

to have the same sign, paralleling the observations for norbornenes (XXII). All three coupling constants, J_{12} , J_{13} , and J_{23} , are all significantly larger in bicyclo-[2.2.2]octene derivatives (XXIII)⁷¹⁻⁷⁴ than in corresponding norbornane compounds, despite the similarity of the dihedral angles. This suggests the operation of "ring size effect" similar to that already observed for vicinal olefinic coupling constants.^{31-33,84}

¹³C-H Coupling Constants. Variation with Ring Size.—Foote⁷⁵ has demonstrated that a linear correlation exists between the J_{13CH} coupling constant of methylene groups and the C-C-C interatomic angle, interpreted as indicating a relationship between hybridization and bond angle.^{59,76} The C₁-C₅-C₆ angle of norbornene is strained (*ca.* 104.5°).⁵⁴⁻⁵⁶ The Cl-¹³C-H coupling constants observed here for δ -chloronorbornene derivatives I and IV were 155 c.p.s., significantly higher than expected for unstrained chlorides (150-151 c.p.s.).⁷⁷ By way of confirmation, we have measured the Cl-¹³C-H coupling constant of the more highly strained cyclo-

butane and cyclopropane derivatives 1,1,2,2,3-pentachloro-4,4-difluorocyclobutane ($J_{13C-H} = 165.5$ c.p.s.) and pentachlorocyclopropane ($J_{13C-H} = 193$ c.p.s.). (The extra halogen substituents in these molecules probably have a small but relatively insignificant effect.^{51,77}) The variation of J_{13C-H} with ring size (internal angle) is demonstrated again in these examples.^{75,76}

A direct extension of the Foote J_{13C-H} bond angle relationship⁷⁵ to the olefinic proton of C=C-C systems is possible. Pertinent data are collected in Table VIII and plotted in Fig. 6. The sensitivity of J_{13C-H} to bond angle changes of olefinic C-H is comparable to that found for saturated C-H.⁷⁵

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(75) C. S. Foote, *Tetrahedron Letters*, **No. 9**, 579 (1963). Foote (personal communication) has also found the J_{13CH} bond angle relations of olefinic hydrogens (Table VIII and Fig. 6).

(76) R. Lippert and H. Prigge, *Ber. Bunsen Ges. Physik. Chem.*, **67**, 415 (1963).

(77) E. R. Malinowski, *J. Am. Chem. Soc.*, **83**, 4479 (1961); G. S. Reddy and J. H. Goldstein, *J. Chem. Phys.*, **38**, 2738 (1963).

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Reactions between Secondary Alcohols, Ketones, and Hydrogen on Metallic Catalysts¹

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In the presence of large amounts of hydrogen and at temperatures of 115-150°, the reaction 2-propanol + 2-butanone = acetone + 2-butanol occurs as a coupled surface reaction on metallic copper at about 2.5 times the rate of net hydrogenation. The same reaction occurs on palladium-on-alumina at 96-130° but accompanied by some hydrogenolysis, and it occurs on nickel-silica at 77° in the liquid phase in the absence of added hydrogen. In experiments on copper in which deuterium was substituted for hydrogen, the 2-butanol which was formed was nearly completely 2-butanol-2-*d*. In the presence of deuterium, optically active 2-butanol reacts on copper at 135-155° to form racemic 2-butanol-2-*d* and butanone. Only small amounts of exchange occur in the side chains. At low degrees of dehydrogenation, α , the fractional loss in rotation, is nearly proportional to α . Values of α considerably in excess of that which would correspond to equilibrium in the presence of hydrogen can be attained because of a kinetic isotope effect: the reaction of butanone is slower with deuterium than with

hydrogen. A mechanism is proposed in which adsorbed alcohol is RO-* and adsorbed ketone is R'₂C=O[⊕]⊖*. Indirect reaction between these two species somewhat analogous to that in the Meerwein-Ponndorf reaction is suggested as interconverting adsorbed alcohol and adsorbed ketone.

Hydrogenations of the carbon-oxygen double bond in ketones and of the carbon-carbon double bond in olefins are catalyzed by the same metallic catalysts. Both types of hydrogenation have been studied from a mechanistic point of view, but ketone hydrogenation has received much less attention. The present study is an attempt to specify more closely the nature of the adsorbed intermediates in the reaction, ketone + hydrogen \rightleftharpoons secondary alcohol.

The heat of hydrogenation of a ketone is much less than that of an olefin (acetone, 14 kcal.; isobutylene, 28 kcal.). Largely owing to this, K_p sinks to unity at a much lower temperature in ketone than in olefin hydrogenation (acetone, 200°; isobutylene, over 600°). Thus, ketone hydrogenation and its reverse, dehydrogenation of secondary alcohols, can be studied in conjunction at relatively modest temperatures, a situation which facilitates mechanistic studies.

The addition of deuterium to olefins on metallic catalysts usually gives an alkane product with a rather complicated distribution of deuterium atoms.³ The addition of deuterium to acetone is simpler. The principal product is CH₃-CDOD-CH₃⁴⁻⁶ although there is some introduction of deuterium into the methyl groups.⁶ It is clear, then, that no large fraction of acetone is hydrogenated *via* an enolic intermediate which would of necessity lead to the introduction of one deuterium atom on a methyl group.

The mechanism shown in eq. 1 has been proposed to account for these data. The last step is assumed to be rate determining.⁶ In addition, it is known that the interaction of deuterium and isopropylalcohol on metallic catalysts to form CH₃CHODCH₃ is rapid compared to

(3) G. C. Bond, "Catalysis by Metals," Academic Press, Inc., London, 1962, sect. 11.53.

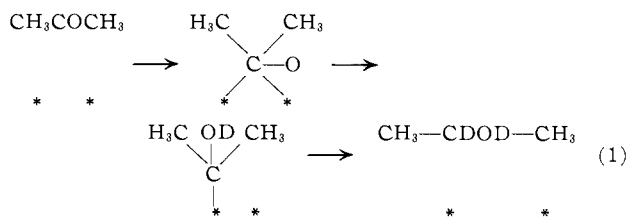
(4) L. C. Anderson and N. W. MacNaughton, *J. Am. Chem. Soc.*, **64**, 1456 (1942).

(5) L. Friedman and J. Turkevich, *ibid.*, **74**, 1669 (1952).

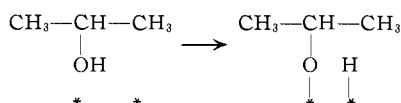
(6) C. Kemball and C. T. H. Stoddart, *Proc. Roy. Soc. (London)*, **A241**, 208 (1957).

(1) Presented at the 142nd National Meeting of the American Chemical Society, Atlantic City, N. J., Sept., 11, 1962.

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alcohol dehydrogenation or ketone hydrogenation.^{5,6} If this proceeds by the reaction



it must be fast. In mechanism 1, this isotopic exchange reaction would appear as a side step not in the direct line of hydrogenation-dehydrogenation.

At least on copper catalysts at about 170°, there is a possible difficulty with this mechanism. In the dehydrogenation of optically active *sec*-butyl alcohol, substantial amounts of racemic alcohol are formed at low degrees of dehydrogenation.⁷ Of course, the reverse reaction, hydrogenation of methyl ethyl ketone, will generate racemic alcohol when the conversion is large enough to make the reverse reaction significant. It is not clear, however, how mechanism 1 can lead to racemic alcohol at low conversions.

Accordingly, we have investigated the interaction between optically active 2-butanol and deuterium. Copper was chosen as the catalyst for the following reason. We wished to work in the vapor phase, at temperatures at which a significant fraction of butanol would be dehydrogenated at equilibrium, and at total pressures of about 1 atm. These criteria require temperatures in excess of about 110°. At such temperatures copper is one of the few catalysts, which appears not to give serious hydrogenolysis to alkane. However, pure copper loses activity with use. We have used a 99% copper-1% nickel catalyst which seems to have essentially the same catalytic properties as pure copper⁸ but to be longer lived probably because of a reduced tendency toward sintering.

Experimental

Electrolytic hydrogen (Matheson Co., Inc.), and deuterium (General Dynamics Corp.) were purified by passage through traps of heated copper, Drierite, Linde Molecular Sieve (Type 4A), sodium-potassium alloy, and activated charcoal. Isopropyl alcohol, 2-butanone, and 2-butanol of commercial origin were fractionated and found to be chromatographically pure. (-)-2-Butanol was prepared by resolution of the *sec*-butyl hydrogen phthalate with brucine. Reagent grade ethanol, 2-pentanone, 3-pentanone, and propyl alcohol were used without further purification.

The copper catalyst was prepared by coprecipitation of the carbonates by adding a solution of ammonium carbonate to a solution of copper and nickel nitrates present in a mole ratio of 100. The precipitates were washed, dried at 100°, powdered, calcined in oxygen at 250° for 1 day, pelleted at 2000 lb. per sq. in. and sieved to 60-100 mesh. Samples were reduced *in situ* at 250° for 8 hr. in flowing hydrogen. The 3% palladium-on-alumina catalyst was prepared by impregnating 8.4 g. of Harshaw Chemical Co. hard alumina with 100 cc. of 0.024 *M* H₂PdCl₂ at 65° for 3 hr. After drying at 110°, catalyst samples were reduced *in situ* at 450° for 8 hr. Catalyst weights are given as computed weights of metal.

Between runs, the catalysts were allowed to stand in hydrogen either at room temperatures or at the temperature of the previous reaction. The copper catalyst proved to be rather stable. For example, catalyst C was used for 51 runs before it lost activity seriously.

Apparatus.—A flow system was employed. Vapor phase mixtures of alcohol and hydrogen or deuterium were prepared in a saturator. The alcohol/hydrogen ratio was set by thermostating

a helix through which the mixture passed. The helix was preceded by a small saturator which was kept 10 to 15° above the temperature of the helix. The catalyst chamber was the annular space between a thermocouple well and an outer tubing, 10 mm. i.d. The walls of the outer tubing were reduced to about half of their original thickness by aqueous hydrofluoric acid. The catalyst chamber was surrounded by a furnace. The reaction product stream was passed through a Dry Ice trap to condense the alcohol-ketone mixture.

A few runs were made in the liquid phase with 60-100 mesh nickel-kieselguhr (Harshaw Chemical Co.) reduced *in situ* at 450° for 8 hr. in flowing hydrogen. The apparatus involved hydrogen or nitrogen bubbling from a porous disk through a suspension of the catalyst in a mixture of alcohol and ketone.⁹

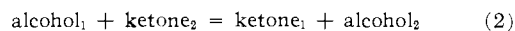
Analysis.—Chemical composition was determined by gas chromatography employing 30% polyester, LAC-2-R-446 (Cambridge Industries Co.), on 30-60 mesh firebrick. Where mixtures involved 2-butanol and butanone or these plus acetone and isopropyl alcohol, calibration runs were made with known mixtures. The precision for analysis of the butanone-butanol mixture seemed to be about 0.3%.

Optical rotations of total product were measured at 30° in a semimicro 0.5-dm. tube. These data were converted to rotation of the component 2-butanol by allowing for the ketone content as previously described.⁷

Deuterium distributions were determined on a Consolidated 21-130 mass spectrometer provided this department by a matching grant from the National Science Foundation. Even at low ionizing voltages the parent peak of 2-butanol is too small to be useful. The compound was analyzed by measurement of the ions C₂H₅CHOH⁺ and CH₃CHOH⁺. Low ionizing voltages were used to minimize fragmentation of these ions. It has been shown that the deuterium atom in CH₃CDOHCH₃ is not rearranged prior to formation of CH₃CDOH⁺.¹⁰ We assume that the two fragment ions from 2-butanol are formed without significant deuterium rearrangement. 2-Butanol was examined at an ionizing voltage of 68. Butanol-butane mixtures were separated by gas chromatography before mass spectrometric analysis.

Results

Alcohol-Ketone Pair Interchange.—Previous work⁷ had suggested the possibility of the reaction



This reaction was investigated with the results shown in Table I. In run B-1, butanone plus hydrogen passed over the copper-1% nickel catalyst at 117° led to 8.7% hydrogenation. An azeotropic mixture of isopropyl alcohol and butanone was then passed over the catalyst (run B-2). The molar product composition was acetone, 12.7%; isopropyl alcohol, 22.1%; butanone, 42.7%; and 2-butanol, 22.4%. Here and in similar experiments there was a small loss in the propane derivatives *vs.* the butane probably owing to preferential loss of acetone in the Dry Ice trap which followed the catalyst. We give the molar product ratios, C₃one/C₄alc and C₄one/C₄alc in Table I. The first ratio is probably consistently a little low.

Similar results were observed at temperatures in the vicinity of 137 and 150° and in the system 2-butanol + 3-pentanone (run B-10). However, in passing ethyl alcohol plus butanone (50% of each) over the catalyst at 146°, only 1.6% of the ethanol was dehydrogenated while 16.4% of the butanone was hydrogenated. Alcohol-ketone pair interchange is much slower in this system if indeed it occurs at all. Propyl alcohol plus 2-pentanone behaved similarly.

Before the experiments described above, we ran similar experiments on 3% palladium-on-alumina. Reaction 2 was observed at 96, 118, and 130°. At the latter two temperatures the relative extents of hydrogenation and of alcohol-ketone pair interchange were nearly the same as on copper. Per unit weight of metal, the palladium catalyst was about 20 times as active as the copper. However, additional peaks were observed in the gas chromatograms which appeared to result from

(7) R. L. Burwell, Jr., *J. Am. Chem. Soc.*, **70**, 2865 (1948).

(8) H. J. Kolb and R. L. Burwell, Jr., *ibid.*, **67**, 1084 (1945).

(9) G. V. Smith and R. L. Burwell, Jr., *ibid.*, **84**, 925 (1962).

(10) I. Friedman and J. Turkevich, *ibid.*, **74**, 1666 (1952); see also, K. Mislow, R. E. O'Brien, and H. Schaefer, *ibid.*, **84**, 1940 (1962).

TABLE I
 KETONE-ALCOHOL PAIR INTERCHANGE ON COPPER (1% NICKEL)

Run	Reactant	Temp., °C.	Flow rate in ^a mmoles/hr./g.—		$\frac{C_{\text{one}}}{C_{\text{alc}}}$	$\left(\frac{C_{\text{one}}}{C_{\text{alc}}}\right)_{\text{eq}}$	$\left(\frac{C_{\text{one}}}{C_{\text{alc}}}\right)$	$\left(\frac{C_{\text{one}}}{C_{\text{alc}}}\right)_{\text{eq}}$
			H ₂	Alc. + ketone				
B-1	C ₄ one	117	200	32	10.5	0.051
B-2	Azeo ^b	115	171	32	0.57	0.045	1.91	.047
A-2	Azeo ^b	118	17.7	3.3	.042	.052	0.059	.055
B-3	Azeo ^b	131	238	46	.132	.092	10.5	.098
B-4	Azeo ^b	136	204	38	.53	.113	3.16	.121
B-5	C ₄ one	139	194	32	12.9	.135
B-6	Azeo ^b	138	204	38	0.80	0.123	2.13	.131
B-10	C ₄ + C ₅ ^c	150	200	6.9	1.57 ^d	.186 ^d	0.274	.186
B-11	Azeo ^b	149	196	38	0.332	.191	4.32	.204

^a Flow rate of hydrogen and of alcohol plus ketone in millimoles per hour per gram of catalyst. In series A, the catalyst was 3.9 g. of Cu-1% Ni; in series B, 0.46 g. of Cu-1% Ni mixed with 3.2 g. of glass beads of the same mesh. ^b The reactant was the azeotropic mixture of isopropyl alcohol and 2-butanone, 35.6 mole % of the former. ^c The reactant was the azeotropic mixture of 2-butanol and 3-pentanone, 61.4% of the former. ^d C₅one/C₅alc.

hydrogenolysis. These additional products seemed to be formed at roughly 10% of the rate of hydrogenation of ketone. A 1% impregnated palladium-on-silica gel gave even more of the by-products.

Nickel catalysts were investigated in a liquid phase system at about 77°. Raney nickel in ethyl alcohol was inserted in the system and the alcohol evaporated by a stream of nitrogen. The isopropyl alcohol-butanone azeotrope was then added. Considerable acetone was formed and about one-third of the butanone was hydrogenated by the hydrogen dissolved in the Raney nickel. To test whether hydrogen was essential for reaction 2, 0.32 g. of Harshaw nickel-silica was reduced *in situ* at 450° and the catalyst was swept with nitrogen at this temperature. After cooling to 77°, 1.0 cc. of the azeotrope was added. After 500 sec., the system was very nearly in equilibrium with respect to reaction 2. Hydrogenolytic products would have escaped detection in the liquid phase experiments.

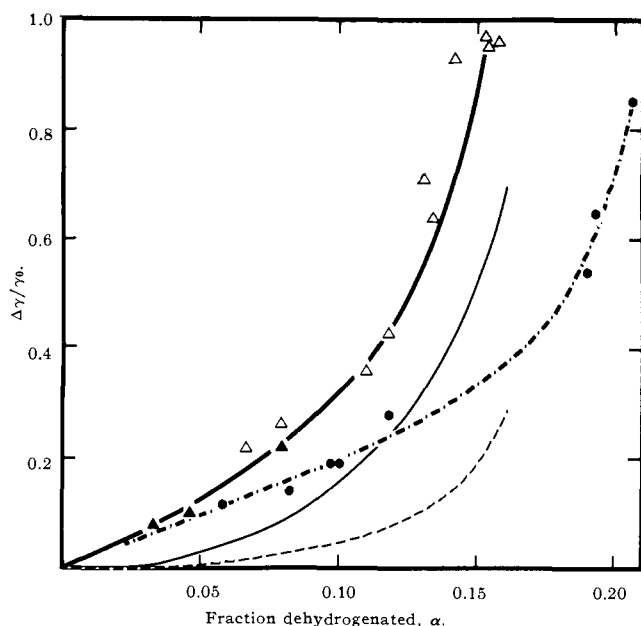


Fig. 1.—Racemization of (–)-2-butanol at 155°: Δ, runs in the presence of hydrogen; ▲, runs in the presence of hydrogen with 1-dm. polarimeter tube; ●, runs in the presence of deuterium.

Racemization of (–)-2-Butanol.—In these experiments, hydrogen plus (–)-2-butanol was passed over 0.346 g. of the copper catalyst diluted with 4.0 g. of glass beads. The molar ratio of hydrogen to butanol was 33. Experiments were run at about 155 and 135°. Flow rates were varied to get a range of conversions. The actual temperatures of these experiments lay

within 5° ranges, centered on 155 and 135°. Data are presented in Fig. 1 and 2 where we plot $\Delta\gamma/\gamma_0$, the fractional loss in rotation of (–)-2-butanol against α , the fraction of butanol converted to butanone.

The method by which we determined $\Delta\gamma/\gamma_0$ is one of rather low accuracy. The possible error in $\Delta\gamma/\gamma_0$ is probably about 0.02. In three runs at lower conversion at 155°, the rotation was measured more accurately in a 1-dm. water-jacketed tube.

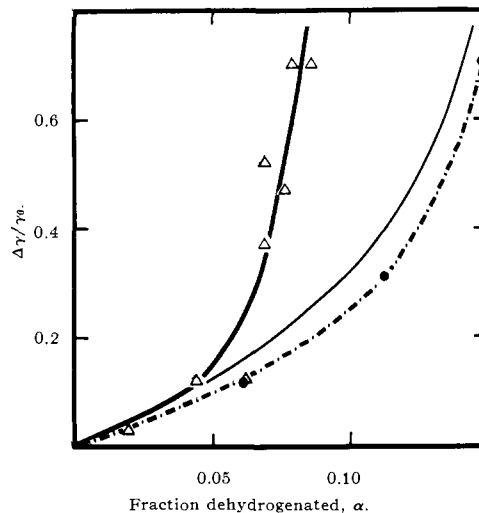


Fig. 2.—Racemization of (–)-2-butanol at 135°: Δ, runs in the presence of hydrogen; ●, runs in the presence of deuterium.

Gas chromatography indicated the presence of an additional product at about the 0.1% level. Judged by its elution time it was butane or a butene. In our ordinary procedure the contents of the Dry Ice trap which followed the catalyst were allowed to warm to 25° before samples were taken for analysis. Since considerable butane might have been lost in this procedure, we carried out a run at 183° which went nearly to equilibrium and removed a sample for analysis without warming the contents of the trap. The by-product amounted to 0.4%. Since our other runs were at less drastic conditions, we have ignored this side reaction.

Isotopic Exchange with Deuterium.—Similar experiments were performed on the same sample of catalyst with deuterium replacing hydrogen. Loss in rotation vs. α is shown in Fig. 1 and 2.

After polarimetry, about 0.1 cc. of product was separated into 2-butanol and butanone by gas chromatography and each fraction was analyzed mass spectrometrically. One would expect the group –OD to be converted to –OH by exchange with the surface –OH groups of the firebrick support in the gas chromatographic column. Further, previous workers have shown

TABLE II
 ISOTOPIC DISTRIBUTION IN 2-BUTANOL AND 2-BUTANONE^a

Run	C ₂ H ₅ CHOH ⁺ ions					-CH ₃ CHOH ⁺ ions					Butanone			
	d ₀	d ₁	d ₂	d ₃	d ₄	d ₀	d ₁	d ₂	d ₃	d ₄	d ₀	d ₁	d ₂	d ₃
At 155°														
C-39	86.4	13.4	0.23	0.03	87.2	12.2	0.48	0.17	0.05	96.6	2.7	0.55	0.15	
C-36					85.0	14.6	.32	.07	.01	98.3	1.44	.23	.02	
C-40	79.7	19.9	0.27	0.06	80.7	18.6	.51	.10	.02	96.9	2.24	.79	.12	
C-35	79.6	20.3	.08	.01	81.1	18.7	.22	.02	.00	Not analyzed				
C-38	69.5	30.2	.25	.05	71.0	28.4	.52	.11	.00	98.0	1.43	0.54	0.06	
C-41	44.4	55.2	.42	.03	45.7	53.4	.84	.05	.01	96.7	2.54	.76	.04	
C-37	33.4	65.9	.36	.10	34.8	64.4	.75	.08	.02	97.9	2.00	.13	.03	
C-42	15.7	82.1	1.93	.17 ^b	16.2	79.4	3.96	.36	.14	92.8	6.45	.58	.12 ^c	
At 135°														
C-45	87.9	12.0	0.09	0.03	88.4	11.4	0.12	0.06	0.03	97.9	1.89	0.20	0.01	
C-44	68.5	31.2	.31	.05	69.8	29.6	0.56	.05	.01	98.6	1.28	.11	.00	
C-43	30.3	69.3	.49	.01	31.2	66.6	1.88	.24	.02	95.9	3.90	.19	.01	
Azeotrope at 155° ^d														
C-52	3.9	95.4	0.73	0.00	4.7	94.4	0.88	0.00						
C-51	4.3	94.9	0.87	.00	4.5	94.0	1.47	.01						
C-54	3.7	95.1	1.18	.00	3.9	94.5	1.63	.02						

^a For exact conditions, see Table III. ^b d₄ = 0.02. ^c d₄ = 0.03. ^d The isopropyl alcohol-butanone azeotrope; for exact conditions and product analysis, see Table IV.

that the -OD group of alcohols exchanges in the mass spectrometer itself.^{5,6} Thus, any deuterium in the hydroxyl groups of butanol will be lost in analysis.

Isotopic analyses for 2-butanol derived from the CH₃CH₂CHOH⁺ and the CH₃CHOH⁺ ions are given in Table II. If one assumes that the group -CDOH- is present in all exchanged butanols, then d₀ should be the same whether computed from the C₂H₅CHOH⁺ or from the CH₃CHOH⁺ ion. The agreement between the two computed values of d₀ is as good as one could expect considering that there may be an isotope effect upon the fragmentation of the parent ion and that one may have a species such as CH₂DCHOH⁺ provided there is any significant quantity of hydrogen in the surface hydrogen-deuterium pool.

Table III gives the conditions for the runs with deuterium and, in the three columns at the right, the fractional dehydrogenation, the fractional loss in rotation of (-)-2-butanol, and the fraction of butanol molecules which underwent isotopic exchange.

 TABLE III
 RACEMIZATION vs. EXCHANGE OF (-)-2-BUTANOL

Run	Temp., °C.	Flow rate, ^a mmoles/hr./g.	α ^b	Δγ/γ ^c	1 - d ₀ ^d
C-39	153	114	0.058	0.115	0.13
C-36	154	73	.082	.14	.15
C-40	157	86	.097	.19	.20
C-35	153	46	.100	.19	.20
C-38	153	44	.118	.28	.30
C-41	153	35	.190	.54	.55
C-37	154	21	.193	.65	.66
C-42	154	19	.206	.85	.84
C-45	136	55	.061	.115	.12
C-44	137	27	.112	.31	.31
C-43	138	17	.148	.705	.69

^a Flow rate of H₂ was 33 times that of 2-butanol given in this column. ^b Fraction of 2-butanol dehydrogenated. ^c Fractional loss in rotation in undehydrogenated 2-butanol. ^d Fraction of 2-butanol molecules which underwent isotopic exchange.

Reaction between Deuterium and Isopropyl Alcohol-Butanone Azeotrope.—The azeotrope and deuterium were passed over the copper catalyst at about 155°. Conditions and product analyses are given in Table IV. The 2-butanol which was formed during reaction was separated from the reaction mixture by gas chroma-

tography and analyzed by mass spectroscopy. Results are given in the last three lines of Table II.

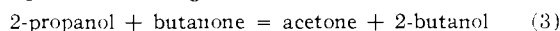
 TABLE IV
 COMPOSITION OF PRODUCT FROM REACTION OF ISOPROPYL ALCOHOL-BUTANONE AZEOTROPE WITH DEUTERIUM

Run	Temp., °C.	Flow rate, ^a mmoles/hr./g.	C ₃ one,	C ₃ alc,	C ₁ one,	C ₁ alc,
			%	%	%	%
C-52	154	74	5.6	28.3	60.3	5.8
C-51	155	171	13.7	22.5	48.6	15.1
C-54	158	20	14.9	18.1	48.1	18.9

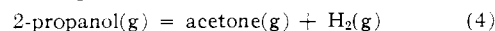
^a Flow rate of azeotrope; flow rate of deuterium is 4.2 times greater.

Discussion

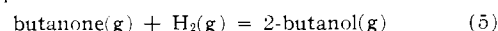
Alcohol-Ketone Pair Interchange.—The alcohol-ketone pair interchange



occurs at a substantial rate on copper at 115–150°. Consider run B-2 of Table I. The ratio, C₃one/C₃alc, started at 0.00 and reached 0.57. This ratio is far larger than the value of the ratio, 0.045,⁸ which would be obtained at equilibrium in the reaction



Thus reaction 3 occurs as a direct surface reaction and not merely by the simultaneous, independent progress of reaction 4 plus



Hydrogen transfer reactions between alcohol and ketones or aldehydes are not new.^{11,12} Acrolein can be converted to allyl alcohol by reaction with primary and secondary alcohols on magnesium and other group II oxides.¹¹ Mechanistically, one might expect this to be a heterogeneous Meerwein-Ponndorff reaction. The reaction was also reported¹¹ to occur on copper-magnesia accompanied by formation of propionaldehyde (an internal hydrogen transfer reaction of acrolein). 3-Methylbutanol reacts with ethyl and isopropyl alcohols on a copper-on-pumice catalyst at temperatures of 200° and above.¹² The dehydrogenation of ethyl alcohol goes faster than the interchange reaction under these conditions. Nickel-on-pumice gives simi-

(11) S. A. Ballard, H. D. Finch, and D. E. Winkler, *Advan. Catalysis*, **9**, 754 (1957).

(12) S. Malinowski and T. Kobylinski, *J. prakt. Chem.*, **14**, 34 (1961).

lar reactions but at lower temperatures. Because of the temperatures involved, it was not clear whether these reactions proceeded by the independent progress of reactions 3 and 4 or by a direct surface reaction (5). Still other hydrogen transfer reactions are known and one example is the formation of benzene derivatives during the hydrogenation of cyclohexenes.¹³

Although, in our experiments, acetone was formed in quantities well in excess of the equilibrium quantity in reaction 4, sufficient reduction in space velocity should bring the system into equilibrium with regard to all three reactions, 3, 4, and 5. This was indeed observed in run A-2 of Table I.

The rate of reaction 3 is greater than the net rate of hydrogenation. In B-4, for example, 11.6% acetone and 16.0% 2-butanol were formed. The net % hydrogenation was thus 4.4, and the ratio, (rate of reaction 3)/(rate of net hydrogenation), was $11.6/(16.0 - 11.6) = 2.6$. This value is probably a little low because of preferential loss of acetone. Similar data for several runs are given in Table V.

TABLE V

RELATIVE RATES OF HYDROGENATION AND ALCOHOL-KETONE PAIR INTERCHANGE				
Run	B-4	B-5	B-6	B-3
Temp., °C.	136	139	138	131
Reactant	Azeo	C ₄ one	Azeo	Azeo
Rate hydrogenation, mmoles/hr./g.	1.7	2.3	2.5	0.8
<u>Rate reaction 3</u>	2.6	...	2.3	2.4
Rate hydrogenation				

The ratio of the rates of the two reactions is also 2.5 at 149° (run B-11) but it appears to be lower at 115° where the data of run B-2 give 1.3. Reaction of a mixture of 2-butanol and 3-pentanone at 150° (run B-10) also gives 2.5. With ethyl and propyl alcohols reaction 3 is relatively much slower if, indeed, it occurs at all. This could be related to a much smaller equilibrium constant for the dehydrogenation of ethyl alcohol.¹⁴

Reaction 3 was also investigated on a palladium-alumina catalyst at 96–130°. Ratios C₃one/C₃alc were obtained which were considerably in excess of those corresponding to equilibrium in reaction 4. At 118°, values of 0.5 were reached. At this temperature, (rate of reaction 3)/(rate of hydrogenation) was about 1.5. However, the dehydrogenation reaction was accompanied by hydrogenolysis to a degree which made interpretation of the results difficult. Accordingly, further study of palladium catalysts was abandoned.

Reaction 3 was also investigated in the liquid phase at about 77° using nickel-kieselguhr. During reaction, a stream of nitrogen passed through the liquid containing the suspended catalyst. The reaction conditions are analogous to those employed by Claes and Jungers¹⁵ in the study of the dehydrogenation of secondary alcohols by nickel. After reduction and before use, the nickel-kieselguhr was swept with nitrogen at 450°. Any reaction, then, should not depend upon the presence of added hydrogen. Reaction 3 was found to be very much more rapid than reaction 4 under these conditions. Similar alcohol-ketone interchange occurs when cyclohexanone is refluxed in toluene with such alcohols as cholesterol, benzhydrol, and fluorenol in the presence of Raney nickel.¹⁶

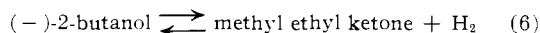
(13) For a recent example, see S. Siegel and G. V. Smith, *J. Am. Chem. Soc.*, **82**, 6082 (1960).

(14) This equilibrium constant seems not to be known very accurately, but at 100–140° it is about 0.01 that of the dehydrogenation of isopropyl alcohol: K. S. Pitzer and W. Weltner, Jr., *ibid.*, **71**, 2842 (1949).

(15) F. Claes and J. C. Jungers, *Bull. soc. chim. France*, 1167 (1958).

Racemization of Optically Active 2-Butanol.—When (–)-2-butanol and hydrogen are passed over the copper catalyst, the recovered alcohol is partially racemized. In Fig. 1, the triangles represent the loss in rotation, $\Delta\gamma/\gamma_0$, plotted against the fraction dehydrogenated, α . Temperatures were in the range 153 to 158°, 10 of the 14 points being between 154 and 156°. At 155°, α_{eq} is 0.17.⁸

The initial slope of $\Delta\gamma/\gamma_0$ vs. α appears to be finite although our values for $\Delta\gamma$ are not accurate enough to establish this completely. Different experimental techniques would be needed to establish the initial slope rigorously. The racemization approaches unity at about the equilibrium conversion. Progress of the reaction



must generate racemic 2-butanol since methyl ethyl ketone is incapable of optical activity. Reaction 6 requires that the racemization go to unity as α approaches α_{eq} .

In deriving a functional relation between $\Delta\gamma/\gamma_0$ and α according to eq. 6 let us assume that

$$\text{rate forward reaction/rate reverse reaction} = K' \quad (7)$$

where K' is the reciprocal of the equilibrium constant for eq. 6. If we consider that hydrogen is in such large excess that the change in its pressure may be ignored ($p^0_{\text{H}_2}/p^0_{\text{alc}}$ was 33) then

$$r = k\phi \left(1 - \frac{K'\alpha}{1-\alpha} p^0_{\text{H}_2} \right) \quad (8)$$

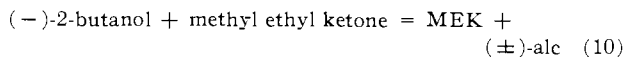
where r is the rate of the forward reaction, k is a rate constant, and ϕ is a function of the partial pressures of reactants and products. By the method previously employed,⁷ it follows that

$$\ln \frac{\gamma}{\gamma_0} = -\ln(1-\alpha) + \alpha_{eq} \ln \left(1 - \frac{\alpha}{\alpha_{eq}} \right) \quad (9)$$

The thin dashed curve of Fig. 1 represents this function. The observed degree of racemization far exceeds that resulting from eq. 9.

A similar result was observed previously in experiments in which pure (–)-2-butanol rather than a mixture of (–)-2-butanol in hydrogen was passed over a copper catalyst.⁷

However, since we now know that alcohol-ketone pair interchange occurs rather rapidly on copper catalysts at the temperatures under consideration, we must consider the possible occurrence of additional racemization *via* the reaction



where products and reactants are in the gas phase. Under the conditions of Table V, the rate of this reaction would be 2.5 times that of methyl ethyl ketone hydrogenation. For the purpose of setting an upper limit let us assume that this same factor would apply to the ratio of the rates of reactions 10 and the reverse of reaction 6 even though concentrations of methyl ethyl ketone would be much lower. This would make the rate of formation of racemic alcohol 3.5 times that implicit in eq. 8 and

$$\ln \frac{\gamma}{\gamma_0} = 3.5 \left[-\ln(1-\alpha) + \alpha_{eq} \ln \left(1 - \frac{\alpha}{\alpha_{eq}} \right) \right] \quad (11)$$

Equation 11 is plotted as the thin full line in Fig. 1. It does not appear likely that any combination of reactions 6 and 10 can account for the racemization which is observed at low values of α . In both eq. 9 and 11, the initial slope of $\Delta\gamma/\gamma_0$ is zero, *i.e.*, both equations reduce to an equation of the form $\Delta\gamma/\gamma_0 \propto \alpha^2$ at small

(16) E. C. Kleiderer and E. C. Kornfeld, *J. Org. Chem.*, **13**, 455 (1948).

values of α . Yet, from the experimental data, initially $\Delta\gamma/\gamma_0$ seems to be proportional to α .

Equation 7 is not necessarily valid.¹⁷ In fact, K' may appear raised to any power. Thus, eq. 7 may not apply to eq. 6; *i.e.*, the stoichiometric number of eq. 6 may not be unity. Alternatively, some additional process may contribute to the racemization.

Figure 2 is the same as Fig. 1 but for a reaction temperature of about 135°. The full line represents the smoothed data from Fig. 1. Racemization rises toward unity at an appropriately smaller value of α_{eq} . At the lowest values of α , the degrees of racemization are nearly the same at the two temperatures.

Racemization and Exchange in the Presence of Deuterium.—Figures 1 and 2 show by filled circles the degree of racemization observed in the presence of deuterium. At higher values of α , the racemization is much less than with hydrogen, but at low values of α it is nearly the same. In fact, our data are not sufficiently precise to exclude the possibility that hydrogen and deuterium may give the same degree of racemization at the lowest conversions.

At both temperatures, conversions exceeding $\alpha/\alpha_{eq} = 1.00$ were readily obtained. Fortunately, this does not violate the second law of thermodynamics; rather it represents an uncommonly observed kinetic isotope effect. The forward reaction of eq. 6 proceeds as indicated, but the reverse reaction involves the addition of deuterium to methyl ethyl ketone. As shown by Kemball and Stoddart, this is distinctly slower than the addition of hydrogen.⁶ Presumably, at still slower flow rates, all of the alcohol would become deuterated and α/α_{eq} would drop to that which results from the equilibrium isotope effect.

Samples obtained in the racemization studies were separated by gas chromatography into alcohol and ketone and examined mass spectrographically. Under our conditions, as described in the Introduction, one would expect the hydrogen atom of the hydroxyl group of 2-butanol to have exchanged to equilibrium during reaction. However, the deuterium atom introduced was replaced by hydrogen during the course of analysis as described under Experimental. Thus, the isotopic distributions of Table II ignore any exchange in hydroxyl.

As will be seen from Table II, the concentration of 2-butanol- d_1 is much larger than those of d_2 , d_3 , and d_4 . Since d_0 computed from $C_2H_5CHOH^+$ and from CH_3CHOH^+ are nearly identical, d_1 is essentially $C_2H_5CDOHCH_3$ and d_2 , d_3 , and d_4 consist of this species with one or more additional deuterium atoms substituted in the alkyl side chains. Thus, the total percentage of molecules containing the group $-CDOH-$ is $d_1 + d_2 + d_3 + d_4$ and that containing the group $-CHOH-$ is d_0 . These results accord with those of previous workers.⁴⁻⁶ Correspondingly, the degree of exchange of butanone is small relative to that into 2-butanol (there is no possibility of deuterium at carbon atom 2).

The use of 2-butanol rather than isopropyl alcohol or acetone does give us some new information of potential mechanistic interest: the probability of introducing deuterium into a methyl group is about twice that into an ethyl group.

The principal purpose of these experiments with deuterium was comparison of the rate of racemization with that of isotopic exchange. As shown in Table III, over a wide degree of conversion, the fraction racemized is equal to the fraction of molecules which underwent

exchange. Thus, racemization and exchange occur by a common process and introduction of deuterium at carbon atom 2 leads to racemization and not, for example, to inversion of configuration in which the fraction racemized would be twice the fraction exchanged.

The Alcohol-Ketone Pair Interchange in the Presence of Deuterium.—As shown in Table IV, the chemical course of the alcohol-ketone pair interchange is little changed by replacing hydrogen by deuterium. However, about 96% of the 2-butanol product contains deuterium at carbon atom 2.

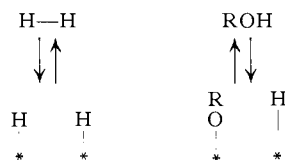
Mechanism.—It is difficult to see how isotopic exchange between deuterium and the hydroxylic hydrogen atom on an alcohol can avoid involving adsorbed hydrogen atoms as an intermediate. Since the exchange reaction is very rapid, adsorption and desorption of hydrogen must be rapid and the surface pool of hydrogen and deuterium atoms must be essentially in equilibrium with the gas phase. As is well known, this is not usually true during the hydrogenation of olefins on metallic catalysts (although there are no data for copper) but it is true during the exchange between alkanes and deuterium.

Considering that the deuterium gas originally contains about 1% HD and that additional hydrogen is introduced from the exchange of the hydroxylic hydrogen atoms and from some exchange in the other hydrogen atoms of 2-butanol, the 96% introduction of deuterium during the alcohol-ketone pair interchange indicates that the deuterium atom originates from some species in equilibrium with gas phase deuterium. The near identity of racemization and exchange (Table III) also indicates that the hydrogen atom introduced during exchange comes from some species in equilibrium with gas phase deuterium.

The formation of ketone and alcohol isotopically exchanged on the side chains is slow compared to the other reactions. Let us disregard it at this point. Then the conclusions which appear to be of key mechanistic interest with respect to reaction on copper at 110–160° are: (a) Isotopic exchange on the hydroxylic hydrogen atom of 2-butanol is very rapid.⁶ (b) Hydrogen adsorption and desorption are very rapid. (c) At low conversions, racemization of 2-butanol appears to be about proportional to the fraction dehydrogenated, α . (d) Racemization and the exchange of the hydrogen atom at carbon atom 2 occur at identical rates. (e) The degree of racemization at a particular value of α is nearly the same with either hydrogen or deuterium at low conversions, but racemization is much less in the presence of deuterium at high conversions. (f) The alcohol-ketone pair interchange reaction proceeds as a coupled reaction. (g) The alcohol-ketone pair interchange reaction is faster than hydrogenation-dehydrogenation. (h) The hydrogen atom which is transferred during the alcohol-ketone pair interchange has been equilibrated with the surface hydrogen-deuterium atom pool.

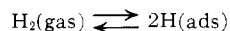
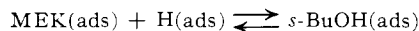
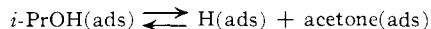
It should be emphasized that we assume in item a that copper would give the same result as those metals for which item a has actually been demonstrated.⁶

If we assume that rapid isotopic exchange of the hydroxylic hydrogen atom (items a and b) proceeds by a conventional mechanism, then the following reactions are much more rapid than those which determine the rates of formation of ketone and racemic 2-butanol-2- d .



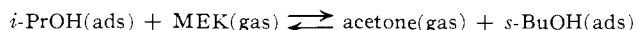
(17) A. A. Frost and R. G. Pearson, "Kinetics and Mechanism," 2nd Ed., John Wiley and Sons, Inc., New York, N. Y., 1961, p. 191; M. Manes, I. J. F. Hofer, and S. Weller, *J. Chem. Phys.*, **18**, 1355 (1950); J. Horiuti, *Advan. Catalysis*, **9**, 339 (1957); C. Bokhoven, M. J. Gorgels, and P. Mars, *Trans. Faraday Soc.*, **55**, 315 (1959).

One might imagine the alcohol-ketone interchange to occur consequent to the reactions

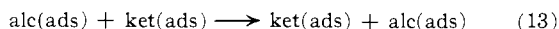


Here, we assume that adsorbed ketone has the same formula as gas phase ketone but that adsorbed alcohol has lost one hydrogen atom. This assumption does not, however, affect the validity of the argument. If, now, the third reaction is much slower than the others, the second reaction consumes hydrogen and lowers the free energy of adsorbed hydrogen well below that of $1/2\text{H}_2$ in the gas phase. Accordingly, the first reaction shifts to the right and acetone appears in the gas phase in concentrations exceeding the equilibrium constant for isopropyl alcohol dehydrogenation. However, as shown above, the third reaction must be fast, so this mechanism may be excluded.

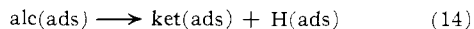
If one also excludes exotic elementary reactions of the type



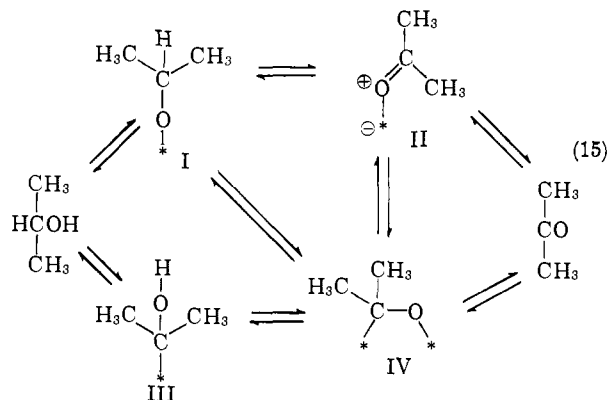
then one must conclude that there is not just a single surface intermediate common both to alcohol and to ketone. Thus, the following reaction must occur although not necessarily in one step.



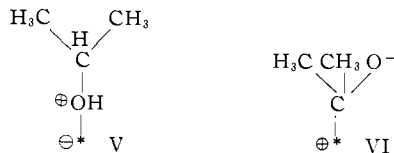
Further, it must be faster than the following reaction if it is to disturb the equilibrium in that reaction and lead to yields of ketone in excess of equilibrium for that reaction considered alone.



If, as we have argued, hydrogen adsorption-desorption is fast, it follows that species adsorbed at the carbon atoms of the side chains play no major role. There are not, then, many possibilities for adsorbed alcohol and ketone



Of the following adsorbed species

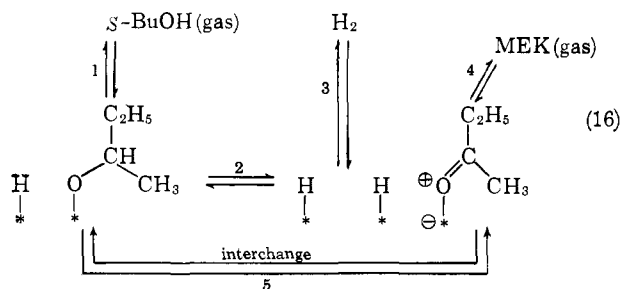


V should rapidly interconvert with I and should be less stable than I; VI should rapidly interconvert to and should be less stable than IV. Accordingly, we shall ignore V and VI, although V might be the precursor of I and VI might be an intermediate between III and IV.

Species II is a planar molecule with a quite different geometry from IV. Compounds II and IV may, then, interconvert slowly although, in the absence of detailed knowledge about surface geometry, it is difficult to

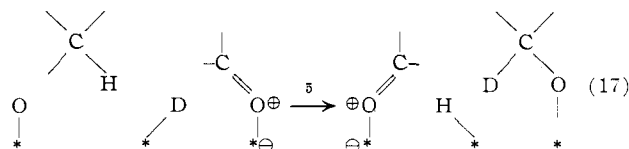
estimate how difficult the isomerization of II to IV might be.

Since species I is necessary for the exchange of the hydroxylic hydrogen atom by a conventional mechanism (eq. 12), it is tempting to assume that it is the important form of adsorbed alcohol and that interconversion of gas phase alcohol and species III is slow. Complexes of Lewis acids and ketones constitute homogeneous analogies to species II. Species II is a symmetric species which can be used to explain the racemization of 2-butanol. Furthermore, hydride ion transfer to carbon atom 2 converts it to species I as in the Meerwein-Ponndorff reaction. The over-all reactions can be represented by the scheme



Here, reactions 1 and 3 are very fast and reaction 2 is the slowest. The sequence 1, 2, 3, and 4 gives dehydrogenation. Reaction 5 gives the alcohol-ketone pair interchange reaction. Since the adsorbed ketone is incapable of optical activity, reactions -2 and 5 generate racemic 2-butanol and the rate of racemization will equal the sum of the rates of reactions -2 and 5.

Since isotopic exchange of the hydroxyl hydrogen atom is very much faster than that of the hydrogen atom at carbon atom 2, the great majority of species I is devoid of deuterium at low conversions; *i.e.*, species I is essentially in equilibrium with gas phase 2-butanol. In view of item h of conclusions, the interchange reaction is unlike the Meerwein-Ponndorff reaction to the extent that a hydride ion is not transferred directly from I to II. A hydride ion leaves I and a deuteride ion adds to II. Perhaps the packing on the surface is such that a direct transfer is difficult and the process proceeds thus



In a sense this involves the concerted progress of steps 2 and -2 of eq. 16. Reaction 17 also satisfies requirement d. We have not seen how to satisfy requirements d and h by any conventional mechanism employing the species of eq. 15. In particular, species II, being optically inactive, is the only species which can lead directly to racemization. As has been shown, requirement c excludes gas phase ketone from being the only source of racemization. Mechanisms 16 and 17 seem to accord with c. In Langmuir-Hinshelwood kinetics, the rate of formation of ketone is

$$k_4\theta_K - k_{-4}\theta_*p_K \quad (18)$$

The rate of formation of racemic 2-butanol is

$$k_{-2}\theta_K\theta_H + k_5\theta_K\theta_A\theta_H \quad (19)$$

whence

$$\frac{d\gamma/d\alpha}{\gamma} = \frac{1}{1-\alpha} \left(\frac{k_{-2}\theta_K\theta_H + k_5\theta_K\theta_A\theta_H}{k_4\theta_K - k_{-4}\theta_*p_K} \right)$$

Thus, at low conversions

$$\frac{d\gamma/d\alpha}{\gamma} = \frac{\theta_H(k_{-2} + k_5\theta_A)}{k_4} \quad (20)$$

It is not easy to assess the isotope effect to be expected of eq. 20. It is not entirely clear, therefore, that eq. 16 and 17 would predict that the isotope effect at low conversions would be small, requirement e.

We have been able to place a number of restrictions upon the nature of the mechanisms which operate in these reactions and these establish that the mechanism previously advanced, eq. 1, is unsatisfactory for copper and probably for palladium and nickel. Mechanism 16 + 17 is a possible alternative, but further work will be necessary to elaborate and test it. It does, however, exemplify most of the features necessary in any mechanism for these reactions. It hardly seems worthwhile at this time to discuss the more complicated mechanisms which can be devised. One should mention, though, that a symmetric adsorbed species is not the only way in which racemization can be achieved. Thus, in eq. 15, one might imagine the interconversion of I to IV to involve two paths, one leading to retention and the other to inversion of configuration. This concept has been advanced by Rooney, Gault, and Kemball for similar stereochemical purposes.¹⁸ In attempting to apply this, we have seen no *simple* way to avoid the assumption that the rates of the two processes are accidentally identical at both 135 and 156°. While not impossible, this is not very attractive.

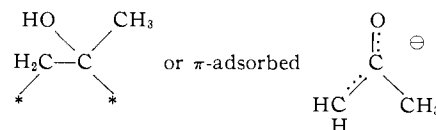
Exchange in Side Chains.—As shown in Table II, at low conversions the ratio

$$\frac{\text{fraction of reacted 2-butanol exchanged in side chains}}{\text{fraction of 2-butanone exchanged in side chains}} \approx 1.5$$

(18) J. J. Rooney, F. G. Gault, and C. Kemball, *Proc. Chem. Soc.*, 407 (1960).

In computing the numerator of this expression, we sum d_2 , d_3 , and d_4 and divide by $1 - d_0$. Thus the reaction which leads to multiply exchanged species is more closely associated kinetically with adsorbed alcohol than with adsorbed ketone. The amount of multiply exchanged alcohol is too small to decide whether it is racemic or not. Further, the multiple exchange reaction might proceed by some side reaction on special sites. If, however, it proceeds by a branching from mechanism 16, the branch is not directly from species I of 15 because this would make the ratio much larger than 1.5, species I being essentially in equilibrium with vapor phase 2-butanol. Nor could the branching be direct from species II since, then, the ratio would be less than unity.

In any case the most likely species leading to multiple exchange are⁶



If one of these is to be associated with mechanism 16 it seems necessary to assume that IV is an intermediate in the interconversion of species I and II and that IV converts to I somewhat more rapidly than II; IV could readily convert to either of the two possible intermediates pictured above by conventional processes.

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[CONTRIBUTION FROM THE PULP MILLS RESEARCH, THE INSTITUTE OF FOREST PRODUCTS, DEPARTMENTS OF CHEMISTRY AND CHEMICAL ENGINEERING, UNIVERSITY OF WASHINGTON, SEATTLE, WASH.]

Lignin. XII.¹ The High Resolution Nuclear Magnetic Resonance Spectroscopy of Protons in Compounds Related to Lignin

BY CHARLES H. LUDWIG, BERNARD J. NIST, AND JOSEPH L. MCCARTHY

RECEIVED JULY 12, 1963

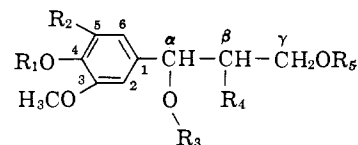
The chemical shifts of n.m.r. signals from protons in a number of compounds related to gymnosperm lignins have been determined. Evidence has been found supporting the presence of stable hydrogen bonds between the α -hydroxyl and β -ether groups in arylglycerol β -aryl ether type model compounds. The n.m.r. of dehydrodiconiferyl alcohol indicates a *cis* configuration in its furan ring. The diequatorial configuration of pinoresinol is confirmed by n.m.r. characteristics. The potential utility of n.m.r. for studies on lignin structures is demonstrated.

Introduction

In spite of numerous investigations summarized in recent reviews²⁻⁴ the chemical structures of plant lignins have remained incompletely known. While it is generally agreed that lignins represent polymeric materials composed of various phenylpropane units bonded together by a complex system of ether and carbon-to-carbon linkages, the nature of this bonding system has remained a matter of more or less well-founded speculation.²⁻⁴

The phenylpropane, C₉, units as they are visualized to exist in the lignin macromolecules (Fig. 1) contain protons connected with carbon and oxygen atoms that give signals with widely varying τ -values in the n.m.r. spectrum. In view of the potential usefulness of these signals for studies on the structure of lignins, the n.m.r. spectra of a number of small molecular weight lignin

model compounds were determined in order to obtain



R₁ = H, C'_β, or C'_α
 R₂ = H, OCH₃, C'_β, or C'₅
 R₃ = H, C'_α, C'_γ, C'₄, or linkage with polysaccharides
 R₄ = OC'₄, C'₅, or C'_β
 R₅ = H or C'_α

Fig. 1.—Some probable linkages in lignins.

information applicable to the more complex lignin spectra which are to be reported in a forthcoming publication.

The model compounds used are enumerated in Table I. Of these, the dimeric models VI_d, VII_a, VII_d, and VIII_c are particularly interesting, because they represent structures indicated to be present in the lignin macromolecules.^{2,3} Similarly, a linkage of the 5-5' type in IX_a is thought to be a common occurrence in lignins.⁵

(1) J. Moacanin, H. Nelson, E. Back, V. F. Felicetta, and J. L. McCarthy, *J. Am. Chem. Soc.*, **81**, 2054 (1959).

(2) E. Adler, *Paperi Puu*, **43**, 634 (1961).

(3) K. Freudenberg, *Pure Appl. Chem.*, **5**, 9 (1962).

(4) E. F. Brauns, *Holzforchung*, **16**, 97 (1962).