

Anal. Calcd for $C_{22}H_{22}O_4$: C, 74.97; H, 6.86. Found: C, 75.38; H, 6.43.

(C) With H_2O_2 under N_2 . To the deep red solution of 205 mg (0.61 mmol) of **3** in 15 mL of methanol made by addition of 200 mg of sodium methoxide under nitrogen was added dropwise 1 mL of 30% hydrogen peroxide with stirring for 15 min at 0 °C. The solution was warmed to room temperature and stirred for an additional 15 min under nitrogen. The solution was then poured into excess dilute hydrochloric acid, extracted with methylene chloride, dried (Na_2SO_4), and evaporated to give a colorless viscous liquid. An NMR spectrum shows that the oil was a mixture of 24% of **30** and 76% of the starting **3**.

Epoxidation of 2 with Alkaline H_2O_2 . A solution of 1.00 g (3.5 mmol) of **2** and 1.02 mL (10 mmol) of 30% aqueous hydrogen peroxide in 20 mL of methanol was cooled to 10 °C, and 2 mL of 1 N sodium hydroxide was added dropwise with stirring over a period of 1 h. The mixture was maintained with stirring at 15–20 °C for 3 h and then diluted with 100 mL of water and one drop of dilute hydrochloric acid. Extraction with ether (3 × 30 mL) followed by evaporation of the solvent in vacuo gave a solid which when recrystallized from cyclohexane gave colorless

crystals (**32**): mp 141.5–142.5 °C; NMR δ 0.93 (3 H, s), 1.05 (3 H, s), 1.38 (3 H, s), 1.45 (3 H, s), 1.67 (3 H, m), 1.80 (3 H, m), 3.20 (1 H, d, $J = 12$ Hz), 3.60 (2 H, s), 3.62 (1 H, d, $J = 12$ Hz); UV max (methanol) 299 nm ($\log \epsilon$ 2.48); mass spectrum, m/e (rel intensity) 302 (17), 232 (27), 178 (11), 174 (16), 161 (32), 135 (18), 134 (55), 119 (28), 91 (13), 79 (11), 58 (80), 43 (100), 41 (25).

Anal. Calcd for $C_{18}H_{22}O_4$: C, 71.50; H, 7.74. Found: C, 71.01; H, 7.35.

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Registry No. 1, 3854-96-4; 2, 72049-34-4; 3, 72049-35-5; 4, 72049-36-6; 5, 72049-37-7; 6, 72049-38-8; 8, 72049-39-9; 9, 72059-82-6; 10, 72049-40-2; 11, 72049-41-3; 12, 72049-42-4; 13, 72049-43-5; 14, 72049-44-6; 23, 72049-45-7; 24, 72049-46-8; 25, 72049-47-9; 26, 72049-48-0; 27, 72049-49-1; 28, 72059-83-7; 29, 72049-50-4; 30, 72049-51-5; 31, 33583-79-8; 32, 72049-52-6; *p*-benzoquinone, 106-51-4; 1,4-naphthoquinone, 130-15-4.

Liquid-Phase Catalytic Hydrogenation of 1,4-Cyclohexanedione: Activity and Selectivity

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Liquid-phase catalytic hydrogenation of 1,4-cyclohexanedione was carried out by using various metal catalysts on SiO_2 (Ni, Cu, Pd, Pt, Ir, Ru) in 2-propanol as solvent under low hydrogen pressure, 6.2 bar, and 20 °C. A kinetically consecutive process, diketone \rightarrow ketol \rightarrow diol, is obtained, and 4-hydroxycyclohexanone may be obtained in a single step at a yield of 70% by utilizing Ru/ SiO_2 . The rate and the selectivity for the first step of the reaction giving the ketol were examined as a function of several parameters: hydrogen pressure, substrate concentration, and temperature. The kinetic orders are 1 in H_2 and -0.6 in diketone with an activation energy of 11 kcal/mol.

One of the main objectives of chemistry is to devise and improve methods which allow the selective reaction of only one of the functional groups in a bifunctional molecule.

Our interest in this area is in the selective reduction of 1,4-cyclohexanedione to its corresponding ketol, 4-hydroxycyclohexanone. We chose to examine this ketone since its conformation has been definitively established as the twist-boat in the liquid phase.¹⁻⁴ This structure allows us to disregard the existence of the enol form and suggests a simultaneous adsorption of the two carbonyls on the surface of the catalyst.

The catalytic hydrogenation was carried out in the liquid phase by using a hydroxylic solvent, 2-propanol or water. The metal used was generally ruthenium, since this catalyst has often been utilized for the hydrogenation of ketones, as reported by Augustine,⁵ Rylander,⁶ and Frei-

felder.⁷ However, other metals such as platinum, iridium, and copper were also examined and compared.

In this work, we report on (1) the rate of disappearance of the diketone as a function of several parameters such as the hydrogen pressure, the amount of substrate, the temperature, the amount of catalyst, and the nature of the metal and (2) the selectivity of the reaction, which is defined by the ratio of the number of moles of product ketol to the total number of moles of ketol plus diol.

Experimental Section

Apparatus. Two different types of apparatus were used: an apparatus for the work at hydrogen pressures less than 1 bar⁸ and one for higher pressures, an autoclave (Autoclave Engineers type Magnedrive) with a capacity of 0.3 L, which allowed the removal of samples without stopping the agitation.

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Products. Both 1,4-cyclohexanedione and the corresponding diol, 1,4-cyclohexanediol, were commercial products (Fluka). Commercial 1,4-cyclohexanediol is a mixture of diols which are not separated under our conditions of analysis.

4-Hydroxycyclohexanone was obtained from 1,4-cyclohexanedione by the method of Jones and Sondheimer⁹ by blocking one of the hydroxyl groups as the monobenzoate, followed by chromium oxidation of the second group and regeneration of the first hydroxyl group by hydrolysis. Alternatively, the method of Kariv and Cohen¹⁰ was used, involving chromium oxidation of the diol with a single equivalent of chromium and then separating the products by silica chromatography [bp 100 °C (35 mm)].

The catalysts were prepared by impregnation from an aqueous solution of the metal commercial salts or acids, copper and nickel nitrates, ammonium hexachloropalladate, hexachloroiridic and hexachloroplatinic acids, and ruthenium red from Fluka or Merck by weighing the necessary amount in order to get 5% by weight of metal catalyst.

The support which is the fraction between 0.05- and 0.125-mm particle size of a screened Davison silica is then added, and the mixture is agitated during 2 h before evaporating the excess water in a stove at 80 °C during 18 h.

The catalysts were generated by reduction under a stream of hydrogen (6 L/h) at 350 °C for Pt, Ir, and Pd and at 450 °C for Ru, Ni, and Cu during 8 h. Before reduction the Ru catalyst is maintained at 250 °C during 6 h under a stream of air (6 L/h).

Operation. In the case of reactions conducted at low pressure, the apparatus was purged with nitrogen after introduction of the catalyst. For hydrogen pressures less than 1 bar, the reaction was conducted in a mixture of nitrogen and hydrogen at a total pressure of 1 bar. When equilibrium with the gas was reached (about 1 h), a solution of the reactant in the solvent, generally water, was introduced. The total quantity of liquid phase was 40 mL.

In the case of reactions at high pressure, the catalyst, the substrate, and the solvent (2-propanol, 80 mL) were placed directly in the autoclave. The choice of 2-propanol was dictated by the facts that 1,4-cyclohexanedione is practically insoluble in hydrocarbons and that this alcohol does not readily form ketals. After the apparatus was purged with nitrogen, shaken for 1 h at 6 bars, and evacuated of this gas, hydrogen was introduced at the desired pressure.

Gas Chromatography. The different aliquots of the reacting mixture were analyzed by vapor-phase chromatography on a Girdel Series 3000 apparatus equipped with a flame-ionization detector and a $\frac{1}{8}$ in. \times 5 ft 3% Carbowax 20M on Chromosorb W column. The conditions used for separation were as follows: injector temperature 250 °C; detector temperature 300 °C; temperature programming from 90 to 150 °C at 6 °C/min. The carrier gas was nitrogen, and its flow rate was 30 mL/min.

Results

The results of the hydrogenation of 1,4-cyclohexanedione (A) to give 4-hydroxycyclohexanone (B) and 1,4-cyclohexanediol (C) will be analyzed in terms of the rate of the disappearance of the diketone (eq 1) and in terms of the

$$r = -dc_A/dt = kp_{H_2}^\alpha c_A^\beta \quad (1)$$

selectivity of the reaction to give product B, expressed as a function of τ , where τ represents the number of moles of hydrogen consumed per mole of ketone during the hydrogenation. Knowing that 1 mol of hydrogen is required for each mole of ketone and 2 mol are needed for each mole of diol, we may write eq 2, where n_i is the molar fraction of the species i at time t .

Here τ may vary from 0 to 2.

$$\tau = (n_B + 2n_C)/n_A^0 \quad (2)$$

These plots of molar percentages vs. $f(\tau)$ have the advantage of eliminating the time factor and permitting a

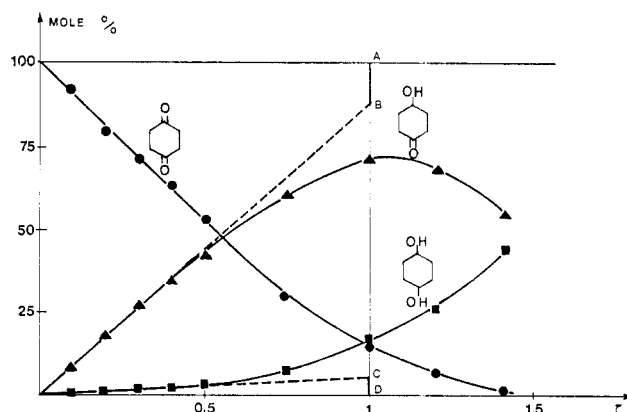


Figure 1. Consecutive process in the catalytic hydrogenation of 1,4-cyclohexanedione; $\tau = (n_B + 2n_C)/n_A^0$ with n_i = molar fraction of the species i at time t ; catalyst Ru/SiO₂; solvent 2-propanol; temperature 20 °C; p_{H_2} = 6.2 bars.

more precise determination of the initial selectivity of the ketone (S_B^0). The tangents of the curves [mole % of B = $f(\tau)$ and mole % of C = $f(\tau)$] as shown in Figure 1 give intercepts at $\tau = 1$ which determine two line segments AB and CD such that $AB = 2CD = 2x$.

The initial selectivity of B may be defined as in eq 3.

$$S_B^0 = dn_B/dn_C = (1 - 2x)/x \quad (3)$$

The percentage of product B is given by the expression $[(1 - 2x)/(1 - x)]100\%$.

We note also that, at 50% reaction, a value of $\tau = 0.5$ represents a reaction which goes in two steps $A \rightarrow B \rightarrow C$, whereas a direct reaction of A to the diol C would give a value of $\tau = 1$ at the half-reaction point.

The variables to be considered include the nature of the metal, the hydrogen pressure, the mass of the substrate, and the temperature.

Influence of the Nature of the Metal. This study was designed as an examination of the catalytic abilities of metals near Ru and Pt in the periodic table. In order to facilitate a comparison of these metals, we used identical conditions, the same support, and the same dispersion (5% metal by weight). The results are shown in Table I.

The least active metals were copper, nickel, and palladium which were not used under the normally employed conditions. Platinum is more active than ruthenium, but the initial selectivity and the maximum percentage of ketone are lower. Iridium, which is rarely utilized in catalytic hydrogenation of ketones, was more active than platinum and more selective than ruthenium.

Influence of the Hydrogen Pressure. Two series of results are reported in Tables II and III. The first series describes a study at pressures less than 1 bar (low-pressure apparatus) using water as the solvent, due to the low catalytic activity of ruthenium in 2-propanol, whereas the second corresponds to the work at pressures greater than 4 bars using under these conditions 2-propanol as the solvent.

The results in both series demonstrate that the reaction velocity increases with increasing pressure. At low pressure, a plot of $\log r_0^i$ as a function of $\log p_{H_2}$ is reasonably linear with a slope of about 0.8 (correlation coefficient 0.97). The reaction is thus approximately first order in hydrogen. This conclusion was confirmed by the studies at pressures greater than 4 bars, in which we obtained a curve whose first points are in agreement with an order near 1, this order tending then to zero at higher pressures.

As far as the selectivity is concerned in the case of 2-propanol, the initial selectivity did not seem to be affected by a rise of hydrogen pressure; the selectivity was greater

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Table I. Influence of the Nature of the Metal^a

metal at 5% by wt	amt of catalyst, g	temp, °C	initial rate × 10 ⁶ , mol/min	initial selectivity			selectivity % max of ketol, %
				S _B ^o ^c	% of ketol obtained	% max of ketol	
Ni/SiO ₂	0.5049	20	<i>b</i>	<i>b</i>	<i>b</i>	<i>b</i>	<i>b</i>
Cu/SiO ₂	0.5050	100	5.2	7	87	<i>b</i>	<i>b</i>
		190	2.4	14	93	<i>b</i>	<i>b</i>
Pd/SiO ₂	0.5111	20	2.2	<i>b</i>	<i>b</i>	<i>b</i>	<i>b</i>
		100	1.8	23	96	<i>b</i>	<i>b</i>
Pt/SiO ₂	0.5052	20	12.5	<i>b</i>	<i>b</i>	<i>b</i>	<i>b</i>
Ir/SiO ₂	0.5221	20	45	2	67	48	55
Ru/SiO ₂	0.4956	20	615	18	95	78	76
			15	11	92	<i>b</i>	<i>b</i>

^a $p_{H_2} = 6.2$ bars; solvent 2-propanol. ^b Could not be determined. ^c Initial selectivity $S_B^o = \% \text{ ketol} / \% \text{ diol}$.

Table II. Influence of the Hydrogen Pressure ($p_{H_2} < 1$ Bar)^a

p_{H_2} , bar	init selectivity				
	initial rate × 10 ⁵ , mol/min	S _B ^o ^b	% of ketol obtained	% max of ketol	selectivity at % max of ketol, %
6.6×10^{-2}	1.0	7.1	87	53	72
1.32×10^{-1}	2.2	5.4	85	51	73
2.10×10^{-1}	2.9	4.7	82	48	57
3.68×10^{-1}	3.8	3.4	77	49	63
5.02×10^{-1}	5.2	3.1	76	47	62

^a Catalyst Ru/SiO₂ at 5% by weight; temperature 22 °C; solvent water. ^b $S_B^o = \% \text{ ketol} / \% \text{ diol}$.

Table III. Influence of the Hydrogen Pressure ($p_{H_2} > 4$ Bars)^a

p_{H_2} , bar	initial selectivity				
	initial rate × 10 ⁵ , mol/min	S _B ^o ^b	% of ketol obtained	% max of ketol	selectivity at % max of ketol, %
4	1.7	48	98	<i>c</i>	<i>c</i>
6.2	3.7	65	98	<i>c</i>	<i>c</i>
17	10.6	65	98	73	78
34	12.4	65	98	72	77
54.4	13.4	65	98	68	74
61.2	14.7	65	98	68	70

^a Catalyst Ru/SiO₂ at 5% by weight; temperature 20 °C; solvent 2-propanol. ^b $S_B^o = \% \text{ ketol} / \% \text{ diol}$. ^c Could not be determined.

than it was in water where the activity is greater.

Influence of the Amount of Substrate. The values given in Table IV show that there is a decrease in the initial rate of hydrogenation as the amount of the substrate (and, therefore, its concentration) increases for pressures where the order in hydrogen is still near 1.

A value of β may be obtained from the slope of a plot of $\log r_0^i$ as a function of $\log c_A$: $\beta = -0.6$ (correlation coefficient 0.98). However, the initial selectivity is not affected by an increase in the mass of the substrate.

Influence of the Temperature. An apparent energy of activation of 11 kcal/mol may be obtained from the results in 2-propanol at a pressure of 6.2 bars (Table V). An increase in temperature yields to an increase in activity and a decrease in the initial selectivity and the maximum percentage of 4-hydroxycyclohexanone which may be obtained.

Discussion

The above results allow us to rewrite eq 1 as eq 4.

$$r = -dc_A/dt = kp_{H_2}c_A^{-0.6} \quad (4)$$

Table IV. Influence of the Amount of Substrate^a

amt of substrate, g	initial rate × 10 ⁴ , mol/min	initial selectivity			selectivity at % max of ketol, %
		S _B ^o ^b	% of ketol obtained	% max of ketol	
0.5148	2.8	48	98	68	72
0.7163	2.5	48	98	68	74
1.0010	2.0	48	98	68	82
1.5079	1.5	48	98	72	80

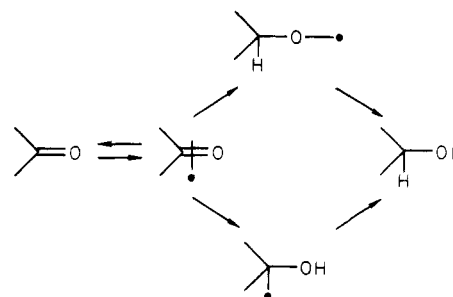
^a Catalyst Ru/SiO₂ at 5% by weight; temperature 22 °C; $p_{H_2} = 34$ bars; solvent 2-propanol. ^b $S_B^o = \% \text{ ketol} / \% \text{ diol}$.

Table V. Influence of the Temperature^a

temp, K	initial rate × 10 ⁵ , mol/min	temp, K	initial rate × 10 ⁵ , mol/min
293	3.7	341	55
315	20	355	97

^a Catalyst Ru/SiO₂ at 5% by weight; $p_{H_2} = 6.2$ bars; solvent 2-propanol.

Scheme I. General Mechanism of the Hydrogenation Reaction



The kinetic order of 1 in hydrogen at low pressure is different from that obtained for the cyclanones for which the experimental value is 0.5.¹¹ On the basis of the Horiuti-Polanyi-type reaction mechanism (Scheme I) this suggests that the slow step in the formation of 4-hydroxycyclohexanone is the addition of the second hydrogen atom as in the case of the olefins.⁸

The kinetic order in substrate is negative, -0.6 . This inhibition effect in the region of pressure where the reaction rate is controlled by a step between adsorbed species suggests either that there is a competitive adsorption between hydrogen and substrate or that the second hydrogenable function may inhibit the whole reaction.

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Under the same conditions, the experimental results¹² found in the catalytic hydrogenation of acetophenone—kinetic order of 1 in hydrogen and of -0.5 in substrate—led us to think that the similar kinetic behavior for these two very dissimilar molecules may be due to the presence of the second hydrogenable function (benzenoid ring or carbonyl).

On the other hand, the initial selectivity in 4-hydroxycyclohexanone is only slightly affected by variations in the amount of substrate, the hydrogen pressure, or the amount of catalyst. In contrast, the temperature does affect the selectivity from 93% at 20 °C to 81% at 80 °C. A similar effect was also noted with respect to the nature of the solvent: 93% in 2-propanol, 86% in methanol, and 80% in water.

Generally, for a given metal, most of the factors which favor activity decrease the selectivity.

By utilizing ruthenium as the metal and 2-propanol as the solvent, we were able to obtain 4-hydroxycyclo-

hexanone by hydrogenation in a single step starting from the diketone with a yield of about 70%.

In contrast, the majority of the prior preparations of this compound in homogeneous solution, whether from the diol^{9,10,13} or the diketone,¹⁴ take several steps and/or suffer from difficulties in extraction or separation, leading to decreasing yields.

Under these experimental heterogeneous conditions it is possible to stop the hydrogenation at any time, and in particular, when the maximum yield of ketol has been reached.

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Registry No. 1,4-Cyclohexanedione, 637-88-7; 1,4-cyclohexanediol, 556-48-9; 4-hydroxycyclohexanone, 13482-22-9; Ni, 7440-02-0; Cu, 7440-50-8; Pd, 7440-05-3; Pt, 7440-06-4; Ir, 7439-88-5; Ru, 7440-18-8.

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Malonate Anion Induced Favorskii-Type Rearrangement. Reaction of Cyclic α -Halo Ketones with Sodiomalonates¹

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The reaction of 2-chlorocyclohexanone (**1b**) with ethyl sodiomalonate in benzene at 0–25 °C gave 6-[bis(ethoxycarbonyl)methyl]bicyclo[3.1.0]hexan-6-ol (**4c**), the Favorskii-type intermediate, in 49% yield, in place of the substitution product ethyl C-(2-oxocyclohexyl)malonate (**3**). Derivatives of bicyclo[4.1.0]heptan-7-ol (**4a,b**) and those of bicyclo[3.1.0]hexan-6-ol (**4d,e**) were also obtained in good yields by similar means. Compound **4c** was transformed into **3** readily by heating with 0.05 equiv of NaH in benzene. The hydrolysis of **4a–d** with 0.2 N NaOH followed by pyrolysis at 110–120 °C gave the ring-contracted β -keto esters **9a–d**. Pyrolysis after the hydrolysis with 2 N NaOH gave the corresponding ketones **11a–d** in good yields. Oxidation of **4c** with CrO₃ and HClO₄ afforded ethyl C-(2-hydroxycyclopentanecarbonyl)malonate (**14**) in 45% yield. Treatment of **4c** with Br₂ gave ethyl C-(1-bromocyclopentanecarbonyl)malonate (**18**) in 64% yield.

The reaction of an α -halo ketone with hydroxide or alkoxide is well-known to give a carboxylic acid or ester via the Favorskii rearrangement.² On the other hand, the reaction of α -halo ketone with carbanions, such as sodiomalonate^{3,4} and sodioacetoacetate,⁵ has been reported to produce exclusively an α -substituted ketone via an S_N2 reaction.

Cocker³ and Schemiakin⁴ obtained ethyl C-(2-oxocyclohexyl)malonate (**3**) in the reaction of 2-chlorocyclohexanone (**1b**) with ethyl sodiomalonate (**2**) in benzene under reflux conditions. We carried the same reaction out at lower temperatures (0–25 °C) and contrarily obtained 6-[bis(ethoxycarbonyl)methyl]bicyclo[3.1.0]hexan-6-ol (**4c**) in 49% yield.

In this paper, we report the formation and the first isolation of cyclopropanol derivatives **4a–e**, the Favorskii-type intermediates in the reaction of cyclic α -halo ketones with sodiomalonates. Transformations of **4** to the corresponding ring-contracted β -keto esters **9a–d** and ketones **11a–d** are also described.

The structure of the bicyclo[3.1.0]hexane skeleton of **4c** was elucidated by spectral data and chemical transformations to known compounds, such as ethyl β -oxocyclopentanepropanoate (**9c**), cyclopentyl methyl ketone (**11c**), and 1-cyclopentenyl methyl ketone (**15**). The IR spectrum of **4c** showed a strong absorption of a hydroxyl group at 3500 cm⁻¹. The ¹H NMR spectrum exhibited a singlet (1 H) at δ 2.91 due to the α -H of the malonate moiety and the ¹³C NMR spectrum indicated a signal at 29.8 ppm. This was split into a doublet (off-resonance decoupling) due to the two equivalent angular methine carbons. In the mass spectrum, a molecular ion peak was observed at *m/e* 256.

A conceivable mechanism for this reaction is shown in Scheme I. It is reasonable to consider that malonate anion reacts as a base initially to produce an equilibrium mixture

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