Hydrogenolysis of ketals. The ketal was placed in the hydrogenation vessel and 0.2 g. of rhodium (5%) on alumina and 1 drop of concentrated hydrochloric acid were added (0.5 g. of rhodium catalyst and 0.5 ml. of acid were used with the acetone dimethyl ketal). The mixture was then shaken with hydrogen at 35–60 p.s.i.g. for the time and at the temperature shown in Table I. If the alcohol produced were soluble in water, the mixture was extracted with water and the alcohol and ether isolated from the separated phases by distillation. To facilitate separation of the ethers from butanol and cyclohexanol, these alcohols were converted respectively to their acid maleate and phthalate esters by refluxing the product mixture with the anhydride. The acid esters were then extracted into aqueous bicarbonate solution, and the ethers were obtained by distillation. The butanol was recovered by distillation after saponification of its acid ester. The hydrogenation of the dimethyl and dibutyl ketals was started at room temperature, then conducted at a higher temperature until no change in hydrogen pressure could be detected in a 2-hr. interval. The amount of hydrogen consumed at each temperature, the material balance for the total hydrogenation, and other pertinent data are given in Table I.

FREEPORT, TEX.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, TEXAS SOUTHERN UNIVERSITY]

Formylation of Pyrones in the Presence of Trifluoroacetic Acid

L. L. WOODS[1] AND P. A. DIX

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This paper describes a new method of formylating pyrones through the use of carbon monoxide-hydrogen chloride mixture in the presence of trifluoroacetic acid as a catalyst.

Mononuclear pyrones, particularly the 4-pyrones which are our primary interest have, so far, resisted all our efforts to oxidize the appended alkyl or hydroxyalkyl groups to aldehydes or acids. Therefore, it was decided to devise a method to formylate these compounds without oxidation.

The method worked remarkably well for the formation of aldehydes from kojic acid, α-chloro-α-deoxy kojic acid and 2-hydroxymethyl-5-methoxy-4-pyrone to produce compounds of the $\mathrm{I_{A-C}}$ series given in Table I.

TABLE I

FORMYL DERIVATIVES OF PYRONES

No.	Pyrone	Yield, %	M.P.	Formula	Carbon Calcd.	Carbon Found	Hydrogen Calcd.	Hydrogen Found	Chlorine Calcd.	Chlorine Found
$\mathrm{I_A}$	2-Hydroxymethyl-5-methoxy-4-pyrone	82	165–166	$C_8H_8O_5$	52.17	52.53	4.37	4.64		
$\mathrm{I_B}$	α-Chloro-α-deoxy-kojic acid	100	168–170	$C_7H_5ClO_4$	44.58	44.29	2.67	2.89	18.80	19.11
$\mathrm{I_C}$	Kojic acid	67	159–160	$C_7H_6O_5$	49.42	49.54	3.55	3.82		
$\mathrm{I_D}$	6-Methyl-2-pyronone	72	193.5–194	$C_7H_6O_4$	54.55	55.09	3.92	4.09		
$\mathrm{I_E}$	Coumarin	94	70–71.5	$C_{10}H_6O_3$	68.96	68.72	3.47	3.29		

Compounds $\mathrm{I_{D-E}}$ were subsequently prepared merely to ascertain if the method was effective on 2-pyrones. 2,6-Dimethyl-4-pyrone for some unaccountable reason failed to form more than a water insoluble oil which could not be crystallized and could not be distilled, and benzodihydro-4-pyrone was so reactive that the monoformyl derivative was never isolated.

The malonic acid derivatives of most of the formylated pyrones were prepared because of the failure of methone to react in the expected way and because no consistent results could be obtained with any of the usual nitrogenous reagents commonly used to characterize carbonyl-containing compounds. All efforts to oxidize the pyrone aldehydes to the corresponding acids were failures.

It was visualized that the malonic acid derivatives resulting in the formation of a pyrone–acrylic acid (Table II) would serve the dual purpose of demonstrating the presence of the formyl group and also indicate the position of its attachment on the pyrone ring. This latter premise would be effectively demonstrated if the aldehyde group were in position of 6 of kojic acid or α-chloro-α-deoxykojic acid since the resultant pyrone–acrylic acid would spontaneously cyclize to form coumaropyrones similar to those prepared previously.[2]

However, not only did the compounds fail to cyclize, spontaneously they also failed to cyclize when heated with 100% phosphoric acid at 120–

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(1) To whom communications regarding this contribution should be addressed.

(2) L. L. Woods and P. A. Dix, *J. Org. Chem.*, **24**, 1148 (1959).

TABLE II

ACRYLIC ACID DERIVATIVE

Pyrone Alde- hyde	Yield, %	M.P.	Formula	Carbon		Hydrogen		Chlorine	
				Calcd.	Found	Calcd.	Found	Calcd.	Found
II_A	40	157.5	$C_9H_8O_6$	50.95	50.49	3.80	3.62		
II_B	54	166–167.5	$C_9H_7ClO_5$	46.87	46.39	4.36	4.08	15.37	15.68
II_C	46	167.5–169.5	$C_{10}H_{10}O_6$	53.10	53.19	4.45	4.68		
II_D	51	189–190	$C_9H_8O_5$	55.10	55.42	4.11	4.21		

130° and with concentrated sulfuric acid when heated at 90° for one hour.

The failure to obtain coumaropyrones proves unequivocally that the formyl group must be on position 3, as it is the only other position available for such attachment and the only position in which a formyl group would be sufficiently stable to form a pyrone–acrylic acid derivative.

Proof of the validity of the previous statement was obtained by producing the bisaldehyde of α-chloro-α-deoxy-kojic acid which when converted into the pyrone acrylic acid derivative gave the same melting point and mixed melting point of the pyrone–acrylic acid derivative of the monoformylated I_B, indicating the instability of the formyl group in position 6.

The orientation of substituents on a pyrone ring is not surprising if consideration is given to the fact that trifluoroacetic acid is a powerful solvating agent[3] and that the compound acted upon by a substituent is no longer a pyrone but an activated complex of the pyrone hydrogenchloride salt. This, of course, now makes reasonable an assumption that the 3-position is activated due to the conversion of the nuclear oxygen to a positive pole created by coordination with the solvating trifluoroacetic acid.

Infrared data (Table III) did not give what we considered to be conclusive proof of formylation in compounds I_{A-C}; other physical means of demonstration were sought. An effort to determine molecular weights of these compounds was attempted by mass spectrographic means but the compound would not volatilize, so NMR studies were made to give the desired evidence.

The NMR spectra for compounds I_{A-C} are given in Table IV using 2,6-dimethyl-4-pyrone as a reference substance. The resonances appear at about the positions predicted by the Chamberlain[4] chemical shift charts except for the hydrogen of the formyl group. Any conjecture by the author, at this time, as to why the formyl group gives a peak at −0.7 would be valueless. The hydrogen of the hydroxyl group does not appear because rapid exchange broadens the peak beyond detection.

TABLE III

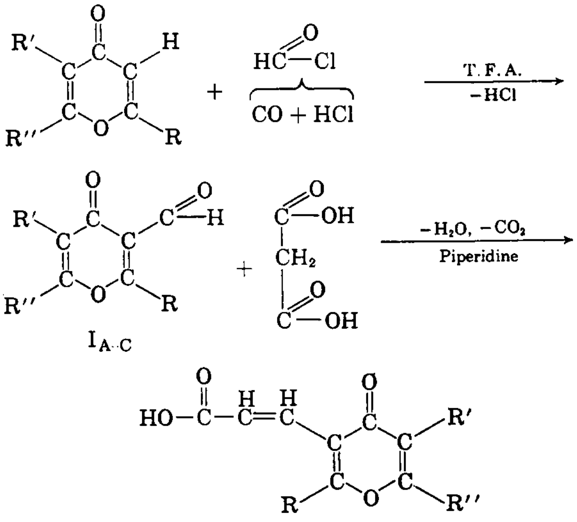
INFRARED ABSORPTION BANDS IN CM.$^{-1}$
(KBr Pellet)

I_A	3125, 2857 shoulder, 1653, 1626, 1610, 1600, 1471, 1389, 1284, 1227, 1143, 1078, 943, 854
I_B	3125, 1653, 1618, 1587, 1453, 1374, 1282, 1225, 1166, 1117, 865, 8000
I_C	3125, 1631, 1603, 1266, 1221, 1152, 1092, 1005, 9615, 877

TABLE IV

DELTA (δ) VALUE OF NMR SPECTRA IN DIMETHYL SULFOXIDE

I_A	H, 1; $—CH_2OH$, 3.2; $—\overset{\overset{O}{/\!\!/}}{C}—H$, −0.7; $—OCH_3$, 3.7
I_B	H, 0.7; $—CH_2Cl$, 2.8; $—\overset{\overset{O}{/\!\!/}}{C}—H$, −0.7
I_C	H, 1; $—CH_2OH$, 3.2; $—\overset{\overset{O}{/\!\!/}}{C}—H$, −0.7
2,6-Dimethyl-4-pyrone	H (nuclear), 1; H (methyl), 4.7



II A-C

I_A. R = CH_2OH, R′ = OH, R″ = H
[2-Hydroxymethyl-3-formyl-5-hydroxy-4-pyrone]
I_B. R = CH_2Cl, R′ = OH, R″ = H
[2-Chloromethyl-3-formyl-5-hydroxy-4-pyrone]
I_C. R = CH_2OH, R′ = OCH_3, R″ = H
[2-Hydroxymethyl-3-formyl-5-methoxy-4-pyrone]
II_A = β—[2-Hydroxymethyl-5-hydroxy-4-pyrone-3] acrylic acid
II_B = β—[2-Chloromethyl-5-hydroxy-4-pyrone-3] acrylic acid
II_C = β—[2-Hydroxymethyl-5-methoxy-4-pyrone-3] acrylic acid

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[3] L. J. Andrews and R. M. Keefer, *J. Am. Chem. Soc.*, **82**, 3059 (1960).

[4] N. F. Chamberlain, *Anal. Chem.*, **31**, 56 (1959).

EXPERIMENTAL[5]

Compounds of I_{A-E} *series.* In a wash bottle—tall form—fitted with a fritted aspirator plate was placed 0.15 mole of the pyrone with 30 ml. of trifluoroacetic acid. A 50–50 mixture of carbon monoxide and dry hydrogen chloride from a tank was bubbled fairly rapidly through the solution at room temperature for not less than 3 hr. Usually during the initial portion of the reaction period the mixture warmed up somewhat but as the pyrone dissolved the temperature decreased and the viscosity of the material increased to a thick sirup. At the termination of the reaction period the product was diluted with 100 ml. of water and chilled overnight in the freezing compartment of the refrigerator. The precipitate was suctioned off and dried in air. With compounds I_{A-C} the crude material was recrystallized twice from absolute ethanol. However, for I_D three recrystallizations from distilled water was necessary and I_E was purified by recrystallizing it twice from heptane.

Compounds of II_{A-D} *series.* A mixture consisting of 0.01 mole of the pyrone aldehyde, 0.01 mole of malonic acid, 5 drops of piperidine in 30 ml. of absolute ethanol was placed in a flask, protected from moisture, then immersed in a water bath at 80° for at least 5 hr. The solutions were then acidified with 10–15 drops of concentrated hydrochloric acid and chilled. The precipitates were recrystallized once from absolute ethanol. In the case of sample II_D the alcoholic solution was acidified, 50 ml. of water added, and then heated to drive off some of the ethanol. Upon chilling, a chocolate-colored precipitate was obtained which was taken up in distilled water, decolorized with Norite, and then chilled to give colorless crystals.

Reduction of I_C. Two grams of I_C was dissolved in 50 ml. of ethanol and 4 g. of potassium borohydride was added. The reaction flask was stoppered with cotton and allowed to stand overnight, following which 10 ml. of concentrated hydrochloric acid was added and an additional 40 ml. of ethanol. The solution was heated, filtered while warm, and the solution evaporated to dryness over a steam bath to give a brown compound which was 2,3-bis(hydroxy-methyl)-5-hydroxy-4-pyrone, crude yield 1.4 g.

The material was recrystallized twice from ethanol; it softened above 164° and melted at 167°.

Anal. Calcd. for $C_8H_{10}O_5$: C, 51.61; H, 5.42. Found: C, 51.90; 5.19.

Bisformylation of α-chloro-α-deoxykojic acid. To 30 g. of α-chloro-α-deoxy kojic acid in a wash bottle, described previously, 40 ml. of trifluoroacetic acid was added and the mixture of carbon monoxide–hydrogen chloride was bubbled in at a rapid rate for 6.5 hr. The solution was diluted with 200 ml. of water and chilled as previously stated; crude yield 21.3 g. Recrystallization of the compound three times from absolute ethanol gave a tan substance m.p. 165–166.5°.

Anal. Calcd. for $C_8H_5ClO_5$: C, 44.65; H, 2.32; Cl, 16.37. Found: C, 44.82; H, 2.52; Cl. 16.22.

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HOUSTON 4, TEX.

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

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, DUKE UNIVERSITY]

Acylations of Bisacetylferrocene with Esters by Potassium Amide to Form Bis-β-diketones. Consideration of Mechanism[1]

CHARLES E. CAIN,[2] T. ARTHUR MASHBURN, JR., AND CHARLES R. HAUSER

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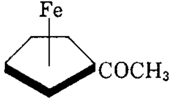
Acylations at both of the methyl groups of bisacetylferrocene with esters by potassium amide in liquid ammonia to form bis-β-diketones appears to be quite general. Unsuccessful attempts were made to isolate the corresponding mono-β-diketones, which might be expected as intermediates. The bis-β-diketones were allowed to react with an excess of hydrazine to form bis-pyrazoles. A mechanism for the diacylations is suggested.

It has recently been observed[3] that both of the methyl groups of bisacetylferrocene (I) can be benzoylated readily with methyl benzoate by means of potassium amide to form the bis-β-diketone II in good yield.

It has now been found that I can similarly be acylated with ethyl acetate and ethyl propionate to form the bis-β-diketones III and IV respectively.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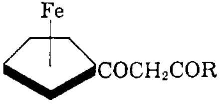
II. R = C_6H_5
III. R = CH_3
IV. R = C_2H_5

Although mono-β-diketones of type V might be expected to be formed as intermediates, no such compound could be isolated either in the previous work or in the present investigation.

That the products isolated were the bis-β-diketones II, III, and IV was supported not only by their analyses and molecular weight (for II),[4] but also by their infrared spectra, which showed

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[1] Supported in part by the Office of Ordnance Research, U. S. Army.

[2] Esso Research and Engineering Company Fellow, 1957–1958.

[3] C. R. Hauser and C. E. Cain, *J. Org. Chem.*, **23**, 1142 (1958).