Two and sixty-two hundredths grams (0.01 mole) of the unsaturated diketone was dissolved in 50 cc. of absolute alcohol, 0.05 g. of platinum oxide was added, and the system was filled with hydrogen to a pressure of forty-five pounds. The reduction was stopped after shaking for three and one-half minutes, when the mercury column had dropped 260 mm. The alcohol solution, which was still colored a light yellow, was filtered and evaporated at room temperature by means of a water pump. The residue consisted of a mass of fine colorless needles contaminated by a yellow oil; this was washed with a small quantity of cold ether and filtered. The product so obtained melted at 121–122°; recrystallization from ligroin containing a small amount of benzene did not raise the melting point. More of this product was contained in the ether. This compound is evidently identical with the *cis*-1,2-dibenzoylcyclobutane obtained by Kao and Fuson.[1]

Anal. Calcd. for $C_{18}H_{16}O_2$: C, 81.8; H, 6.06. Found: C, 81.6; H, 6.13.

The ether solution remaining was evaporated to dryness on the steam-bath, and was inadvertently allowed to remain for about five minutes after the ether had evaporated. The residue was then mixed with a little methyl alcohol, whereupon it formed a colorless crystalline product which was only slightly soluble in hot methyl and ethyl alcohols. After several recrystallizations from benzene, the product melted at 222–223°; yield, 1 g.

Anal. C, 79.5, 79.6; H, 6.5, 6.3.

Cis-1,2-dibenzoylcyclobutane was subjected to the following tests to characterize it and further to substantiate its identity: (1) potassium permanganate in acetone gave no reaction. (2) A solution in ethyl alcohol plus a few drops of dilute sodium hydroxide was allowed to stand at room temperature for one hour. A yellow color developed, and when the solution was poured into water pure *trans*-1,2-dibenzoylcyclobutane was precipitated; m. p. 96–97°. A mixed melting point with an authentic sample of the *trans* diketone showed no depression; a mixture with the original *cis* diketone melted at 85–100°. (3) A suspension in aqueous sodium carbonate solution was heated in a steam-bath for several hours. The *cis* diketone changed to an oily product which solidified on cooling; m. p. 88–105°. (4) A solution in glacial acetic acid, allowed to stand for one hour at room temperature, yielded the original *cis* diketone unchanged. (5) Anhydrous aluminum chloride was added to a solution of the diketone in dry benzene which was then shaken for about ten minutes. The mixture was worked up in the usual manner for Friedel–Crafts reactions, and the *cis* diketone was recovered only slightly changed; m. p. 114–119°. (6) A suspension in concentrated hydrochloric acid was heated on the steam-bath for one-half hour. Pure *trans* diketone was recovered; m. p. 96–97°. (7) Bromination in carbon tetrachloride yielded a mixture of *cis*- and *trans*-1,2-dibenzoyl-1,2-dibromocyclobutanes, the latter in the predominating amount. This result is the same as that obtained by bromination of the pure *trans* diketone.

The Dioxime of Cis-1,2-dibenzoylcyclobutane.—The dioxime melted at 174–175°. A mixed melting point showed it to be different from the dioxime of *trans*-1,2-dibenzoylcyclobutane obtained by Kao and Fuson.[1]

Anal. Calcd. for $C_{18}H_{18}O_2N_2$: C, 73.4; H, 6.2; N, 9.52. Found: C, 73.6; H, 6.2; N, 9.56.

Summary

Cis-1,2-dibenzoylcyclobutane has been synthesized from its *trans* isomer through the dibromide of the latter. The dibromide was converted into 1,2-dibenzoyl-1,2-cyclobutene, which was catalytically hydrogenated to the *cis* diketone.

The ease with which the *cis* diketone is isomerized to the *trans* form offers an explanation for the fact that *cis*-1,2-cyclobutanedicarboxylic acid and its anhydride yield derivatives which have the *trans* configuration.

URBANA, ILLINOIS RECEIVED MAY 14, 1934

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

The Action of Phenylmagnesium Bromide on the Anhydride and the Phenylimide of 1,2-Cyclobutanedicarboxylic Acid

BY ELLSWORTH ELLINGBOE AND REYNOLD C. FUSON

The synthesis of 1,2-dibenzoylethane by the action of phenylmagnesium bromide on N-methylsuccinimide[1] suggests the possibility of preparing *cis*-1,2-dibenzoylcyclobutane by an application of the same method to analogous derivatives of 1,2-cyclobutanedicarboxylic acid. In the case of the succinimide the addition of two moles of reagent leads to the formation of α,α'-diphenyl-N-methylpyrrole, presumably by the loss of two molecules of water from the primary addition product. For steric reasons the formation of a pyrrole derivative in this manner seemed unlikely in the cyclobutane series.

Experiments with the N-phenylimide (V) of 1,2-cyclobutanedicarboxylic acid, however, did not lead to the formation of the diketone. The first molecule of the reagent added normally to yield *cis*-2-benzoylcyclobutanecarboxanilide

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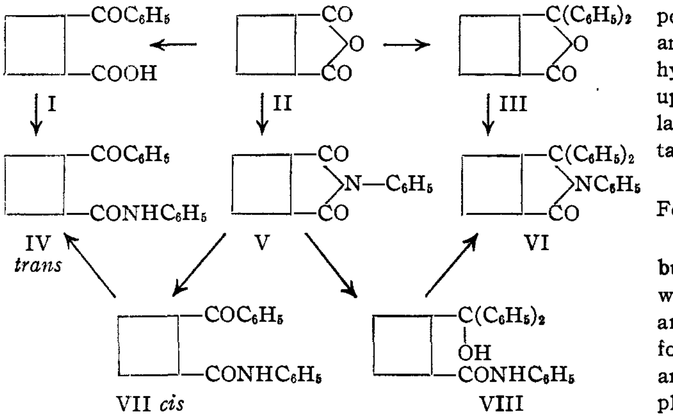
[1] Lukes and Prelog, *Coll. Czech. Chem. Comm.*, **1**, 334 (1929).

(VII); and when two molecules of phenylmagnesium bromide were employed the unsymmetrical addition product—the anilide (VIII) of 2-(α-hydroxybenzohydryl)-cyclobutanecarboxylic acid—was formed. This compound could be hydrolyzed to III; dehydration converted it into the lactam (VI) of 2-(α-anilinobenzohydryl)-cyclobutanecarboxylic acid, which is also produced from III by the action of aniline and aniline hydrobromide at 160–170°.[2]



Condensation of the anhydride (II) with phenylmagnesium bromide also led to unsymmetrical products as was to be expected by analogy with the results obtained with phthalic anhydride.[3] One mole of the reagent gave the keto acid (I), and two moles produced the lactone (III) of 2-(α-hydroxybenzohydryl)-cyclobutanecarboxylic acid. The *trans* configuration for I was established by the fact that its acid chloride reacted with aniline to give the anilide (IV) previously obtained by the rearrangement of the monoxime of *trans*-dibenzoylcyclobutane.[4] The *cis* anilide (VII), mentioned above, rearranges to the *trans* isomer when dissolved in alcohol containing a little alkali.

Experimental

The Action of Phenylmagnesium Bromide (Two Moles) on 1,2-Cyclobutanedicarboxylic Anhydride.—Three and two-tenths grams of the anhydride[5] was dissolved in 100 cc. of absolute ether contained in a 200-cc. three-necked flask equipped with a mercury-sealed stirrer and a reflux condenser. To this was slowly added 24 cc. of 2.1 *N* phenylmagnesium bromide. The mixture was stirred and refluxed for three hours; a heavy precipitate formed. The reaction mixture was then decomposed with ice and hydrochloric acid and the ether extract was washed with sodium carbonate solution. The ether layer, upon evaporation, yielded a colorless solid product which, after three recrystallizations from alcohol, melted at 116–117°. More of the same compound was obtained by acidification of the sodium carbonate wash solution; it did not react with bromine in carbon tetrachloride; it decolorized potassium permanganate in acetone only very slowly; and it dissolved slowly, on heating, in dilute sodium hydroxide from which it was reprecipitated unchanged upon acidification. The product was evidently the lactone (III) of 2-(α-hydroxybenzohydryl)-cyclobutanecarboxylic acid.

Anal. Calcd. for $C_{18}H_{16}O_2$: C, 81.8; H, 6.06. Found: C, 81.6, 81.8; H, 5.96, 6.13.

Lactam (VI) of 2-(α-Anilinobenzohydryl)-cyclobutanecarboxylic Acid.—One gram of III was mixed with 1.3 g. of aniline hydrobromide and 1 g. of aniline and heated at 160–170° for seven hours in an oil-bath, following the procedure which was used by O. Fischer and Hepp[6] in the preparation of the anilide of diphenyl phthalide. A solid product was obtained when the mixture was poured into dilute hydrochloric acid. When decolorized with norite and recrystallized from methyl alcohol the product came out as colorless needles; m. p. 136–137°.

Anal. Calcd. for $C_{24}H_{21}ON$: C, 85.0; H, 6.19. Found: C, 85.1; H, 6.25.

The Action of Phenylmagnesium Bromide (One Mole) on 1,2-Cyclobutanedicarboxylic Anhydride.—Three and two-tenths grams (0.025 mole) of the anhydride was dissolved in absolute ether and treated with 12 cc. (0.025 mole) of 2.1 *N* phenylmagnesium bromide according to the foregoing procedure. This time, however, the reaction mixture was decomposed with ice and ammonium chloride solution. The ether layer was extracted with sodium bicarbonate solution, and this, when acidified, deposited an oil which partially solidified after standing for several days. The solid was washed free of residual oil with benzene and was recrystallized from alcohol; it proved to be *trans*-2-benzoylcyclobutanecarboxylic acid; m. p. 127–128°.

Anal. Calcd. for $C_{12}H_{12}O_3$: N. E., 204; C, 70.6; H, 5.88. Found: N. E., 205.5; C, 70.5; H, 6.05.

Evaporation of the ether layer yielded a small amount of III contaminated with diphenyl.

The anilide of the keto acid was prepared through the acid chloride and aniline. It melted at 129–130° after recrystallization from alcohol and, by means of a mixed melting point, was shown to be identical with the anilide of *trans*-2-benzoylcyclobutanecarboxylic acid prepared by Kao and Fuson by rearrangement of the monoxime of *trans*-1,2-dibenzoylcyclobutane.

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(2) Beis [*Compt. rend.*, **138**, 987 (1904)], Sachs and Ludwig [*Ber.*, **37**, 385 (1904)], and Kohn and Lakner [*Monatsh.*, **45**, 617 (1925)] studied the action of one mole of various Grignard reagents on N-substituted phthalimides. They obtained 2,3-dialkyl-3-hydroxyisoindoleinones, which could be saponified to γ-keto acids. They do not report the addition of two moles of Grignard reagent.

(3) Bauer, *Ber.*, **37**, 735 (1904); Pickles and Weizmann, *Chem. News*, **90**, 276 (1904). See also Courtot, "Le Magnesium en chimie Organique," Imprimerie Lorraine-Rigot et Cie, Nancy, 1926, p. 264.

(4) Kao and Fuson, This Journal, **54**, 1120 (1932).

(5) Perkin, *J. Chem. Soc.*, **65**, 584 (1894); Ellingboe and Fuson, This Journal, **56**, 1774 (1934).

(6) O. Fischer and Hepp, *Ber.*, **27**, 2793 (1894).

The Action of Phenylmagnesium Bromide (One Mole) on N-Phenyl-1,2-cyclobutanedicarboximide (V).—Five grams (0.025 mole) of V, prepared according to Perkin's directions,[5] was dissolved in 75 cc. of absolute ether. Fourteen cubic centimeters (0.025 mole) of 2.1 *N* phenylmagnesium bromide was then added, and the mixture was refluxed and stirred for three hours. A white precipitate was formed, and when the reaction mixture was decomposed with ice and hydrochloric acid and the ether extract evaporated, a mass of colorless, leafy needles was obtained. After three recrystallizations from alcohol the compound melted at 149.5–150.5°. That it was *cis*-2-benzoylcyclobutanecarboxanilide (VII) was demonstrated by its quantitative conversion into the known *trans* isomer IV when it was allowed to stand a short time in alcohol solution containing a few drops of dilute sodium hydroxide.

Anal. Calcd. for $C_{18}H_{17}O_2N$: C, 77.4; H, 6.09. Found: C, 77.1; H, 6.11.

The Action of Phenylmagnesium Bromide (Two Moles) on N-Phenyl-1,2-cyclobutanedicarboximide (V).—Four grams (0.02 mole) of V was dissolved in 75 cc. of absolute ether and treated with 20 cc. (0.04 mole) of 2.1 *N* phenylmagnesium bromide. The mixture was stirred and refluxed for four hours, during which time a heavy white precipitate appeared. The reaction mixture was decomposed with ice and hydrochloric acid to yield a crystalline solid which was only slightly soluble in the ether layer. After three recrystallizations from alcohol the product melted at 193.5–194.5°. The analysis and properties of the compound indicated that it was the anilide (VIII) of 2-(α-hydroxybenzohydryl)-cyclobutanecarboxylic acid.

Anal. Calcd. for $C_{24}H_{23}O_2N$: C, 80.7; H, 6.44. Found: C, 80.4; H, 6.55.

The properties of the anilide which contribute toward a knowledge of its structure are as follows: (1) It was transformed into III by boiling with acetic anhydride or by boiling with alcohol containing a small amount of either sulfuric acid or sodium hydroxide. (2) Dehydration by boiling for two hours in xylene with a small quantity of anhydrous potassium acid sulfate yielded VI. (3) It was unaffected by permanganate, or by dilute aqueous sodium hydroxide after two hours of boiling. Four hours of boiling with 4 *M* sulfuric acid changed it only partially into VI.

Summary

Phenylmagnesium bromide has been shown to react with 1,2-cyclobutanedicarboxylic anhydride (II) in a fashion analogous to its reaction with phthalic anhydride. One mole of the Grignard reagent produces the keto acid, 2-benzoylcyclobutanecarboxylic acid (I); and two moles give the lactone (III) of 2-(α-hydroxybenzohydryl)-cyclobutanecarboxylic acid.

The phenylimide (V) of 1,2-cyclobutanedicarboxylic acid reacts in a manner similar to the anhydride when treated with phenylmagnesium bromide. The products obtained with one and two moles, respectively, of the Grignard reagent are *cis*-2-benzoylcyclobutanecarboxanilide (VII) and the anilide (VIII) of 2-(α-hydroxybenzohydryl)-cyclobutanecarboxylic acid.

URBANA, ILLINOIS RECEIVED MAY 14, 1934

[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT OF THE UNIVERSITY OF NEBRASKA]

The Reactivity of Nuclear Chlorine in 2-Chloro-5-nitrophenylarsonic Acid

BY MARVIN J. HALL AND CLIFF S. HAMILTON

In this investigation the reactivity of the chlorine in 2-chloro-5-nitrophenylarsonic acid was found to be less than that in 3-nitro-4-chlorophenylarsonic acid,[1] and the introduction of a nitro group into *o*-chlorophenylarsonic acid para to the halogen increased the reactivity of the chlorine as shown, in general, by a comparison of the ease of condensation and yields obtained.[2]

In order to determine the most favorable experimental conditions for the reaction studied, variations were made in the solvent, temperature, catalyst, proportion of reactants, and the reaction time. Amyl alcohol proved to be an excellent solvent and the optimum reaction temperature was approximately 135°, which permitted active refluxing of the solvent. The reaction time varied with the type of reactant. A small piece of carefully cleaned sheet copper, when used as a catalyst, produced better results than either cuprous iodide or finely divided copper obtained by precipitation from copper sulfate.

The aliphatic amines (isobutyl, iso- and *n*-amyl, ethylenediamine and ethanolamine) condensed quite readily with 2-chloro-5-nitrophenylarsonic acid, and these were reduced to the corresponding amino derivatives. Condensations between 2-chloro-5-nitrophenylarsonic acid and several substituted phenols resulted in a number of phenyl ether derivatives. Phenol, *p*-chlorophenol, *o*- and *p*-cresol were found to condense under the same conditions employed with the amines.

When 2-chloro-5-nitrophenylarsonic acid was

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(1) Maclay and Hamilton, THIS JOURNAL, **54**, 3310 (1932).

(2) Etzelmiller and Hamilton, *ibid.*, **53**, 3085 (1931).