methyl alcohol melted at 134.5°; yield of crude material, 52%. The substance is soluble in benzene, acetone, ether, chloroform or acetic acid but only slightly soluble in methyl or ethyl alcohol. The product obtained by Conant and Lutz melted at 148°.

Di-*p*-toluyl-dibromo-ethane.—Two g. of the ditoluyl-ethylene was dissolved in 100 cc. of acetic acid and bromine slowly added. The bromine was immediately absorbed and colorless, needle-shaped crystals appeared; m. p., 200–200.5°. These were insoluble in benzene, toluene, ether or acetone, slightly soluble in acetic acid and more soluble in chloroform.

Analysis. Calc. for $C_{18}H_{16}O_2Br_2$: Br, 37.7. Found: 37 25.

Identification of Di-*p*-toluyl-dibromo-ethane.—One g. of the bromine addition compound was fused with 2 g. of potassium hydroxide for 10 minutes at 130°. The product on acidification gave *p*-toluic acid. This also identifies the di-toluyl-ethylene as di-*p*-toluyl-ethylene.

Di-*p*-toluyl-ethylene (*cis*).—Two g. of the *trans* compound was dissolved in acetic acid and allowed to remain in the sunlight for 3 days. At the end of this time some colorless crystals had appeared in the solution and more were obtained by evaporation of the solution; m. p., 148.5°. When the substance was recrystallized from ethyl alcohol the melting point became 152°. In acetic acid solution this product absorbed bromine and gave colorless needles identical with the bromine addition compound of the original compound. When the substance, m. p. 134.5°, was dissolved in acetone and exposed to sunlight for 2 days the product after one recrystallization melted at 147°. Further exposure to brighter sunlight for 2 days gave a small quantity of a substance melting at 120°. Conant and Lutz obtained the *cis* compound, m. p. 123°, and this is probably identical with my last product as I had not enough material for recrystallization.

Di-2,4-xylyl-ethylene (*trans*).—Seven g. of fumaryl chloride, 45 cc. of *m*-xylene, and 20 g. of aluminum chloride were used and the reaction proceeded at room temperature for several hours. After decomposition of the intermediate compound an oil was obtained, but on solution in methyl alcohol and gradual evaporation of the alcohol a yellow solid separated which on recrystallization from ethyl alcohol melted at 125.5–126°. It is quite soluble in benzene, acetone, ether, chloroform or acetic acid and slightly soluble in methyl or ethyl alcohol; yield, 15%.

Di-2,4-xylyl-dibromo-ethane.—Two g. of the dixylyl-ethylene was dissolved in 150 cc. of hot acetic acid and bromine gradually added. White needles formed; m. p., 145°. This product is insoluble in benzene, acetone or ether and slightly soluble in chloroform.

Analysis. Calc. for $C_{20}H_{20}O_2Br_2$: Br, 35.36. Found: 35.38.

Identification of the Di-2,4-xylyl-dibromo-ethane.—One g. of the bromine addition compound was fused with 2 g. of potassium hydroxide for 10 minutes at 135°. The product on acidification gave 2,4-dimethyl-benzoic acid. This also identifies the dixylylethylene as di-2,4-xylyl-ethylene.

Di-2,4-xylyl-ethylene (*cis*).—Two g. of the *trans* compound was dissolved in methyl alcohol and allowed to stand in sunlight for a week. A great deal of the original material was unchanged, but on evaporation of the alcohol the last precipitate was an oil which on recrystallization from ligroin gave colorless, needle-shaped crystals; m. p., 65–65.5°. These crystals are soluble in acetone, ether, benzene or chloroform. The bromine addition compound was made in acetic acid solution and was identical with that made from the *trans* form. A mixed melting point was not lower.

Di-*p*-phenyl-benzoyl-ethylene (*trans*).—A mixture of 8 g. of fumaryl chloride, 12 g. of diphenyl, 60 cc. of benzene, and 20 g. of aluminum chloride was kept at room temperature for 1 day. After decomposition of the intermediate compound and removal of the benzene and diphenyl by distillation with steam, the product was washed with hot benzene and a yellow powder was left; m. p., 247.5–248°. It is slightly soluble in benzene, and acetic acid and somewhat more soluble in chloroform. The solution in chloroform was exposed to 36 hours' sunlight but no product other than the original *trans* compound was obtained.

Di-*p*-phenyl-benzoyl-dibromo-ethane.—One g. of the di-*p*-phenyl-benzoyl-ethylene was dissolved in chloroform and bromine added. The color disappeared gradually and on evaporation of the solution a white solid, m. p., 218–218.5°, was obtained. This compound is slightly soluble in acetone or ether. Both this substance and the original ethylene derivative are assumed to contain the *p*-phenyl-benzoyl group.

Analysis. Calc. for $C_{28}H_{20}O_2Br_2$: Br, 30.3. Found: 29.85.

This work was done under the direction of Professor F. B. Allan and was made possible through assistance in the form of a Studentship received from the Research Council of Canada.

Summary

1. Rubidge and Qua's method for the preparation of diphenyl-phthalide was found not to be applicable to the preparation of diphenyl-croton lactone from maleic anhydride. An attempt to prepare this lactone from the anhydride of β-benzoyl-acrylic acid and acetic acid was also unsuccessful.

2. Several unsaturated keto acids have been prepared from maleic anhydride, and some of their addition compounds have been obtained. Some of these unsaturated keto acids readily formed addition compounds with bromine; others did not.

3. Using fumaryl chloride, several unsaturated diketones have been prepared as well as their bromine addition compounds. In two of these the yellow *trans* form has been changed to the colorless *cis* form by exposure to sunlight. The behavior of ditoloyl-ethylene seems to be peculiar; further work will be done on this.

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