greenish-yellow color was first produced, being accompanied by the formation of some dregs, then turning pink-purple), gently reduced ammoniacal silver nitrate on heating and decolorized bromine water.

Anal. Calcd. for $C_{10}H_{10}O$: C, 82.16; H, 6.90. Found: C, 81.57; H, 6.83.

Its semicarbazone was prepared in aqueous methanol and recrystallized from methanol to yield long faintly greenish-yellow plates, m.p. 206–206.5° (dec.) (reported 205.5–206.5°,[2] 206°[3] for semicarbazone of II).

Its 2,4-dinitrophenylhydrazone was prepared in alcoholic sulfuric acid, and recrystallized from pyridine containing some alcohol as dark red crystals, slightly soluble in alcohol, easily soluble in pyridine, m.p. 209–210°.

Anal. Calcd. for $C_{16}H_{14}O_4N_4$: C, 58.89; H, 4.32; N, 17.17. Found: C, 59.07; H, 4.26; N, 17.04.

The same 2,4-dinitrophenylhydrazone also was obtained directly from the above semicarbazone. A small amount of another semicarbazone, apparently isomeric, was obtained from the original mother liquor of the above semicarbazone and was recrystallized from methanol containing some water as colorless crystals, easily soluble in methanol, m.p. *ca.* 174°.

Anal. Calcd. for $C_{11}H_{13}ON_3$: N, 20.68. Found: N, 20.01.

This semicarbazone was converted to the corresponding 2,4-dinitrophenylhydrazone as mentioned above, and was washed with ethanol to give orange-red crystals, m.p. *ca.* 173° (*Anal.* C, 58.45; H, 4.10).

Autoxidation of Fraction (2).—The fraction was allowed to stand for a few days in the air, whereupon the greater part crystallized as colorless plates which were washed with ethanol and then had m.p. 98–99.5° (reported 98–99°, 97–98°, 97–98.5° for lower-melting β-methylcinnamic acid[10]).

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(10) Beilstein, "Organische Chemie," Band 9, p. 614; Erstes Ergänzungswerk, Band 9, p. 254.

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Methoxy 3-Carbethoxy-1-tetralones

BY GORDON N. WALKER

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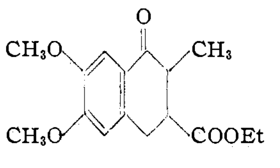
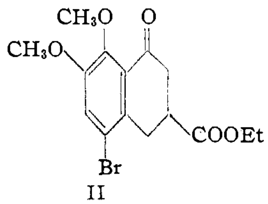
The carbethoxytetralones, I and II, are examples of a class of compounds which are difficult to synthesize by methods involving conventional cyclizations. These two compounds have now been prepared by polyphosphoric acid cyclization of the required acid esters, a method which has been applied successfully to other ketoesters of this type.[1,2]



I



II

The precursor of I was obtained by Stobbe condensation of veratraldehyde with ethyl α-methylsuccinate, hydrolysis *in situ*, partial esterification, and hydrogenation of the resulting acid ester. Cyclization with polyphosphoric acid gave a mixture of I and the corresponding keto acid. Ketoester I was identified by the 2,4-dinitrophenylhydrazone. The synthesis of II involved Stobbe condensation of veratraldehyde with ethyl succinate, hydrogenation of the acid ester, and bromination. The latter reaction led primarily to nuclear monosubstitution under the conditions described in the Experimental section. When the bromo acid ester so obtained was cyclized with polyphosphoric acid, II was formed in moderately good yield. The over-all yield of II from veratraldehyde was 14%. Although II could not be analyzed successfully, it was identified as the 2,4-dinitrophenylhydrazone.

It is possible that II will be of interest in connection with morphine synthetic studies. However, II appeared to be unstable, and attempts to alkylate it with halo-esters did not meet with success.

Experimental[3,4,5]

α-Methyl-3,4-dimethoxyphenylitaconic Acid.—Veratraldehyde (87 g., 0.524 mole) and α-methylsuccinic ester (111 g., 0.591 mole) were added to a solution of 26.5 g. (1.15 g. atoms) of sodium in 500 ml. of absolute ethanol. The mixture was stirred and refluxed for three hours, and excess ethanol (270 ml.) was distilled. The residue was treated with 475 ml. of water. The solution was distilled until 430 ml. of solvents had been collected, and was refluxed for two hours. It was diluted with 1000 ml. of cold water and acidified with 75 ml. of concentrated hydrochloric acid. The solution at this point was decanted from the tar which separated, and was washed with ethyl acetate. Further acidification, refrigeration, and trituration of the crystals with ether afforded 11.2 g. (8%) of di-acid, m.p. 172–176° (dec.). Recrystallization from methanol gave colorless crystals, m.p. 178–180.5° (dec.).

Anal. Calcd. for $C_{14}H_{16}O_6$: C, 59.99; H, 5.76. Found: C, 59.99; H, 5.79.

Monoethyl Ester of α-Methyl-3,4-dimethoxyphenylitaconic Acid.—A solution of 9.4 g. (0.034 mole) of the itaconic acid in 115 ml. of absolute ethanol containing 6 ml. of concentrated sulfuric acid was refluxed for four hours. The neutral product, after isolation in the usual way, consisted of 5.4 g. of oil. This material, apparently the diester, gave the original acid upon hydrolysis with 20% sodium hydroxide solution for three hours. The acidic fraction of the product, isolated by acidification of a dilute alkaline solution, was 4.0 g. of yellow crystals and gum. Recrystallization of this material from aqueous methanol gave 2.8 g. of pale yellow crystals, m.p. 133–135°. Further recrystallization did not raise this melting point.

Anal. Calcd. for $C_{16}H_{20}O_6$: C, 62.32; H, 6.54. Found: C, 62.46; H, 6.98.

2-Methyl-3-carbethoxy-6,7-dimethoxy-1-tetralone and 2-Methyl-3-carboxy-6,7-dimethoxy-1-tetralone. (A) **Hydrogenation.**—A solution of 2.5 g. of the acid-ester from the preceding experiment in 100 ml. of glacial acetic acid containing 2.0 g. of 5% palladium–charcoal catalyst was shaken under hydrogen (40 lb.) at 75° for 1.5 hours. Filtration of the catalyst and evaporation of the solvent gave 2.5 g. of an oil.

(B) **Cyclization.**—The hydrogenated material was stirred with 14 g. of polyphosphoric acid, and the mixture was heated at 100° for 15 minutes. Hydrolysis of the cooled solution with cold water led to a gum, which was extracted with ethyl acetate. The organic solution was washed with dilute sodium hydroxide solution, dilute acetic acid, sodium bicarbonate solution and water, and was dried over magnesium sulfate. Evaporation of the solvent gave 1.7 g. of neutral product. Trituration with ether afforded 0.9 g. of crystals, m.p. 97–109°. Recrystallization from methanol gave pale yellow crystals, m.p. 120.5–121.5°.

Anal. Calcd. for $C_{16}H_{20}O_5$: C, 65.74; H, 6.90. Found: C, 65.70; H, 6.64.

The 2,4-dinitrophenylhydrazone was recrystallized from ethyl acetate; red crystals, m.p. 241.5–243°.

Anal. Calcd. for $C_{22}H_{24}O_8N_4$: C, 55.93; H, 5.12. Found: C, 56.08; H, 5.22.

The basic solution, upon acidification with hydrochloric acid, deposited 0.4 g. of crystalline material, m.p. 194–201°,

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(1) E. C. Horning and G. N. Walker, THIS JOURNAL, **74**, 5147 (1952).

(2) G. N. Walker, *ibid.*, **75**, 3387 (1953).

(3) Melting points are corrected.

(4) Analyses were carried out by Dr. William C. Alford and his staff.

(5) Infrared spectral measurements were carried out by Mrs. Iris Siewers and Miss Alice Bernardi of the Instrument Laboratory.

after trituration with methanol. Recrystallization from methanol gave golden crystals of **2-methyl-3-carboxy-6,7-dimethoxy-1-tetralone**, m.p. 202–204.5°.

Anal. Calcd. for $C_{14}H_{16}O_5$: C, 63.62; H, 6.10. Found: C, 63.51; H, 6.32.

This compound was soluble in sodium bicarbonate solution, and gave a red precipitate with 2,4-dinitrophenylhydrazine.

Monoethyl Ester of 2-Bromo-4,5-dimethoxybenzylsuccinic Acid. (A) Stobbe Condensation.—A reaction of 89 g. (0.537 mole) of veratraldehyde with 110 g. (0.632 mole) of ethyl succinate in the presence of sodium ethoxide prepared from 13 g. (0.565 g. atom) of sodium was carried out as described previously.[1] The crude acid-ester was isolated (126 g.) and was not purified.

(B) **Hydrogenation.**—The acid-ester obtained as described in (A) was hydrogenated in glacial acetic acid in the presence of 10 g. of 5% palladium-charcoal catalyst at 80°, as described previously.[1] Ninety per cent. of the theoretical amount of hydrogen was absorbed during a period of 8 hours. The crude product was isolated by filtration of the catalyst and evaporation of the acetic acid, and weighed 128 g.

(C) **Bromination.**—A solution of the crude acid-ester from (B) (128 g., 0.43 mole) in 600 ml. of dry benzene was treated with 70 g. (0.44 mole) of bromine and 0.5 g. of magnesium. The solution was warmed on the steam-cone for two hours after the initial exothermic reaction subsided. It was cooled, diluted with ethyl acetate, washed with four portions of water, and dried over magnesium sulfate. Evaporation of the solvents and trituration of the dark residue with ether afforded 72 g. (36% from veratraldehyde) of crystalline product, m.p. 95–98°, which was sufficiently pure for further reactions. Recrystallization from ether gave colorless crystals, m.p. 110–112°.

Anal. Calcd. for $C_{15}H_{19}O_6Br$: C, 48.01; H, 5.10. Found: C, 48.19; H, 4.85.

3-Carbethoxy-5-bromo-7,8-dimethoxy-1-tetralone.—A mixture of 72 g. of the bromo-acid-ester from the preceding experiment and 400 g. of polyphosphoric acid was heated on the steam-cone with stirring for a half-hour. The cooled solution was hydrolyzed with ice and water, and the product was extracted with ethyl acetate. The organic solution was washed with dilute sodium hydroxide solution, dilute acetic acid and sodium bicarbonate solution, and was dried over magnesium sulfate. Evaporation of the solvent and distillation *in vacuo* of the dark, residual oil afforded 33.5 g. of bright-yellow oil, b.p. 218–227° (2-3 mm.), which crystallized very slowly, and which darkened gradually upon exposure to air. Recrystallization of the distilled material from the ether gave 26.3 g. (39%) of colorless crystals, m.p. 96.5–98.5°, which *exploded* when an attempt was made to burn a sample for carbon-hydrogen analysis. The infrared spectrum (chloroform) had peaks at 5.78 and 5.92 μ.

The 2,4-dinitrophenylhydrazone was recrystallized from ethyl acetate; orange crystals, m.p. 232–232.5°.

Anal. Calcd. for $C_{21}H_{21}O_8N_4Br$: C, 46.94; H, 3.94. Found: C, 46.41; H, 3.66.

Attempts to alkylate this keto-ester with γ-bromobutyronitrile and ethyl bromoacetate in the presence of sodium amide led to the formation of dark, tarry products and partial recovery of the starting material.

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Acetoacetylation of Aromatic Compounds by Boron Fluoride to Form β-Diketones. Failure with Boron and Aluminum Chlorides[1]

BY HOWARD G. WALKER, JR., JAMES J. SANDERSON[2] AND CHARLES R. HAUSER

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Meerwein and Vossen[3] observed that the Friedel–Crafts type of acetylation of benzene or toluene with acetic anhydride by boron fluoride produced small amounts of the corresponding acetoacetophenones along with the acetophenones. The β-diketone was obtained in good yield by further treatment of acetophenone with the anhydride and the reagent.

We have obtained satisfactory yields of the corresponding β-diketones from toluene, anisole and mesitylene by employing a larger excess (four moles) of the anhydride (Table I). Some of the intermediate ketone was also usually isolated. The acetoacetylation is illustrated below with toluene. The procedure employed was unsatisfactory with benzene and acetic anhydride and with toluene and propionic anhydride even though the intermediate ketones were formed in fair yields (23–30%).

$$p\text{-}CH_3C_6H_5 \xrightarrow[BF_3]{(CH_3CO)_2O} p\text{-}CH_3C_6H_4COCH_3 \xrightarrow[BF_3]{(CH_3CO)_2O} p\text{-}CH_3C_6H_4COCH_2COCH_3$$

TABLE I

ACETOACETYLATION OF AROMATIC COMPOUNDS WITH ACETIC ANHYDRIDE BY BORON FLUORIDE

Aromatic cpd.	β-Diketone	B.p. or m.p.,[a] °C.	Yield, %
Benzene	Benzoylacetone	....	2[b]
Toluene	*p*-Methylbenzoylacetone	149–151 (13.5 mm.)[c]	43
Anisole	*p*-Methoxybenzoylacetone	M.p. 53–54.5[d,e]	51
Mesitylene	Mesitoylacetone	139–141 (8.5 mm.) M.p. 44.5–45.5[f,g]	57

[a] Melting points and boiling points are uncorrected. [b] Isolated as copper salt, m.p. 195–196° (W. Wislicenus and W. Stoeber, *Ber.*, **35**, 545 (1902)). [c] *Anal.* Calcd. for $C_{11}H_{12}O_2$: C, 74.96; H, 6.87. Found: C, 74.85; H, 7.12. The copper salt (light greenish blue) melted at 213–215°. Meerwein and Vossen (ref. 3) reported 155–156° (13 mm.) as the b.p. of the β-diketone and 129–130° as the m.p. of the copper salt. [d] E. Besthorn and G. Jaegle, *Ber.*, **27**, 910 (1894). [e] The copper salt (blue-green) melted at 210–211.5°. [f] R. C. Fuson and C. F. Woodward (THIS JOURNAL, **55**, 3474 (1933)) reported 45–46°. [g] The copper salt (dark grayish blue) melted at 193–194°.

That the products were β-diketones and not diketones having both of the acetyl groups attached to the aromatic rings was established by their characteristic enol test with ferric chloride, their complete solubility in alkali, and their conversion in high yield to copper salts with copper acetate. In these cases, exclusive acetylation at the α-hydrogen of the intermediate ketone evidently occurred even with acetomesitylene. However, in another connection, we have observed acetylation at the aromatic ring as well as at the α-hydrogen on treating mesitylacetone and acetic anhydride with boron fluoride, although no pure product was isolated.

In contrast to boron fluoride, boron chloride and aluminum chloride failed to effect the acetoacetylation of toluene in the presence of excess acetic anhydride, only the usual Friedel–Crafts acetylation to form the ketone being observed. Not even a trace of β-diketone could be detected by means of the sensitive ferric chloride enol test. Aluminum chloride has been observed to effect the diacetylation of mesitylene with excess acetyl chloride, but the second acetyl group as well as the first entered the aromatic ring.[4]

We further found that boron chloride fails to ef-

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(1) Paper L on Condensations.

(2) Carbide and Carbon Chemicals Company Fellow, 1946–1947.

(3) H. Meerwein and D. Vossen, *J. prakt. Chem.*, **141**, 149 (1934).

(4) C. A. Thomas, "Anhydrous Aluminum Chloride in Organic Chemistry," Reinhold Publ. Corp., New York, N. Y., 1941, pp. 220, 222.