The polymeric product is light (flesh) in color; a benzopyrilium salt of this kind would be very dark in color (purple, dark maroon or black). Moreover, it contains no halogen and must therefore have the structure (X). This result is rather unexpected if the ease of ring closure of 2-hydroxychalcones to flavilium salts and the difficulty of ring closure of 2'-hydroxychalcones to flavanones are recalled by way of analogy.

It is understood, of course, that analogs of lignin having the same polymeric structure as (IV) may well occur naturally. It is also possible, but not nearly so probable, that polymers having the same structure as (X) may be found.

Experimental

Fries Rearrangement of *p*-Acetoxybenzaldehyde.—*p*-Acetoxybenzaldehyde (10 g., 1 mol.) was dissolved in dry nitrobenzene (50 g.) and anhydrous aluminum chloride (18 g., 2 moles) added portionwise, with shaking, over five minutes. The reaction mixture was heated to 110–120° for ninety minutes, cooled and decomposed with dilute hydrochloric acid (200 cc., 5%). The nitrobenzene was removed by steam distillation and the light brown, amorphous reaction product collected. It was difficultly, or only very slightly if at all, soluble in ethanol, acetone and dioxane; totally insoluble in ether, hydrocarbons, and halogenated solvents. Finally, for purification, it was dissolved in dilute (1 to 2%) alkali and reprecipitated by filtering into ice cold dilute (*ca.* 3%) hydrochloric acid. After several reprecipitations the pink, near gelatinous, material was collected, washed with water until free of acid, and dried completely (twenty days, 23 mm., potassium hydroxide). As anticipated, the wet material was easily soluble in sodium bisulfite solution (*ca.* 10%), the dried material much less so, and the solubility diminished as aging proceeded.

Anal.[4] Calcd. for $(C_9H_6O_2)_n$: C, 74.0; H, 4.11. Found: C, 74.2, 73.7; H, 4.6, 4.5.

Methylation of 2,6-Polydihydrobenzopyrone.—2,6-Polydihydrobenzopyrone (2 g.) was dissolved in 10% aqueous sodium hydroxide (40 cc.). At the temperature of the steam-bath, dimethyl sulfate (12 g.) was added portionwise with shaking. Then, with heating and shaking, a further quantity of dimethyl sulfate (24 g.) was added in portions and the reaction mixture kept alkaline by addition of portions of 20% aqueous sodium hydroxide as needed. Finally the alkali insoluble reaction product was collected, washed, and dried.

Anal. Calcd. for $(C_9H_5O.OCH_3)_n$: "OCH_3," 19.37. Found: "OCH_3," 19.8, 20.1.

Fries Rearrangement of Salicylaldehyde Monoacetate.—Salicylaldehyde monoacetate (12.3 g., 1 mol.) was dissolved in dry nitrobenzene (75 cc.) and anhydrous aluminum chloride (20.2 g., 2 mol.) added portionwise, with occasional shaking, over ten minutes. The reaction mixture was held at 120° for an hour, cooled and decomposed with ice cold dilute hydrochloric acid (400 cc., 3%). After removal of the nitrobenzene by steam distillation, the light (flesh) colored solid was collected, washed with water until free of acid, and reprecipitated three times with water from solution in acetone. After drying, it formed a fawn-colored amorphous solid, somewhat soluble in acetone, rather insoluble in ethanol and dioxane, and insoluble in hydrocarbon and halogenated solvents. It showed the same solubility characteristics in aqueous sodium bisulfite as the analogous polymers already described.

Anal. Calcd. for $(C_9H_6O_2)_n$: C, 74.00; H, 4.11. $C_9H_8O_3$: C, 65.9; H, 4.87. Found: C, 71.0, 71.2; H, 4.57, 4.59.

Summary

The polymerization reaction used in the synthesis from vanillin of a polymeric material having the structure proposed for spruce lignin has been extended to the preparation of analogous polymeric materials from *o*- and *p*-hydroxybenzaldehydes.

PEORIA, ILLINOIS RECEIVED MARCH 19, 1948

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[4] Analyses are microdeterminations by C. H. Van Etten and Mary B. Wiele of this Laboratory.

[CONTRIBUTION FROM THE DEPARTMENTS OF CHEMISTRY OF TRINITY COLLEGE AND NORTHWESTERN UNIVERSITY]

Catalytic Racemization and Dehydrogenation of Optically Active Secondary-butyl Alcohol by Copper and by Zinc Chromite

BY ROBERT L. BURWELL, JR.

Optically active *s*-butyl alcohol is both racemized and decomposed in passage over certain catalysts.[1] Copper gives pure dehydrogenation and a distinctly smaller ratio of racemization to decomposition than that found with other catalysts. Zinc chromite exhibits dehydrogenation accompanied by a small amount of condensation and a large amount of racemization. It could not be decided, particularly for copper, whether racemization resulted solely from inactive alcohol produced by hydrogenation of the dehydrogenation product, methyl ethyl ketone.

Dehydrogenation of alcohols by copper was extensively investigated in the classical work of Palmer and Constable[2,3,4] though this work was largely confined to primary alcohols. Certain kinetic data dealing with the dehydrogenation of secondary alcohols by copper do, however, exist: isopropyl alcohol,[3,5,6] *s*-butyl alcohol,[6,7] cyclohexyl alcohol,[3,5] and 2-octanol.[6]

Analogous kinetic studies with zinc chromite have not been reported but this substance has

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[1] Burwell, THIS JOURNAL, **59**, 1609 (1937).

[2] Palmer, *Proc. Roy. Soc.* (*London*), **98A**, 13 (1920).

[3] Palmer and Constable, *ibid.*, **107A**, 255 (1925).

[4] Constable, *ibid.*, **107A**, 279 (1925).

[5] Balandin, Marushkin and Ikonnikov, *Uchenye Zapiski Moskov. Ordena Lenina Gosudarst. Univ. im. M. V. Lomonosova*, **2**, 221 (1934); *Chem. Centr.*, **106**, II, 1528 (1935).

[6] Neish, *Can. J. Research*, **23B**, 49 (1945).

[7] Balandin and Liberman, *Compt. rend. acad. sci. U. R. S. S.*, **28**, 794 (1940).

been shown to hydrogenate ketones and aldehydes[8,9,10,11] with the accompaniment usually of some condensation. Required temperatures were considerably above those used in Ref. 1.

Since the degree of maintenance of configuration of *l*-*s*-butyl alcohol is conditioned by the nature of processes which affect the carbinol carbon atom, quantitative study of the rates of racemization with simultaneous measurement of rates of dehydrogenation should assist in elucidating the mechanisms of both reactions.

Experimental

Materials.—Butanol-2 was partially resolved by the method of Viditz,[12] dried by refluxing with lime and distilled through a Vigreux column, $\alpha^{31.5}\text{D}$ −3.96°. Inactive *s*-butyl alcohol, isopropyl alcohol and *n*-propyl alcohol (Eastman Kodak Company) were given the same final purification.

The copper catalyst was made by reducing 0.55 g. of 20 to 40 mesh Schering-Kahlbaum "Copper Oxide for anal." with hydrogen at 260° for four hours. Professor P. W. Selwood and Dr. H. Morris kindly investigated the magnetic properties. Upon reduction with hydrogen at 150° for twenty-four hours, the copper was ferromagnetic, exhibiting a specific susceptibility of 282 × 10^{-6} in a field of 1000 gauss. 0.1% iron could account for this. They also found that at 100° the material was ineffective in hydrogenating benzene at a contact time of fifteen seconds.[13]

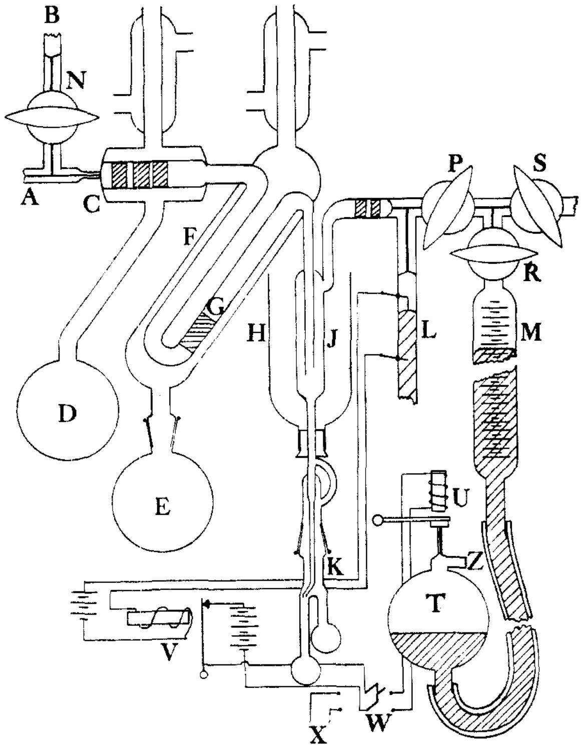

Fig. 1.—Apparatus.

The zinc chromite catalysts were prepared by reducing at 420° 0.27 g. (0.57 cc.)[14] of ignited zinc ammonia chromate.

Apparatus.—The apparatus is shown in Fig. 1. Alcohol fed into the system at A from a feed device which displaced alcohol by gases evolved by electrolysis of caustic solution.[15] A tiny gas flame played on the small capillary just before the preheater C with consequent very uniform volatilization. Chlorobenzene, boiling in bulb D, kept the preheater at even temperature. The alcohol vapors then entered the catalyst thermostat F and passed over the catalyst at G. The effluent vapor was condensed in trap J by ice in its jacket H. The liquid condensate could be distributed in any of the three receivers of collector K (only two shown).

To protect the catalyst from mercury vapor, the preheater and a section following trap J were packed with gold foil and cadmium turnings. Hydrogen evolved during the passage over alcohol was collected and measured in buret M at constant pressure. A portion of one arm of the control manometer is shown at L. When the mercury in the manometer was not touching the upper tungsten contact, no current flowed through relay V which was of the normally closed type. Consequently current flowed through the coils of the electromagnet U (a converted buzzer) holding the arm below U in the up position. Mercury had originally been forced up into the buret by compressed air supplied to the reservoir bulb T through inlet Z. As air escaped through the fine capillary above T, hydrogen was drawn into the buret. When the pressure had fallen enough to close the contact in the control manometer, the capillary leak was closed. With proper choice of capillary very smooth control was secured.

Collection in the buret was begun only after a "warm-up" period. During such periods the pressure was kept constant by turning stopcocks S and R to feed a solenoid valve connected beyond stopcock S. The valve was connected at X and was energized by switch W.

The temperature of the catalyst chamber was controlled by use of vapor baths, or above 265° by a furnace. Hydrogen or nitrogen entered at B. Hydrogen was generated electrolytically, passed over glowing platinum wire, soda-lime and calcium chloride. Tank nitrogen was passed over hot copper, soda-lime and calcium chloride.

Measurement of alcohol feed, hydrogen evolution and time gave feed rate and rate of dehydrogenation. Correction was made for the 2-butanol and 2-butanone vapors in the hydrogen. The partial pressures derived from the laws of ideal solutions were corrected by the assumption that the departure from ideality was the same as that found by Parks and Chaffee[16] for isopropyl alcohol–acetone mixtures.

From the optical rotation of the condensate determined in a semi-micro tube and its composition found as above, the degree of racemization of the alcohol was found. A calibration curve of rotation *vs.* composition was prepared from the following data giving fraction of rotation of the pure alcohol and mole fraction of methyl ethyl ketone, respectively: 0.932, 0.098; 0.864, 0.183; 0.795, 0.263; 0.692, 0.368.

Results.—Table I gives results on copper catalysts. The first series, with inactive 2-butanol, was run on one sample of catalyst; the series with active alcohol was run on a new sample. After a steady state had apparently been reached, each run was continued until 1.3–1.5 cc. of condensate had been separately collected. Precision in fraction racemized is about ±0.005, in feed rate about 1%, and in hydrogen evolved about 0.003 micromole per second. Rates of dehydrogenation were constant during any one run. The runs lasted from one to two and a half hours. Runs with "b" in the serial were direct continuations of previous runs with "a."

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[8] Lazier, U. S. Patent 1,746,783; *C. A.*, **24**, 1649 (1930).

[9] Adkins and Connor, THIS JOURNAL, **53**, 1091 (1931).

[10] Adkins, Folkers and Kinsey, *ibid.*, **53**, 2714 (1931).

[11] Vaughen and Lazier, *ibid.*, **53**, 3719 (1931).

[12] Viditz, *Biochem. Z.*, **259**, 294 (1933).

[13] For techniques, Morris and Selwood, THIS JOURNAL, **65**, 2245 (1943).

[14] This and also the copper oxide were from the batches employed in ref. 1.

[15] Burwell, *Ind. Eng. Chem., Anal. Ed.*, **12**, 681 (1940).

[16] Parks and Chaffee, *J. Phys. Chem.*, **31**, 439 (1927).

TABLE I

DEHYDROGENATION AND RACEMIZATION OF *l*-2-BUTANOL ON COPPER CATALYSTS

Run	Temp., °C.	Press., mm.	Feed rate micro-moles per sec.	H_2 evolved micro-moles per sec.	Fraction dehydro-genated	Fraction racemized
1a	131.7	500	4.96	0.048	0.0097	
1b			2.52	.049	.0194	
2		250	2.44	.047	.0192	
3a	132.3	740	2.73	.058	.0213	
3b			4.71	.061	.0129	
4a		125	2.66	.048	.0184	
4b			5.19	.052	.0101	
5	155.5	125	2.94	.200	.068	
6a			4.82	.202	.042	
6b			1.72	.195	.113	
10a	132.0[a]	360	6.45	.048	.0074	Nil
10b			3.11	.040	.0130	Nil
11	155.5	360	6.60	.149	.0225	Nil
12			2.04	.122	.0597	Not found
13	184.2	360	2.04	.755	.369	0.585
14	184.4	360	6.77	1.222	.181	.173
15			2.03	0.799	.393	.690
16a			2.96	1.037	.350	.587
16b			5.70	1.351	.237	.286
17a		180	6.26	1.128	.180	.118
17b			2.89	0.984	.340	.399
18			5.75	1.156	.201	.165
19		360	5.72	1.193	.208	.219
20a	184.3	360	5.65	1.180	.209	.223
20b			2.95	0.954	.323	.524
21a	171.4	360	5.59	.501	.090	.054
21b			2.81	.449	.160	.152
22	171.7	360	5.72	.453	.079	.036
23	184.1	360	5.55	.769	.138	.068

[a] A new sample of catalyst was employed for this and subsequent runs.

Zinc Chromite.—Runs on zinc chromite were at 180 mm. and at feed rates of 5.4 micromoles per second save as otherwise noted. At feed rates of 2.0 micromoles per second, rates of dehydrogenation at 211, 238 and 265° were roughly 0.05, 0.2 and 0.9 micromoles per second. Rates rose or fell during runs in dependence upon previous history of the catalyst. Evacuating at 238° had no effect.

Racemization was negligible at 184°. In one run at 238°, 90 mm. pressure and a feed rate of 2.2 micromoles per second, the average rate of hydrogen evolution was 0.19 micromole per second, the racemization, 0.316. In the succeeding run at 238°, 180 mm. and a feed rate of 2.0, the average rate was 0.15 and the racemization, 0.274. Owing to insufficient reproducibility in rates no further samples of active alcohol were expended.

Upon flushing the catalyst with hydrogen at 400°, evacuating and cooling *in vacuo* reproducibility greatly improved and much faster rates of dehydrogenation resulted. Typical initial rates at 184 and 211° were 0.2 and 0.9 micromole per second. Rates declined steadily during runs, initially the more rapidly. A decline to about two-thirds the initial occurred in one and one-half hours. In a series of 21 successive runs on one sample, initial rates rose by a factor of about four.

Upon allowing the catalyst to cool from 400° in hydrogen, rates were, if anything, slightly increased. Several different methods of drying and purifying the alcohol gave similar results. Upon adding 1.0 and 2.3% water to the alcohol, rates resulted which were steady and nearly the same. These were about 0.25 those with dry alcohol.

Interrupting the alcohol feed for several minutes resulted in rate decline considerably greater than that in a corresponding period with flow.

Behavior of isopropyl alcohol was similar. Initial rates appeared 20% lower but they declined much less during a run. Normal propyl alcohol exhibited the same general characteristics but temperatures nearly 100° higher were needed for equivalent rates. Temperature of run, rate during first ten minutes and rate from fifty to sixty minutes were: 184°, 0.015 micromole per second and 0.006 micromole per second; 211°, 0.031 and 0.011; 238°, 0.076 and 0.040; 264°, 0.15 and 0.11; 283°, 0.30 and 0.24. The corresponding adjacent values for initial rates with *s*-butyl alcohol are 184°, 0.29; and 211°, 0.92.

Discussion

The activity of the second copper catalyst apparently increased slightly at first and then declined slowly. A more pronounced decline followed run 21. However, the catalyst was in use over thirty hours. Palmer and Constable[3] had found that impurities in certain alcohols poisoned their copper catalysts rapidly. In view of the exhaustive purification to which the acid *s*-butyl ester of phthalic acid was subjected during its resolution, such is probably not the origin of the decline observed in this case.

As shown in Table I, the rate of dehydrogenation is nearly but not quite zero order at low conversions (runs 1–6, 16b, 17a, 18 and 19). It seems to rise slightly with pressure. It falls with increasing α much more rapidly than the reverse reaction can account for if a zero order reaction is assumed. Inhibition is less at lower pressures (run 17).

For any given sample of catalyst the rate of dehydrogenation will be

$$r = k\phi(1 - pK'\alpha^2/(1 - \alpha^2)) \qquad (1)$$

where α is the fraction of alcohol dehydrogenated, K' is the reciprocal of the equilibrium constant at constant pressure for the reaction

$$\text{alcohol} = \text{ketone} + \text{hydrogen}$$

p is the total pressure, ϕ is a function of the partial pressures of reactant and products, and k is a function of temperature.

In this paper, rates are expressed in terms of moles per sec. Values of K' have been taken from Kolb and Burwell.[17]

Data much more extensive than those on dehydrogenation accumulated in these racemization studies will be needed uniquely to fix the form of ϕ in equation (1), but it must approximate unity at low values of α and it must decline with increasing α (inhibition by reaction products).

Palmer and Constable[2,4] reported rates of dehydrogenation of ethyl and isopropyl alcohols to be zero order and independent of feed rate at 216 to 275°, but α was always less than 0.1.

At greater conversions, Balandin and Liberman[7] and Neish[6] report dependence of the rate of dehydrogenation of secondary alcohols upon degree of conversion. The equations, which they propose to express this dependence, fail when applied to the present data, but the temperatures employed (particularly by Neish) were higher than those reported here. Neish's equation, which he interprets as first order, is equivalent to equation

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[17] Kolb and Burwell, THIS JOURNAL, **67**, 1084 (1945). See also Cubberly and Mueller, *ibid.*, **68**, 1149 (1946).

(1) with the reverse reaction neglected and with

$$\phi = p_{\text{alc.}}/(p_{\text{alc.}} + p_{\text{prods.}})$$

Racemization over Copper.—If L be the flow rate and V_0 the total volume of catalyst, the change in α in a layer of catalyst $\mathrm{d}V$ is

$$\mathrm{d}\alpha = \frac{r}{L}\frac{\mathrm{d}V}{V_0} = \frac{k\phi}{L}\left[1 - \frac{pK'\alpha^2}{1 - \alpha^2}\right]\frac{\mathrm{d}V}{V_0} \qquad (2)$$

The gross rate of formation of alcohol by the reverse reaction is given by the second part of equation (1).

$$r_2 = k\phi pK'\alpha^2/(1 - \alpha^2) \qquad (3)$$

$L(1 - \alpha)$ moles of alcohol of rotation γ cross a layer of catalyst $\mathrm{d}V$ per sec. An amount $r_2\mathrm{d}V/V_0$ is racemized; $r\mathrm{d}V/V_0$ is dehydrogenated. In the effluent stream there is $(L(1 - \alpha) - r\mathrm{d}V/V_0 - r_2\mathrm{d}V/V_0)$ moles of active alcohol and $(L(1 - \alpha) - r\mathrm{d}V/V_0)$ total moles of alcohol. Thus

$$\gamma + \mathrm{d}\gamma = \gamma\left(\frac{L(1 - \alpha) - r_1\dfrac{\mathrm{d}V}{V_0} - r_2\dfrac{\mathrm{d}V}{V_0}}{L(1 - \alpha) - r_1\dfrac{\mathrm{d}V}{V_0}}\right)$$

whence

$$\frac{\mathrm{d}\gamma}{\gamma} = -\frac{r_2}{L(1 - \alpha)}\frac{\mathrm{d}V}{V_0} \qquad (4)$$

Substituting for $\mathrm{d}V/V_0$ from equation (2)

$$\frac{\mathrm{d}\gamma}{\gamma} = -\frac{pK'\alpha^2\mathrm{d}\alpha}{(1 - \alpha)(1 - \kappa^2\alpha^2)} \qquad (5)$$

where $\kappa^2 = 1 + pK'$ and $1/\kappa$ is the equilibrium value of α. Integrating

$$\ln\frac{\gamma}{\gamma_0} = -\frac{pK'}{\kappa^2 - 1}\left[\frac{1}{2\kappa}\ln\frac{1 + \kappa\alpha}{1 - \kappa\alpha} - \frac{1}{2\kappa^2}\ln(1 - \kappa^2\alpha^2) + \ln(1 - \alpha)\right] \qquad (6)$$

Thus, if racemization results only from the reverse reaction, the fraction racemized is a function of total pressure, equilibrium constant and fraction dehydrogenated and is independent of feed rate and of the particular kinetics.

In the expansion of equation (6) as a power series, the first power of α which enters is the third. Consequently, racemization is small at low values of α and rises rapidly as the equilibrium value of α is approached. Racemizations so computed are far below the observed as shown in curve B of Fig. 2 where $10 \cdot \Delta\gamma/\gamma_0$ is plotted *vs.* α. The contribution of the reverse reaction is nearly negligible and some other mechanism must be involved.

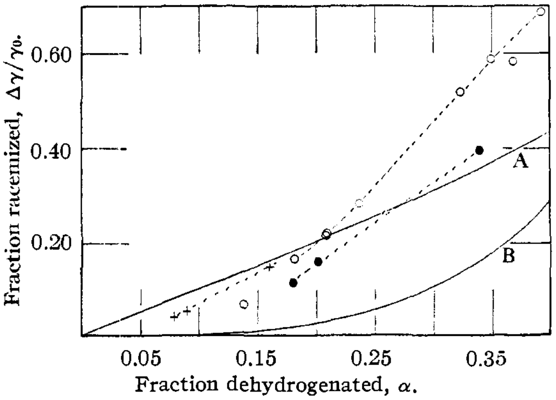

Fig. 2.—Fraction racemized *vs.* fraction dehydrogenated: ○ ○ ○, 360 mm. pressure, 184.4°; ● ● ●, 180 mm. pressure, 184.4°; + + +, 360 mm. pressure, 171.6°; Curve A, Equation (8) with $k_3/k = 1$; Curve B, Equation (6) with ordinates multiplied by ten.

If alcohol is racemized catalytically by another mechanism

$$\frac{\mathrm{d}\gamma}{\gamma} = -\frac{k_3\psi}{L(1 - \alpha)}\frac{\mathrm{d}V}{V_0} = -\frac{k_3\psi}{k\phi}\left(\frac{1 + \alpha}{1 - \kappa^2\alpha^2}\right)\mathrm{d}\alpha \qquad (7)$$

where $k_3\psi$ is the rate of formation of inactive alcohol. The right term in equation (5) must be added to this, but at lower values of α this correction is negligible.

If $\psi = \phi$

$$\ln\frac{\gamma}{\gamma_0} = -\frac{k_3}{k}\left[\frac{1}{2\kappa}\ln\frac{1 + \kappa\alpha}{1 - \kappa\alpha} - \frac{1}{2\kappa^2}\ln(1 - \kappa^2\alpha^2)\right] \qquad (8)$$

The right side of equation (6) must be added to this. Up to rather large values of α this is nearly equivalent to

$$1 - \gamma/\gamma_0 = k_3\alpha/k \qquad (9)$$

Equation (8) with k_3/k equal to unity is plotted in Fig. 2. It is evident that no value of k_3/k would fit the data.

The experimental dependence of fraction racemized upon fraction converted requires that dehydrogenation be inhibited by reaction products relative to racemization and that this relative inhibition decline at lower pressures since at a given racemization, greater dehydrogenation occurs at lower pressures. Three possibilities present themselves. (a) The racemization may proceed on a section of surface not active in dehydrogenation. (b) The adsorption which preceeds dehydrogenation involves racemization. The rate determining step in the dehydrogenation is the transformation of adsorbed alcohol into adsorbed ketone and hydrogen and this transformation is inhibited by the products. (c) Racemization proceeds by direct hydrogen exchange between adsorbed optically active alcohol and adsorbed methyl ethyl ketone to form ketone and racemic alcohol.[18] If $\psi = k_3C_{\text{alc.}}C_{\text{ketone}}$, where the C's refer to concentrations on the surface and depend upon the corresponding pressures so as to make ϕ of the form $\phi = p_{\text{alc.}}/(p_{\text{alc.}} + bp_{\text{ketone}})$ where b depends upon pressure and temperature, then all the experimental data can be reasonably well reproduced. This proposal can be checked by measuring the rate of isopropyl alcohol formation resulting from passage of a mixture of acetone and *s*-butyl alcohol over a catalyst.

Zinc Chromite.—Apparent conflict as to the temperature at which the so-called zinc chromite is catalytically active is now resolved.

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[18] This author expresses his indebtedness to Professor Frank H. Westheimer, who pointed out this possibility.

The activity at comparatively low temperatures reported by Burwell[1] results from his having evacuated the catalysts at 400° between each run. This is shown in the present investigation to remove poison which otherwise steadily diminished the activity of the catalyst. The poison seems not to be contained in the alcohol but to result from a condensation reaction such as this catalyst is known to promote.[9] The poison is not removed by evacuating at 238° but is by flushing with hydrogen at 400°. This behavior resembles that reported by Woodman and Taylor[19] in the hydrogenation of ethylene by zinc oxide.

With a freshly flushed catalyst a rate starts high and steadily declines during a run apparently coming to a steady state at a rate equivalent to a 60° decrease in temperature. The addition of water to the alcohol reduces the rate by three-quarters but eliminates the decline. Poisoning may, thus, be partly due to water produced by condensation reactions.

Considerable racemization occurs upon passing *s*-butyl alcohol over freshly evacuated catalysts.[1] It is now shown that at a higher temperature a similar process occurs on previously used and unflushed catalyst. The values of racemization and fraction converted exclude the possibility that the racemization can be the result merely of rehydrogenation of ketone. Owing to the lack of constancy in activity which appears inherent in the catalyst under these conditions it appeared fruitless to expend much optically active alcohol.

Isopropyl alcohol dehydrogenates at rates rather near those of *s*-butyl. This corresponds with previous reports[5,6] of rates of dehydrogenation of some secondary alcohols on copper. Also, *n*-propyl alcohol dehydrogenates much more slowly than the secondary alcohol, a result analogous to that of Palmer and Constable[3] on copper.

Summary

Rates of catalytic dehydrogenation and racemization of *l*-*s*-butyl alcohol have been measured simultaneously over copper and over zinc chromite catalysts.

Racemization is far more extensive than can be accounted for by the production of inactive alcohol by rehydrogenation of methyl ethyl ketone. On copper, dehydrogenation is inhibited by the reaction products relative to the racemization.

With zinc chromite, the reactions are poisoned probably by adsorption of products of concurrent condensation reactions. The activity of the catalyst is temporarily greatly increased by flushing with hydrogen at 400°. The rate of dehydrogenation of isopropyl alcohol is about equal to that of *s*-butyl while that of *n*-propyl is far less.

EVANSTON, ILLINOIS RECEIVED FEBRUARY 20, 1948

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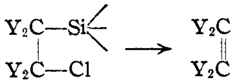
[19] Woodman and Taylor, THIS JOURNAL, **62**, 1393 (1940).

[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY AND PHYSICS OF THE PENNSYLVANIA STATE COLLEGE]

Further Studies of β-Eliminations Involving Silicon[1]

BY LEO H. SOMMER, DONALD L. BAILEY AND FRANK C. WHITMORE

The remarkable reactivity of β-carbon–chlorine bonds in β-chloroalkyltrichlorosilanes ($RCHClCH_2SiCl_3$) with dilute alkali and Grignard reagents is associated with cleavage of the carbon–silicon bond.[2] These reactions, which are β-eliminations involving silicon and halogen, take place according to the general equation



$$\begin{matrix} Y_2C{-}Si\diagup\!\diagdown \\ | \\ Y_2C{-}Cl \end{matrix} \longrightarrow \begin{matrix} Y_2C \\ \| \\ Y_2C \end{matrix} \qquad (1)$$

The present paper reports further studies of these interesting reactions as given by

β-chloroethyldiethylchlorosilane, $(ClCH_2CH_2)(C_2H_5)_2SiCl$ (I)

β-chloroethyldiethylfluorosilane, $(ClCH_2CH_2)(C_2H_5)_2SiF$ (II)

and β-chloroethyltriethylsilane, $(ClCH_2CH_2)(C_2H_5)_3Si$ (III)

Effective reagents are: alcoholic bases, aqueous alkali, water, potassium acetate in glacial acetic acid, methylmagnesium bromide, small amounts of aluminum chloride, silver nitrate in methanol, and heat alone with compound III.

It is evident from equation (1) that these reactions are formally similar to the dehydrohalogenation of ordinary organic halides. Further similarities, particularly with regard to mechanism and electronegativity relations, will be discussed below.

Experimental

β-Chloroethyldiethylchlorosilane and β-Chloroethyldiethylfluorosilane.—The synthesis and characterization of these two compounds by the chlorination of the corresponding triethylhalosilane with sulfuryl chloride and benzoyl peroxide catalyst has been described in a previous paper.[3]

β-Chloroethyltriethylsilane.—This compound was prepared by the chlorination of tetraethylsilane using phosphorus pentachloride catalyst and ultraviolet light according to the method of Ushakov and Itenberg.[4] Chlorination of tetraethylsilane with sulfuryl chloride and benzoyl peroxide catalyst gave only the α-chloro compound.

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[1] Paper XVI in a series on organosilicon compounds. For Paper XV see THIS JOURNAL, **70**, 484 (1947). Paper XVI was presented in part before the Division of Organic Chemistry, American Chemical Society, New York City, September, 1947.

[2] Sommer, Goldberg, Dorfman and Whitmore, *ibid.*, **68**, 1083 (1946).

[3] Sommer, Bailey, Strong and Whitmore, THIS JOURNAL, **68**, 1881 (1946).

[4] Ushakov and Itenberg, *J. Gen. Chem. U. S. S. R.*, **7**, 2495 (1937).