catalyst,[3] 0.01 mole of propene-1-d, a trace of iodine, and 8 ml. of anhydrous ether were sealed in a 25-ml. Pyrex vessel and shaken for 20 hr. at 60° Methylcyclopropane was recovered by distillation of the reaction mixture and was purified on a preparative GLPC column.

Similar technique with *trans*-ethylene-d_2 and methylene iodide (molar ratio of 1:2) gave yields based on olefin of 35% at 60° and 7% at 35° (50-hr. reaction time). Reactions employing methylene iodide gave side products of ethylene, resulting from reagent coupling, as well as cyclopropane from subsequent addition to the ethylene.

In two experiments, the organometallic reagent was prepared in the absence of olefin by stirring 0.02 mole of zinc-copper catalyst, 0.01 mole of methylene iodide, and a trace of iodine in anhydrous ether at reflux temperature for 4 hr.; the reaction with ethylene was completed in the normal manner at 60° after removal of the excess catalyst by filtration and addition of 0.003 mole of *trans*-ethylene-d_2. Pure *trans*-cyclopropane-d_2 was obtained in 2% and 4% yield.

Reaction of ethylene with ethylidene iodide. The following procedure minimized the undesirable side reactions of ethylene formation through rearrangement, and butene production from coupling, of the ethylidene iodide. *trans*-Ethylene-d_2 (0.02 mole), ethylidene iodide (0.007 mole), a trace of iodine, catalyst (0.015 mole), and 8 cc. of ether were sealed in a Pyrex vessel of volume such that, ignoring the solubility in the ether, the ethylene pressure would have been 35 atm. Explosions were prevented by filling the reaction vessel at liquid nitrogen temperature and placing it within a small diameter iron pipe which was pressurized to 15 atm. before the assembly was permitted to warm. The reaction was then completed by shaking in an oil bath at 60° for 10 hr. Methylcyclopropane was recovered and purified in the previously described manner. The yield of methylcyclopropane was 12% based on iodide and was 90%-d_2 and 10% light. 5% of the ethylidene iodide coupled to give butene and the remainder gave light ethylene.

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The Reaction of Lactones with Pyrones in the Presence of Trifluoroacetic Acid

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Received December 5, 1960

This report is part of a continuing study of the fundamental chemistry of the 4-pyrones and is a portion of the investigation of the reaction of pyrones in the presence of the powerful solvating agent, trifluoroacetic acid.[2-4]

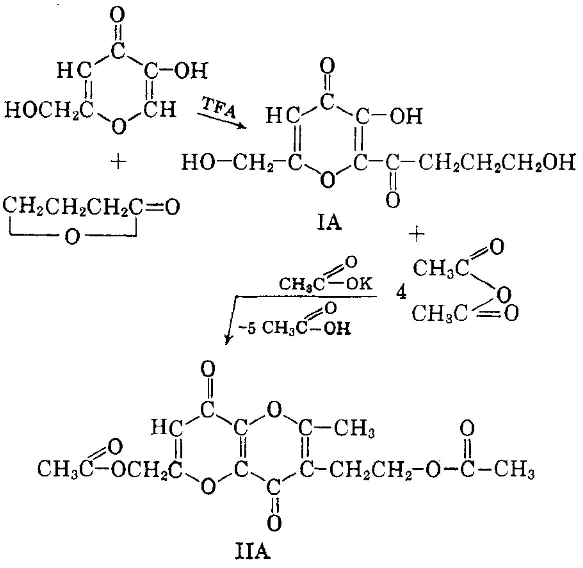
The reaction of lactones with pyrones gives good yields and requires only a short period of time for completion. Table I lists the various pyrones used in the experiment. Coumarin and 6-methyl-2-pyronone were tried to ascertain if the generalized method was applicable to pyrones other than 4-pyrones. Only coumarin gave a product which could be isolated under the conditions employed.

The point of attachment of the hydroxy-acyl radical to the ring was ascertained by converting all those pyrones having a 5-hydroxy group to the corresponding pyrano[3,2,-b]pyran-6-methyl-4,8-diones given in Table II.

As I_A upon conversion to II_A gave a poor analysis, compound III was prepared as added confirmation of its structure.

EXPERIMENTAL[4]

Preparation of members of I_{A-G} series. A mixture consisting of 0.1 mole of the pyrone, 0.1 mole of the lactone and 10 ml. of trifluoroacetic acid was refluxed for 1 hr. The resulting material was cooled somewhat, diluted with about 40 ml. of absolute ethanol and chilled. In the case of coumarin, only 20 ml. of ethanol was used.



The chilled solutions were filtered and dried in air to give the crude yields reported in Table I.

Analytical samples were obtained by two further recrystallizations from ethanol.

All the 5-hydroxy compounds gave red colorations with ferric chloride.

Preparation of members of (IIa-d) *series.* A 100-ml. flask containing 3 g. of the hydroxy-acylated pyrone of the I_{A-G} series, 3 g. of fused potassium acetate, and 10 ml. of acetic anhydride was connected with an air cooled condenser and immersed in a Fisher Hi Temp oil bath and heated at 130° for 2 hr. The melt was then diluted with 30 ml. of water, cooled, neutralized with sodium bicarbonate, chilled in the freezing compartment of the refrigerator, and filtered. The air dried compound was recrystallized twice from heptane to give the analytical sample.

Preparation of compound III. Two grams of compound Ia was allowed to react with 5 ml. of ammonium hydroxide overnight in a stoppered flask. The mixture was evaporated to dryness to give the pyridone of 2-hydroxymethyl-5-hydroxy-6-(γ-hydroxybutyryl)-4-pyrone.

The brown solid was converted, without purification, to

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[1] The authors express their gratitude to the Robert A. Welch Foundation for the support of this investigation.

[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 and H. L. Williams, *J. Org. Chem.*, **25**, 1052 (1960).

[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.

TABLE I

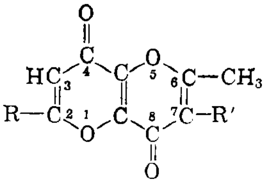
HYDROXYACYLATED PYRONES

	Pyrone Used	Lactone Used	M.P.	% Yield	Empirical Formula	Calculated (Found) Carbon	Calculated (Found) Hydrogen	Calculated (Found) Chlorine
Ia[a]	Kojic acid	γ-Butyrolactone	159–160	56.5	$C_{10}H_{12}O_6$	52.63 52.27	5.30 5.14	
Ib[b]	2-Hydroxymethyl-5-methoxy-4-pyrone	γ-Butyrolactone	164–165	61	$C_{11}H_{14}O_6$	54.54 54.37	5.82 5.58	
Ic[c]	Coumarin	γ-Butyrolactone	69–70	40	$C_{13}H_{12}O_4$	67.23 66.89	5.20 5.01	
Id[d]	Kojic acid	β-Propiolactone	154.5	62	$C_9H_{10}O_6$	50.47 50.31	4.70 4.49	
Ie[e]	α-Chloro-α-deoxy kojic acid	β-Propiolactone	158	78	$C_9H_9ClO_5$	46.46 46.19	3.89 3.67	15.24 15.03
If[f]	2-Hydroxymethyl-5-methoxy-4-pyrone	β-Propiolactone	150	32	$C_{10}H_{12}O_6$	52.63 52.19	5.30 4.88	
Ig[g]	Kojic acid	γ-Valerolactone	155–156	54	$C_{11}H_{14}O_6$	54.54 54.32	5.82 5.62	

[a] Ia = 2-Hydroxymethyl-5-hydroxy-6-(γ-hydroxybutyryl)-4-pyrone. [b] Ib = 2-Hydroxymethyl-5-methoxy-6-(γ-hydroxybutyryl)-4-pyrone. [c] Ic = 3-(γ-Hydroxybutyryl)-coumarin. [d] Id = 2-Hydroxymethyl-5-hydroxy-6-(β-hydroxypropionyl)-4-pyrone. [e] Ie = 2-Chloromethyl-5-hydroxy-6-(β-hydroxypropionyl)-4-pyrone. [f] If = 2-Hydroxymethyl-5-methoxy-6-(β-hydroxypropionyl)-4-pyrone. [g] Ig = 2-Hydroxymethyl-5-hydroxy-6-(γ-hydroxyvaleryl)-4-pyrone.

TABLE II

PYRANO[3,2-b]PYRAN-6-METHYL-4,8-DIONES FROM MEMBERS OF Ia–g SERIES



No.	Pyrone Used	Pyranopyran Product M.P.	R	R′	Empirical Formula	Calculated (Found) Carbon	Calculated (Found) Hydrogen	Calculated (Found) Chloride
IIa	Ia	126–127	Acetoxymethyl	Acetoxyethyl	$C_{16}H_{16}O_7$	59.99 55.49	5.03 4.84	
IIb	Id	91	Acetoxymethyl	Acetoxymethyl	$C_{15}H_{14}O_8$	55.90 55.69	4.37 4.19	
IIc	Ie	93–94	Chloromethyl	Acetoxymethyl	$C_{13}H_{11}ClO_6$	52.27 52.50	3.71 3.94	11.87 11.69
IId	Ig	102–104	Acetoxymethyl	2-Acetoxypropyl	$C_{17}H_{18}O_8$	58.28 58.44	5.17 5.29	

the 2,4-dinitrophenylhydrazone by dissolving it in 100 ml. of boiling ethanol to which 1 g. of 2,4-dinitrophenylhydrazine was added. The solution was boiled for 5 min. and filtered. The brown compound was recrystallized once from ethanol to give a m.p. of 195–196°.

Anal. Calcd. for $C_{16}H_{17}N_5O_8$: N, 17.27. Found: N, 17.48.

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Preparation of 3-Keto-9-methyl-$\Delta^{4,6}$- and 3-Keto-4,9-dimethyl-$\Delta^{4,6}$-hexahydronaphthalenes

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Received December 14, 1960

We required 3-keto-9-methyl-$\Delta^{4,6}$-hexahydronaphthalene (IIa) and 3-keto-4,9-dimethyl-$\Delta^{4,6}$-hexahydronaphthalene (IIb) for synthetic projects in the field of terpenoids. These compounds were previously prepared[1–3] in varying yields by bromination of 3-keto-9-methyl-Δ^4-octahydronaphthalene (Ia) and 3-keto-4,9-dimethyl-Δ^4-octa-

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[1] (a) F. D. Gunstone and R. M. Heggie, *J. Chem. Soc.*, 1437 (1952); (b) F. D. Gunstone and A. P. Tulloch, *J. Chem. Soc.*, 1130 (1955).

[2] M. Yanagita, S. Inayama, M. Hirakura, and F. Seki, *J. Org. Chem.*, **23**, 690 (1958).

[3] T. Harukawa, *J. Pharm. Soc. Japan*, **75**, 521 (1955).