EXPERIMENTAL[5]

Preparation of compounds of I_{A-F} Series. A mixture consisting of 0.1 mole of 6-methyl-2-pyronone (11.4 g.), 0.1 mole of the acyl halide and 20 ml. of trifluoroacetic acid was refluxed in an all-glass assembly until hydrogen chloride vapors ceased to be evolved. This usually required between 90 min. and 2 hr. At the end of the reaction period the mixture was poured into 100 ml. of water and chilled. Those compounds which remained as oils or semi-solids such as II_A and $_B$ were taken up in alcohol and reprecipitated with water; chilling at this stage produced soft crystals which could be dried in air and weighed, as were the higher melting compounds.

The analytical samples were obtained by recrystallizing the compound several times from boiling heptane.

Those compounds in which the pyronone had been bisacylated were prepared by using 0.2 mole of the acyl halide. All other conditions for the preparation and purification of the compounds were the same.

Synthesis of 2-(m-nitrophenyl)-3,5-di(m-nitrobenzoyl-6-methyl-4-pyrone (II). To 20 ml. of trifluoroacetic acid was added 0.05 mole (6.2 g.) 6-methyl-2-pyronone followed by 0.15 of mole (27.9) of *m*-nitrobenzoyl chloride. This mixture was refluxed in an all-glass assembly over a glass heating mantle for 4 hr., and then diluted while hot with 100 ml. of water. The precipitate was filtered off, dried in air to give 32.1 g. of the crude compound, which was then recrystallized twice from ethanol. An 8 g. sample of the partially purified substance was refluxed with 70 ml. of concd. hydrochloric acid for 3 hr., diluted with water and chilled to give 6.2 g. of the air-dried compound. The purified material was recrystallized once from heptane to give a melting point of 143–144°.

Anal. Calcd. for $C_{26}H_{15}N_3O_{10}$: C, 58.98; H, 2.85; N, 7.93. Found: C, 58.79; H, 2.74; N, 7.67.

Synthesis of 2-phenyl-6-methyl-4-pyrone (III). A 5 g. sample of I_A was heated for 30 min. at 155–160° in a Fisher constant temperature oil bath. The resulting melt was poured into 100 ml. of water and chilled to give 4.5 g. of an air-dried sample.

Refluxing 5 g. of I_A with 70 ml. of concd. hydrochloric acid for 2 hr. gave a similar yield.

The crude III was recrystallized once from heptane, m.p. 84–85° which is in good agreement with the results of Light and Hauser[6] and in fair agreement with those of Ruhemann.[7]

Anal. Calcd. for $C_{12}H_{10}O_2$: C, 77.40; H, 5.41. Found: C, 77.69; H, 5.27.

Synthesis of 2-phenyl-5-benzoyl-6-methyl-4-pyrone (IV). Ten grams of I_B was refluxed in 60 ml. of concd. hydrochloric acid for 3 hr., diluted with 100 ml. of water and then chilled to produce 7.5 g. of crude IV. The compound was crystallized once from heptane to give the analytical sample, m.p. 124–125°.

Anal. Calcd. for $C_{19}H_{14}O_3$: C, 78.60; H, 4.86. Found: C, 78.29; H, 4.69.

Preparation of compounds of V_{A-D} Series. One tenth of a mole of the pyrone along with 0.05 mole of chloranil was vigorously refluxed for 3 hr. in 100 ml. of absolute ethanol. The brown solution was filtered while hot and placed in the freezing compartment of the refrigerator overnight. The precipitate was filtered off, dried in air and the analytical sample prepared by recrystallizing it three times from absolute ethanol.

Ultraviolet absorption spectra of V_A and $_B$ were taken on a Bausch and Lomb Spectronic-505 and compared with spectra of the pyrones from which they were prepared. The spectra were made in the wave length range of 222–372 mμ in spectro grade methanol:

Substance	Maxima
Kojic acid	264 mμ
V_A	269.5 mμ
α-Chloro-α-deoxy kojic acid	272 mμ
V_B	277 mμ

Preparation of dibromopyrones (VI_{A-D}). A mixture consisting of 0.1 mole of the pyrone, 20 ml. of trifluoroacetic acid and 32 g. of bromine was placed in the hood in an all glass assembly with two standard taper 300 mm. condensers fitted in tandem and gently refluxed for a period of 2 hr. The reaction mixture was poured into water, thoroughly chilled, filtered and dried in air.

Samples of the tarry materials were recrystallized twice from heptane to give the analytical sample.

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(5) All analyses were performed by Dr. Carl Tiedcke, Teaneck, N. J., and all melting points were determined on a Fisher-Johns Melting Point Assembly.

(6) R. J. Light and C. R. Hauser, *J. Org. Chem.*, **25**, 538 (1960).

(7) S. Ruhemann, *J. Chem. Soc.*, **93**, 431 (1908).

Behavior of α-Substituted Chalcones on Attempted Friedel-Crafts Arylation

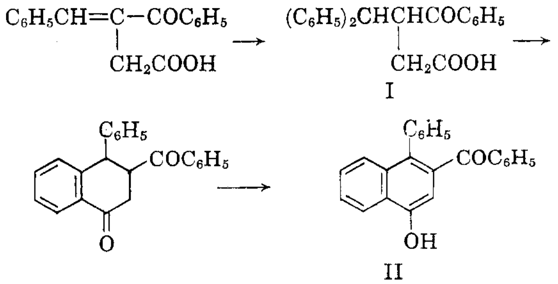
C. F. KOELSCH

Received November 7, 1960

Addition of an aromatic nucleus to an α,β-unsaturated compound under the influence of aluminum chloride is a well known process;[1] for example, benzene and chalcone yield β,β-diphenylpropiophenone.[2]

$$C_6H_6 + C_6H_5CH{=}CHCOC_6H_5 \longrightarrow (C_6H_5)_2CH{-}CH_2COC_6H_5$$

It was thought that this reaction could be applied in a synthesis of 3-benzoyl-4-phenyl-1-naphthol (II)[3] in the following way.



I

II

However the expected keto acid (I) was not formed, and further processing gave a compound

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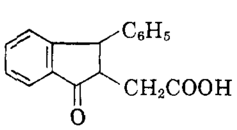
(1) Vorlander and Friedberg, *Ber.*, **56**, 1144 (1923); R. C. Fuson and H. G. Cooke, *J. Am. Chem. Soc.*, **73**, 3515 (1951) and previous papers by Fuson and co-workers; J. F. J. Dippy and A. L. L. Palluel, J. Chem. Soc., 1415 (1951).

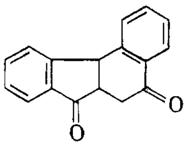
(2) P. R. Shildneck, *Org. Syntheses*, **Coll. Vol. II**, 236 (1943).

(3) C. F. Koelsch, *J. Org. Chem.*, **26**, 1003 (1961).

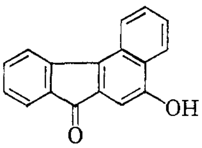
which was not the substituted naphthol desired (II). The keto acid was found to be III, the intermediate diketone was IV, and the end product was V.



III

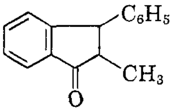


IV

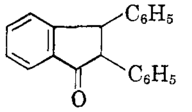


V

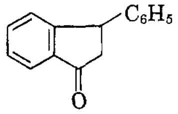
Formation of III appeared anomalous, and therefore a simpler compound, α-methylchalcone, was treated with aluminum chloride in benzene. Here too, a similar reaction occurred, forming VI in 93% yield. Also α-phenylchalcone yielded VII. Careful examination of the products from interaction of chalcone itself with aluminum chloride in benzene allowed isolation of 0.3% of VIII in addition to 90% of β,β-diphenylpropiophenone, the normal product.



VI



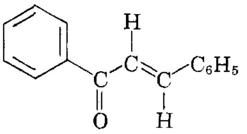
VII



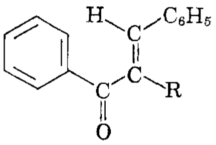
VIII

It was apparent from these results that an α-substituent in a chalcone caused the main reaction to involve addition of the benzoyl nucleus to the α,β-double bond. At first it was thought that the results might be explained by an electronic effect, but Professor R. M. Dodson, with whom the matter was discussed, held strongly to the belief that a steric effect was responsible. Investigation of the behaviors of α-bromo- and α-carbethoxychalcone then supported this belief completely. The α-substituents here are entirely different electronically from methyl, etc., and yet the compounds gave hydrindones and not phenylation products.

Thus, it was concluded that a nearly flat chalcone has configuation IX only when hydrogen is in its α-position and is crowded into configuration X when a larger group is present, and orientation about the C—CO bond (*s-cis* or *s-trans*) controls reaction type.



IX



X

If the configurations were exactly as in IX and X, the latter compounds should show stronger O=C—C=C absorption, corresponding to their linear structures and consequent greater oscillator strength, as contrasted with the folded system in IX. However, this is not the case: chalcone has ϵ_{307} = 24,300, whereas α-methylchalcone has ϵ_{290} = 17,400 and α-bromochalcone has ϵ_{305} = 15,400.[4] It is probable that the anomaly is caused by incomplete planarity in X, a result of interference between β-H and *o*-H.

The present reaction is analogous to Fuson's hydrindone synthesis,[5] where α-substituted acrylophenones and β-hydroxypropiophenones are used. However in that synthesis, the reaction medium is sulfuric acid, and no question of competition between cyclization and phenylation arises.

EXPERIMENTAL

3-Phenylhydrindone-2-acetic acid (III). Addition of 10 g. of 3-benzoyl-4-phenyl-3-pentenoic acid[6] to a suspension of 12 g. of aluminum chloride in 50 ml. of benzene gave an orange gum which dissolved during 15-min. boiling, forming a deep orange-red solution. Decomposition with iced hydrochloric acid and extraction with dilute sodium carbonate then gave 9.4 g. of acidic product that crystallized completely when it was rubbed with ether. It formed colorless plates from dilute acetic acid, m.p. 131–133°.

Anal. Calcd. for $C_{17}H_{14}O_3$: C, 76.7; H, 5.27; Found: C, 76.5; H, 5.39.

Addition of 0.06 g. of bromine to a solution of 0.1 g. of III in 1 ml. of acetic acid, followed by gentle warming led to rapid evolution of hydrogen bromide. Evaporation gave a crystalline residue, completely soluble in cold 2% sodium carbonate. When it was boiled, this solution became deep yellow and deposited 25 mg. of waxy material. Acidification and crystallization from dilute acetic acid gave 50 mg. of 3-phenylindone-2-acetic acid, m.p. 165–167° alone or mixed with an authentic sample.[7]

3,4-Benzo-1,2,4a,9a-tetrahydro-2,9-fluorenedione (IV). A mixture of 1.2 g. of III and 6 ml. of sulfuric acid was heated 4 min. on a water bath, then poured on ice, giving 0.6 g. of pink crystals. Recrystallization from alcohol furnished 0.4 g. of long colorless needles, m.p. 165–167°.

Anal. Calcd. for $C_{17}H_{12}O_2$: C, 82.2; H, 4.85. Found: C, 82.0; H, 4.93.

3,4-Benzo-2-oxy-9-fluorenone (V). Addition of 0.4 g. of bromine to a suspension of 0.8 g. of IV in 5 ml. of acetic acid caused rapid evolution of hydrogen bromide and separation of dark purple crystals. Recrystallization from 75 ml. of acetic acid gave 0.55 g. of flat red-purple needles, m.p. above 235°.

Anal. Calcd. for $C_{17}H_{10}O_2$: C, 82.9; H, 4.09. Found: C, 82.3; H, 4.18.

When 0.2 g. of V was boiled with 5 ml. of 2% sodium hydroxide, it gave a deep blue solution, which deposited purple-gray needles on cooling. Addition of a little methanol caused the salt to dissolve, and the resulting solution was treated alternately with methyl sulfate and sodium hydroxide until the latter no longer developed a blue color. The precipitate was then removed and crystallized from ethyl acetate–ligroin, giving 0.2 g. of *2-methoxy-3,4-benzo-9-fluorenone*, deep red needles, m.p. 155–156°.

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[4] W. B. Black and R. E. Lutz, *J. Am. Chem. Soc.*, **77,** 5134 (1955).

[5] J. H. Burckhalter and R. C. Fuson, *J. Am. Chem. Soc.*, **70,** 7184 (1948), and previous papers. J. Colonge and G. Weinstein, *Bull. Soc. Chim.*, 462 (1952).

[6] W. Borsche, *Ber.*, **47,** 1108 (1914).

[7] C. F. Koelsch and H. J. Richter, *J. Am. Chem. Soc.*, **57,** 2010 (1935).

Anal. Calcd. for $C_{18}H_{12}O_2$: C, 83.0; H, 4.65. Found: C, 82.8; H, 4.71.

The same compound (0.35 g.) (mixed melting point and infrared spectrum) was obtained when 0.5 g. of 4-methoxy-1-phenyl-2-naphthoic acid[8] was boiled for 15 min. with thionyl chloride, and the resulting oily acid chloride was treated with 0.4 g. of aluminum chloride in 5 ml. of benzene.

Chalcone and aluminum chloride in benzene. When a suspension of 70 g. of aluminum chloride in 300 ml. of benzene was treated with 100 g. of chalcone, a smooth exothermic reaction took place during 15 min., forming a bright yellow solid complex. Boiling for 15 min. more gave an orange-red solution, and this was hydrolyzed with iced hydrochloric acid. Most of the benzene was then distilled and replaced with 60–70° ligroin, giving 97 g. of nearly pure β,β-diphenylpropiophenone. The mother liquor was concentrated and treated again with ligroin, giving 21 g. more of the same ketone. The material (17.4 g.) remaining in the second mother liquor was separated by fractional distillation and chromatography into 6.4 g. of β,β-diphenylpropiophenone, 2 g. of diphenylmethane, and 0.29 g. of 3-phenylhydrindone, m.p. 76–77° alone or mixed with an authentic sample.

α-Methylchalcone. A mixture of 5.5 g. α-methylchalcone, 4 g. of aluminum chloride, and 20 ml. of benzene gave an orange-red solution when it was boiled 15 min. Decomposition with iced hydrochloric acid, etc., furnished 5.1 g. of *2-methyl-3-phenylhydrindone*, a colorless oil b.p. 195–198° at 16 mm.

Anal. Calcd. for $C_{16}H_{14}O$: C, 86.4; H, 6.35. Found: C, 86.5; H, 6.30.

Treatment with the calculated amount of bromine in acetic acid, followed by potassium hydroxide in methanol gave a nearly quantitative yield of 2-methyl-3-phenylindone, yellow prisms m.p. 83–84° alone or mixed with an authentic sample.[8]

α-Phenylchalcone. A mixture of 1.5 g. of aluminum chloride and 2.8 g. of α-phenylchalcone in 15 ml. of benzene gave a clear yellow-brown solution after it had been boiled 2 min. There was obtained 2.8 g. of solid product, separated by fractional crystallization from alcohol into 0.9 g. of 2,3-diphenylhydrindone, m.p. 98–100° alone or mixed with an authentic sample,[9] and 1.3 g. of colorless needles m.p. 135–153°. The latter substance was probably largely a stereoisomeric form of 2,3-diphenylhydrindone, since both products gave 2,3-diphenylindone on treatment with bromine and then potassium hydroxide.

α-Bromochalcone. Crystalline α-bromochalcone (1.5 g.) in 10 ml. of benzene containing 1.5 g. of aluminum chloride gave a green-brown solution after 10-min. boiling. There was obtained 1.5 g. of 2-bromo-3-phenylhydrindone which had m.p. 84–87° after crystallization from alcohol.

Anal. Calcd. for $C_{15}H_{11}BrO$: C, 62.7; H, 3.84. Found: C, 62.6; H, 3.92.

This product was a stereoisomer of the compound m.p. 88–90°, obtained by brominating 3-phenylhydrindone.[10] A mixture of the two had m.p. 78–83°; infrared spectra were identical except that the 87° isomer absorbed at 765, 745, and 703 cm.$^{-1}$, whereas in the 90° isomer these bands occurred at 760, 742, and 700 cm.$^{-1}$ Each of the compounds gave 3-phenylindone-semicarbazone, m.p. 205° dec. (reported[11] 212° dec.), characterized by infrared spectra.

α-Carbethoxychalcone. This substance (1.5 g.) reacted rapidly with 2 g. of aluminum chloride in 10 ml. of benzene to form a yellow oily complex which dissolved after the mixture had been boiled for 15 min. There was obtained 1.45 g. of pale yellow product that crystallized completely when it was rubbed with ether. Recrystallization from alcohol gave *2-carbethoxy-3-phenylhydrindone*, faintly pink needles, m.p. 86–88° that gave a blue-violet color with ferric chloride.

Anal. Calcd. for $C_{18}H_{17}O_3$: C, 76.9; H, 6.05. Found: C, 77.1; H, 5.90.

The product was identical (mixed melting point and infrared spectrum) with the one obtained from 2-carbethoxy-3-phenylindone by (a) catalytic reduction[12] or (b) reduction with zinc and acetic acid. Condensation of 3-phenylhydrindone with ethyl carbonate[13] in this laboratory also gave the same substance and not the form m.p. 103–104° reported by the British investigators. The latter form is more likely an allotropic modification than a stereoisomer, for it is difficult to believe configuration would be preserved in a substance so easily enolized. The instability reported by Yost and Burger is not simply steric inversion, as suggested by Baker, and is really not very pronounced. A sample kept in this laboratory for two years had become brown and sticky in spots, but still contained over 50% unchanged material.

Acknowledgment. The author thanks Mrs. O. Hamerston for analytical results.

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(8) E. Bergmann and H. Weiss, *Ann.*, **480**, 73 (1930).

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(11) E. P. Kohler, G. L. Heritage, and M. C. Burnley, *Am. Chem. J.*, **44**, 73 (1910).

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The Stevens Rearrangement in the Benzomorphan Synthesis

EDWARD M. FRY AND EVERETTE L. MAY

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Synthesis of analgesics of the benzomorphan type has been accomplished either by means of the Grewe synthesis[1] as in diagram A, or through a β-tetralone.[2] This note concerns a synthesis based on the Stevens rearrangement of the *N*-benzyl quaternary salt (III) and is diagrammed in B.

The action of basic reagents on quaternary ammonium salts may yield a variety of products depending on the nature of the reactants.[3] A recent example related to this work is that of benzylmethylpiperidinium iodide which with sodium amide in liquid ammonia gave three rearrangement products as a result of aryl- and alkyl-migrations.[4] One of these was 2-benzyl-1-methylpiperidine, obtained in 23% yield. It was felt that in the tetrahydro system (III) the most readily formed ylid would be that conjugated with the double bond and that substitution at the desired site (2- position) might thereby be favored. At present it is not possible to say what percentage of the total re-

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(1) R. Grewe, *Agnew. Chem.*, **59**, 194 (1947).

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(3) S. W. Kantor and C. R. Hauser, *J. Am. Chem. Soc.*, **73**, 4122 (1951); G. Wittig and T. F. Burger, *Ann.*, **631**, 85 (1960).

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