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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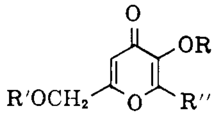
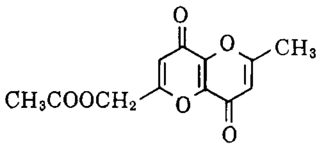
Woods[1] reported the C-acylation of kojic acid (I) by the Friedel–Crafts reaction with benzoyl chloride and claimed to have obtained the ketone, 6-benzoyl-5-hydroxy-2-hydroxymethyl-4*H*-pyran-4-one (VI). In view of this work and of our interest in the possibilities of transforming such ketones into 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).

repeated efforts to isolate the dione (XI) by the latter method failed, and in every case, the starting material, m.p. 102°, was recovered unchanged. Surprisingly, Woods and Dix did not record the mixed melting point, although the melting point of the starting material (V) and their reaction product (XI) were the same. Since our results differ from those of Woods and Dix, we have no opinion regarding the identity of their reported ketonic materials. It should be pointed out, however, that their formulas were not supported by the usual ketone derivatives.

The foregoing results of our investigation led us to re-examine Wood's C-acylation[1] of I with benzoyl chloride by the Friedel–Crafts reaction in carbon disulfide. Repetition of his experiment furnished a product, m.p. 180–181°. Woods reported the m.p. 188°, but repeated crystallizations of our product did not raise the melting point. The same compound, melting at 180–181°, was isolated when nitrobenzene was used in the reaction. It gave a red coloration with ferric chloride, and did not form the 2,4-dinitrophenylhydrazone. We identified it as 2-benzoyloxymethyl-5-hydroxy-4*H*-pyran-4-one (VII) by a mixed melting point determination with an authentic specimen, m.p. 180–181°, prepared according to Beelik and Purves[7]; and by its conversion into the previously known[2,3,8] kojic acid dibenzoate (VIII), by the action of benzoyl chloride in pyridine. Recently, Woods[8] again prepared his compound, m.p. 188°, by the C-acylation of I with benzoic acid in trifluoroacetic acid. He assigned the structure VI without preparing any ketone derivative. The formulation was supported by the infrared and analytical data[8]; but little credence can be attached to these, as the data would fit the monobenzoate (VII) quite well. Since we were unable to obtain the compound, m.p. 188°, we cannot speak about it with confidence, but we have reasons to conclude that the C-acylation of kojic acid (I) by the Friedel–Crafts method does not take place.

The Friedel–Crafts reaction of I with chloroacetyl chloride yielded a product, m.p. 141°, which gave a red coloration with ferric chloride and was characterized as the ester, 2-chloroacetoxymethyl-5-hydroxy-4*H*-pyran-4-one (X) by comparison with a specimen prepared by the action of chloroacetyl chloride on kojic acid (I) alone. Recently, Woods[8] reported obtaining the ketone, 6-chloroacetyl-5-hydroxy-2-hydroxymethyl-4*H*-pyran-4-one (IX), m.p. 143°, by treating I with chloracetic acid in the presence of trifluoroacetic acid. No ketone derivative has been reported. The structural assignment was based only on the infrared and analytical data which would also fit X quite well. His experiment could not be repeated as we were unable to procure trifluoroacetic acid, and his product, purporting to be IX, could not be compared with our Friedel–Crafts reaction product. Nevertheless, it should be pointed out that his method of acylation was the same as that employed in the preceding case, and the melting point of our product (X) is close to that of Wood's compound (IX).

The result of our investigations showed that the Friedel–Crafts reaction of kojic acid (I) with the three acyl chlorides led to the selective O-acylation of the 2-hydroxymethyl group of I. It was thought that, if the hydroxyl groups of I were protected by acyl groups prior to carrying out the Friedel–Crafts reaction, C-acylation might occur. On subjecting kojic acid diacetate (V) to the Friedel–Crafts reaction, it was found that C-acylation did not take place, but deacetylation of the 5-acetoxy group occurred, yielding the monoacetate (III). Similar results were obtained by Hurd and Sims[4] when they tried to effect the Fries rearrangement of kojic acid diacetate with anhydrous aluminum chloride.

Experimental

2-Acetoxymethyl-5-hydroxy-4*H*-pyran-4-one (III).—(a) To a well stirred mixture of I (2 g.), anhydrous aluminum chloride (2.8 g.), and nitrobenzene (14 ml.) at 0°, acetyl chloride (1.2 ml.) was added dropwise. After 30 min., the cooling bath was removed and the mixture allowed to stand overnight at the room temperature. The product was decomposed with iced hydrochloric acid with stirring for 1 hr. and the solid, which separated, was allowed to settle. Nitrobenzene and water were decanted, the solid filtered and washed repeatedly with petroleum ether (b.p. 60–80°) and finally with water. Crystallization from ethyl acetate furnished III (1 g.) in white needles, m.p. 137°, undepressed on admixture with an authentic specimen.[2] A further quantity (0.3 g.), m.p. 136°, was recovered from the mother liquor; total yield, 50%. It gave a red coloration with aqueous alcoholic ferric chloride.

Anal. Calcd. for $C_8H_8O_5$: C, 52.17; H, 4.35. Found: C, 51.8; H, 4.5.

(b) The directions[6] of Woods and Dix were followed: A mixture of V (12 g.) and potassium acetate (12 g.) was heated at 130–135° for 90 min. and worked up to yield the solid (0.4 g.); sublimation *in vacuo* followed by several crystallizations from ethanol afforded the pure specimen, m.p. 137°, undepressed on admixture with an authentic sample of III.[2]

Anal. Calcd. for $C_8H_8O_5$: C, 52.17; H, 4.35. Found: C, 52.48; H, 4.12.

(c) A mixture of V (1.75 g.) and anhydrous aluminum chloride (2.8 g.) in nitrobenzene (14 ml.) was treated with acetyl chloride (0.6 ml.) at 0° and worked up as described above. The product, on crystallization from ethyl acetate, gave needles (0.5 g.), m.p. 136°, undepressed when mixed with an authentic specimen[2] of III.

2-Benzoyloxy-5-hydroxy-4*H*-pyran-4-one (VII).—(a) Benzoyl chloride (3.75 ml.) was added dropwise to a well stirred ice-cold mixture of I (4 g.), anhydrous aluminum chloride (5.8 g.), and nitrobenzene (28 ml.). Following the procedure detailed above, VII was isolated and crystallized from ethanol in white prisms (5.7 g.; 82.6%), m.p. 180–181°, undepressed on admixture with an authentic specimen.[7] It sublimed *in vacuo* and gave a red coloration with aqueous alcoholic ferric chloride.

Anal. Calcd. for $C_{13}H_{10}O_5$: C, 63.41; H, 4.09. Found: C, 63.20; H, 3.92.

A solution of VII (0.5 g.) in pyridine (2 ml.) was treated with benzoyl chloride (1 ml.) and left overnight. It was diluted with water, extracted with chloroform, the extract washed with dilute hydrochloric acid followed by water. Evaporation of the solvent left a solid, which on sublimation *in vacuo* followed by crystallization from ethyl acetate afforded VIII, m.p. 134° undepressed on admixture with an authentic specimen.[2]

(b) Using carbon disulfide in the Friedel–Crafts reaction, according to Woods's directions,[1] the product obtained had m.p. 181° (Woods reported 188°), undepressed when mixed with an authentic specimen[8] of VII.

Anal. Calcd. for $C_{13}H_{10}O_5$: C, 63.41; H, 4.09. Found: C, 63.67; H, 4.23.

2-Chloroacetoxymethyl-5-hydroxy-4*H*-pyran-4-one (X).—(a) Adopting the procedure described above, the interaction of I (4 g.) with chloroacetyl chloride (2.34 ml.), anhydrous aluminum chloride (2.8 g.) in nitrobenzene (14 ml.) afforded X (3.4 g.), which was crystallized from methanol or ethyl acetate to give irregular prisms, m.p. 141°. It gave a red coloration with aqueous-alcoholic ferric chloride.

Anal. Calcd. for $C_8H_7ClO_5$: C, 43.95; H, 3.22; Cl, 16.21. Found: C, 44.12; H, 3.28; Cl, 16.41.

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(7) A. Beélik and C. B. Purves, *Can. J. Chem.*, **33**, 1361 (1955).

(8) L. L. Woods, *J. Org. Chem.*, **27**, 696 (1962).

(b) A mixture of I (1 g.) and chloroacetyl chloride (3 ml.) was left at room temperature for 24 hr. The solution was poured into ice-water (20 ml.), the dark solid which separated, was filtered and crystallized several times from methanol to yield brown prisms (0.4 g.), m.p. 136–139°. It was purified by sublimation *in vacuo* followed by crystallization from ethyl acetate to afford white irregular prisms, m.p. 141°, undepressed on admixture with specimen obtained in (a).

Anal. Calcd. for $C_8H_7ClO_5$: C, 43.95; H, 3.22. Found: C, 43.72; H, 3.08.

Formation of Hexamethylbenzene from Phenol and Methanol

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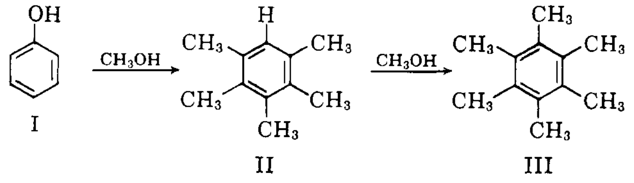
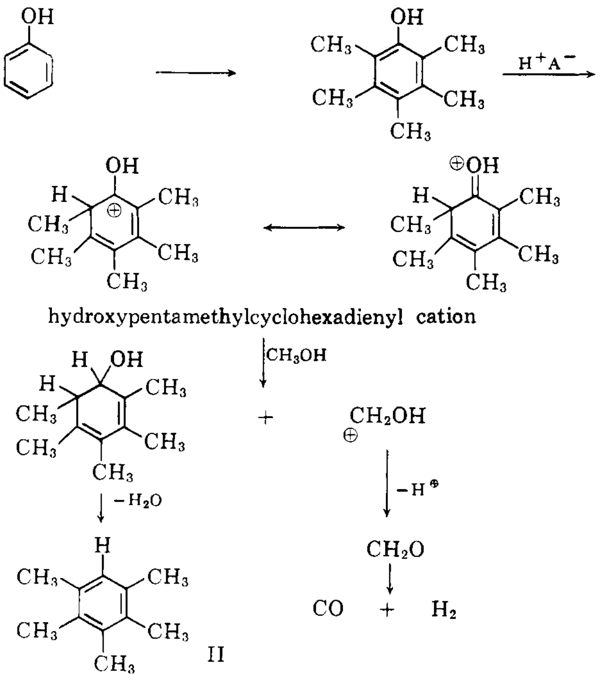
In the reaction of phenol with methanol at 400° over an acidic alumina catalyst to form hexamethylbenzene,[1–3] we have obtained evidence that the reaction proceeds through pentamethylbenzene as an intermediate.



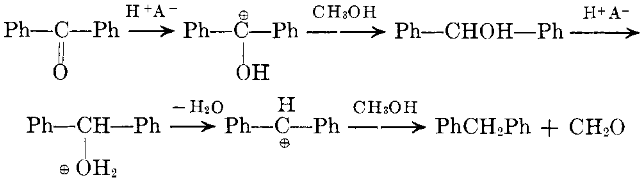
The amount of II in the crude reaction product increased with increasing space velocity (shorter contact time). Furthermore, II was readily converted exclusively to III under the reaction conditions.

A plausible reaction mechanism for the conversion of I to II is the following:



In agreement with this mechanism we have found substantial amounts of formaldehyde in addition to the previously reported carbon monoxide, hydrogen, and methane. Also, no di-, tri-, or tetramethylbenzene could be detected in the crude reaction products.

One important step in the above mechanism is a hydride ion transfer reaction between a relatively stable cyclohexadienyl carbonium ion and methanol. A similar mechanism can apply to the reaction of benzophenone with methanol over alumina at 450°, wherein diphenylmethane and formaldehyde were found as the only products:



$$Ph-\underset{\underset{O}{\|}}{C}-Ph \xrightarrow{H^+A^-} Ph-\overset{\oplus}{\underset{\underset{OH}{|}}{C}}-Ph \xrightarrow{CH_3OH} Ph-CHOH-Ph \xrightarrow{H^+A^-}$$

$$Ph-\underset{\underset{\oplus OH_2}{|}}{CH}-Ph \xrightarrow{-H_2O} Ph-\overset{H}{\underset{\oplus}{C}}-Ph \xrightarrow{CH_3OH} PhCH_2Ph + CH_2O$$

The intermediates here are again resonance-stabilized benzylic carbonium ions which undergo hydride ion transfer reactions. There are a number of analogies in the literature including the formation of cyclohexanol (among other products) from 1,4-cyclohexanediol and methanol over alumina[4] and the reaction of aryldiazonium saltswith methanol to form aromatic hydrocarbons and formaldehyde.[5]

Experimental

Penta- and Hexamethylbenzene.—Ten grams of 8–15-mesh Alcoa F-10 alumina was placed in a $^3/_4 \times 12$ in. Vycor reactor heated by external heating wire. With the temperature at 400° a solution of 9.4 g. (0.1 mole) of phenol in 20 ml. of methanol was introduced through a syringe needle from a constant rate syringe drive pump (JKM Instrument Co., Durham, Pa.). Products were collected in a series of air-cooled and ice-cooled receivers. The products included a light yellow solid suspended in water and unchanged methanol. Filtration and thorough drying yielded 8 g. of crude solid, m.p. 130–155°. Vapor phase chromatography using silicone rubber packing, and high molecular weight mass spectrometry, easily established the presence of 9% pentamethylbenzene, 89% hexamethylbenzene, and 2% of a mixture of high molecular weight methylated polyaromatics. Recrystallization of the crude solid using cyclohexane yielded hexamethylbenzene, m.p. 164–165°. Pentamethylbenzene was subsequently separated from the crude mixture by preparative VPC and its identity confirmed by mixed m.p. (52–53°) and by infrared comparison.

Diphenylmethane.—Using the previously described technique, 9.1 g. of benzophenone in 100 g. of methanol was passed over 10 g. of F-10 alumina. There was obtained 7.1 g. of white solid m.p. 27°, established as diphenylmethane by analysis, infrared, and mixed m.p. comparison with an authentic sample.

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(1) E. Briner, W. Pluss, and H. Paillard, *Helv. Chim. Acta*, **7**, 1046 (1924).

(2) H. J. Backer, *Rec. trav. chim.*, **54**, 745 (1935).

(3) N. M. Cullinane and S. J. Chard, *J. Chem. Soc.*, 821 (1945).

(4) R. C. Olberg, H. Pines, and V. N. Ipatieff, *J. Am. Chem. Soc.*, **66**, 1096 (1941).

(5) D. F. Detar and T. Kosuge, *ibid.*, **80**, 6072 (1958).

A New Synthesis of Ureas. V. The Preparation of Methyl-N-phenylurethane from Carbon Monoxide, Sulfur, Aniline, and Methanol

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Earlier publications in this series describe a new method for the synthesis of substituted ureas from