1-Methyl-2-acetyl-3-phenylhexahydropyridazine (III).—Three grams of 1-methyl-3-phenyl-Δ^2-tetrahydropyridazine (V) in acetic acid (4 ml.) and acetic anhydride (20 ml.) was reduced at a hydrogen pressure of 66 p.s.i. in the presence of 400 mg. of platinum oxide. The resulting acetic anhydride solution was refluxed for 3 min. and the excess acetic anhydride was removed *in vacuo*. The residue was neutralized with sodium bicarbonate solution and was extracted with ether. The ether solution was dried over potassium carbonate and the ether was removed. The infrared spectrum of the material showed N–H absorption bands. The residue (1.71 g.) when chromatographed on a alumina using hexane–benzene and benzene–ethyl acetate as eluents gave two fractions which gave 1-methyl-2-acetyl-3-phenylhexahydropyridazine (III) (0.48 g.). Two recrystallizations from pentane gave white prisms melting at 52.5–53.5°, identical in all respects with the product obtained from the pyrolysis of the aminimide.

1,1,1-Trimethyl-2-benzoylhydrazonium *p*-Toluenesulfonate.—A mixture of 1,1-dimethyl-2-benzoylhydrazine (114 g.) and methyl *p*-toluenesulfonate (130 g.) in benzene (1100 ml.) was refluxed for 23 hr. The resulting solid (225 g.) melted at 179–180.5°. Recrystallization from chloroform–ethyl acetate raised the melting point to 179.5–181°.

Anal. Calcd. for $C_{17}H_{22}N_2O_4S$: C, 58.27; H, 6.33; N, 7.99. Found: C, 58.18; H, 6.25; N, 7.79.

Trimethylaminebenzimide.—1,1,1-Trimethyl-2-benzoylhydrazonium methyl-*p*-toluenesulfonate (247 g.) in water (2000 ml.) was treated with 28.2 g. of sodium hydroxide. The resulting solution was extracted with eight 250-ml. portions of chloroform. Removal of the chloroform gave a solid which was recrystallized from chloroform–hexane: m.p. 165.5–167° (lit.[7] m.p. 168–169°); yield, 81g.

Pyrolysis of Trimethylaminebenzimide.[12]—Trimethylaminebenzimide (109 g.) upon heating at 220–230° underwent a vigorous decomposition and gave a gaseous product and a liquid which solidified in the reservoir. The solid (44.2 g.) melted at 289–290° after recrystallization from toluene and did not lower the melting point of 1,3,5-triphenyl-s-triazine-2,4,6(1H,3H,5H)-trione.

The gaseous product (19.1 g.) collected at −78° was converted to a hydrochloride and then to a picrate which melted at 223.5–225° and was identical with trimethylamine picrate.

The tarry residue (21.4 g.) remaining from the distillation gave in addition to the phenyl isocyanate trimer 10 g. of a solid which was insoluble in toluene and melted at 270–281°. The infrared spectrum was complex and showed no carbonyl absorption. Elemental analysis pointed to the presence of only carbon, hydrogen, and nitrogen.

Acknowledgment.—Support of this research by the National Science Foundation is gratefully acknowledged.

(12) Since the submission of the manuscript, similar results for the pyrolysis of trimethylaminebenzimide have been reported: M. S. Gibson and A. W. Murray, *J. Chem. Soc.*, 880 (1965).

2-Aryl-3-acetyl-4(1H)-quinolones[1]

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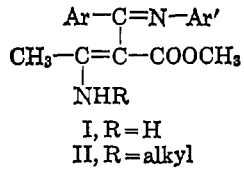
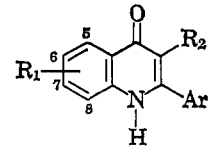
Several compounds claimed to be 2-aryl-3-acetyl-4(1H)-quinolones (III) in the literature have been reformulated as the isomeric VI. The conversion of 2-phenyl-3-acetyl-4-chloroquinoline to 6-phenyl-7-methyldibenzo-[*b*,*h*][1,6]naphthyridine (X) and to 2,4-diphenyl-3-methyl-2H-pyrazolo[4,3-*c*]quinoline (XI) is described. β-Methylamino-α-(N-arylimidoyl)crotonic esters (II, R = CH_3) were thermally cyclized to 2-aryl-3-N-methylacetimidoyl-4(1H)-quinolones (V, R = CH_3).

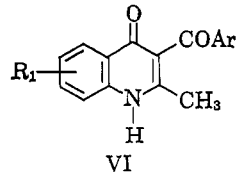
Cyclization of β-amino-α-(N-arylimidoyl)crotonates (I) in polyphosphoric acid (PPA)[3] gave the 2-aryl-3-acetyl-4(1H)-quinolones (III) listed in Table I. Also shown in Table I are the melting points of the products alleged by Shah[4,5] and by Usgaonkar[6] to be the title compounds but which are, as shown originally by Singh and Nair,[7] the isomeric 2-methyl-3-aroyl-4-(1H)-quinolones (VI).



I, R = H
II, R = alkyl



III, R_2 = $COCH_3$
IV, R_2 = H
V, R_2 = C(=NR)CH_3



VI

The structure of 2-*p*-anisyl-3-acetyl-4(1H)-quinolone (III, R_1 = H; Ar = *p*-$CH_3OC_6H_4$) was established unequivocally by oxidation with selenium dioxide and hydrogen peroxide[7] which converted it to a carboxylic acid identical with 2-*p*-anisyl-3-carboxy-4(1H)-quinolone prepared by the Just reaction[8] from N-phenyl-*p*-anisimidoyl chloride and diethyl sodiomalonate. Both acid samples on thermal decarboxylation gave 2-*p*-anisyl-4(1H)-quinolone (IV, R_1 = H; Ar = *p*-$CH_3OC_6H_4$) obtained also by cyclization of crotonate I (Ar = *p*-$CH_3OC_6H_4$; Ar′ = C_6H_5) in liquid paraffin.[9] In concentrated hydrochloric acid 2-*p*-anisyl-3-acetyl-4(1H)-quinolone underwent deacetylation[7] and demethylation to 2-*p*-hydroxyphenyl-4(1H)-quinolone (IV, R_1 = H; Ar = *p*-HOC_6H_4).

The infrared spectra of the 2-aryl-3-acetyl-4(1H)-quinolones (III) showed the carbonyl band at 5.9–6.0 μ[3] (Table I); in 2-methyl-3-benzoyl-4(1H)-quinolone and 2-methyl-3-*p*-anisoyl-4(1H)-quinolone this was at 6.05 and 6.08 μ, respectively. The frequency of CO absorption in the 2-methyl-3-aroyl-4-chloroquinolines IX (6–6.06 μ) was likewise slightly less than in the isomeric 2-aryl-3-acetyl-4-chloroquinolines VII

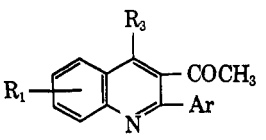
(1) The title compounds are named and formulated in terms of the tautomeric form predominating as evidenced byinfrared measurements: *cf.* A. R. Katritzky and J. M. Lagowski, *Advan. Heterocyclic Chem.*, **1**, 341 (1963).
(2) To whom inquiries should be addressed.
(3) B. Staskun, *J. Org. Chem.*, **26**, 2791 (1961).
(4) S. A. Kulkarni and R. C. Shah, *J. Indian Chem. Soc.*, **27**, 111 (1950).
(5) T. B. Desai and R. C. Shah, *ibid.*, **26**, 121 (1949).
(6) U. R. Usgaonkar and G. V. Jadhav, *ibid.*, **40**, 75 (1963).
(7) G. Singh and G. V. Nair, *J. Am. Chem. Soc.*, **78**, 6105 (1956).
(8) F. Just, *Ber.*, **19**, 984 (1886).
(9) B. Staskun, *J. S. African Chem. Inst.*, **9**, 89 (1956).

TABLE I
2-ARYL-3-ACETYL-4(1H)-QUINOLONES (III)

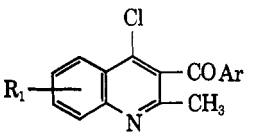
Crotonate cyclized	3-Acetyl-4(1H)-quinolone derivative formed	M.p., °C. Obsd.	M.p., °C. Lit.	Formula	Nitrogen, % Calcd.	Nitrogen, % Found	Infrared acetyl CO absorption, μ
I, Ar = *p*-$CH_3C_6H_4$; Ar′ = C_6H_5	2-*p*-Tolyl	239–240[a]	>297[b,c]				5.91
I, Ar = Ar′ = *p*-$CH_3C_6H_4$	2-*p*-Tolyl-6-methyl	236–237		$C_{19}H_{17}NO_2$	4.81	4.78	5.91, 6.0
I, Ar = *p*-$CH_3OC_6H_4$; Ar′ = *o*-$CH_3C_6H_4$	2-*p*-Anisyl-8-methyl	192–194	246–247[c,d]	$C_{19}H_{17}NO_3$	4.56	4.57	6.0
I, Ar = Ar′ = *p*-$CH_3OC_6H_4$	2-*p*-Anisyl-6-methoxy	229–231[e]	295–296[c,d]	$C_{19}H_{17}NO_4$	4.33	4.36	5.90
I, Ar = C_6H_5; Ar′ = 1-$C_{10}H_7$	2-Phenyl-7,8-benzo	190–191	263–265[c,f]				5.93

[a] Ref. 3. [b] Ref. 4. [c] The higher melting point may be that of the isomeric VI. [d] Ref. 6. [e] Obtained also as a hydrate, m.p. ~135° dec. [f] Ref. 5.

(5.9 μ) owing to the greater conjugation of the CO group in the 3-aroyl structures.[10]

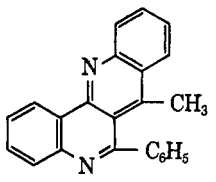


VII, R_3 = Cl
VIII, R_3 = NHC_6H_5

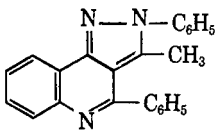


IX

Phosphorus oxychloride acting on III readily formed the 4-chloro derivatives VII which are useful intermediate compounds for the synthesis of more complex heterocyclics[11]: for example, (a) 6-phenyl-7-methyldibenzo[*b*,*h*][1,6]naphthyridine (X)[12] resulted upon cyclodehydration of 2-phenyl-3-acetyl-4-anilinoquinoline (VIII), derived from 2-phenyl-3-acetyl-4-chloroquinoline and aniline, in PPA; and (b) warming together the above 4-chloroquinoline and phenylhydrazine gave 2,4-diphenyl-3-methyl-2H-pyrazolo[4,3-*c*]-quinoline (XI)[12] isomeric with the 1,4-diphenyl-3-methyl-1H-pyrazolo[4,3-*c*]quinoline previously formed from 2-phenyl-3-acetyl-4(1H)-quinolone and phenylhydrazine.[3]



X



XI

β-Alkylamino-α-(N-arylimidoyl)crotonates (II), prepared from imidoyl chlorides and β-alkylaminocrotonates, were converted into III by means of PPA or concentrated sulfuric acid. In contrast to the compounds I, which are transformed in hot liquid paraffin or diphenyl ether to 2-aryl-4(1H)-quinolones (IV), with loss of acetonitrile,[9] the crotonates II when similarly heated formed quinoline derivatives which appear to be of type V (or a tautomer thereof). Thus, methyl β-methylamino-α-(N-phenylbenzimidoyl)crotonate (II, R = CH_3; Ar = Ar′ = C_6H_5) underwent reaction in liquid paraffin at 250° and furnished a base which was not 2-phenyl-3-methyl-4(1H)-quinolone. The crude product was hydrolyzed with dilute acid to 2-phenyl-3-acetyl-4(1H)-quinolone, and its infrared spectrum was in keeping with a structure such as V (R = CH_3; R_1 = H; Ar = C_6H_5).

Experimental[13]

β-Alkylaminocrotonic Esters.—Methyl (or ethyl) acetoacetate (1 mole) and the appropriate amine (1.2 moles) were allowed to react in absolute ethanol at room temperature for several days (Table II). Ice–water was added and the precipitated product was filtered or, if an oil, extracted by ether. The solid crotonates were crystallized from methanol and were obtained as colorless needles; the liquid esters were obtained as pale yellow oils after distillation under reduced pressure. The compounds tend to decompose on prolonged contact with water.

β-Alkylamino-α-(N-arylimidoyl)crotonates (II).—Equimolar proportions of the β-alkylaminocrotonate (0.02 mole) and arylimidoyl chloride were reacted in dry chloroform (~50 ml.) at 0–5° for several days (Table III).[14] Dilute (2 *N*) hydrochloric acid (~50 ml.) was added to the yellow-orange solution (from which, usually, a little II hydrochloride had settled out) and the mixture was steam distilled as rapidly as possible so as to minimize possible hydrolysis of the product. The resulting bright yellow aqueous residue was immediately chilled and any acid-insoluble material was removed. Addition of 2 *N* sodium hydroxide to the yellow filtrate deposited the crotonate II, usually as a gum, which solidified on standing and was recrystallized from dilute ethanol (charcoal). In those instances where the product was not conveniently filterable, it was isolated from the alkaline reaction mixture by ether extraction. The crotonates II dissolved in dilute mineral acids to give bright yellow solutions. Also included in Table III are the crotonates I which were prepared in a similar manner. NH absorption in the infrared spectra of II was indicated by a single weak peak; in the crotonates I this was shown by two weak–medium peaks.

Methyl β-Amino-α-(N-phenyl-*p*-hydroxybenzimidoyl)crotonate (I, Ar = *p*-HOC_6H_4; Ar′ = C_6H_5).—As attempts to prepare *p*-hydroxybenzoyl chloride from the acid and thionyl chloride or phosphorus pentachloride led only to complex products, *p*-hydroxybenzoic acid in ice-cold dilute sodium hydroxide solution was treated with methyl chloroformate and converted to *p*-carbomethoxybenzoic acid. This and phosphorus pentachloride gave *p*-carbomethoxybenzoyl chloride which with aniline formed *p*-carbomethoxybenzanilide, colorless crystals from ethanol, m.p. 177–178°.

Anal. Calcd. for $C_{15}H_{13}NO_4$: N, 5.17. Found: N, 5.20.

The infrared spectrum of this compound showed the NH and ester carbonyl bands at 2.99 (m) and 5.70 (s) μ, respectively. Warming the anilide with 2 *N* sodium hydroxide readily afforded *p*-hydroxybenzanilide, shining plates from dilute ethanol, m.p.

(10) L. J. Bellamy, "The Infrared Spectra of Complex Molecules," 2nd Ed., Methuen and Co. Ltd., London, 1958, p. 132.

(11) The unsuccessful attempts made earlier[3] to obtain the 4-chloro derivatives from III and phosphorus oxychloride has made doubtful the authenticity of the oxychloride sample then employed.

(12) A. M. Patterson, L. T. Capell, and D. F. Walker, "The Ring Index," 2nd Ed., American Chemical Society, Washington, D. C., 1960.

(13) Melting points are uncorrected. Infrared spectra were taken on a Perkin-Elmer Infracord Model 137 spectrophotometer using 1 mg. of sample/300 mg. of potassium bromide.

(14) B. Staskun and H. Stephen, *J. Chem. Soc.*, 4696 (1956).

TABLE II

β-AMINO- AND β-ALKYLAMINOCROTONATES

$$CH_3C(NHR)=CHCOOR_4$$

Product R	Product R_4	Reaction time, days	Crude yield, %	M.p. or b.p. (mm.), °C. Obsd.	M.p. or b.p. (mm.), °C. Lit.	Formula	Nitrogen, % Calcd.	Nitrogen, % Found
H	CH_3	1[a]	80	84–85	84–85[b]			
CH_3	CH_3	10[c]	52	65–67	60.5[d]			
CH_3	C_2H_5	15[e]	40	114 (22)	133 (50)[f]			
C_2H_5	CH_3	16[g]	57	108 (18)		$C_7H_{13}NO_2$	9.79	9.57
n-C_3H_7	CH_3	16[h]	73	120–121 (20)		$C_8H_{15}NO_2$	8.92	8.87

[a] Methyl acetoacetate (100 ml.), concentrated ammonia solution (100 ml., d 0.88) in ethanol (100 ml.). This method of preparing the crotonate was found more convenient than the usual procedure of M. Conrad and W. Epstein [*Ber.*, **20**, 3055 (1887)]. [b] M. Conrad and W. Epstein, footnote *a*. [c] Methyl acetoacetate (45 ml.), methylamine (60 ml. of a 33% aqueous solution) in ethanol (150 ml.). [d] T. V. Korschun and K. V. Roll, *Bull. soc. chim. France*, **33**, 1106 (1923). [e] Ethyl acetoacetate (10 ml.), methylamine (12 ml. of a 25% aqueous solution) in ethanol (25 ml.). [f] J. Décombe, *Ann. chim.* (Paris), **18**, 81 (1932). [g] Methyl acetoacetate (10 ml.), ethylamine (10 ml. of a 50% aqueous solution) in ethanol (25 ml.). [h] Methyl acetoacetate (10 ml.), n-propylamine (6.5 ml.) in ethanol (25 ml.).

TABLE III

β-AMINO- AND β-ALKYLAMINO-α-(N-ARYLIMIDOYL)CROTONATES (I AND II)

$$CH_3C(NHR)=CHCOOCH_3 + Ar{-}C(Cl)=N{-}Ar' \longrightarrow CH_3{-}C(NHR)=C(Ar{-}C=N{-}Ar')-COOCH_3$$

Product R	Product Ar	Product Ar′	Reaction time, days	Yield, % (recrystallized product)	M.p., °C.	Formula	Nitrogen, % Calcd.	Nitrogen, % Found.
H	p-$CH_3C_6H_4$	p-$CH_3C_6H_4$	4	63[a]	155–156	$C_{20}H_{22}N_2O_2$	8.70	8.49
H	p-$CH_3OC_6H_4$	C_6H_5	14	32[b]	166–168	$C_{19}H_{20}N_2O_2$	8.64	8.68
H	p-$CH_3OC_6H_4$	o-$CH_3C_6H_4$	12	40	155–156	$C_{20}H_{22}N_2O_2$	8.28	8.24
H	p-$CH_3OC_6H_4$	p-$CH_3OC_6H_4$	7	34	190–191	$C_{20}H_{22}N_2O_4$	7.91	7.87
H	p-$CH_3OC_6H_4$	o-$C_2H_5OC_6H_4$	12	39	155–156	$C_{21}H_{24}N_2O_4$	7.61	7.68
CH_3	C_6H_5	C_6H_5	13	56	104–106[c]	$C_{19}H_{20}N_2O_2$	9.09	9.27
CH_3	C_6H_5	p-$CH_3C_6H_4$	11	66[a]	117–118	$C_{20}H_{22}N_2O_2$	8.70	8.76
CH_3	p-$CH_3C_6H_4$	C_6H_5	11	65[a]	135–136	$C_{20}H_{22}N_2O_2$	8.70	8.62
CH_3	C_6H_5	2,4-$(CH_3)_2C_6H_3$	20	94[a]	155–156	$C_{21}H_{24}N_2O_2$	8.33	8.23
CH_3	C_6H_5	1-$C_{10}H_7$	14	40	102–103	$C_{23}H_{22}N_2O_2$	7.82	7.60
CH_3	C_6H_5	2-$C_{10}H_7$	14	12	142–143	$C_{23}H_{22}N_2O_2$	7.82	7.72
CH_3	1-$C_{10}H_7$	C_6H_5	17	52	140–141	$C_{23}H_{22}N_2O_2$	7.82	8.03
C_2H_5	C_6H_5	C_6H_5	14	58	105–106	$C_{20}H_{22}N_2O_2$	8.70	8.66
n-C_3H_7	C_6H_5	C_6H_5	12	42	87–88	$C_{21}H_{24}N_2O_2$	8.33	8.26

[a] Crude yield. [b] The product was not easily soluble in dilute (2 N) hydrochloric acid. [c] Ethyl ester, m.p. 73–75°. *Anal.* Calcd. for $C_{20}H_{22}N_2O_2$: N, 8.70. Found: N, 8.85.

200–201° (lit.[15] m.p. 201–202°). Condensation of crude N-phenyl-*p*-carbomethoxybenzimidoyl chloride (prepared from 4 g. of the anilide and phosphorus pentachloride) with methyl β-aminocrotonate (2 g.) in chloroform (60 ml.) for 10 days produced 3.5 g. (67%, crude) of methyl β-amino-α-(N-phenyl-*p*-carbomethoxybenzimidoyl)crotonate (I, Ar = *p*-$CH_3OCOOC_6H_4$; Ar′ = C_6H_5), colorless needles from ethanol, m.p. 105°.

Anal. Calcd. for $C_{20}H_{20}N_2O_5$: N, 7.61. Found: N, 7.76.

The crotonate dissolved on warming the 2 N sodium hydroxide; neutralization of the solution with acetic acid deposited the amphoteric, crude methyl β-amino-α-(N-phenyl-*p*-hydroxybenzimidoyl)crotonate, colorless needles from methanol, m.p. 219–220°.

Anal. Calcd. for $C_{18}H_{18}N_2O_3$: N, 9.03. Found: N, 9.25.

2-Aryl-3-acetyl-4(1H)-quinolones (III). A. By Cyclization of Crotonates I and II in PPA.—The methyl β-amino-α-(N-arylimidoyl)crotonate I was stirred with ten times its weight of PPA (supplied by Riedel-de Haën) at 150–170° until effervescence had ceased (about 30 min.) and the quinolone III was isolated as previously described[3] and recrystallized from dilute ethanol. Table I lists the bases obtained in this manner (in 70–90% crude yield). 2-Phenyl-3-acetyl-4(1H)-quinolone was prepared also by similar PPA treatment of methyl β-methylamino-α-(N-phenylbenzimidoyl)crotonate (II, R = CH_3; Ar = Ar′ = C_6H_5) and methyl β-*n*-propylamino-α-(N-phenylbenzimidoyl)crotonate (II, R = n-C_3H_7; Ar = Ar′ = C_6H_5), in 70 and 90% yields, respectively.

2-*p*-Anisyl-3-acetyl-4(1H)-quinolone was obtained from 2 g. of methyl β-amino-α-(N-phenyl-*p*-anisimidoyl)crotonate (I, Ar = *p*-$CH_3OC_6H_4$; Ar′ = C_6H_5) and 20 g. of PPA as above, in 66% crude yield. Recrystallization from dilute ethanol gave a colorless hydrate, m.p. 130–135°; this was carefully heated at ~150° where the melt resolidified to the anhydrous form, m.p. ~200°. Recrystallized from ethanol the product was obtained as colorless needles, m.p. 202–203° (lit.[6] m.p. 236–237°). The infrared spectrum showed strong carbonyl and methoxyl absorption at 5.9 and 9.7 μ, respectively.

Anal. Calcd. for $C_{18}H_{15}NO_3$: N, 4.78; CH_3O, 10.58. Found: N, 4.61; CH_3O, 10.54.

The crystals, m.p. 202–203°, when warmed with water were converted to the hydrated form, m.p. 130–135°.

Treatment of the base (0.5 g.) with selenium dioxide and hydrogen peroxide according to the procedure of Singh and Nair[7] afforded 2-*p*-anisyl-3-carboxy-4(1H)-quinolone (0.25 g., 50%), identical (infrared spectrum) with the carboxylic acid obtained from diethyl sodiomalonate and N-phenyl-*p*-anisimidoyl chloride (see below). Decarboxylation of the respective acids was effected by gentle heating at ~250° and gave 2-p-anisyl-4(1H)-

(15) A. Klemenc, *Ber.*, **49**, 1371 (1916).

quinolone which was identical (mixture melting point and infrared spectrum) with the quinolone derived by cyclization of methyl β-amino-α-(N-phenyl-*p*-anisimidoyl)crotonate (I, Ar = *p*-$CH_3OC_6H_4$; Ar′ = C_6H_5) in liquid paraffin (see below).

B. By Cyclization of Crotonates I and II in Concentrated Sulfuric Acid.—The crotonates I (Ar = Ar′ = C_6H_5, 1 g.) and II (R = CH_3; Ar = Ar′ = C_6H_5, 1 g.) were each treated with concentrated sulfuric acid (10 g.) and dissolved rapidly with effervescence. The yellow-orange solutions were heated on the water bath for 1 hr., cooled, diluted with water, and neutralized with ammonia to deposit crude 2-phenyl-3-acetyl-4(1H)-quinolone in ~80% yield, colorless needles from ethanol, identical (mixture melting point and infrared spectrum) with the PPA-derived base. 2-*p*-Tolyl-3-acetyl-4(1H)-quinolone was likewise obtained from II (R = CH_3; Ar = *p*-$CH_3C_6H_4$; Ar′ = C_6H_5).

C. By Cyclization of Crotonate II in Liquid Paraffin.—A solution of methyl β-methylamino-α-(N-phenylbenzimidoyl)-crotonate (II, R = CH_3; Ar = Ar′ = C_6H_5, 1 g.) in (medicinal) liquid paraffin (10 g.) was stirred at 240–250° for 15–20 min. Petroleum ether (b.p. 40–60°) was added to the cooled viscous mass and the insoluble material was removed, washed with petroleum ether, and dried (0.4 g.). The infrared spectrum of the crude, orange-brown product showed NH absorption and displayed a very weak carbonyl absorption in the 5.9–6.0-μ region; moreover, the absence of III (R_1 = H; Ar = C_6H_5) and of II (R = CH_3; Ar = Ar′ = C_6H_5) as impurities was revealed. Attempts at purifying the product (which dissolved in dilute hydrochloric acid to give an orange solution) were unsuccessful and it was eventually heated with dilute sulfuric acid (25 vol. %) for 30 min. to effect its hydrolysis; the mixture was made alkaline, insoluble material was removed, and the filtrate was acidified with glacial acetic acid to deposit crude 2-phenyl-3-acetyl-4(1H)-quinolone (as shown by its infrared spectrum) in ~10% (over-all) yield. The recrystallized base was identical (mixture melting point and infrared spectrum) with authentic III (R_1 = H; Ar = C_6H_5).

Methyl β-methylamino-α-(N-phenyl-*p*-toluimidoyl)crotonate (II, R = CH_3; Ar = *p*-$CH_3C_6H_4$; Ar′ = C_6H_5) similarly furnished a petroleum ether insoluble intermediate (V, R = CH_3; R_1 = H; Ar = *p*-$CH_3C_6H_4$, 50% yield) which was hydrolyzed to 2-*p*-tolyl-3-acetyl-4(1H)-quinolone.

D. From Imidoyl Chlorides and Ethyl Sodioacetoacetate. 1.—N-Phenylbenzimidoyl chloride was allowed to react with ethyl sodioacetocetate in absolute ethanol according to the procedure of Singh and Nair[7] and, as reported, gave a mixture of 2-phenyl-3-acetyl-4(1H)-quinolone and 2-methyl-3-benzoyl-4(1H)-quinolone. The former quinolone (m.p. 250–251°) proved identical (mixture melting point and infrared spectrum) with III (R_1 = H; Ar = C_6H_5) obtained in method A. The 3-benzoyl compound had m.p. 287–289° (lit.[7] m.p. 287–289°) and its infrared spectrum showed strong CO absorption at 6.05 μ.

N-Phenyl-*p*-anisimidoyl chloride when similarly treated afforded only 2-methyl-3-*p*-anisoyl-4(1H)-quinolone, m.p. 235–237°, identical (mixture melting point and infrared spectrum) with Usgaonkar's product[6] (see below).

2.—The condensation of N-phenyl-*p*-anisimidoyl chloride and ethyl sodioacetoacetate in toluene was performed as described by Usgaonkar and Jadhav[6] and yielded a base, m.p. 235–237° (lit.[6] m.p. 236–237°), said to be 2-*p*-anisyl-3-acetyl-4(1H)-quinolone. The infrared spectrum, which showed a strong CO band at 6.08 μ, differed from that of authentic III (R_1 = H; Ar = *p*-$CH_3OC_6H_4$), m.p. 202–203°, and accorded with the formula VI (R_1 = H; Ar = *p*-$CH_3OC_6H_4$). However, on employment of N-*o*-tolyl-*p*-anisimidoyl chloride, N-phenyl-*o*-toluimidoyl chloride, and N-*p*-anisyl-*p*-anisimidoyl chloride, respectively, in the Usgaonkar method, the reaction product isolated was in each case the corresponding 3-acetyl derivative, *viz.*, 2-*p*-anisyl-8-methyl-3-acetyl-4(1H)-quinolone, 2-*o*-tolyl-3-acetyl-4(1H)-quinolone, and 2-*p*-anisyl-6-methoxy-3-acetyl-4(1H)-quinolone, as was established by comparison (mixture melting point and infrared spectrum) with the bases prepared in method A.[16]

2-Aryl-3-acetyl-4-chloroquinolines (VII) and 2-Methyl-3-aroyl-4-chloroquinolines (IX).—The 4-chloro derivatives were obtained by refluxing the quinolone (III or VI, 1 g.) with redistilled phosphorus oxychloride (10 ml.) for 15 min. The cooled solution was carefully added portionwise to ice–water and the product separated as a gummy solid. After neutralization of the mixture with ammonia, the insoluble crude VII or IX was removed (in 90–100% yield) and recrystallized from dilute ethanol.

2-Phenyl-3-acetyl-4-chloroquinoline was obtained as colorless platelets, m.p. 138–140° (lit.[7] m.p. 136°), carbonyl band at 5.9 μ.

2-*p*-Anisyl-3-acetyl-4-chloroquinoline was obtained as needles, m.p. 146–148°, carbonyl band at 5.91 μ.

Anal. Calcd. for $C_{18}H_{14}ClNO_2$: N, 4.49. Found: N, 4.43.

2-Methyl-3-benzoyl-4-chloroquinoline was obtained as colorless platelets, m.p. 123–124° (lit.[7] m.p. 121°), carbonyl band at 6.0 μ.

Anal. Calcd. for $C_{17}H_{12}ClNO$: N, 4.97. Found: N, 4.85.

2-Methyl-3-*p*-anisoyl-4-chloroquinoline was obtained as needles, m.p. 138–140°, carbonyl band at 6.60 μ.

Anal. Calcd. for $C_{18}H_{14}ClNO_2$: N, 4.49. Found: N, 4.35.

2-Aryl-4(1H)-quinolones (IV). A. By Cyclization of Crotonate I in Liquid Paraffin.—The crotonate (I, 1 g.) was added in one portion to hot (~200°) liquid paraffin (medicinal, 20 g.) and the yellow solution was stirred at ~250° for 20–30 min.[9] During this period reaction proceeded with effervescence and the sparingly soluble quinolone IV usually separated from solution. After cooling to room temperature, the viscous mass was treated with dry ether and the insoluble crude IV was removed, washed with ether, and dried (70–85% yield). The usually discolored crude product was purified by dissolving in hot dilute sodium hydroxide (charcoal), precipitating from the filtrate with acetic acid, and recrystallizing from ethanol.

2-*p*-Anisyl-8-methyl-4(1H)-quinolone was obtained as colorless needles, m.p. 264–266°.

Anal. Calcd. for $C_{17}H_{15}NO_2$: N, 5.28. Found: N, 5.29.

2-*p*-anisyl-6-methoxy-4(1H)-quinolone was obtained as colorless platelets, m.p. 312–314° [lit.[17] m.p. 295° (hydrate)].

Anal. Calcd. for $C_{17}H_{15}NO_3 \cdot H_2O$: N, 4.68. Found: N, 4.63.

2-*p*-Anisyl-4(1H)-quinolone was obtained in 78% (crude) yield by heating I (Ar = *p*-$CH_3OC_6H_4$; Ar′ = C_6H_5, 1 g.) in liquid paraffin (10 g.) at 250° for 10 min., colorless needles from glacial acetic acid or from ethanol, m.p. 295–297° (lit.[18] m.p. 315°).

Anal. Calcd. for $C_{16}H_{13}NO_2$: N, 5.58; CH_3O, 12.35. Found: N, 5.55; CH_3O, 12.42.

The compound was synthesized unambiguously by the application of the Just reaction.[19] Diethyl malonate (3.6 g.) was stirred with sodium sand (0.26 g.) in dry toluene (25 ml.) at room temperature for 2 hr. After the addition of N-phenyl-*p*-anisimidoyl chloride (2.6 g.), the mixture was refluxed for 2 hr. and poured into ice–water. The product was extracted by ether and heated under reduced pressure to remove toluene and excess malonic ester, and the residue was dissolved in hot diphenyl ether (20 g.). The solution was refluxed for 30 min., about half of the solvent was removed by distillation, and the cooled residue, treated with ether, deposited crude 2-*p*-anisyl-3-carbethoxy-4(1H)-quinolone as a gum. This material was triturated with ether and it solidified (2.4 g.). The crude ester was refluxed with 2 *N* alcoholic sodium hydroxide for 2 hr.; on acidification of the solution with glacial acetic acid, 2-*p*-anisyl-3-carboxy-4(1H)-quinolone was precipitated, colorless needles from glacial acetic acid, m.p. about 250° dec. (lit.[18] m.p. 270°). The acid was decarboxylated by heating at ~250° and gave 2-*p*-anisyl-4(1H)-quinolone, colorless needles from glacial acetic acid, m.p. 294–296°.

B. By Deacetylation of 2-Aryl-3-acetyl-4(1H)-quinolones (III) in Concentrated Hydrochloric Acid.—Concentrated hydrochloric acid (20 ml.) and the PPA-derived quinolone III (1 g.) in a sealed Carius tube were heated at 200–220° for 5–8 hr.[7] The cooled reaction mixture was treated with ice–water and the crude insoluble IV (90–100% yield) was removed and purified by reprecipitation from dilute alkali and subsequent recrystallization as in A above. The following 4(1H)-quinolones were obtained on deacetylation of the corresponding III; the identity of the product was confirmed in each case by comparison (mixture melting point and infrared spectrum) with IV produced by method A[9] or other-

(16) It may well be that the Shah synthesis[5] normally produces a mixture of quinolones III and VI in poor yield. The molar ratio of the two components is, presumably, determined to some extent by the nature of the substituent in the imidoyl chloride, and may vary greatly in different reactions. Under the circumstances, and with the work-up procedure used,[5,6] the quinolone VI only would be isolated from reaction on certain occasions.

(17) R. Seka and W. Fuchs, *Monatsh. Chem.*, **57**, 52 (1931).

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(19) V. R. Heeramaneck and R. C. Shah, *J. Chem. Soc.*, 867 (1937).

wise available[20]: 2-phenyl, 2-phenyl-8-methyl, 2-phenyl-6,8-dimethyl, 2-*o*-tolyl, and 2-*p*-tolyl.

2-*p*-Hydroxyphenyl-4(1H)-quinolone.—2-*p*-Anisyl-3-acetyl-4(1H)-quinolone and concentrated hydrochloric acid formed IV (R_1 = H; Ar = *p*-HOC_6H_4) in almost theoretical yield. It was crystallized from dilute ethanol and was obtained as a monohydrate, m.p. 175–180°.

Anal. Calcd. for $C_{15}H_{11}NO_2 \cdot H_2O$: N, 5.49. Found: N, 5.52.

Dehydration was effected by heating at ~200°, and the resolidified base (m.p. ~280°) was recrystallized from glacial acetic acid and gave IV (R_1 = H; Ar = *p*-HOC_6H_4) as colorless platelets, m.p. 284–285° (lit.[21] m.p. 216°).

Anal. Calcd. for $C_{15}H_{11}NO_2$: N, 5.91. Found: N, 5.71.

The absence of methoxyl in the anhydrous sample was confirmed by a Zeisel determination and also by the infrared spectrum which, in contrast to the spectra of III (R_1 = H; Ar = *p*-$CH_3OC_6H_4$) and IV (R_1 = H; Ar = *p*-$CH_3OC_6H_4$), showed no strong methoxyl band in the 9.7–9.8-μ region.

2-*p*-Hydroxyphenyl-4(1H)-quinolone, m.p. 284–285°, was likewise produced on subjecting 2-*p*-anisyl-4(1H)-quinolone and 2-*p*-anisyl-3-carboxy-4(1H)-quinolone, respectively, to a similar degradation. Confirmation of its structure was obtained by cyclization of methyl β-amino-α-(N-phenyl-*p*-hydroxybenzimidoyl)crotonate (I, Ar = *p*-HOC_6H_4; Ar′ = C_6H_5, 0.15 g.) in liquid paraffin (2 g.) at 250° for 5 min.; the product (0.1 g., 87%) separated from dilute ethanol as a hydrate, m.p. 175–180°, and was converted to the anhydrous base, m.p. 284–285°, which proved to be identical (mixture melting point and infrared spectrum) with the product from degradation of 2-*p*-anisyl-3-acetyl-4(1H)-quinolone.

2-Phenyl-3-acetyl-4-anilinoquinoline (VIII, R_1 = H).—A two-molar proportion of aniline (0.33 g.) was stirred with 2-phenyl-3-acetyl-4-chloroquinoline (0.5 g.) on the water bath for 15 min. The solidified mixture was dissolved in ethanol and the 4-anilinoquinoline was precipitated in good yield (0.6 g.) by the addition of water. A recrystallization from dilute ethanol furnished ether-soluble, pale yellow needles, m.p. 114–116°, insoluble in dilute alkali and readily soluble in dilute hydrochloric acid to give a bright yellow solution.

Anal. Calcd. for $C_{23}H_{18}N_2O$: N, 8.28; mol. wt., 338. Found: N, 8.26; mol. wt., 310.

The infrared spectrum showed NH and CO absorption at 3.1 and 6.03 μ, respectively, and was in keeping with the structure assigned.

2-*p*-Anisyl-3-acetyl-4-anilinoquinoline was similarly obtained from VII (R_1 = H; Ar = *p*-$CH_3OC_6H_4$) in 60% crude yield, yellow needles from dilute ethanol, m.p. 121–123° (lit.[6] m.p. 213–214°); NH and CO bands were at 3.05 and 6.02 μ, respectively.

Anal. Calcd. for $C_{24}N_{20}N_2O_2$: N, 7.61. Found: N, 7.82.

6-Phenyl-7-methyldibenzo[*b*,*h*][1,6]naphthyridine (X).—VIII, 2-Phenyl-3-acetyl-4-anilinoquinoline (0.25 g.), was stirred with PPA (3 g.) at 150° for 30 min., the reaction proceeding with effervescence. The solution was cooled and neutralized with dilute sodium hydroxide and the precipitated product was collected and recrystallized from acetic acid, pale brown needles, m.p. 178–180°. These were sparingly soluble in dilute hydrochloric acid, ether, and ethanol.

Anal. Calcd. for $C_{23}H_{16}N_2$: N, 8.75; mol. wt., 320. Found: N, 8.59; mol. wt., 297.

The infrared spectrum showed no NH or carbonyl absorption and was consistent with structure X.

2,4-Diphenyl-3-methyl-2H-pyrazolo[4,3-*c*]quinoline (XI).—Equimolar proportions of 2-phenyl-3-acetyl-4-chloroquinoline (1.1 g.) and phenylhydrazine (0.45 g.) were stirred together at 140° for 30 min. The mixture liquified and effervesced and became semisolid. It was cooled and triturated with ether to yield a fawn-colored powder (1.3 g.), m.p. 250–260°, which was possibly a hydrochloride. This was recrystallized from dilute ethanol and formed colorless platelets, m.p. 185–186°, insoluble in dilute sodium hydroxide.

Anal. Calcd. for $C_{23}H_{17}N_3$: N, 12.54; mol. wt., 335. Found: N, 12.75; mol. wt., 317.

The infrared spectrum of XI, like that of the isomeric 1,4-diphenyl isomer,[3] showed no NH and no carbonyl absorption; significant differences between the two spectra were, however, evident in the 6–7- and 10–11-μ regions particularly.

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Ozonation of Aromatic Aldehydes[1]

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The order of reactivity with ozone–nitrogen mixtures for the aromatic aldehydes studied was anisaldehyde > benzaldehyde > *p*-nitrobenzaldehyde, showing that a nucleophilic ozone attack on the carbonyl group of the aldehyde is not an important, or rate-determining, step. The major product from ozone attack on benzaldehyde is perbenzoic acid whether ozone–nitrogen or ozone–oxygen mixtures are employed. Much more ozone is required per benzaldehyde molecule with ozone–nitrogen than with ozone–oxygen, however. It is suggested that the predominant ozone attack on an aromatic aldehyde is a concerted 1,3-dipolar insertion, producing unstable intermediate ArC(=O)OOOH, which decomposes, predominantly, to aroylperoxy radicals. These produce peracids by abstraction of hydrogen from the solvent or the aldehyde. Therefore, autoxidation, which occurs in the presence of oxygen, is initiated by these radicals rather than by ozone itself.

The ozonation of aldehydes has been studied by several investigators, including Harries,[3] Fischer,[4] Briner,[5] Spath,[6] von Wacek,[7] and Dick.[8] Harries[3] studied aliphatic aldehydes and reported that a peroxidic intermediate was produced which rearranged to the corresponding acid. He represented the reaction as follows: RCHO + O_3 → O_2 + RC(H)=O=O → RC(=O)OH. Other workers found that not only the carboxylic acid but also the peracid,[4,5,8] and with some aromatic aldehydes the corresponding phenol,[6,7] is produced. Fischer, Düll, and Volz[4] suggested an initial adduct between ozone and the aldehyde (RCH=$O \cdot O_3$) which then can react with another mole of aldehyde to give 1 mole of acid and 1 mole of peracid, or with 2 moles of aldehyde to give 3 moles of acid. Briner and co-workers[5] studied the oxidation of benzaldehyde with ozone–oxygen–nitrogen mixtures of various ozone–oxygen ratios. When present in high concentration,

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