TABLE II

SUMMARY OF DATA ON THE THERMAL ISOMERIZATION OF PALUSTRIC ACID AT 200°

Time (Hr.)	$[\alpha]_D$ 2% C_2H_5OH	α at 241 mμ	Palustric, %	Abietic, %	Neoabietic, %	Calcd. $[\alpha]_D$	Calcd. α at 241 mμ
0	+71		99+				
0.25	+19	27	72	27	2	+26	31
0.50	−3	37	54	42	4	0	42
0.75	−26	45	40	54	6	−21	51
1	−35	51	34	61	6	−31	56
1.5	−48	56	26	67	6	−42	60
2	−53	61	19	72	7	−51	63
4	−63	62	15	77	7	−59	66
8	−68	68	11	80	7	−66	68

The identity of the palustric, abietic and neoabietic acids was confirmed by checking the ultraviolet absorption spectrum of the peaks from a chromatographic analysis.

Thermal isomerization of palustric acid at 200°. The isomerization of palustric acid at 200° was observed by the same method as at 170°. A summary of the data on the thermal isomerization of palustric acid at 200° is given in Table II.

Thermal isomerization of methyl palustrate at 200°. Methyl palustrate was prepared by treating an ether solution of palustric acid with an excess of an ether solution of diazomethane. The solution was extracted with dilute alkali, washed neutral with water and the ether removed by distillation. The ester crystallized from methanol, m.p. 24–27°, $[\alpha]_D + 67.0°$, α 26.5 at 265–266 mμ. The ester was sealed in an evacuated tube and after heating at 200° for 72 hr. had the following constants; $[\alpha]_D + 62.9°$, α 22.4 at 265–266 mμ.

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Hydrogenolysis of Ketals

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Hydrogenolysis of ketals in the presence of acid and rhodium or palladium yields ethers and alcohols. Ketals of secondary alcohols react faster than those of primary alcohols. A mechanism is suggested.

The literature contains several references to the hydrogenolysis of aldehyde acetals to ethers and alcohols, usually under conditions of rather high temperature and pressure.[1] Hydrogenolysis of aldehyde and ketone acetals to hydrocarbons has also been reported,[2] but in each of these cases the —C(OR)$_2$— group was a substituent on an aromatic nucleus. By hydrogenation Gorin[3] opened the ring of some cyclic ketals of sugars and obtained ether derivatives of the sugars. Bond scission occurred at the oxygen attached to the secondary carbon atoms of the sugars, indicating that secondary alkoxyl groups are more labile than primary ones in this reaction. Staff[1] stated that ketals could be hydrogenated to ethers and alcohols but gave no experimental data.

We have found that hydrogenation of acidified ketals gives high yields of saturated ethers and alcohols under mild conditions (Reaction 1). The reaction

$$R_2C(OR')_2 + H_2 \xrightarrow{H^+,\ Rh} R_2CHOR' + R'OH \qquad (1)$$

has been demonstrated with the dimethyl, dibutyl, diisopropyl, and dicyclohexyl ketals of acetone and with cyclohexanone diisopropyl ketal. With ketals of secondary alcohols the hydrogenation proceeds rapidly to completion at room temperature, and with ketals of primary alcohols appreciable rates are obtained at 50 to 80°. Yields of isolated products, based on conversions calculated from the hydrogen uptake, ranged from 70% to nearly 100%. Recovery of starting materials, absence of byproducts, and infrared analyses indicate that actual yields were approximately quantitative.

Tests of several platinum metal catalysts for the hydrogenation of isopropenyl methyl ether showed rhodium the most active. Platinum and ruthenium were almost inactive, and palladium was about half as active as rhodium. As these metals had the same

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[1] F. Sigmund and G. Marchart, *Monatsh.*, **48**, 267 (1927); M. Cabanac, *Compt. rend.*, **188**, 1257 (1929); C. E. Staff (to Carbide and Carbon Chemicals Corp.), U. S. Patent 2,397,514 (April 2, 1946); N. V. Polak and Schwarz's Essencefabrieken, Dutch Patent 68,125 (June 15, 1951); J. W. Copenhaver (to General Aniline and Film Corp.), U. S. Patent 2,590,598 (March 25, 1952) and U. S. Patent 2,604,493 (July 22, 1952).

[2] T. Kariyone and Y. Kimura, *J. Pharm. Soc. Japan*, No. 500, 746 (1923); P. E. Papadakis, *J. Am. Chem. Soc.*, **58**, 665 (1936); T. Kariyone, T. Kajiura, A. Ueno, and N. Suzuki, *J. Pharm. Soc. Japan*, **73**, 493 (1953).

[3] P. A. J. Gorin, *J. Org. Chem.*, **24**, 49 (1959).

TABLE I

HYDROGENOLYSIS OF KETALS $R_2C(OR')_2$ TO ETHERS R_2CHOR' AND ALCOHOLS $R'OH$

Ketal			Time, Hr.	Temp.	H_2 Consumed, % of Theory	Material Balance, Moles			Properties of Ether			
R	R′	Moles				Ether	Alcohol	Recovered ketal	B.P.°	Mm.	n_D(T)	Density, g./ml. (T)
CH_3	n-C_4H_9	0.20	4	25	34							
			23	60	47	0.16	0.14	—[a]	105[b]	760	1.3853(25)	0.754(25)
CH_3	CH_3	2.00	17	25	5							
			73	50–80	24	0.47	—[a]	1.42	32[c,d]	760	1.3490(24)	0.722(24)
CH_3	i-C_3H_7	0.20	1	25	97	0.15	0.19	—[a]	69	760	1.3664(24)	0.724(24)
—[e]	i-C_3H_7	0.10	2.5	25	100	0.09	0.10	—[a]	155–156[f,g]	760	1.4283(25)	0.846(25)
CH_3	cyclo-C_6H_{11}	0.116	3	25	90	0.12[h] 0.07[i]	0.11[h] —[a]	0[h] —[a]	155	760	1.4305(25)	—

[a] Recovery not attempted. [b] Lit.[8] b.p. 108°(738), d_{15} 0.7594, $n^{24.9}_{5461}$ 1.3889. [c] Lit.[9] b.p. 32.5° (777), d^{20}_{20} 0.735, n^{20}_D 1.3576. [d] Purity determined by gas chromatography 98%. [e] R_2C = cyclohexyliden. [f] Lit.[6] b.p. 168–169° (716), n^{20}_D 1.4833, d^{20}_4 0.9285. [g] Purity determined by gas chromatography 98%. *Anal.* Calcd. for $C_9H_{18}O$: C, 76.00; H, 12.75. Found: C, 75.97, 76.13; H, 12.82, 12.88. [h] Determined by infrared spectroscopy. [i] Isolated by distillation after conversion of the cyclohexanol to an acid ester.

order of activity with acetone diisopropyl ketal, rhodium was selected for use with the other ketals.

There is considerable evidence[4] that acidification of ketals results in the establishment of an equilibrium whose components are ketal, unsaturated ether, and alcohol (Equation 2). If R″ is a primary alkyl radical, the concentration of

$$R_2CH{-}CR'(OR'')_2 \overset{H^+}{\rightleftharpoons} R_2C{=}CR'(OR'') + R''OH \quad (2)$$

unsaturated ether is usually very small at room temperature but is large enough at elevated temperatures for the ether to be distilled from the mixture. Reichle[5] noted the ease with which ketals of secondary alcohols are decomposed by acids to unsaturated ethers, and this corresponds with our experience. We have also found that the infrared spectrum at room temperature of an acidified solution of acetone diisopropyl ketal in nine volumes of isopropyl alcohol contains a distinct absorption band at 6.05 μ, due to the unsaturated ether, which completely disappears when one volume of methanol is added. Evidently ketals of secondary alcohols are much more dissociated in this manner than are those of primary alcohols.

The dissociation of the ketal to unsaturated ether and alcohol probably constitutes the first step in the apparent hydrogenolysis of ketals. Hydrogenation then removes the unsaturated ether and this allows further conversion of the ketal. Accumulation of the alcohol opposes this dissociation and with the depletion of the ketal there finally results such a small concentration of unsaturated ether that hydrogenation virtually stops. Several experimental facts support this hypothesis. First, hydrogenolysis requires acid. It fails in neutral or alkaline media, even at 100°. Second, rates are in accord with the effects predicted from other reactions. They are in the same order as we have observed qualitatively for the ease of the acid-catalyzed splitting of ketals to unsaturated ethers and alcohols. Third, conversions of ketals of primary alcohols are less complete than those of secondary alcohols, probably because the equilibrium of Reaction 2 is less favorable to formation of unsaturated ether when the alkoxyl groups are primary. Fourth, the activity of catalysts is in the same order for both the ketals and unsaturated ethers.

Waser and co-workers[6] reported properties for cyclohexyl isopropyl ether which are abnormal among the properties of a series of related compounds which they prepared. The values we obtained fit well in Waser's series and together with other characterization data indicate that they are the properties of cyclohexyl isopropyl ether. Waser probably obtained a mixture of this ether and his starting material.

EXPERIMENTAL

Materials. Acetone dimethyl ketal (2,2-dimethoxypropane) was commercial material used as received from The Dow Chemical Company. The other ketals were specially prepared.[7] Electrolytic hydrogen was used in a Parr hydrogenation apparatus, Model No. 3911. The hydrogenation catalysts were obtained from Baker and Co., Incorporated.

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(4) F. Sigmund and R. Uchann, *Monatsh.*, 51, 234 (1929); A. Johannissian and E. Akunian, *Bull. univ. état R. S. S. Arménie*, No. 5, 245 (1930); D. B. Killian, G. F. Hennion, and J. A. Nieuwland, *J. Am. Chem. Soc.*, 57, 544 (1935); C. D. Hurd and M. A. Pollack, *J. Am. Chem. Soc.*, 60, 1905 (1938); W. H. Carothers and H. B. Dykstra, U. S. Patent 2,124,686, July 26, 1938; H. P. Crocker and R. H. Hall, *J. Chem. Soc.*, 1955, 2052; W. L. Howard and N. B. Lorette, *J. Org. Chem.*, 25, 525 (1960).

(5) W. T. Reichle, dissertation, The Ohio State University, 1958.

(6) E. Waser, H. Sommer, C. Landweer, and C. Gaza, *Helv. Chim. Acta*, 12, 418 (1929).

(7) N. B. Lorette and W. L. Howard, *J. Org. Chem.*, 25, 521, 525 (1960).

(8) H. Henstock, *J. Chem. Soc.*, 1931, 372.

(9) *Handbook of Chemistry*, 8th ed., N. A. Lange, Ed., Handbook Publishers, Inc., Sandusky, Ohio, 1952, p. 592, 1374.

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

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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 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
I_A	2-Hydroxymethyl-5-methoxy-4-pyrone	82	165–166	$C_8H_8O_5$	52.17	52.53	4.37	4.64		
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
I_C	Kojic acid	67	159–160	$C_7H_6O_5$	49.42	49.54	3.55	3.82		
I_D	6-Methyl-2-pyronone	72	193.5–194	$C_7H_6O_4$	54.55	55.09	3.92	4.09		
I_E	Coumarin	94	70–71.5	$C_{10}H_6O_3$	68.96	68.72	3.47	3.29		

Compounds 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).