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Friedländer Syntheses with *o*-Aminoaryl Ketones. III. Acid-Catalyzed Condensations of *o*-Aminobenzophenone with Polyfunctional Carbonyl Compounds (1,2)

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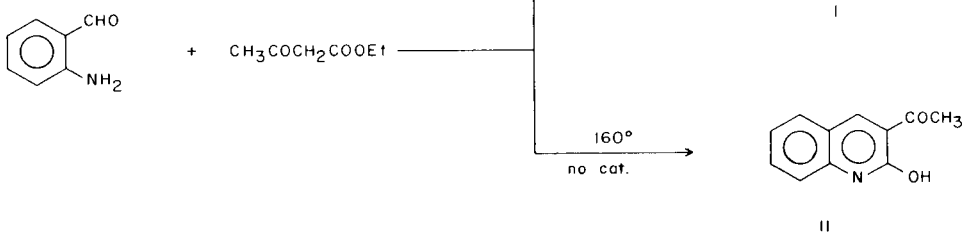
The acid-catalyzed condensations of *o*-aminobenzophenone with a variety of diketones, ketoesters, ketoacids, and representatives of several other classes of polyfunctional carbonyl compounds containing the -$COCH_2$- moiety have been investigated. Under the conditions used, normal Friedländer-type ring-closure was found to occur in all cases, giving good yields of substituted quinolines which have been identified as the 4-phenyl analogs of the products obtained in classical base-catalyzed Friedländer condensations with *o*-aminobenzaldehyde. The method appears to be quite general and should provide a convenient synthetic route to a previously inaccessible series of 4-arylquinolines.

In the first paper in this series (3), it was shown that under appropriate conditions involving acid catalysis *o*-aminobenzophenone can be induced to undergo Friedländer-type condensations with monofunctional ketones having α-methyl or α-methylene groups. The present paper describes an extension of this method to condensations of *o*-aminobenzophenone with more complex types of carbonyl compounds containing the -$COCH_2$- moiety, including a variety of diketones, ketoesters, ketoacids, and representatives of several other classes of polyfunctional ketones. The compounds used and the results obtained are summarized in Table I.

Although most of the polyfunctional carbonyl compounds used in the present investigation have previously been found to react normally with *o*-aminobenzaldehyde in classical base-catalyzed Friedländer syntheses (4-16), no

SCHEME 1



SCHEME 2

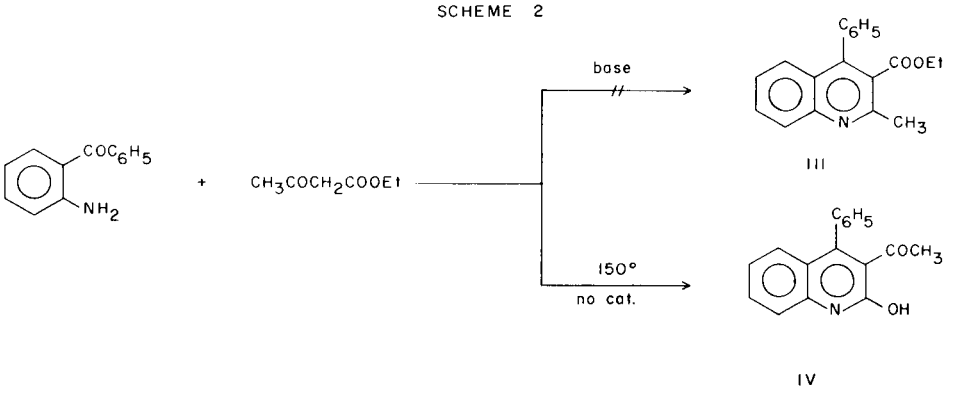
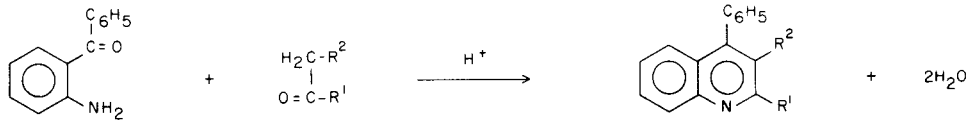


TABLE I

Acid-Catalyzed Condensations of *o*-Aminobenzophenone with Polyfunctional Carbonyl Compounds



Carbonyl compound	R^1	R^2	Reaction time, hr.	Product	Yield (a) %
1-Phenyl-1,2-propanedione	COC_6H_5	H	4	2-Benzoyl-4-phenylquinoline	57
Acetylacetone	CH_3	$COCH_3$	2	3-Acetyl-4-phenylquinaldine (b)	84
Dibenzoylmethane	C_6H_5	COC_6H_5	12	3-Benzoyl-2,4-diphenylquinoline	59 (c)
Benzoylacetone	CH_3	COC_6H_5	2	3-Benzoyl-4-phenylquinaldine (d)	86
1,3-Cyclohexanedione	$CH_2CH_2CH_2CO$		2	1,2,3,4-Tetrahydro-1-oxo-9-phenylacridine	85
5,5-Dimethyl-1,3-cyclohexanedione	$CH_2C(CH_3)_2CH_2CO$		2	1,2,3,4-Tetrahydro-3,3-dimethyl-1-oxo-9-phenylacridine	86
1,3-Indandione	*o*-C_6H_4CO		2	10-Phenyl-11*H*-indeno[1,2-*b*]quinolin-11-one	83
Ethyl acetoacetate	CH_3	$COOC_2H_5$	2	Ethyl 4-phenyl-3-quinaldinecarboxylate	85
Ethyl benzoylacetate	C_6H_5	$COOC_2H_5$	12 (e)	Ethyl 2,4-diphenyl-3-quinolinecarboxylate	73
Diethyl oxalacetate	$COOC_2H_5$	$COOC_2H_5$	6 (e)	Diethyl 4-phenylacridinate	66
Diethyl acetonedicarboxylate	$CH_2COOC_2H_5$	$COOC_2H_5$	10 (e)	Ethyl 3-carbethoxy-4-phenyl-2-quinolineacetate	69
Dimethyl acetonedicarboxylate	CH_2COOCH_3	$COOCH_3$	12 (f)	Methyl 3-carbomethoxy-4-phenyl-2-quinolineacetate	89 (g)
Tetronic acid	CH_2OCO		1	2-Hydroxymethyl-4-phenyl-3-quinolinecarboxylic acid lactone (h)	86
Ethyl benzoylpyruvate	$COOC_2H_5$	COC_6H_5	6 (e)	Ethyl 3-benzoyl-4-phenylquinaldate	65
Ethyl phenylpyruvate	$COOC_2H_5$	C_6H_5	6 (e)	Ethyl 3,4-diphenylquinaldate	53
Phenylpyruvic acid	COOH (i)	C_6H_5	2	3,4-Diphenylquinoline	69 (j)
Levulinic acid	CH_3	CH_2COOH	12	4-Phenyl-3-quinaldineacetic acid	61 (k)
β-Benzoylpropionic acid	C_6H_5	CH_2COOH	24	2,4-Diphenyl-3-quinolineacetic acid	52 (l)
Benzoylacetonitrile	C_6H_5	CN	4	2,4-Diphenyl-3-quinolinecarbonitrile	72
α-Methoxyacetophenone	C_6H_5	OCH_3	3	3-Methoxy-2,4-diphenylquinoline	69
Hydroxyacetone (m)	CH_3	OH	4	2-Methyl-4-phenyl-3-quinolinol	51

(a) After one recrystallization from ethanol, unless otherwise noted; melting points of these products were not more than 2° below those reported for analytically pure samples. (b) Reported in the preceding paper in this series; see ref. 1. (c) Recrystallized twice. (d) NMR spectrum in deuteriochloroform: complex multiplets between τ 1.7-2.9 (14 H, aromatic), singlet at τ 7.36 (3 H, α-CH_3). (e) Reaction solvent, ethanol. (f) Reaction solvent, methanol. (g) Recrystallized from methanol. (h) Previously prepared by cyclodehydration of β-(*o*-benzoylphenylimino)-butyrolactone; see E. A. Fehnel, J. A. Deyrup, and M. B. Davidson, *J. Org. Chem.*, 23, 1996 (1958). (i) R^1 = COOH in reactant only; in product R^1 = H because of spontaneous decarboxylation of initially formed quinaldic acid. (j) In this case, 43% was isolated directly as 3,4-diphenylquinoline and an additional 26% was isolated as the picrate derivative. (k) Monohydrate. (l) Ethanol solvate. (m) Prepared *in situ* by hydrolysis of acetonyl acetate as described in the Experimental Section.

TABLE II

New Compounds Prepared by Acid-Catalyzed Friedländer Condensations with *o*-Aminobenzophenone

Compound	M.p., °C	Formula	Calcd., %			Found, %			Picrate derivative			
			C	H	N	C	H	N	M.p., °C	Formula	N, % Calcd.	N, % Found
2-Benzoyl-4-phenylquinoline	121-122	$C_{22}H_{15}NO$	85.41	4.89	4.53	85.21	4.66	4.58	167-168	$C_{28}H_{18}N_4O_8$	10.41	10.16
3-Benzoyl-2,4-diphenylquinoline	146-147	$C_{28}H_{19}NO$	87.25	4.97	3.63	87.00	4.94	3.83	163-164	$C_{34}H_{22}N_4O_8$	9.12	9.03
3-Benzoyl-4-phenylquinaldine	138-139	$C_{23}H_{17}NO$	85.41	5.30	4.33	85.29	5.33	4.47	210-211	$C_{29}H_{20}N_4O_8$	10.14	9.94
1,2,3,4-Tetrahydro-1-oxo-9-phenylacridine	156-157	$C_{19}H_{15}NO$	83.49	5.53	5.13	83.98	5.64	5.15	188-189 dec.	$C_{25}H_{18}N_4O_8$	11.15	11.00
1,2,3,4-Tetrahydro-3,3-dimethyl-1-oxo-9-phenylacridine	190-191	$C_{21}H_{19}NO$	83.68	6.35	4.65	83.50	6.46	4.64	213-214 dec.	$C_{27}H_{22}N_4O_8$	10.56	10.53
10-Phenyl-11*H*-indeno[1,2-*b*]-quinolin-11-one	187-188	$C_{22}H_{13}NO$	85.97	4.26	4.56	85.96	4.45	4.57	209-210	$C_{28}H_{16}N_4O_8$	10.44	10.46
Ethyl 4-phenyl-3-quinaldine-carboxylate	99-100	$C_{19}H_{17}NO_2$	78.34	5.88	4.81	78.27	5.81	4.76	159-160	$C_{25}H_{20}N_4O_9$	10.77	10.70
Ethyl 2,4-diphenyl-3-quinoline-carboxylate	98-99	$C_{24}H_{19}NO_2$	81.56	5.42	3.96	81.95	5.53	3.98	142-143	$C_{30}H_{22}N_4O_9$	9.62	9.61
Diethyl 4-phenylacridinate	93-94	$C_{21}H_{19}NO_4$	72.19	5.48	4.01	72.19	5.47	3.98	(a)	....	...	...
Ethyl 3-carbethoxy-4-phenyl-2-quinolineacetate	60-61	$C_{22}H_{21}NO_4$	72.71	5.83	3.85	72.57	5.87	3.89	121-122	$C_{28}H_{24}N_4O_{11}$	9.46	9.48
Methyl 3-carbomethoxy-4-phenyl-2-quinolineacetate	112-113	$C_{20}H_{17}NO_4$	71.63	5.11	4.18	71.53	5.06	4.15	150-151	$C_{26}H_{20}N_4O_{11}$	9.93	9.96
Ethyl 3-benzoyl-4-phenylquinaldate	155-156	$C_{25}H_{19}NO_3$	78.72	5.02	3.67	78.56	5.03	3.84	(a)	....	...	...
Ethyl 3,4-diphenylquinaldate	128-129	$C_{24}H_{19}NO_2$	81.56	5.42	3.96	81.61	5.41	3.94	134-135	$C_{30}H_{22}N_4O_9$	9.62	9.66
3,4-Diphenylquinoline	140-141	$C_{21}H_{15}N$	89.65	5.37	4.98	89.85	5.34	4.99	195-196	$C_{27}H_{18}N_4O_7$	10.98	10.81
4-Phenyl-3-quinaldineacetic Acid	194-195 dec.	$C_{18}H_{15}NO_2$	77.96	5.45	5.05	77.98	5.38	5.08	(a)	....	...	...
Monohydrate	~135-140 dec.(b)	$C_{18}H_{17}NO_3$	73.21	5.80	4.74	73.26	5.74	4.57	(a)	....	...	...
2,4-Diphenyl-3-quinolineacetic Acid Ethanol solvate	168-171 dec.	$C_{23}H_{17}NO_2$	81.39	5.05	4.13	81.37	5.35	4.01	(a)	....	...	...
	116-118 dec.	$C_{25}H_{23}NO_3$	77.91	6.02	3.64	77.99	6.08	3.46	(a)	....	...	...
2,4-Diphenyl-3-quinolinecarbonitrile	177-178	$C_{22}H_{14}N_2$	86.25	4.61	9.15	86.33	4.88	9.27	144-145 (c)	$C_{34}H_{20}N_8O_{14}$	14.66	14.44
3-Methoxy-2,4-diphenylquinoline	145-146	$C_{22}H_{17}NO$	84.86	5.51	4.50	84.61	5.40	4.49	202-204	$C_{28}H_{20}N_4O_8$	10.37	10.48
2-Methyl-4-phenyl-3-quinolinol	236-237 dec.	$C_{16}H_{13}NO$	81.68	5.57	5.95	81.91	5.49	5.84	(a)	....	...	...

(a) Picrate failed to form under usual conditions. (b) Melting point dependent on the rate of heating. (c) Dipicrate, $C_{22}H_{14}N_2 \cdot 2C_6H_3N_3O_7$.

analogous base-catalyzed reactions between compounds of this type and *o*-aminoaryl ketones have been reported (17). Condensations between *o*-aminoaryl carbonyl compounds and β-ketoesters having active methylene groups have been brought about by heating mixtures of the reactants to relatively high temperatures (~150-165°) in the absence of solvents and catalysts (4, 10, 18-21), but under these conditions the reactions take an abnormal course and the cyclization products are 3-acylcarbostyrils instead of 3-quinolinecarboxylic esters. Thus *o*-aminobenzaldehyde can be condensed with ethyl acetoacetate to yield either ethyl 3-quinaldinecarboxylate (I) or 3-acetylcarbostyril (II), depending on the conditions under which the reaction is carried out (4) (Scheme 1). *o*-Aminobenzophenone, on the other hand, fails to react with ethyl acetoacetate in the presence of base under the usual Friedländer reaction conditions, although it can be induced to undergo the uncatalyzed thermal condensation with this β-ketoester to give 3-acetyl-4-phenylcarbostyril (IV) in 60% yield (21) (Scheme 2).

As is shown by the results listed in Table I, good yields of normal Friedländer reaction products can be obtained in condensations of *o*-aminobenzophenone with β-ketoesters and other types of polyfunctional carbonyl compounds having active α-methylene groups when the reactions are carried out in the presence of acid catalysts under conditions similar to those employed successfully in our earlier work (3) with monofunctional ketones. Of particular interest is the finding that β-ketoesters can be condensed with *o*-aminobenzophenone under these conditions to give the previously inaccessible 4-phenyl-3-quinolinecarboxylic esters. The mode of cyclization observed in the acid-catalyzed condensations of these ketoesters with *o*-aminobenzophenone thus corresponds to that observed in their base-catalyzed condensations with *o*-aminobenzaldehyde. An examination of the results obtained with these and other unsymmetrical 1,3-dicarbonyl compounds reveals that, in general, when more than one mode of cyclization is theoretically possible, ring-closure in the acid-catalyzed reaction occurs predominantly at the $-COCH_2-$ moiety containing the more electrophilic carbonyl group (22). This is also the observed mode of cyclization in *base*-catalyzed condensations of unsymmetrical 1,3-dicarbonyl compounds with *o*-aminobenzaldehyde. The acid-catalyzed condensations of *o*-aminobenzophenone with appropriate polyfunctional carbonyl compounds should thus provide a convenient synthetic route to a series of 4-phenylquinolines analogous to the products obtained in classical Friedländer syntheses with *o*-aminobenzaldehyde.

Structures of the products listed in Table I were assigned on the basis of elemental analyses and spectroscopic properties and in most cases were confirmed by chemical transformations to quinoline derivatives whose structures have previously been established. Pertinent data and procedural details are given in the Experimental Section.

EXPERIMENTAL (23)

General Procedures.

The carbonyl compounds listed as reactants in Table I were obtained from commercial sources or were prepared according to directions in the literature. All were checked against literature criteria for purity and, when necessary, were purified by recrystallization or redistillation immediately before use. Except in the cases noted below, acid-catalyzed condensations with *o*-aminobenzophenone were carried out in glacial acetic acid containing a trace of sulfuric acid by the method previously described (24). Reaction times and product yields are listed in Table I. Physical and analytical data for products and derivatives not previously reported in the literature are given in Table II.

In the reactions with ethyl benzoylacetate, diethyl oxalacetate, diethyl acetonedicarboxylate, ethyl benzoylpyruvate, and ethyl phenylpyruvate, better results were obtained when ethanol was used as a solvent in place of acetic acid. Product isolation was then achieved by the addition of sufficient ammonium hydroxide to neutralize the acid catalyst, followed by cooling in an ice bath until crystallization was complete. A similar procedure was used in the reaction with dimethyl acetonedicarboxylate, except that methanol was employed as a solvent, both in the reaction and in subsequent recrystallizations of the crude product.

The reactions with β-benzoylpropionic acid and levulinic acid were carried out in acetic acid in the usual way, but the product isolation procedure was modified as follows. On completion of the reaction, the mixture from a 0.01-mole run was cooled and poured into 80 ml. of ice-cold 10% sodium hydroxide solution. The resultant mixture was extracted several times with small portions of ether and the aqueous layer was heated on a steam bath to expel dissolved ether. The aqueous solution was then acidified with acetic acid and allowed to stand in an ice bath until precipitation was complete. The precipitate was collected, washed with water, and dried *in vacuo* at room temperature. In the reaction with levulinic acid, the product obtained in this way was found by elemental analysis (after recrystallization from 50% aqueous ethanol) to be the monohydrate of the expected product (m.p. ~135-140° with loss of water of crystallization, followed by resolidification and remelting at 193-195° dec.). Recrystallization from absolute ethanol provided the anhydrous compound (m.p. 194-195° dec.). In the reaction with β-benzoylpropionic acid, recrystallization of the crude product from ethanol gave a compound (m.p. 116-118° dec.) with a composition corresponding to that calculated for a solvate containing one molecule of ethanol per molecule of the expected product. Conversion of this solvate to the solvent-free compound (m.p. 168-171° dec.) was accomplished by recrystallization from a benzene-ligroin mixture.

The *in situ* preparation of hydroxyacetone and its condensation with *o*-aminobenzophenone were carried out by refluxing a mixture of 1.16 g. (0.01 mole) of acetonyl acetate (Aldrich), 10 ml. of glacial acetic acid, 2 ml. of water, and 0.1 ml. of concentrated sulfuric acid for 5 minutes, then adding 1.97 g. (0.01 mole) of *o*-aminobenzophenone and continuing to reflux for another 4 hours. Product isolation was accomplished by the method described above for the reactions with levulinic and β-benzoylpropionic acids.

Oxidation of 3-Benzoyl-4-phenylquinaldine.

A mixture of 1.00 g. (3.1 mmoles) of the product obtained in the acid-catalyzed condensation of *o*-aminobenzophenone with

benzoylacetone, 0.69 g. (6.2 mmoles) of freshly resublimed selenium dioxide, 5 ml. of dioxane, and 0.3 ml. of water was refluxed for 1 hour and was then filtered and diluted with 75 ml. of water. The resultant precipitate was collected, washed with water, and dried *in vacuo* to provide 1.10 g. of pale orange powder. A mixture of this product with 25 ml. of acetone and 2.5 ml. of 30% hydrogen peroxide was refluxed for 45 minutes and was then concentrated by distillation to about one-third of its original volume. The residue was diluted with 100 ml. of water and allowed to stand until precipitation was complete, after which the precipitate was collected, washed with water, and dried to provide 1.09 g. of almost colorless powder, m.p. ~70° with effervescence and resolidification followed by remelting at 173-177° dec. Recrystallization from ethanol gave 0.81 g. (74%) of colorless crystals which melted at ~177-180° dec. (25) and showed no melting-point depression when mixed with a sample of 3-benzoyl-4-phenylquinaldic acid prepared by hydrolysis of ethyl 3-benzoyl-4-phenylquinaldate as described below.

Hydrolysis of Ethyl 3-Benzoyl-4-phenylquinaldate.

A solution of 0.33 g. of potassium hydroxide in 1 ml. of water was added to 3 ml. of an ethanolic solution containing 1.00 g. of the product obtained in the acid-catalyzed condensation of *o*-aminobenzophenone with ethyl benzoylpyruvate. The mixture was refluxed for 2 hours and was then cooled, diluted with 20 ml. of water, and acidified with acetic acid. The precipitate was collected, washed with water, and dried to provide 0.93 g. (100%) of white powder, m.p. ~178-180° dec. (25). Recrystallization from ethanol gave colorless crystals of 3-benzoyl-4-phenylquinaldic acid, m.p. ~182-183° dec. (25). The infrared spectrum of this compound was identical with that of the compound prepared by oxidation of 3-benzoyl-4-phenylquinaldine as described above.

Anal. Calcd. for $C_{23}H_{15}NO_3$: C, 78.17; H, 4.28; N, 3.96; Found: C, 78.32; H, 4.41; N, 3.99.

Decarboxylation of 3-Benzoyl-4-phenylquinaldic Acid.

A mixture of 0.22 g. of 3-benzoyl-4-phenylquinaldic acid and 2 ml. of diethylene glycol was heated in a metal bath at 175-195° for 5 minutes and was then cooled and diluted with 20 ml. of water. The resultant waxy suspension was extracted with two 10-ml. portions of ether, and the combined ether extracts were washed with 5% sodium hydroxide and dried over anhydrous magnesium sulfate. Evaporation of the ether left a waxy residue which was recrystallized from ethanol to give 0.11 g. (57%) of almost colorless microcrystalline powder melting at 110-112°. Further recrystallization raised the melting point to 113-114°; lit. m.p. for 3-benzoyl-4-phenylquinoline, 115-116° (26).

Hydrolysis of Ethyl 4-Phenyl-3-quinaldinecarboxylate.

A solution of 2.61 g. of the product obtained in the acid-catalyzed condensation of *o*-aminobenzophenone with ethyl acetoacetate in 26 ml. of concentrated hydrochloric acid was refluxed for 5 days and was then diluted with an equal volume of water, cooled in an ice bath, and made alkaline by the addition of 15 ml. of concentrated ammonium hydroxide. A small amount (0.21 g.) of unreacted ester (m.p. 97-99°) which precipitated at this point was removed and the filtrate was acidified with acetic acid. The resultant precipitate was collected, washed with water, and dried at 110° to give 1.94 g. (89%, based on unrecovered ester) of white powder, m.p. 266-268° dec., which showed no melting-point depression when mixed with a sample of 4-phenyl-3-quinaldinecarboxylic acid prepared by the method described in the preceding paper in this series (1).

Hydrolysis of Ethyl 2,4-Diphenyl-3-quinolinecarboxylate.

A solution of 0.70 g. of the product obtained in the acid-catalyzed condensation of *o*-aminobenzophenone with ethyl benzoylacetate in 8 ml. of concentrated hydrochloric acid was refluxed for 10 days, and the reaction mixture was worked up by a procedure similar to the one described in the preceding experiment. Recrystallization of the crude product from benzene afforded 0.29 g. of colorless microcrystalline powder which melted at 136-138° with effervescence followed by resolidification and remelting at 206-207° and which had an elemental composition corresponding to that of a benzene solvate of 2,4-diphenyl-3-quinolinecarboxylic acid.

Anal. Calcd. for $C_{22}H_{15}NO_2 \cdot C_6H_6$: C, 83.35; H, 5.25; N, 3.47. Found: C, 83.46; H, 5.38; N, 3.81.

When a sample of this product was heated in an oven at 150° for 10 minutes, a white powder melting at 207-208° was obtained which gave analytical data consistent with its formulation as solvent-free 2,4-diphenyl-3-quinolinecarboxylic acid.

Anal. Calcd. for $C_{22}H_{15}NO_2$: C, 81.21; H, 4.65; N, 4.31. Found: C, 81.13; H, 4.65; N, 4.44.

Decarboxylation of 2,4-Diphenyl-3-quinolinecarboxylic Acid.

A sample of the above product was placed in a melting-point capillary and heated in an oil bath at 250-265° until effervescence stopped (*ca.* 15 minutes). On cooling, the product resolidified and was then found to remelt at 109-111° and to show no melting-point depression when mixed with an authentic sample of 2,4-diphenylquinoline (m.p. 110-111°) (27).

Hydrolysis of Ethyl 3,4-Diphenylquinaldate.

A solution of 0.25 g. of potassium hydroxide in 1 ml. of water was added to 3 ml. of an ethanolic solution containing 0.60 g. of the product obtained in the acid-catalyzed condensation of *o*-aminobenzophenone with ethyl phenylpyruvate. The mixture was refluxed for 2 hours and was then worked up as described above for the hydrolysis of ethyl 3-benzoyl-4-phenylquinaldate. A white powder (0.53 g., 96%) was obtained which melted at 184-185° dec. (25) and showed no melting-point depression when mixed with an authentic sample of 3,4-diphenylquinaldic acid (3).

Decarboxylation of 3,4-Diphenylquinaldic Acid.

A sample of 3,4-diphenylquinaldic acid (0.28 g.) was heated in a metal bath at 200-210° for 10 minutes. The resultant syrup was dissolved in a small amount of hot ethanol and induced to crystallize by the gradual addition of water to the hot solution. The crude 3,4-diphenylquinoline (0.13 g., m.p. 131-136°) thus obtained was treated with ethanolic picric acid to give the picrate, m.p. 194-195.5°, which showed no melting-point depression when mixed with the picrate of 3,4-diphenylquinoline prepared by the acid-catalyzed condensation of *o*-aminobenzophenone with phenylpyruvic acid.

Partial Hydrolysis and Decarboxylation of Ethyl 3-Carbethoxy-4-phenyl-2-quinolineacetate.

A solution of 1.0 g. of potassium hydroxide in 1 ml. of water was added to 6 ml. of a methanolic solution containing 1.71 g. of the product obtained in the acid-catalyzed condensation of *o*-aminobenzophenone with diethyl acetonedicarboxylate, and the mixture was allowed to stand at room temperature for 1 hour. Enough acetic acid was then added to neutralize the base, and the mixture was evaporated almost to dryness on a steam bath. Thirty milliliters of water were added to the oily residue and the solution was extracted with several small portions of ether. The combined ether

extracts were washed with 5% sodium hydroxide and dried over anhydrous magnesium sulfate. After removal of the ether on a steam bath, the residue (1.22 g., 84%) was recrystallized twice from aqueous ethanol to give 0.75 g. of almost colorless crystals which melted at 97-99° and showed no melting-point depression when mixed with a sample of ethyl 4-phenyl-3-quinaldinecarboxylate prepared by the acid-catalyzed condensation of *o*-aminobenzophenone with ethyl acetoacetate.

Decarboxylation of 4-Phenyl-3-quinaldineacetic Acid.

A sample (0.1 g.) of the product obtained in the acid-catalyzed condensation of *o*-aminobenzophenone with levulinic acid was heated in a metal bath at 200-215° for 10 minutes. Recrystallization of the crude product from ligroin (b.p. 65-75°) followed by recrystallization from aqueous ethanol provided almost colorless powder, m.p. 117-119°, which showed no melting-point depression when mixed with a sample of 2,3-dimethyl-4-phenylquinoline prepared by the acid-catalyzed condensation of *o*-aminobenzophenone with methyl ethyl ketone (3).

Decarboxylation of 2,4-Diphenyl-3-quinolineacetic Acid.

A sample (0.2 g.) of the product obtained in the acid-catalyzed condensation of *o*-aminobenzophenone with β-benzoylpropionic acid was heated in a metal bath at 200-215° for 10 minutes. Recrystallization of the crude product from ethanol gave colorless microcrystalline powder, m.p. 144-146°, which showed no melting point depression when mixed with an authentic sample of 2,4-diphenyl-3-methylquinoline (3).

Wolff-Kishner Reduction of 2-Benzoyl-4-phenylquinoline.

To a solution of 0.72 g. of potassium hydroxide in 5 ml. of diethylene glycol were added 0.5 g. of hydrazine (95+%) and 1.99 g. of the product obtained in the acid-catalyzed condensation of *o*-aminobenzophenone with 1-phenyl-1,2-propanedione. The mixture was heated in an open test tube in a metal bath at 110-125° for 1 hour, then at gradually increasing temperatures up to 200° for 30 minutes, and finally at 200-210° for 2 hours. The mixture was then cooled, washed several times by decantation with water, and the residue was dissolved in 25 ml. of benzene. The benzene solution was washed with water, dried over anhydrous magnesium sulfate, and evaporated on a steam bath. The oily residue was recrystallized from aqueous ethanol to provide 1.07 g. (56%) of crude 2-benzyl-4-phenylquinoline, m.p. 70-74°. Recrystallization from ligroin (b.p. 65-75°) gave pale yellow crystals melting at 77-78.5°.

Anal. Calcd. for $C_{22}H_{17}N$: C, 89.45; H, 5.80; N, 4.74. Found: C, 89.35; H, 5.81; N, 4.74.

The picrate derivative was obtained in the form of bright yellow crystals, m.p. 178-179° dec. (28), after recrystallization from ethanol.

Anal. Calcd. for $C_{28}H_{20}N_4O_7$: C, 64.11; H, 3.84; H, 10.68. Found: C, 64.26; H, 4.11; N, 10.33.

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