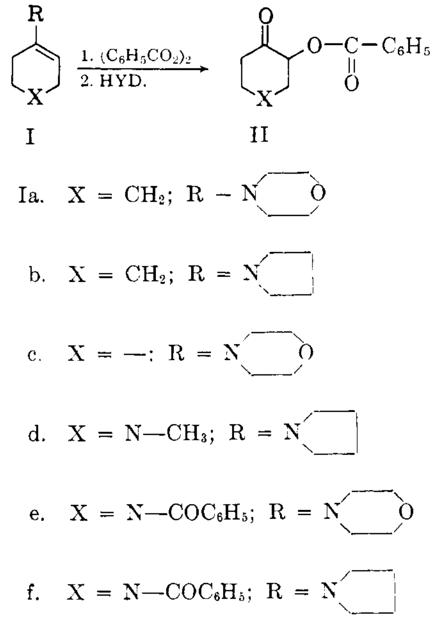

IIa. $X = CH_2$
c. X = —
d. $X = N—CH_3$
e. $X = N—COC_6H_5$

the solution was warmed at 50–70° for 3 hr. After this time 200 ml. of water was added and the resulting solution refluxed overnight. The solution was cooled, poured into an additional 500 ml. of water, and extracted with ether. The ether was washed with 10% hydrochloric acid, saturated aqueous sodium carbonate, and water. The dried ethereal solution was evaporated and the product recrystallized from aqueous ethanol. In some instances the reaction was cooled in an ice bath during the addition, allowed to warm to room temperature for 3 hr. and hydrolyzed by stirring with water at room temperature overnight. These precautions did not appreciably alter the outcome of the reaction.

2-Benzoyloxycyclohexanone (IIa) was formed in 30% yield with a m.p. of 85–86° on recrystallization from aqueous ethanol (reported[5] m.p. 87°).

Anal. Calcd. for $C_{13}H_{14}O_3$: C, 71.54; H, 6.46. Found: C, 71.64; H, 6.53.

2-Benzoyloxycyclopentanone (IIc) was formed in 25% yield with a m.p. of 90–91° on recrystallization from aqueous ethanol.

Anal. Calcd. for $C_{12}H_{12}O_3$: C, 70.57; H, 5.92. Found: C, 70.57; H, 5.92.

The 2,4-dinitrophenylhydrazone had a m.p. of 128–129° (95% ethanol).

Anal. Calcd. for $C_{18}H_{16}N_4O_6$: C, 56.24; H, 4.19; N, 14.57. Found: C, 56.34; H, 4.26; N, 14.70.

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(5) M. Bergmann and M. Greith, *Ann.*, **448**, 48 (1926).

Preparation of Hydrogen Phthalate Derivatives of Tertiary Alcohols

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Received August 1, 1962

Interest in this laboratory in low temperature liquid phase pyrolysis of esters has necessitated the development of a good procedure for the preparation of tertiary alcohol ester derivatives which decompose at relatively low temperatures. Zeiss[3] reported that the hydrogen phthalate derivative of 2-phenyl-2-butanol decomposed at its melting point (111°). Although no study was made of the decomposition products, it seemed reasonable to assume that an ordinary ester pyrolysis occurred and at a low temperature. Doering and Zeiss[4] previously reported on the preparation of the hydrogen phthalate derivative of 2,4-dimethylhexan-4-ol. The oil obtained was characterized as the barium salt. The procedure used by these workers involved the conversion of the tertiary alcohol to its potassium salt in boiling benzene followed by the addition of phthalic anhydride.

Fessler and Shriner[5] reported on the preparation of hydrogen phthalate derivatives of six aliphatic tertiary alcohols from tetrachlorophthalic anhydride. The yields range from 36 to 66%. The method involved treatment of the alcohols with ethylmagnesium to obtain the alkoxy magnesium bromide which was then treated with tetrachlorophthalic anhydride. No derivatives of mixed aliphatic–aromatic tertiary alcohols were recorded and all attempts to prepare an acid phthalate of triphenylcarbinol failed.

We have developed a convenient procedure for the preparation of hydrogen phthalate derivatives of aliphatic, mixed aliphatic–aromatic, and aromatic tertiary alcohols. The procedure involves treatment of the alcohol with ethereal triphenylmethylsodium at room temperature. The addition of phthalic anhydride followed by a short period of stirring (1–2 hr.) yields the solid derivative. The method is very convenient both as a characterization and a preparative procedure since the triphenylmethylsodium which has a blood-red color in ether can be titrated rapidly into the colorless ethereal alcohol solution until a red coloration persists. This indicates complete proton removal from the alcohol. As can be seen from the chart, the yields of the acid phthalates are good with the exception of that for triphenylcarbinol (30%). Unlike Shriner's observation, we have found that this procedure yields easily crystallizable hydrogen phthalate derivatives.

It is interesting to note that all of the hydrogen phthalate derivatives of the tertiary aliphatic series have decomposition points between 132–155°. The presence of one or two aromatic rings results in simultaneous melting and decomposition of the derivative. This substitution tends to lower the decomposition point substantially. The derivative from triphenylcarbinol did not decompose at the melting point or even at 300°. In all cases of decomposition, phthalic acid was isolated as the only solid residue. Olefins and olefinic mixtures (where possible) were obtained in yields greater than 85% in those cases which have been studied in detail. A report embodying the results of the pyrolysis of the hydrogen phthalates will appear in a later paper.

Experimental

Alcohols.—Triphenylcarbinol, *t*-amyl alcohol, and *t*-butyl alcohol were obtained from commercial sources. The remaining

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[1] Supported by a grant from the Research Council of Ontario, Canada.

[2] Recipient of a National Research Council of Canada Studentship.

(3) H. H. Zeiss, *J. Am. Chem. Soc.*, **73**, 2391 (1951).

(4) W. von E. Doering and H. H. Zeiss, *ibid.*, **72**, 147 (1950).

(5) W. A. Fessler and R. L. Shriner, *ibid.*, **58**, 1384 (1936).

Table I

Acid Phthalate Derivatives

Alcohol	Average yield of acid phthalate, %	M.p.,[a] °C.	Dec. point[a]	Neutralization equivalent Calcd.	Neutralization equivalent Found	Carbon % Calcd.	Carbon % Found	Hydrogen % Calcd.	Hydrogen % Found
t-Butyl alcohol	65	87–88	151–155	222.23	223.44	64.85	64.90	6.35	6.38
t-Amyl alcohol	70	62–63	144–146	236.26	236.40	66.08	66.09	6.83	6.88
3-Methyl-3-pentanol	65	80–81	136–138	250.28	250.45	67.18	66.79	7.25	6.99
3-Ethyl-3-pentanol	80	77–78	132–133	264.71	264.30	68.06	68.52	7.76	7.72
2,3-Dimethyl-2-butanol	80	95–96	137–140	250.28	249.82	67.18	67.17	7.25	7.28
2,3-Dimethyl-3-pentanol	65	118–120	132–135	264.71	265.77	68.06	68.19	7.76	7.71
1-Methylcyclopentanol	85	68–69	145–148	248.77	248.27	67.73	68.03	6.50	6.62
1-Methylcyclohexanol	85	89–91	154–157	260.69	262.29	68.68	68.31	6.92	6.88
2-Phenyl-2-propanol	80	109–110	109–110	284.30	283.46	71.82	71.82	5.67	5.65
2-Phenyl-2-butanol	80	114–115	114–115	298.32	298.04	72.47	72.52	6.08	6.07
2-Phenyl-2-pentanol	70	105–106	105–106	312.35	313.83	73.05	73.13	6.45	6.47
3-Phenyl-3-pentanol	85	114–115	114–115	312.35	312.67	73.05	73.08	6.45	6.47
1,1-Diphenyl-1-ethanol	80	110	110	345.27	343.99	76.28	76.31	5.24	5.40
Triphenylcarbinol	30	251–253	...	408.43	407.15	79.39	79.44	4.94	5.09

[a] All melting and decomposition points were taken on the Fisher–Johns melting point apparatus.

alcohols were prepared by conventional methods previously reported in the literature.

Preparation of Acid Phthalates.—The following preparation of the acid phthalate of *t*-butyl alcohol will exemplify the procedure. To a solution of 5 g. (0.068 mole) of *t*-butyl alcohol in 150 ml. of anhydrous ether was added rapidly with stirring an ethereal solution of triphenylmethylsodium[6] until a persistent red coloration indicated a slight excess of the base. This procedure was carried out in a 1-l. Erlenmeyer flask fitted loosely with a polyethylene stopper. Phthalic anhydride (10.6 g., 0.068 mole) was added in one portion and the stirring was continued for 1–2 hr. Water (200 ml.) was added, the layers were separated, and the water layer was poured over cracked ice and hydrochloric acid. The precipitate formed was recovered by filtration, air-dried, and recrystallized from a chloroform–petroleum ether (b.p. 30–60°) solvent pair giving white crystals of pure hydrogen-2-methylpropyl-2-phthalate, m.p. 87–88°. The average yield of several runs was 65%.

Anal. Calcd. for $C_{12}H_{14}O_4$: C, 64.85; H, 6.90; neut. equiv., 222.23. Found: C, 64.90; H, 6.38; neut. equiv., 223.44.

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[6] W. B. Renfrow, Jr., and C. R. Hauser, "Organic Syntheses," Coll. Vol. II, John Wiley and Sons, Inc., New York, N. Y., 1943, p. 609.

O-Acylation of Kojic Acid by Friedel–Crafts Reaction

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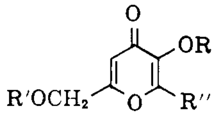
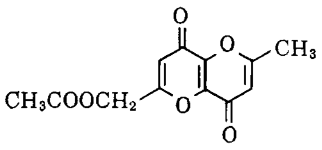
Received September 11, 1962

Woods[1] reported the C-acylation of kojic acid (I) by the Friedel–Crafts reaction with benzoyl chloride and claimed to have obtained the ketone, 6-benzoyl-5-hydroxy-2-hydroxymethyl-4*H*-pyran-4-one (VI). In view of this work and of our interest in the possibilities of transforming such ketones into interesting oxygen heterocyclic compounds, we performed the Friedel–Crafts reaction of I with acetyl chloride in presence of anhydrous aluminum chloride in nitrobenzene with the object of synthesizing the ketone, 6-acetyl-5-hydroxy-2-hydroxymethyl-4*H*-pyran-4-one (II). The product, m.p. 137°, however, did not prove to be a ketone, but was identified as the previously known[2-4] ester, 2-acetoxymethyl-5-hydroxy-4*H*-pyran-4-one (III). Thus, the C-acylation did not take place in this instance, but the hydroxymethyl group of I was selectively esterified.





XI

I. R = R′ = R″ = H
II. R = R′ = H; R″ = $COCH_3$
III. R = R″ = H; R′ = $COCH_3$
IV. R = H; R′ = R″ = $COCH_3$
V. R″ = H; R = R′ = $COCH_3$
VI. R = R′ = H; R″ = COPh
VII. R = R″ = H; R′ = COPh
VIII. R″ = H; R = R′ = COPh
IX. R = R′ = H; R″ = $COCH_2Cl$
X. R = R″ = H; R′ = $COCH_2Cl$

Woods claimed to have isolated the ketone (II),[5] m.p. 156.5°, by boiling 2-acetoxymethyl-6-acetyl-5-hydroxy-4*H*-pyran-4-one (IV),[5,6] m.p. 137°, with water for twenty-four hours. He prepared IV by heating a mixture of I, acetic anhydride, and 85% phosphoric acid or better by the rearrangement of kojic acid diacetate (V) with potassium acetate at elevated temperature. In our hands, the procedure[6] of Woods and Dix gave a product, m.p. 137°, in extremely poor yield. It did not form the 2,4-dinitrophenylhydrazone or the semicarbazone, and we identified it as the previously known kojic acid monoacetate III.[2-4] On boiling with water for twenty-four hours, III was hydrolyzed to I. Thus, we were unable to effect the rearrangement as postulated by Woods, and failed to isolate the ketones formulated as II and IV. Again, Woods and Dix[6] reported to have transformed their compound (IV), m.p. 137°, into 2-acetoxymethyl-6-methyl-4*H*-pyrano[3,2-*b*]-8*H*-pyran-4,8-dione (XI), m.p. 102°, by heating with potassium acetate and acetic anhydride. Alternatively, they described[6] the preparation of XI by heating kojic acid diacetate (V) with potassium acetate and acetic anhydride. Our

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[1] L. L. Woods, *J. Am. Chem. Soc.*, **74**, 1105 (1952).

[2] K. Maurer, *Ber.*, **63**, 25 (1930).

[3] M. G. Brown, *J. Chem. Soc.*, 2558 (1956).

[4] C. D. Hurd and R. J. Sims, *J. Am. Chem. Soc.*, **71**, 2440 (1949).

[5] L. L. Woods, *ibid.*, **75**, 3608 (1953).

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