2-Hydroxy-4-tetrahydropyranyloxybenzoylacetone.—A solution of 5.0 g. of resacetophenone 4-tetrahydropyranyl ether in 35 ml. of dry ethyl acetate was added to 3.0 g. of powdered sodium. The reaction was lively but controlled; it was allowed to proceed at room temperature for 12 hours. Ice was added and the aqueous layer was separated, washed with ether, then poured onto a mixture of crushed ice and dilute sulfuric acid. The pasty precipitate soon became crystalline and after trituration with cold methanol formed a colorless crystalline solid (4.4 g.). Recrystallization from dilute methanol afforded colorless prisms, m.p. 97–98°.

Anal. Calcd. for $C_{15}H_{18}O_5$: C, 64.76; H, 6.51. Found: C, 64.91; H, 6.51.

Treatment of the diketone with methanolic hydrochloric acid resulted in ring closure and the simultaneous loss of the tetrahydropyranyl group with the formation in excellent yield of 2-methyl-7-hydroxychromone.

For preparative purposes, the three stages of the synthesis (tetrahydropyranylation, acylation and ring closure) are best carried out without isolation of the above-described intermediates.

2-Methyl-7-hydroxychromone.—A mixture of 15.2 g. (0.10 mole) of resacetophenone, 50 ml. of dihydropyran and 100 mg. of *p*-toluenesulfonic acid monohydrate was allowed to stand for 12 hours. Ether, 15 ml. of water and 2 ml. of 6 *N* sodium hydroxide were added, and the aqueous layer was separated and acidified. The monotetrahydropyranyl ether which separated was recrystallized from ether–petroleum ether (3.0 g.) and added to the alkali-washed ether solution containing the bulk of the material. The ether solution was dried over potassium carbonate and evaporated under reduced pressure to a semicrystalline residue. (Note: The weight of this residue, determined in another run, indicated that the main product was a bis-tetrahydropyranyl ether. This compound was not isolated.) The crude residue was dissolved in 75 ml. of dry ethyl acetate and 7.5 g. of powdered sodium was added. After two days, ice was added and the aqueous layer separated, washed with ether, and acidified. The gummy solid was stirred with cold methanol, leaving 17.0 g. of a nearly white, crystalline solid. This was dissolved in a mixture of 50 ml. of methanol and 5 ml. of concentrated hydrochloric acid, the solution was refluxed for several minutes, diluted with water, and cooled. The crystalline (pink-buff prisms) chromone weighed 10.0 g. Treatment of the methanol with which the gummy diketone had been triturated with hydrochloric acid afforded an additional 1.8 g. of chromone, m.p. 251–252°. The total yield was 11.8 g. (67% over-all) of chromone sufficiently pure for further use. This yield represents an average yield of 88% on each of the three chief steps in the over-all synthesis. When purified by recrystallization from methanol, the chromone forms colorless prisms, m.p. 253–254° (reported[1] 250°).

2-Methyl-5,8-dimethoxy-7-hydroxychromone.—A solution of 5.0 g. of 2,4-dihydroxy-3,6-dimethoxyacetophenone in 25 ml. of dihydropyran and a trace of *p*-toluenesulfonic acid was allowed to stand overnight. Ether and a few drops of dilute sodium hydroxide were added and the ether layer was separated, dried over anhydrous potassium carbonate and evaporated. The oily residue was dissolved in 50 ml. of dry ethyl acetate and added to 2 g. of powdered sodium. The next day crushed ice was added and the aqueous layer separated, washed with ether, acidified with iced dilute sulfuric acid and extracted with ether. The sirup remaining after removal of the ether was refluxed for an hour with 20 ml. of methanol and 5 ml. of concentrated hydrochloric acid. Water (75 ml.) was added and the solution cooled. The crystalline product which separated was washed with ether, the washings being used to extract the aqueous alcoholic mother liquors. The residual material from this ether extract was treated again with methanol–hydrochloric acid, yielding a second crop of crystalline chromone. The two crops (2.8 and 1.3 g.) were combined and recrystallized from methanol, yielding 2.8 g. (53%) of pure chromone, white needles, m.p. 247–248°.

The identity of the chromone was established by its independent synthesis in the following way:

2-Hydroxy-3,6-dimethoxy-4-benzyloxyacetophenone was prepared by (A) the monobenzylation of 2,4-dihydroxy-5,8-dimethoxyacetophenone (5.0 g.) in acetone (150 ml.) with benzyl chloride (3.5 g.) in the presence of potassium carbonate (15 g.). The product (5.1 g.) formed pale yellow needles, m.p. 109–110°; (B) the reaction of 2,5-dimethoxyresorcinol dibenzyl ether with acetyl chloride and aluminum chloride in benzene solution at 0°. The yield of the desired compound, m.p. 109.5–110°, was about 35%, a non-phenolic by-product being formed in about an equivalent amount.

Anal. Calcd. for $C_{17}H_{18}O_5$: C, 67.54; H, 6.00. Found: C, 67.23; H, 5.95.

2-Methyl-7-benzyloxy-5,8-dimethoxychromone was prepared by the C-acylation of the above acetophenone in the usual way with ethyl acetate and sodium, followed by ring closure of the resulting diketone. The chromone formed rosettes of crisp needles, m.p. 164–165°, from benzene–ethyl acetate.

Anal. Calcd. for $C_{19}H_{18}O_5$: C, 69.91; H, 5.56. Found: C, 69.57; H, 5.55.

2-Methyl-5,8-dimethoxy-7-hydroxychromone.—A solution of 6.2 g. of 2-methyl-5,8-dimethoxy-7-benzyloxychromone in 150 ml. of warm ethanol was hydrogenated in the presence of 3 g. of 10% palladium–charcoal at an initial pressure of about 1.7 atm. of hydrogen. The absorption of the calculated amount (1 mole) of hydrogen was completed in about 5 min. The catalyst was removed by filtration and washed with dilute alcoholic sodium hydroxide (to remove chromone which had crystallized during the hydrogenolysis). The acidified and diluted filtrate yielded 4.1 g. (92%) of the hydroxychromone, m.p. 247–248°, identical with that obtained by way of the tetrahydropyranylation route.

The chromone was characterized by the preparation of the following ethers by treatment with the corresponding halides and potassium carbonate in acetone:

7-Carboethoxymethoxy Ether.—M.p. 124–125° (from ether–petroleum ether).

Anal. Calcd. for $C_{16}H_{18}O_7$: C, 59.62; H, 5.63. Found: C, 59.31; H, 5.68.

7-*n*-Propyl Ether.—M.p. 103–105° (from dilute methanol).

Anal. Calcd. for $C_{15}H_{18}O_5$: C, 64.73; H, 6.52. Found: C, 64.51; H, 6.50.

7-*n*-Butyl Ether.—M.p. 110–112° (from dilute methanol).

Anal. Calcd. for $C_{16}H_{20}O_5$: C, 65.80; H, 6.92. Found: C, 66.02; H, 6.76.

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The Reversibility of the Friedel–Crafts Condensation. Carbomethoxystilbenes

BY REYNOLD C. FUSON AND H. G. COOKE, JR.

The transformation of various types of substituted styryl compounds into the corresponding unsubstituted 1,1-diphenylethyl derivatives takes place in the presence of benzene, hydrogen chloride and aluminum chloride. For example, nuclear halostilbenes yield 1,1,2-triphenylethane.[1] The process involves the replacement of a halophenyl radical by a phenyl radical.

$$XC_6H_4CH{=}CHC_6H_4X \xrightarrow[AlCl_3]{C_6H_6} (C_6H_5)_2CHCH_2C_6H_5 + 2C_6H_5X$$

Experiments have been carried out to determine whether phenyl groups bearing substituents other than halogen could also be expelled from the molecule in this manner. Experiments with *p*-tolyl radicals[2] indicated that the phenomenon might be general for aryl groups that carry only ortho, para-directing substituents. As expected, benzalquinaldines and benzallepidines failed to yield quino-

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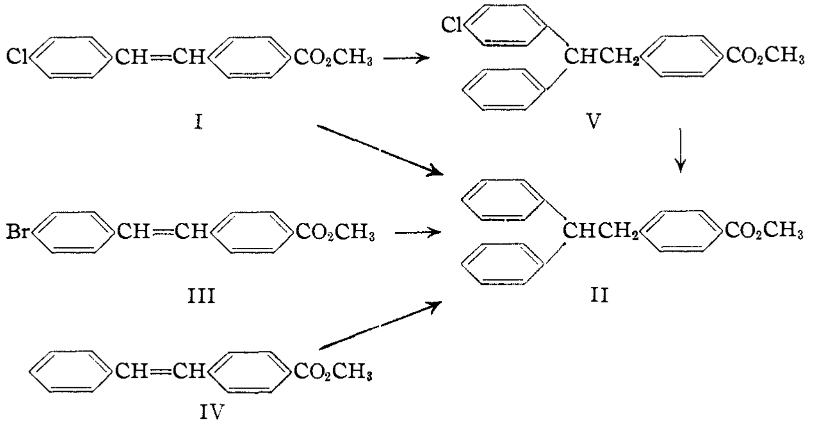
(1) L. L. Alexander and R. C. Fuson, THIS JOURNAL, **58**, 1745 (1936).

(2) J. T. Eaton, D. B. Black and R. C. Fuson, *ibid.*, **56**, 687 (1934).

line when treated with benzene and aluminum chloride.[3] That the addition of the benzene was selective and did not affect the attachment of the quinoline nucleus was attributed to the fact that the ethylenic linkage is part of a heteroconjugated system.

Similar results have now been obtained with a phenyl radical bearing a carbomethoxyl group. A study of the action of benzene and aluminum chloride on *p*-carbomethoxystilbenes, in which the central ethylenic linkage is conjugated (through a benzene ring) with the carbomethoxy group, has shown that benzene adds reversibly to the lateral double bond. The addition takes place in the manner characteristic of heteroconjugated systems and is selective; the entering phenyl radical is joined to the carbon atom remote from the benzoate nucleus.

4-Chloro-4′-carbomethoxystilbene (I) reacts with benzene to yield a chlorine-free product, 1,1-diphenyl-2-*p*-carbomethoxyphenylethane (II). The phenyl group must become attached to the carbon atom adjacent to the chlorophenyl radical in order to eliminate chlorobenzene from the molecule. It was assumed that in the second step benzene was added in the same sense. This assumption was confirmed by oxidative degradation, which produces benzophenone.



The same product (II) was obtained from 4-bromo-4′-carbomethoxystilbene (III) and from 4-carbomethoxystilbene (IV). An indication of the course of the reactions with the halogen compounds was obtained by interrupting the condensation process after a short time. In this way it was shown that the chloro ester (I) condenses with benzene to yield initially 1-phenyl-1-*p*-chlorophenyl-2-*p*-carbomethoxyphenylethane (V). Oxidation of this product produces *p*-chlorobenzophenone. Although chlorobenzene was not isolated as a product of the conversion of V to II, its formation seems certain in view of the results reported for analogous transformations.[4]

Experimental

4-Chloro-4′-carbomethoxystilbene[5] and Benzene.—A solution of 2.5 g. of the stilbene in 100 ml. of dry benzene was saturated with dry hydrogen chloride. Four grams of aluminum chloride was added and the mixture shaken for five hours in a stoppered flask. Decomposition with ice and hydrochloric acid yielded a benzene solution of 1,1-diphenyl-2-*p*-carbomethoxyphenylethane. The solvent was distilled and the ethane recrystallized from methanol; m.p. 113–114°; yield 76%.

Anal. Calcd. for $C_{22}H_{20}O_2$: C, 83.55; H, 6.38. Found: C, 83.75; H, 6.47.

The foregoing preparation was repeated with the reaction time diminished to one hour. The product was 1-phenyl-1-*p*-chlorophenyl-2-*p*-carbomethoxyphenylethane (V). It was recrystallized from methanol; m.p. 107–108°; yield 62%.

Anal. Calcd. for $C_{22}H_{19}O_2Cl$: C, 75.61; H, 5.50. Found: C, 75.53; H, 5.71.

Further treatment of the chloroethane (V) under the conditions outlined above converted it to the chlorine-free ethane (II); melting point and mixed melting point 113–114°; yield 55%.

The same ethane was obtained in a 63% yield by subjecting 4-carbomethoxystilbene to the action of benzene, hydrogen chloride and aluminum chloride. When 4-bromo-4′-carbomethoxystilbene was used and the reaction allowed to continue for five hours, the bromine-free ethane (II) was produced in a 75% yield.

Oxidation of 1-phenyl-1-*p*-chlorophenyl-2-*p*-carbomethoxyphenylethane (V) produced *p*-chlorobenzophenone, which was isolated as the 2,4-dinitrophenylhydrazone; m.p. 192–194°. Grieve and Hey[6] reported a melting point of 184–185°. The 2,4-dinitrophenylhydrazone of a known sample of *p*-chlorobenzophenone was found to melt at 195–196° and gave the following analytical values:

Anal. Calcd. for $C_{19}H_{13}O_4N_4Cl$: C, 57.50; H, 3.30; N, 14.12. Found: C, 57.69; H, 3.36; N, 14.19.

A mixture of this compound and that from the oxidation melted at 192–195°.

1,1-Diphenyl-2-*p*-carbomethoxyethane (II) was oxidized by a method similar to that used by Böeseken and Bastet[7] in the oxidation of 1,1,2-triphenylethane. A mixture of 1 g. of the ethane, 2 g. of chromic anhydride and 50 ml. of glacial acetic acid was heated on a steam-bath for 20 hours. It was poured into 200 ml. of water containing 2 g. of sirupy phosphoric acid, and an excess of ammonium hydroxide was added. Ether extraction of this mixture yielded an oil which reacted with 2,4-dinitrophenylhydrazine to give the 2,4-dinitrophenylhydrazone of benzophenone; melting point and mixed melting point 237–239°.

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[3] R. C. Fuson, L. L. Alexander, E. Ellingboe and A. Hoffman, *ibid.*, **58**, 1979 (1936).

[4] R. C. Fuson, A. P. Kozacik and J. T. Eaton, *ibid.*, **55**, 3799 (1933).

[5] For the preparation of the carbomethoxystilbenes see R. C. Fuson and H. G. Cooke, Jr., *ibid.*, **62**, 1180 (1940).

[6] W. S. M. Grieve and D. H. Hey, *J. Chem. Soc.*, 1797 (1934).

[7] J. Böeseken and M. C. Bastet, *Rec. trav. chim.*, **32**, 184 (1913).

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Complex Formation between Nickel Ion and Hydrazine in Solution

BY E. C. GILBERT AND WM. H. EVANS[1]

When hydrazine is added to a solution of a nickel salt, a deep blue color is formed, followed shortly by the precipitation of a red-violet solid complex salt if the solution is at all concentrated. This is of course accompanied by the disappearance of the blue color. If nickel sulfate is used the precipitation occurs at a very low concentration. The limited solubility of these nickel hydrazine complexes has been used to prepare a considerable number of them, including the sulfate, acetate,

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[1] Abstracted from Ph.D. thesis of Wm. H. Evans, 1947.