(U.C.L.A.) and the Clark Microanalytical Laboratories, Urbana, Illinois.

Summary

1. The total synthesis of khellinone has been carried out.

2. The nitro compound obtained as a by-product in the nitric acid oxidation of pyrogallol tribenzyl ether has been shown to be 5-nitropyrogallol tribenzyl ether.

3. The conversion of dihydrokhellinone to khellinone has been accomplished with the use of N-bromosuccinimide.

LOS ANGELES, CALIFORNIA RECEIVED JUNE 28, 1950

[CONTRIBUTION FROM THE CHARLOTTE DRAKE CARDEZA FOUNDATION, JEFFERSON MEDICAL COLLEGE]

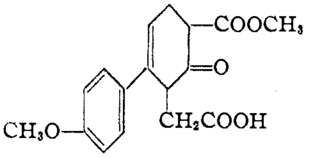
Cyclized Products from the Stobbe Condensation with δ-Keto-esters

BY D. L. TURNER

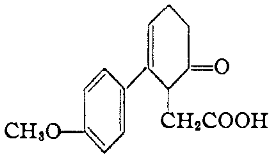
The Stobbe condensation with methyl γ-anisoylbutyrate gives in addition to the normal products, a cyclized half-ester I, which can be converted to IIIb an important intermediate for a potential estrone synthesis. The normal Stobbe products are utilized to produce the same ester IIIb by a longer route. Similar cyclization occurs in the Stobbe condensation with methyl γ-benzoyl-β-phenylbutyrate. Finally, some furyl substituted benzoylbutyric acids are described.

The Stobbe condensation with methyl γ-anisoylbutyrate, when carried out at a higher temperature, has been found to give, in addition to the normal product studied by Johnson, Jones and Schneider,[1] the cyclized ester I in a yield of about 15%. The isolation of this half-ester was facilitated by the insolubility of its potassium salt in *t*-butyl alcohol, the reaction medium. Hydrolysis of the half-ester proceeded as expected with the loss of the carbomethoxy group activated by the adjacent carbonyl group to give the acid II.

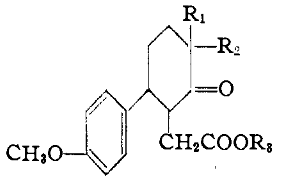
methylation gave the crystalline homolog IIIb. This same product was also obtained by an alternative route utilizing the non-crystalline part of the half-esters from the Stobbe condensation. Reduction and esterification gave dimethyl β-carbomethoxy-γ-anisylsuberate (IV), which was cyclized and methylated to IIIb. W. S. Johnson[4] has prepared IIIb from the trimethyl ester of pure β-carboxy-γ-anisylsuberic acid[1] and has kindly established the identity of his product with the material described here.



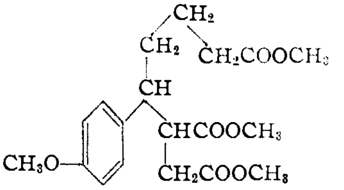
I



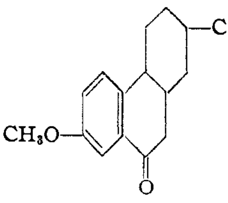
II



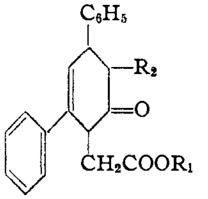
IIIa, $R_1 = H$, $R_2 = COOCH_3$, $R_3 = CH_3$
IIIb, $R_1 = CH_3$, $R_2 = COOCH_3$, $R_3 = CH_3$
IIIc, $R_1 = CH_3$, $R_2 = R_3 = H$



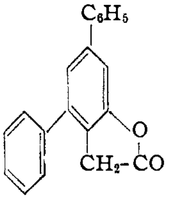
IV



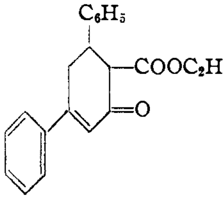
V



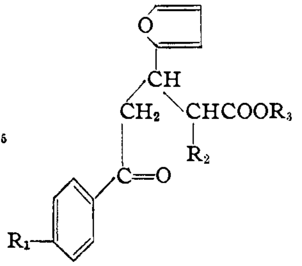
VIa, $R_1 = H$, $R_2 = COOCH_3$
VIb, $R_1 = CH_3$, $R_2 = COOCH_3$
VII, $R_1 = R_2 = H$



VIII



IX



X

The location of the double-bond in I is discussed below. The residual structure was conclusively shown by the following experiments. The unsaturated ester I was hydrogenated using palladium-on-strontium carbonate (2%) as catalyst[2,3] and esterified. The resulting keto-ester IIIa could not be obtained in crystalline form; however,

The structure of IIIb was shown by conversion to 2-methyl-7-methoxyphenanthrene, identified as the trinitrobenzene complex by comparison with an authentic sample.[5] This conversion was effected by Clemmensen reduction of the crystalline hydrolysis product IIIc, followed by cyclization of the acid chloride by the Friedel-Crafts method

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[1] W. S. Johnson, A. R. Jones and W. P. Schneider, THIS JOURNAL, **72**, 2395 (1950).

[2] A. Koebner and R. Robinson, *J. Chem. Soc.*, 1994 (1938).

[3] W. S. Johnson and H. Posvic, THIS JOURNAL, **69**, 1361 (1947).

[4] Private communication from Professor W. S. Johnson.

[5] I wish to thank Professor W. E. Bachmann, who kindly provided a sample of the trinitrobenzene complex of 2-methyl-7-methoxyphenanthrene.

TABLE I

SUBSTITUTED BENZOYLBUTYRIC ACIDS

R_1	Structure X R_2	R_3	Recryst. solvent	Yield, %	M.p., °C.	Formula[a]	Carbon, % Calcd.	Carbon, % Found	Hydrogen, % Calcd.	Hydrogen, % Found
H	$COOC_2H_5$	C_2H_5	Et_2O–pentane	75	42–43	$C_{20}H_{22}O_6$	67.02	66.98	6.19	6.30
H	H	H	EtOAc	30[b]	118–120	$C_{15}H_{14}O_4$	69.75	70.00	5.46	5.53
H	H	CH_3	MeOH	70	59–61	$C_{16}H_{16}O_4$	70.57	70.67	5.92	5.90
C_6H_{11}[c]	$COOCH_3$	CH_3	EtOH–pentane	50	86–87	$C_{24}H_{28}O_6$	69.88	70.12	6.84	6.84
C_6H_{11}[c]	COOH	H	CH_3NO_2, Et_2O–pentane	64	116–118	$C_{22}H_{24}O_6$	68.74	68.46	6.29	6.40
C_6H_{11}[c]	H	H	Et_2O–pentane	87	127–128	$C_{21}H_{24}O_4$	74.09	74.29	7.11	7.10
C_6H_{11}[c]	H	CH_3	MeOH	86	66–68	$C_{22}H_{26}O_4$	74.55	74.61	7.40	7.17
OCH_3	H	H	Et_2O–pentane	71[d]	124–125	$C_{16}H_{16}O_5$	66.66	66.64	5.60	5.46
OCH_3	H	CH_3	Liquid[e]							
Semicarbazone of preceding			EtOAc		140–142	$C_{18}H_{21}N_3O_5$	60.16	60.34	5.89	5.88

[a] All analyses by R.[15] [b] From the precediug ester. [c] C_6H_{11} = cyclohexyl-. [d] From the crude malonic acid. [e] B. p. 236° (3 mm.).

to give 9-keto-7-methoxy-2-methyloctahydrophenanthrene (V), which was converted by hydrogenolysis of the carbonyl group and dehydrogenation to 2-methyl-7-methoxyphenanthrene.

The double-bond in the product from methyl anisoylbutyrate (I) was assigned to the position indicated because the absorption spectrum of this substance shows a maximum at 289 mμ. If the ester I had the α,β-unsaturated ketone structure, it would be expected to absorb at a higher wave length like p-methoxybenzalacetone, which has a band at 318 mμ.[6] The absorption spectrum of I is closer to that of a methoxystyrene[7] (Table II).

The Stobbe condensation with methyl β-phenyl-γ-benzoylbutyrate[8,9] was also studied. The cyclized product, similar to that obtained with methyl anisoylbutyrate, was VIa. This was easily separated from the other products of the Stobbe condensation because of its insolubility in ether; the yield was 43%. The structure of VIa was shown by dehydrogenation to VIII. The ultraviolet absorption spectrum of this benzofuranone and that of m-terphenyl[10,11] are essentially identical, (Table II). The ester VIb was converted to a keto-acid VII by hydrolysis; this ketone was isolated as the semicarbazone.

The double-bond in VI and VII was again assigned to the position not conjugated with the carbonyl group because of the absorption spectrum. For comparison, the absorption spectrum of 2-carbethoxy-3,5-diphenyl-5-cyclohexen-1-one[12] (IX) was studied. This ketone has a maximum at 287 mμ and its semicarbazone has one at 308 mμ, thus showing the bathochromic shift for the semicarbazone as observed by Evans and Gillam[13] for non-aromatic α,β-unsaturated ketones. Since the ester VIb has a maximum at 266 mμ and the semicarbazone of VII has one at 279 mμ, the double-bond is probably not conjugated with the carbonyl group. The shift of the maximum in VI compared with styrene is similar to the shift observed in the spectrum of I compared with p-methoxystyrene (Table II).

TABLE II

ULTRAVIOLET ABSORPTION SPECTRA[a]

Substance	Maxima mμ	Maxima log ε	Minima mμ	Minima log ε
1. New determinations				
Ester I	289	4.19	256	3.96
Ester VIb	266	4.10		
Knoevenagel ketone (IX)	287	4.32	239	3.56
Semicarbazone of VII	279	4.42	241	3.94
Semicarbazone of IX[b]	308	4.41	251	3.80
Benzofuranone (VIII)[c]	244	4.51	223	4.30
2. Data from the literature				
Benzalacetone[d]	286	4.37	237	3.22
p-Anisalacetone[d]	318	4.39	253	3.05
	232	4.02		
α,β-Dimethylstyrene[e]	244	3.94		
3-Methyl-4-methoxystyrene[f,g]	265	4.18		
m-Terphenyl[h]	244–248	4.6	224	4.3

[a] Determinations were made with the Beckman spectrophotometer Model DU using 95% ethanol as solvent except where otherwise stated. [b] The solvent in this case contained 0.02% chloroform. [c] The solvent contained 0.1% chloroform. [d] From Wilds, *et al.*[6] [e] From Y. Hirschberg, THIS JOURNAL, 71, 3241 (1949). [f] From Laitinen, Miller and Parks.[7] [g] The solvent was chloroform. [h] Read from the curve of Pickett, Walter and France.[10]

The availability of some furfurylidene acetophenones[14] suggested the preparation of β-furyl-γ-benzoylbutyric acids for the study of the Stobbe condensation with esters of these acids. The substances shown in Table I were prepared by the general methods used by Vorländer and Knötzsch[8] in their study of the Michael reaction with benzalacetophenone. The Stobbe condensation proceeded smoothly with methyl β-furyl-γ-benzoylbutyrate and methyl β-furyl-γ-p-cyclohexylbenzoylbutyrate, but no crystalline product was obtained.

I wish to thank Professor W. S. Johnson for his coöperation and his kindness in permitting me to refer to his unpublished work. Mrs. R. P. Gerhart gave technical assistance. Part of the work described here was aided by a grant from the American Cancer Society recommended by the Committee on Growth of the National Research Council.

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(6) A. L. Wilds, *et al.*, THIS JOURNAL, **69**, 1985 (1947).

(7) H. A. Laitinen, F. A. Miller and T. D. Parks, *ibid.*, **69**, 2707 (1947).

(8) D. Vorländer and A. Knötzsch, *Ann.*, **294**, 317 (1897).

(9) E. P. Kohler and J. B. Conant, THIS JOURNAL, **39**, 1404 (1917).

(10) L. W. Pickett, G. F. Walter and H. France, *ibid.*, **58**, 2296 (1936).

(11) A. E. Gillam and D. H. Hey, *J. Chem. Soc.*, 1170 (1939).

(12) E. Knoevenagel, *Ann.*, **281**, 58 (1894).

(13) L. K. Evans and A. E. Gillam, *J. Chem. Soc.*, 565 (1943).

(14) D. L. Turner, THIS JOURNAL, **71**, 612 (1949).

Experimental[15]

Methyl γ-Anisoylbutyrate.—γ-Anisoylbutyric acid[16] was esterified by the method of Clinton and Laskowski.[17] The ester was crystallized from ether–pentane, m.p. 49–51°.

Stobbe Condensation.—To a refluxing solution of 74 g. of potassium in 1600 ml. of dry *t*-butyl alcohol[18] under an atmosphere of nitrogen, was added a solution of 490 g. of methyl γ-anisoylbutyrate in 380 g. of dimethyl succinate.[18] The ester mixture was added dropwise because heat was produced. Upon completion of the addition, the mixture was refluxed for 40 minutes, cooled under nitrogen and the solid potassium salt was filtered. It was dissolved in 1500 ml. of water and acidified with concentrated hydrochloric acid. The precipitated oil crystallized after standing overnight. The oily crystals were filtered and dried. They were crystallized from ethyl acetate and weighed 89 g., m.p. 150–160°. Recrystallized from acetic acid and then from ethyl acetate, it had m.p. 163–165° and weighed 45 g. This substance is **3-carbomethoxy-2-keto-6-*p*-anisyl-5-cyclohexen-1-acetic acid.**

Anal. Calcd. for $C_{17}H_{18}O_6$: C, 64.14; H, 5.70. Found: C, 64.10; H, 5.65. (R.)

The *t*-butyl alcohol mother liquor from the crystalline potassium salt was treated in the usual manner,[19] by acidification and transferring to ether.

The half-ester was separated from neutral material by extraction with 5% potassium carbonate. The alkaline solution was acidified with hydrochloric acid and the product was taken up in ether. The ethereal solution was dried and evaporated to give 234 g. of an oil.

2-Keto-6-*p*-anisyl-5-cyclohexen-1-acetic Acid.—The crystalline ester (5 g.) was refluxed for 3 hours with 10 g. of barium hydroxide octahydrate in 100 ml. of water and 150 ml. of ethanol. The solution was cooled and filtered and the barium salts were decomposed by shaking with 2 *N* hydrochloric acid and ether. The ethereal solution was washed, dried and distilled, and the residue was crystallized from ethyl acetate–pentane and then from ether–pentane and ethyl acetate giving 0.95 g., m.p. 137–138.5°.

Anal. Calcd. for $C_{15}H_{16}O_4$: C, 69.21; H, 6.20. Found: C, 69.08; H, 6.21. (R.)

The methyl ester was made with diazomethane in ether and crystallized from ethanol, m.p. 91°.

Anal. Calcd. for $C_{16}H_{18}O_4$: C, 70.05; H, 6.61. Found: C, 69.91; H, 6.63. (R.)

Dimethyl β-Carbomethoxy-γ-*p*-anisylsuberate.—The oily half-ester (115 g.) from the Stobbe condensation was hydrogenated in 250 ml. of methanol with 1 g. of Adams platinum oxide catalyst at 60 p.s.i. When 1 mole of hydrogen was absorbed (after 24 hours) the catalyst was filtered and the solution was treated with a solution of 70 g. of potassium hydroxide in 30 ml. of water and 100 ml. of methanol. After refluxing for 1 hour, the solution was diluted with water and acidified with hydrochloric acid. The oily acid was taken up in ether, the ether was washed, dried and evaporated. The oily residue was esterified by the method of Clinton and Laskowski.[17] The neutral esters were distilled *in vacuo* and a fraction boiling 195–207° at 2 mm. was collected (53 g.).

Anal. Calcd. for $C_{19}H_{26}O_7$: C, 62.28; H, 7.15. Found: C, 62.10; H, 7.17. (R.)

Methyl 3-Carbomethoxy-2-keto-6-*p*-anisyl-3-methyl-cyclohexan-1-acetate (a) From the Crystalline Stobbe Condensation Product.—A pure sample of the half-ester (3-carbomethoxy-2-keto-6-*p*-anisyl-5-cyclohexen-1-acetic acid) (10 g.) was mixed with 10 g. of palladium-on-strontium carbonate (2% palladium)[3] and 150 ml. of methanol. The mixture was shaken with hydrogen at 40° and 50 p.s.i. The theoretical quantity of hydrogen was absorbed in 1 hour. The solution was filtered and evaporated and the oily residue was esterified with ethereal diazomethane. The oily reduced ester was dried thoroughly by distilling benzene from it. It was then dissolved in 30 ml. of dry benzene[18] and added to a solution of 2.3 g. of sodium in 45 ml. of dry methanol.[18] After refluxing for 2 minutes, the mixture was cooled in ice-water and treated with 20 ml. of methyl iodide.[18] After standing overnight at room temperature, an additional 20 ml. of methyl iodide was added and the mixture was refluxed for 30 minutes. It was acidified with acetic acid, water was added to dissolve the sodium iodide, and the solution was evaporated *in vacuo* on the steam-bath. The residue was taken up in benzene; this was washed with water, sodium thiosulfate solution and saturated sodium bicarbonate. The solution was then dried over sodium sulfate and evaporated. The product was crystallized twice from methanol giving 3.9 g. of pure ester, m.p. 93–94°.

Anal. Calcd. for $C_{19}H_{24}O_6$: C, 65.50; H, 6.94. Found: C, 65.83; H, 6.99. (R.)

(b) From Dimethyl β-Carbomethoxy-γ-*p*-anisylsuberate Prepared as Described Above.—To 113 g. of the trimethyl ester dissolved in 500 ml. of benzene,[18] was added 35.4 g. of sodium methylate (dry powder furnished by the Mathieson Chemical Corporation). The mixture was refluxed for 2 hours under nitrogen. The mixture was cooled and treated with 72 ml. of methyl iodide. After standing overnight at room temperature, the mixture was refluxed for 40 minutes. It was then cooled and acidified with acetic acid. The further treatment followed that described above in part (a). Crystallized from methanol, the pure product weighed 34 g. and melted at 93–94° alone or when mixed with the material of section (a). Professor W. S. Johnson found the m.p. 95–95.5° for the same sample with his melting point apparatus.

Anal. Calcd. for $C_{19}H_{24}O_6$: C, 65.50; H, 6.94. Found: C, 65.65; H, 6.90. (R.)

Professor W. S. Johnson[4] has prepared this substance from his pure 6,7-dicarboxy-5-*p*-anisylheptanoic acid.[1] He reports the melting point 95–95.5°, alone or when mixed with the ester described here.

2-Keto-6-*p*-anisyl-3-methyl-cyclohexan-1-acetic Acid.—The preceding ester (1.8 g.) was refluxed in 20 ml. of methanol with 5 ml. of 45% potassium hydroxide solution for 30 minutes. The solution was diluted with 30 ml. of water, the methanol was distilled and the residual solution was cooled, acidified with hydrochloric acid, and extracted with ether. The ether was dried and removed by distillation. The resulting oil was crystallized from ether–pentane, m.p. 135–137°.

Anal. Calcd. for $C_{16}H_{20}O_4$: C, 69.54; H, 7.30. Found: C, 69.57; H, 7.35. (R.)

9-Keto-7-methoxy-2-methyl-1,2,3,4,4a,9,10,10a-octahydrophenanthrene.—Six grams of 2-keto-6-*p*-anisyl-3-methyl-cyclohexan-1-acetic acid was reduced by the Clemmensen method, using 24 ml. of toluene, 15 g. of amalgamated zinc (20 mesh) and 18 ml. of concentrated hydrochloric acid. After refluxing for 6 hours, 18 ml. additional hydrochloric acid was added. After 28 hours refluxing, the mixture was cooled, extracted with ether, and the ethereal solution was washed, dried and distilled. The toluene was removed by distillation *in vacuo* on the steam-bath. The residue was crystallized from ethyl acetate–pentane, but the crystals obtained were identified as impure starting material. They weighed 1.7 g. The mother liquor was evaporated and gave 3.8 g. of an oil. This was dried by distilling benzene from it and then dissolved in 70 ml. of dry benzene[18] and treated with 4 g. of phosphorus pentachloride. After standing for 1 hour at room temperature, the benzene was distilled *in vacuo* from the steam-bath. The residue was dissolved in 30 ml. of dry nitrobenzene and cooled to 5–10° while a solution of 5 g. of aluminum chloride in 15 ml. of nitrobenzene was added dropwise with stirring. After standing at room temperature for 7 days, the mixture was hydrolyzed with ice and hydrochloric acid and steam distilled. The residue was extracted with ether, and the ethereal solution was washed with saturated sodium bicarbonate solution. The ether was dried and distilled and the residue was remethylated by heating for 2 hours on the steam-bath with methyl *p*-toluenesulfonate in 10% sodium

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(15) The melting points were taken using a "Meltpointer" (Scientific Glass Apparatus Co.) with a thermometer calibrated by melting points taken previously with Anschütz thermometers; no other correction was added. The microanalyses are by James Rigas, Brooklyn, N. Y. (R), Dr. Adalbert Elek, Los Angeles, Calif. (E), and Dr. E. W. D. Huffman, Denver, Colo. (H).

(16) E. Berliner, "Organic Reactions," Vol. 5, p. 229 (1949).

(17) R. O. Clinton and S. Laskowski, THIS JOURNAL, **70**, 3135 (1948).

(18) Dried over calcium hydride.

(19) W. S. Johnson, A. Goldman and W. P. Schneider, THIS JOURNAL, **67**, 1357 (1945).

hydroxide.[20] The cooled alkaline solution was decanted from the precipitated methylation product. The latter was crystallized from aqueous methanol using Darco. This gave 0.5 g., m.p. 98–100°. Recrystallized from ether–pentane, it melted at 99–100°.

Anal. Calcd. for $C_{16}H_{20}O_2$: C, 78.65; H, 8.25. Found: C, 78.76, 78.62; H, 8.33, 8.28. (H.)

2-Methyl-7-methoxyphenanthrene.—The preceding substance (200 mg.) was hydrogenated in 40 ml. of acetic acid with 100 mg. of palladium-on-charcoal (30%)[21] in the presence of 1 ml. of perchloric acid 60%[22] at 54 p.s.i. for 5 hours. The mixture was filtered, diluted with water, and extracted five times with ether. The ethereal solution was washed with saturated sodium bicarbonate, dried and distilled. The residue was heated under nitrogen with 200 mg. of palladium-on-charcoal (5%)[23] for 7 minutes at 270°. The product was dissolved in acetone, filtered and evaporated. The residue was treated with an ethanolic solution of *sym*-trinitrobenzene, and the resulting trinitrobenzene complex was crystallized several times from ethanol to give about 10 mg. of pure trinitrobenzene complex in the form of yellow needles, m.p. 143–147°. When mixed with an authentic sample of the trinitrobenzene complex of 2-methyl-7-methoxyphenanthrene (m.p. 144–146°),[24] the m.p. was 144–146°.

Anal. Calcd. for $C_{22}H_{17}N_3O_7$: C, 60.69; H, 3.94. Found: C, 60.85; H, 4.10. (H.)

Stobbe Condensation with Methyl γ-Benzoyl-β-phenylbutyrate.—This was conducted as described above using 216.5 g. of methyl γ-benzoyl-β-phenylbutyrate and 146 g. of dimethyl succinate added to a solution of 39 g. of potassium in 1050 ml. of *t*-butyl alcohol. The product was isolated by the method employed by Johnson, Goldman and Schneider.[19] The neutral fraction gave 66 g. of recovered methyl γ-benzoyl-β-phenylbutyrate. The acid fraction gave 180 g. of an oily product which crystallized readily from ether to give 73 g. of crystals, m.p. 134–138°. Partial evaporation of the ethereal mother-liquor gave additional crystals. The crystalline substance was recrystallized from ether, m.p. 140–142°.

Anal. Calcd. for $C_{22}H_{20}O_5$: C, 72.51; H, 5.53; neut. equiv., 364. Found: C, 72.33; H, 5.61; neut. equiv., 367. (R.)

Methyl 3-Carbomethoxy-2-keto-4,6-diphenyl-5-cyclohexen-1-acetate.—The methyl ester of the above acid prepared by treatment with ethereal diazomethane or by the method of Clinton and Laskowski[17] was crystallized from ethanol, m.p. 121–122°. Both the acid and the ester produce a green color when treated with alcoholic ferric chloride.

Anal. Calcd. for $C_{23}H_{22}O_5$: C, 73.00; H, 5.86. Found: C, 73.10, 73.01; H, 5.96, 5.96. (R.)

Semicarbazone of 2-Keto-4,6-diphenyl-5-cyclohexen-1-acetic Acid.—A 2.0-g. sample of the crystalline half-ester from the Stobbe condensation was suspended in 20 ml. of 10% aqueous sodium hydroxide solution. The mixture was heated on the steam-bath for 15 minutes, cooled, and acidified. The resulting oil was extracted with ether. The extract was washed, dried and distilled. The residual oil was heated on the steam-bath with 1 g. of semicarbazide hydrochloride and 1.8 g. of potassium acetate in 10 ml. water for 30 minutes. The semicarbazone crystallized rapidly while the solution was hot. It was recrystallized from ethyl acetate, in which it is very insoluble, and then from pyridine–pentane. It decomposed at 188–190°. It was freely soluble in cold sodium hydroxide solution.

Anal. Calcd. for $C_{21}H_{21}N_3O_3$: C, 69.40; H, 5.83. Found: C, 70.08, 69.68, 69.53; H, 5.80, 6.09, 6.00. (R.)

4,6-Diphenyl-2-benzofuranone.—(a) The methyl 3-carbomethoxy-2-keto-4,6-diphenyl-5-cyclohexen-1-acetate (2.0 g.) was dissolved in 10 ml. of ethanol. Addition of 10 ml. of 45% potassium hydroxide gave a yellow solution which soon turned into a solid mass of potassium salt. This mixture was heated in an oil-bath kept at 180°. The salt went into solution at first but after evaporation of the ethanol, a new crystalline precipitate appeared which soon turned to a yellow oil. After heating for 20 minutes more, the solution was cooled; the oil, which was a potassium salt, solidified. The mixture was diluted with water, acidified with hydrochloric acid, and extracted with ether. The ethereal solution was washed, dried and evaporated. The oily acid remaining was refluxed with 20 ml. of acetic acid and 12 ml. of hydrochloric acid for 4 hours. The mixture was diluted with water, and extracted with ether. An acid which could not be crystallized was removed by extraction with 5% sodium carbonate solution. The neutral ether solution on evaporation gave violet colored material which was crystallized from ethanol to give 0.15 g. of almost colorless crystals, m.p. 155–156°. The substance gave a red color with alcoholic ferric chloride. It dissolved in hot aqueous alkali to give a non-crystalline acid on acidification. It did not react with diazomethane.

Anal. Calcd. for $C_{20}H_{14}O_2$: C, 83.89; H, 4.93. Found: C, 83.69; H, 5.05. (E.)

(b) Methyl 3-carbomethoxy-2-keto-4,6-diphenyl-5-cyclohexen-1-acetate (5.0 g.) was dehydrogenated with 2.6 g. of 10% palladium-on-Darco G-60[25] at 275–285° for 4 hours and then at 310° for 1 hour. The product was taken up in ether. The solution was washed with dilute sodium bicarbonate. Then a phenolic fraction was removed with 5% sodium hydroxide solution. The ether became green fluorescent and the phenol was removed very slowly, indicating that it was produced by hydrolysis of the benzofuranone. The sodium hydroxide solution was acidified and the product was taken up in ether. The ethereal solution was washed with sodium bicarbonate solution, dried and distilled to remove solvent. The residue was crystallized from methanol, a first crop of impure material being discarded. Recrystallized from ethanol several times the second crop material gave 0.5 g. of crystals, m.p. 155–156° alone, or when mixed with the material of (a) above.

Semicarbazone of 2-Carbethoxy-3,5-diphenyl-5-cyclohexen-1-one.—The ketone prepared according to Knoevenagel[12] had m.p. 114–116° (reported,[12] 111–112°). It was converted to the semicarbazone by the pyridine–ethanol method. The semicarbazone was crystallized from pyridine–ethanol, m.p. 202–204°.

Anal. Calcd. for $C_{22}H_{23}N_3O_3$: C, 70.01; H, 6.14. Found: C, 69.94; H, 6.19. (E.)

Michael Reaction with Malonic Ester and Furfurylidene Ketones[8] (Table I).—A solution of the ketone (1 mole) and ethyl or methyl malonate (1.25 moles) in 300 ml. of the appropriate alcohol[18] was heated to 55° and dry sodium methylate (Mathieson Chemical Corp.) was added until the liquid was just alkaline to brom cresol purple indicator. The mixture was refluxed for 1 hour and then cooled in a Dry Ice chest. Crystallization was brought about by adding pentane and rubbing with a glass rod. The substituted malonates were hydrolyzed by a method similar to that described for the product from benzalacetophenone.[26] The malonic acids were decarboxylated by heating to 180° for 30 minutes, and the substituted benzoylbutyric acids thus produced, were esterified by the method of Clinton and Laskowski.[17]

The malonic acid from furfurylidene acetophenone, after many recrystallizations, was not pure, m.p. 127–136° (gas evolution). It was decarboxylated in crude form.

Difficulty was also experienced with the reaction product from furfurylidene *p*-methoxyacetophenone and ethyl malonate, which could not be crystallized. The reaction mixture was hydrolyzed by adding the calculated quantity of 45% potassium hydroxide, and heating on the steam-bath for 30 minutes. The mixture was cooled, and the recovered furfurylidene ketone was filtered. The filtrate was diluted with water and washed with ether by three extractions. It was then acidified at 0° with hydrochloric acid. The precipitated acid was taken up in ether. The ethereal solution was washed, dried and distilled to remove solvent, and the remaining acid was crystallized from carbon tetrachloride, m.p. 84–93°. Several recrystallizations from various solvents did not effect any further purification. The crude malonic acid was therefore decarboxylated.

PHILADELPHIA 7, PENNA. RECEIVED SEPTEMBER 6, 1950

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(20) A. Cohen, J. W. Cook and C. L. Hewett, *J. Chem. Soc.*, 445 (1935).

(21) Prepared by the method of R. Mozingo, "Org. Synth.," **26**, 77 (1946), method B with an increased quantity of palladium chloride.

(22) *Cf.* K. W. Rosenmund and E. Karg, *Ber.*, **75**, 1850 (1942).

(23) This was a commercial catalyst furnished by the Wilkens-Anderson Company, Chicago.

(24) W. E. Bachmann and J. M. Chemerda, THIS JOURNAL, **70**, 1468 (1948).

(25) R. Mozingo, *Org. Syntheses*, **26**, 77 (1946), method D.

(26) T. L. Davis, THIS JOURNAL, **41**, 1132 (1919).