metallic manganese. It appears therefore that the methyleyclopentadienyl group serves to moderate the reactivity of the manganese atom toward reduction.⁶

An investigation of the stoichiometry of the reaction indicated that five sodium atoms and three carbon monoxide molecules are consumed per $\mathrm{Mn}(\mathrm{CO})_5$ formed regardless of the solvent and temperature up to 200°. The reaction mixture generally contained a brown viscous oil which was insoluble in petroleum ether and did not appear to contain free manganese carbonyl prior to hydrolysis. Unchanged I was generally evident, and methylcyclopentadiene could not be detected before or after hydrolysis. Sodium did not appear to react with carbon monoxide to any significant extent under the conditions employed. Accordingly, it appears that the large excess of sodium required may be due solely to its reaction with the cyclopentadienyl group, and that the sodium methylcyclopentadienide which may be formed reacts further with carbon monoxide. It is suggested that the brown oil contains the sodium salt of manganese carbonyl, probably as a diglyme complex, (diglyme)₂ $Na^+ Mn(CO)_{5}^-$, and that the manganese carbonyl arises by oxidative-hydrolysis of the latter. Further work is required to define the various products of the evidently complex reaction involving I, sodium, and carbon monoxide.

EXPERIMENTAL

To a 1-l. Parr autoclave were added 80 ml. (0.50 mole) of π methylcyclopentadienylmanganese carbonyl (Ethyl Corp.), 300 ml. of dry diglyme, and 100 ml. of a 40% dispersion (1.48 g.-atoms) of sodium in Nujol (Plough, Inc.). The autoclave was then pressurized with 700 p.s.i. of c.p. carbon monoxide and the mixture was heated with stirring to 125° for 8 hr. with intermittent repressurizing to speed up the reaction. The reaction mixture was then carefully quenched with about 500 ml. of water at 0° (or 25–65° under 500 p.s.i. of carbon monoxide) and steam distilled. The yield of manganese carbonyl was 45.7 g. (48%), m.p. 151–153° (uncorrected).

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(6) The oxidation state of manganese in I can be considered formally as +1.

Acylation, Bromination and Oxidation of 4-Pyrones and Pyronones¹

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A review of pertinent literature²⁻⁴ on the chemistry of 6-methyl-2-pyronone fails to show that the compound when treated with acetic anhydride or acetyl chloride regenerates dehydroacetic acid. We have found this to be a very easy transformation to accomplish in the presence of trifluoroacetic acid, further the acid does not degrade dehydroacetic acid to any appreciable degree when refluxed in its presence for as long as twenty-four hours.

Since the acetylation proved to be so facile it was decided to prepare a series of pyronone compounds similar to 3-acetyl-6-methyl-2-pyronone (dehydroacetic acid) by changing the acyl group in position 3.

It was found that not only would different acyl halides place different groups in position 3, but when two equivalents of the acyl halide were used, a second acyl radical was placed on the nucleus without destruction of the ring structure, presumably at position 5 since it is very unlikely that a second acyl group could be put on position 3 without rupture of the ring. The pyronones synthesized are listed as the I_{A-F} series in Table I.

Pyronone when treated in the presence of three equivalents of an acyl halide such as *m*-nitrobenzoyl chloride gave 2-(*m*-nitrophenyl)-3,5-di(*m*-nitrobenzoyl)-6-methyl-4-pyrone (II).

A verification of the structure of the compounds in the I_{A-F} series was obtained by using compounds I_A and $_B$ as models. Carbon dioxide was eliminated from them by the usual hydrochloric acid method and the method of Light and Hauser⁶ to form the 2-aryl-4-pyrones described in the experimental portion of this report as compounds III and IV respectively.

One of the objectives of our study of the pyrones was to devise methods of oxidizing the various mononuclear 4-pyrones without rupture of the ring. A method to effect this oxidation has been found using chloranil as the oxidant. The product of such an oxidation appears to be a 6,6'-bipyrone as indicated by the figure adjacent to Table II in which the substances formed by the oxidation are listed as compounds V_{A-D} . Infrared spectra run on the substances with a Beckman IR-5 failed to show more than an intensification of the absorption bands of the starting materials; however, ultraviolet absorption spectra do show an unmistakable difference.

The absorption maxima for the two model compounds V_A and V_B are slightly but definitely different from the substances from which they are derived, kojic acid and α -chloro- α -deoxy-kojic acid respectively.

The bromination studies included in this report consists of an inelegant generalized method for

(1) The investigations reported here were supported by the Robert A. Welch Foundation.

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NOTES

 $\mathbf{I}_{\mathbf{F}}$

p-Nitrobenzoyl chloride

3-Acyl-6-methyl-2-pyronones from 6-Methyl-2-pyranone								
	Acyl Halide	Equivalents of Acyl	MD	Yield,	Empirical	Carbon	aled. (Found	l)
	Usea	Hande	IVI.P.	70	rormula	Carbon	nyurogen	Nitrogen
$\mathbf{I}_{\mathbf{A}}$	Benzoyl chloride	1	70-71	73	${ m C}_{13}{ m H}_{10}{ m O}_4$	77.40	5.41	
I_{B}	Benzoyl chloride	2	68-69	100	$\mathrm{C}_{20}\mathrm{H}_{14}\mathrm{O}_{5}$	(71.00) (71.85) (71.49)	(3.21) 4.22 (4.40)	
$\mathbf{I}_{\mathbf{C}}$	<i>m</i> -Nitrobenzoyl chloride	1	148-150	99	$\mathrm{C}_{13}\mathrm{H}_9\mathrm{NO}_6$	(71.40) 56.73 (56.84)	(4.40) 3.29 (2.84)	5.08 (4.94)
$\mathbf{I}_{\mathbf{D}}$	Phenylacetyl chloride	1	151 - 152	87	$\mathrm{C}_{14}\mathrm{H}_{12}\mathrm{O}_4$	68.87 (69.08)	(4.95) (5.02)	(10-)
I_E	Phenylacetyl chloride	2	110–111	91	$\mathrm{C}_{22}\mathrm{H}_{18}\mathrm{O}_{6}$	72.91 (72.64)	5.00 (4.82)	
I_F	<i>p</i> -Nitrobenzovl	1	208 - 209	88	$C_{13}H_9NO_6$	56.73	3.29	5.08

TABLE I

 $I_{A} = 3-Benzoyl-6-methyl-2-pyronone. \ I_{B} = 3,5-Di-benzoyl-6-methyl-2-pyronone. \ I_{C} = 3-(m-Nitrobenzoyl)-6-methyl-2-pyronone. \ I_{E} = 3,5-Di-benzoyl-6-methyl-2-pyronone. \ I_{F} = 3-(m-Nitrobenzoyl)-6-methyl-2-pyronone. \ I_{F} = 3-(m-Nitrobenzoyl)-6-methyl-2-pyronone. \ I_{F} = 3-(m-Nitrobenzoyl)-6-methyl-2-pyronone. \ I_{F} = 3,5-Di-benzoyl-6-methyl-2-pyronone. \ I_{F} = 3-(m-Nitrobenzoyl)-6-methyl-2-pyronone. \ I_{F} = 3-(m-Ni$ phenylacetyl)-6-methyl-2-pyronone.

TABLE II BIPYRONES

			Crude Yield,	Empirical	Calcd. (Found)		
No.	Pyrone Used	M.P.	%	Formula	Carbon	Hydrogen	Chlorine
V_{A}	Kojic acid	156-156.5	100	$C_{12}H_{10}O_8$	51.72 (51.44)	3.57 (3.35)	
$V_{\mathbf{B}}$	α -Deoxy- α -chlorokojic acid	168.5	58	$\mathrm{C}_{12}\mathrm{H}_{8}\mathrm{Cl}_{2}\mathrm{O}_{6}$	45.16 (44.94)	2.52 (2.77)	22.22 (22.09)
V_{C}	2-Hydroxymethyl-5- methoxy-4-pyrone	163-164	74	$\mathrm{C}_{14}\mathrm{H}_{14}\mathrm{O}_8$	$54.19' \\ (53.89)$	4.54 (4.29)	, , ,
V_D	2-Chloromethyl-5- methoxy-4-pyrone	119–120	27	$C_{14}H_{12}Cl_2O_6$	(48.43) (48.62)	3.48 (3.57)	$20.42 \\ (20.30)$

 $V_{\rm A} = 2,2'-{\rm Di}({\rm hydroxymethyl})-5,5'-{\rm di-hydroxy-6,6'-bi}(4-{\rm pyrone}), V_{\rm B} = 2,2'-{\rm Di}({\rm chloromethyl})-5,5'-{\rm di-hydroxy-6,6'-bi}(4-{\rm pyrone}), V_{\rm D} = 2,2'-{\rm Di}({\rm hydroxymethyl})-5,5'-{\rm di-hydroxy-6,6'-bi}(4-{\rm pyrone}), V_{\rm D} = 2,2'-{\rm Di}({\rm chloromethyl})-5,5'-{\rm di-hydroxy-6,6'-bi}(4-{\rm pyrone}), V_{\rm D} = 2,2'-{\rm Di}({\rm py$ methoxy-6,6'-bi(4-pyrone).

TUDLE III	TABLE	III
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BISBROMO DERIVATIVES OF 4-PYRONES

			"Crude Yield,	Empirical	Broi	mine
No.	Pyrone Used	M.P.	%	Formula	Caled.	Found
VI_A	Kojic acid	Softens above 135 Melts 143–144	23	$C_6H_4Br_2O_4$	53.28	53.01
VI_B	2,6-Dimethyl-4-pyrone	152	59	$C_7H_6Br_2O_2$	56.68	56.47
VI_{C}	2-Methyl-4-pyrone ^a	148 - 149	58	$C_6H_4Br_2O_2$	59.65	59.41
VID	6-Methyl-2-pyronone	174-176	73	$\mathrm{C_6H_4Br_2O_3}$	56.29	55.87

^a Furnished as a concentrate by the courtesy of Monsanto Chemical Corp. $VI_A = 2$ -Hydroxymethyl-3,6-dibromo-5-hydroxy-4-pyrone. $VI_B = 2$,6-Dimethyl-3,5-dibromo-4-pyrone. $VI_C = 2$ -Methyl-3,6-dibromo-4-pyrone. $VI_D = 3$,5-Dibromo-6-methyl-2-pyronone.

placing two bromine atoms on a pyrone nucleus. The method does produce, for the first time, the compounds sought, but in low yields from tacky semi-solids that often contained considerable tar.

that position 3 in all of them was unoccupied and was one of the sites of halogenation in every case.

The only common denominator among the

The di-bromo pyrones produced in the reaction are given as compounds $\rm VI_{A-D}$ in Table III.

pyrones used as starting materials was the fact

(56.75)

(3.35)

(5.05)

EXPERIMENTAL⁵

Preparation of compounds of I_{A-F} Series. A mixture consisting of 0.1 mole of 6-methyl-2-pyronone (11.4 g.), 0.1 mole of the acyl halide and 20 ml. of trifluoroacetic acid was refluxed in an all-glass assembly until hydrogen chloride vapors ceased to be evolved. This usually required between 90 min. and 2 hr. At the end of the reaction period the mixture was poured into 100 ml. of water and chilled. Those compounds which remained as oils or semi-solids such as II_A and _B were taken up in the taken up in the taken which remained soft crystals which could be dried in air and weighed, as were the higher melting compounds.

The analytical samples were obtained by recrystallizing the compound several times from boiling heptane.

Those compounds in which the pyronone had been bisacylated were prepared by using 0.2 mole of the acyl halide. All other conditions for the preparation and purification of the compounds were the same.

Synthesis of 2-(m-nitrophenyl)-3,5-di(m-nitrobenzoyl-6-methyl-4-pyrone (II). To 20 ml. of trifluoroacetic acid was added 0.05 mole (6.2 g.) 6-methyl-2-pyronone followed by 0.15 of mole (27.9) of m-nitrobenzoyl chloride. This mixture was refluxed in an all-glass assembly over a glass heating mantle for 4 hr., and then diluted while hot with 100 ml. of water. The precipitate was filtered off, dried in air to give 32.1 g. of the crude compound, which was then recrystallized twice from ethanol. An 8 g. sample of the partially purified substance was refluxed with 70 ml. of concd. hydrochloric acid for 3 hr., diluted with water and chilled to give 6.2 g. of the air-dried compound. The purified material was recrystallized once from heptane to give a melting point of 143-144°.

Anal. Calcd. for $C_{36}H_{15}N_{3}O_{10}$: C, 58.98; H, 2.85; N, 7.93. Found: C, 58.79; H, 2.74; N, 7.67.

Synthesis of 2-phenyl-6-methyl-4-pyrone (III). A 5 g. sample of I_A was heated for 30 min. at $155-160^\circ$ in a Fisher constant temperature oil bath. The resulting melt was poured into 100 ml, of water and chilled to give 4.5 g. of an air-dried sample.

Refluxing 5 g. of \hat{I}_A with 70 ml. of concd. hydrochloric acid for 2 hr. gave a similar yield.

The crude III was recrystallized once from heptane, m.p. $84-85^{\circ}$ which is in good agreement with the results of Light and Hauser⁶ and in fair agreement with those of Ruhemann.⁷

Anal. Caled. for C₁₂H₁₀O₂: C, 77.40; H, 5.41. Found: C, 77.69; H, 5.27.

Synthesis of 2-phenyl-5-benzoyl-6-methyl-4-pyrone (IV). Ten grams of I_B was refluxed in 60 ml. of concd. hydrochloric acid for 3 hr., diluted with 100 ml. of water and then chilled to produce 7.5 g. of crude IV. The compound was crystallized once from heptane to give the analytical sample, m.p. 124-125°.

Anal. Caled. for C₁₉H₁₄O₃: C, 78.60; H, 4.86. Found: C, 78.29; H, 4.69.

Preparation of compounds of V_{A-D} Series. One tenth of a mole of the pyrone along with 0.05 mole of chloranil was vigorously refluxed for 3 hr. in 100 ml. of absolute ethanol. The brown solution was filtered while hot and placed in the freezing compartment of the refrigerator overnight. The precipitate was filtered off, dried in air and the analytical sample prepared by recrystallizing it three times from absolute ethanol.

Ultraviolet absorption spectra of V_A and $_B$ were taken on a Bausch and Lomb Spectronic-505 and compared with

spectra of the pyrones from which they were prepared. The spectra were made in the wave length range of 222–372 m μ in spectro grade methanol:

Substance	Maxima
Kojic acid	264 mµ
VA	$269.5 \text{ m}\mu$
α -Chloro- α -deoxy kojic acid	272 mµ
VB	$277 \mathrm{m}\mu$

Preparation of dibromopyrones (VI_{A-D}) . A mixture consisting of 0.1 mole of the pyrone, 20 ml. of trifluoroacetic acid and 32 g. of bromine was placed in the hood in an all glass assembly with two standard taper 300 mm. condensers fitted in tandem and gently refluxed for a period of 2 hr. The reaction mixture was poured into water, thoroughly chilled, filtered and dried in air.

Samples of the tarry materials were recrystallized twice from heptane to give the analytical sample.

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Behavior of α-Substituted Chalcones on Attempted Friedel-Crafts Arylation

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Addition of an aromatic nucleus to an α,β unsaturated compound under the influence of aluminum chloride is a well known process;¹ for example, benzene and chalcone yield β,β -diphenylpropiophenone.²

$$C_{6}H_{5} + C_{6}H_{5}CH = CHCOC_{6}H_{5}$$
$$\longrightarrow (C_{6}H_{5})_{2}CH - CH_{2}COC_{6}H_{5}$$

It was thought that this reaction could be applied in a synthesis of 3-benzoyl-4-phenyl-1-naphthol (II)³ in the following way.



However the expected keto acid (I) was not formed, and further processing gave a compound

⁽⁵⁾ All analyses were performed by Dr. Carl Tiedcke, Teaneck, N. J., and all melting points were determined on a Fisher-Johns Melting Point Assembly.

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