EXPERIMENTAL

Method I. 1-Chloro-3-methylbenzo[*f*]quinoline (0.005 mole) and an equivalent amount of the appropriate amine were dissolved in 90% ethanol and boiled under reflux for 5 to 10 hr. The hydrochloride of the base crystallized during this period and was filtered and washed with ethanol. It was dissolved in hot dilute acetic acid, and the solution neutralized with ammonia to precipitate the base. It was filtered, washed with water, and crystallized from 90% ethanol.

The 4-amino-2-methylbenzo[*h*]quinoline derivatives were prepared in the same way as above, by boiling under reflux for 40 hr.

Method II. A mixture of 0.005 mole of 1-chloro-3-methylbenzo[*f*]quinoline or 4-chloro-2-methylbenzo[*h*]quinoline and a slight excess of thea ppropriate amine was heated in phenol in an oil bath at 130–140° for 30 hr. The reaction mixture was poured into an excess of a solution of sodium hydroxide. The base was obtained as a sticky precipitate which solidified in a day. It was dried in the desiccator, dissolved in ether, and after filtration, the ether solution was treated with a solution of salicylic acid in ether. The salicylate of the base which precipitated was filtered, washed with ether, and crystallized from 90% ethanol.

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Reactions of Pyrones Catalyzed by Trifluoroacetic Acid

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Previous experiments[2,3] with pyrones have shown that trifluoroacetic acid catalyzes the reaction of acyl halides with pyrones to form either mono or diacylated products. These reactions have indicated that the activated complex of a 2- or 4-pyrone with trifluoroacetic acid is a carbanion.

It was therefore decided to try the reaction of pyrones with nitriles and with substituted acrylic acids such as cinnamic acid and crotonic acid.

In every instance in which condensation between a pyrone and a nitrile was attempted, experimental evidence indicated that a reaction had taken place.

The resulting imides are characterized in the I_{A-F} series given in Table I. Compound I_F is a ketone formed from the easily hydrolyzed imide. As Compound I_E represents the simplest molecule, it was selected as representative of the group for hydrolysis to the ketone and thus to the malononitrile derivative (IV). Malononitrile has been demonstrated[3,4] to indicate the presence of the pyrone carbonyl as well as the ketonic carbonyl.

Table II describes the three instances in which the authors were able to isolate the condensation product from the reaction of pyrones with substituted acrylic acids. The *p*-bromophenacyl bromide derivative (V) of II_A was prepared to characterize the acid because it was representative of the group and had the simplest molecule.

The compounds of the III_{A-C} series in Table III represent the nearest approach of a continuing search over a period of several years for a method by which pyrones may be carboxylated. However, every attempt to hydrolyze the carbethoxy compounds was a failure.

In the face of such limited data and so few cases one can only speculate that the position of the carboxyl or carboxyls on the pyrone ring of the carbethoxy compound is such that in the presence of boiling mineral acids the substances rapidly decarboxylate.

EXPERIMENTAL[5]

Compounds I_{A-F} *series.* A mixture of 0.1 mole of the pyrone and 0.1 mole of the nitrile in 20 ml. of trifluoroacetic acid was refluxed for at least 90 min. The cooled solution was diluted with 200 ml. of water and chilled in the freezing compartment of the refrigerator. The precipitate was dried in air and recrystallized twice from absolute ethanol to give the analytical sample.

Compounds of II_{A-C} *series.* One tenth mole of cinnamic or crotonic acid was mixed with 0.1 mole of the pyrone in 15 ml. trifluoroacetic acid and the mixture refluxed for a minimum of 15 hr. At the termination of the reflux period, 100 ml. of water was added to the mixture. The material was cooled somewhat and then filtered. The residue was dried in air and the analytical samples were obtained by recrystallizing the crude compounds twice from boiling heptane.

Compounds of III_{A-C} *series.* To a mixture consisting of 0.1 mole of the pyrone and 30 ml. of trifluoroacetic acid, thoroughly shaken, was added, all at once, either 0.1 mole or 0.2 mole of ethyl chloroformate. The solution was heated under reflux in an all-glass refluxing assembly in the hood for 2 hr. or for a sufficiently longer time that hydrogen chloride vapors were no longer evolved.

At the termination of the reaction period the mixture was poured into 200 ml. distilled water, chilled, and filtered. The air dried precipitate was recrystallized twice from heptane. Compounds of this series are listed in Table III.

Preparation of compound IV. A 5.0-g. sample of compound of I_E was refluxed in a mixture of 90 ml. distilled water and 10 ml. concd. hydrochloric acid for several hours. The solution was filtered while hot and the residue remaining on the paper was dried, then refluxed with 2.5 g. of malononitrile in 15 ml. of acetic anhydride for 1 hr. The solution was poured into water and the light brown precipitate when recrystallized several times from absolute ethanol melted at 122°.

Anal. Calcd. for $C_{21}H_{13}N_5O_3$: N, 18.26. Found: N, 18.27.

p-Bromophenacyl derivative of II_A (V). Two and seven tenths grams (0.01 mole) of II_A was mixed with 0.8 g. of sodium bicarbonate in 8 ml. of water. After the effervescence had subsided, 40 ml. of ethanol and 0.01 mole of *p*-bromophenacyl bromide (2.7 g.) was added. The mixture was

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(1) The person to whom correspondence regarding the contribution should be addressed.

(2) L. L. Woods and P. A. Dix, *J. Org. Chem.*, **24**, 1126 (1959).

(3) L. L. Woods, *J. Org. Chem.*, **24**, 1804 (1959).

(4) L. L. Woods, *J. Am. Chem. Soc.*, **80**, 1440 (1958).

(5) All analyses were performed by Dr. Carl Tiedcke and all melting points were determined on a Fisher-Johns melting point assembly.

TABLE I

REACTIONS OF PYRONES WITH NITRILES

No.	Pyrone	Nitrile	M.P., °	Yield, %	Empirical Formula	Analyses, Calcd. (Found) Carbon	Hydrogen	Nitrogen
I_A	Kojic acid	*p*-Nitrophenylacetonitrile	167.5–168	70	$C_{14}H_{12}N_2O_6$	55.26 55.10	3.97 4.24	9.20 9.04
I_B	α-Chloro-α-deoxy kojic acid	*p*-Nitrophenylacetonitrile	118–120	86	$C_{14}H_{11}N_2ClO_5$	52.10 52.39	3.43 3.58	8.68 8.44
I_C	2-Hydroxymethyl-5-methoxy-4-pyrone	*p*-Nitrophenylacetonitrile	140	94	$C_{15}H_{14}N_2O_6$	56.60 56.41	4.43 4.29	8.80 8.86
I_D	Comenic acid	Benzonitrile	Sublimes above 200, discolors above 270	66	$C_{13}H_9NO_5$	60.23 60.51	3.49 4.70	5.40 5.12
I_E	2,6-Dimethyl-4-pyrone	*p*-Nitrophenylacetonitrile	115.5–116.5	76	$C_{15}H_{14}N_2O_4$	62.93 62.42	4.92 4.55	9.78 10.12
I_F	α-Chloro-α-deoxy kojic acid	Cyanoacetic acid	162–163	54	$C_9H_7ClO_6$[a]	43.83 44.10	2.86 3.11	—

[a] As hydrolysis of the compound failed to change the melting point and composition, the original product was the ketone and not the imide.

TABLE II

REACTIONS OF PYRONES WITH SUBSTITUTED ACRYLIC ACIDS

No.	Pyrone	Unsaturated Acid	Yield, %	M.P.	Formula	Analyses, Calcd. (Found) Carbon	Hydrogen	Chlorine
II_A	2,6-Dimethyl-4-pyrone	Cinnamic acid	98	128–129	$C_{16}H_{16}O_4$	70.59 70.91	5.92 5.70	
II_B	Coumarin	Cinnamic acid	61	142.5–143.5	$C_{18}H_{14}O_4$	73.45 73.19	4.79 4.59	
II_C	α-Chloro-α-deoxy-kojic acid	Crotonic acid	29	145–146	$C_{10}H_{11}O_5Cl$	48.69 48.52	4.49 4.29	14.37 14.19

TABLE III

CARBETHOXY DERIVATIVES OF PYRONES

No.	Pyrone	Moles of Ethyl Chlorocarbonate per Mole Pyrone	M.P.	Formula	Yield, %	Analyses, Calcd. (Found) Carbon	Hydrogen
III_A	Kojic acid	1	162–163	$C_9H_{10}O_6$	41	50.23 50.41	4.68 4.41
III_B	α-Chloro-α-deoxykojic acid	2	140–141	$C_{12}H_{13}ClO_7$	32	47.30 47.54	4.30 4.14
III_D	6-Nitrocoumarin	2	160–161.5	$C_{15}H_{13}NO_8$	51	53.73 53.48	3.90 3.68

refluxed for 90 min. and then poured into 400 ml. of water. Ten milliliters of concd. hydrochloric acid and 1 g. of aluminum chloride was then added; the resulting precipitate was filtered and dried in air, yield 2.5 g. Recrystallization of the precipitate twice from ethanol produced crystals melting at 155°.

Anal. Calcd. for $C_{24}H_{21}BrO_5$: C, 61.41; H, 4.51; Br, 17.02. Found: C, 61.02; H, 4.23; Br, 17.45.

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Coenzyme Q. XIV. Reactions of Ethyl Cyanoacetate with Dimethoxybenzoquinones

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A sensitive color reaction[1] for certain quinones, has been modified so that it is applicable to co-

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[1] R. Craven, *J. Chem. Soc.*, 1605 (1931).