[CONTRIBUTION FROM THE LABORATORY OF ORGANIC CHEMISTRY OF THE UNIVERSITY OF WISCONSIN]

Investigation of the Properties of Alumina *ex*-Aluminum Isopropoxide as a Catalyst for Dehydrations

BY HOMER ADKINS[1] AND SPENCER H. WATKINS[2]

The properties of alumina *ex*-aluminum isopropoxide as a catalyst for dehydrations have been investigated. It was found to have an activity similar to other alkoxide aluminas derived from other aluminum alkoxides, but more than twice as great as that of a commercial alumina catalyst with respect to rate of dehydration of 1-hexanol. It was also more active in the rearrangement of carbon–carbon double bond of the resulting hexene than the commercial alumina. Alumina *ex*-aluminum isopropoxide was found to be active for certain reactions at temperatures 50° lower than were required for the commercial catalyst. Over alumina *ex*-aluminum isopropoxide at atmospheric pressure pinacolone was dehydrated to 2,3-dimethyl-1,3-butadiene. Cyclohexanone and cyclopentanone underwent disproportionation along with dehydration to form cyclohexene and phenol from the former and cyclopentene and 2-cyclopentenone from the latter. Disproportionation was also indicated in the dehydration of 2-pentanone by the formation of pentenes. Diisopropyl ketone was not dehydrated.

The reactions of oxygenated organic compounds over alumina at elevated temperatures depend not only upon the nature of the organic compound, but also to a considerable extent upon the history of the catalyst. Feachem and Swallow[3] have shown that a decrease in sodium content enhances the catalytic activity of alumina with respect to the rate of dehydration of ethanol to ethylene. Adkins and co-workers[4,5,6] have pointed out that it is advantageous to have the smallest spacings possible within the alumina crystal. Other desirable factors such as small crystal size and temperature of activation of the alumina are well established.

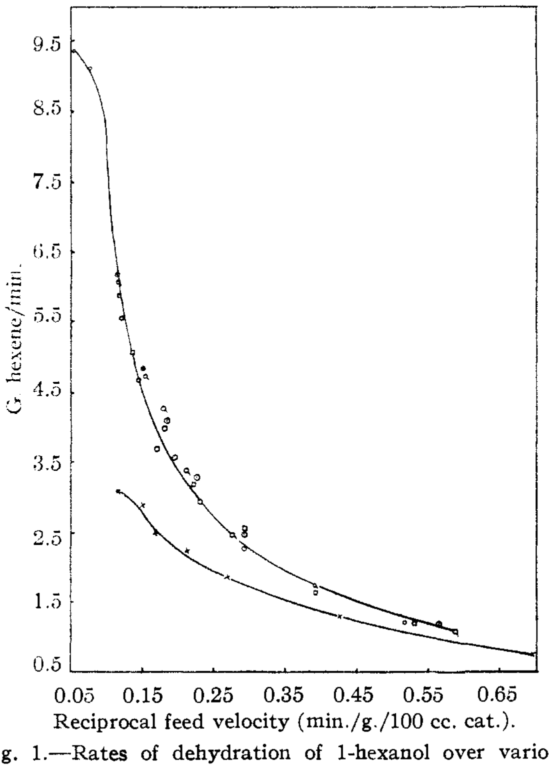


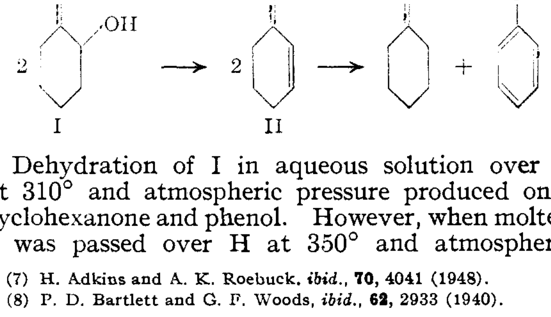
Fig. 1.—Rates of dehydration of 1-hexanol over various catalysts at 450°: ×, H; □, M; ◔, E; ○, P; ⊙, B.

This report is concerned with an investigation of the dehydrative properties of an alumina prepared by the hydrolysis of liquid aluminum isopropoxide followed by dehydration of the hydrated alumina to the active γ-form. This catalyst was used by Adkins and Roebuck[7] for the isomerization of cyclohexenes to cyclopentenes.

The alumina *ex*-aluminum isopropoxide (P) was compared with a standard commercial alumina purchased from the Harshaw Chemical Co. (H), alumina *ex*-aluminum methoxide (M), alumina *ex*-aluminum ethoxide (E) and alumina *ex*-aluminum-*t*-butoxide (B) by rate studies of the dehydration of 1-hexanol. The results are expressed graphically in Fig. 1. The dehydrations were of short duration and consequently are only roughly quantitative. However, it is apparent that the alkoxide aluminas have a similar activity but are more than twice as active as the commercial catalyst with respect to the rate of dehydration of 1-hexanol to hexene.

The hexene produced by the alkoxide catalysts was a mixture of isomers differing only in the position of the double bond whereas the hexene formed over H was very nearly pure 1-hexene. Adkins and Roebuck[7] found P to be approximately ten times as active as the standard commercial catalysts in the rearrangement of cyclohexenes to cyclopentenes and "it was also active in establishing equilibrium between hydrocarbons differing only in the position of a double bond."

Bartlett and Woods[8] reported the preparation of 2-cyclohexenone (II) in yields of 35% by the dehydration of 2-hydroxycyclohexanone (I) over alumina at reduced pressure. They obtained along with the desired product 40% yields of cyclohexanone and phenol in equal molar amounts, doubtless formed by the disproportionation of II.



Dehydration of I in aqueous solution over P at 310° and atmospheric pressure produced only cyclohexanone and phenol. However, when molten I was passed over H at 350° and atmospheric

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[3] G. Feachem and H. T. S. Swallow, *J. Chem. Soc.*, 267 (1948).

[4] H. Adkins, THIS JOURNAL, **44**, 2175 (1922).

[5] H. Adkins and P. P. Perkins, *ibid.*, **47**, 1163 (1925).

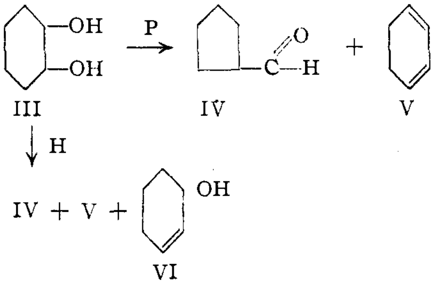
[6] H. Adkins and B. H. Nissen, *ibid.*, **46**, 130 (1924).

[7] H. Adkins and A. K. Roebuck, *ibid.*, **70**, 4041 (1948).

[8] P. D. Bartlett and G. F. Woods, *ibid.*, **62**, 2933 (1940).

pressure, yields of 20% of II, 8% of cyclohexanone and 6% of phenol per pass were obtained.

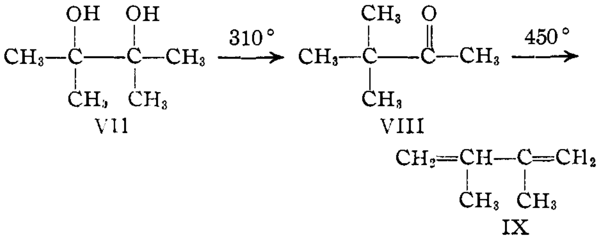
trans-1,2-Cyclohexanediol (III) passed over P at 325–340° yielded the rearranged product, cyclopentyl formaldehyde (IV), and the completely dehydrated product, 1,3-cyclohexadiene (V), in 19 and 29% yields, respectively, per pass. At 325° III was not dehydrated by H. When III was passed over H at 350°, 2-cyclohexenol (VI) was formed as the main product in a yield of 22% per pass. However, at 375° III was dehydrated by H to 27% IV, 10% V and 24% VI. Thus it is apparent that for this reaction there is a distinct temperature differential between the two catalysts.



III IV V

VI

Newton and Coburn[9] reported the preparation of 2,3-dimethyl-1,3-butadiene (IX) in good yields by the dehydration of pinacolone (VIII) over alumina at 450° and reduced pressure. In connection with a further investigation of this interesting reaction, the problem of preparing large quantities of pinacolone arose. Although the "Organic Syntheses" method[10] is satisfactory, it seemed likely that the ketone might be prepared by passing pinacol (VII) or its hydrate over alumina at a relatively low temperature. The results were quite satisfactory; the process is continuous, the reaction temperature low (310°), the yields good (85–87%), and the rate of production high (5–6 kg./l. of catalyst/hr.). The amount of water present in the starting material did not appear to affect the course of the reaction or the yields obtained.



$$CH_3-\underset{CH_3}{\overset{OH}{C}}-\underset{CH_3}{\overset{OH}{C}}-CH_3 \xrightarrow{310°} CH_3-\underset{CH_3}{\overset{CH_3}{C}}-\overset{O}{\overset{\|}{C}}-CH_3 \xrightarrow{450°} CH_2{=}\underset{CH_3}{CH}-\underset{CH_3}{C}{=}CH_2$$

VII VIII IX

The data presented in Table I show the results of varying conditions and catalysts.

TABLE I

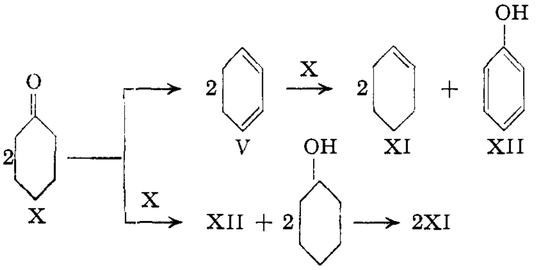
DEHYDRATION OF PINACOL

Cat.	Temp., °C.	Yield of VIII, %	Yield of IX, %
P	310	85–87	11–12
P	450	31	43
H	325	58	8
H	375	80	15

The results listed in the above table show a temperature differential between the two catalysts of over 50° for the dehydration of pinacol to pinacolone.

The work of Newton and Coburn on the dehydration of VIII to IX was repeated. Comparable results were obtained with 100 cc. of H as well as with the 300 cc. of catalyst prescribed by those workers. At atmospheric pressure the yields of IX amounted to only 5–10%. Over P, VIII was dehydrated to IX in 57–71% yields at 450° and atmospheric pressure; reducing the pressure did not improve the yield of diene.

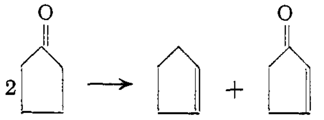
Extending this work to other ketones, cyclohexanone (X) was converted to cyclohexene (XI) and phenol (XII) in the ratio 2:1 over P at 450°. The total yield of these products was 63% based on the amount of X not recovered. The formation of XI and XII may result from the initial formation of cyclohexadiene (V), which is converted by further reaction with X to the products isolated; or three molecules of X may interact to yield XII and cyclohexanol, which is then dehydrated to XI.



X V XI XII

If V were produced in the reaction, it would be expected that at least a trace of it would be found among the reaction products unless its reaction with X is instantaneous and complete. The absence of V among the reaction products leads to the conclusion that it is not an intermediate or that its reaction with X occurs before the adsorbed molecules of these compounds leave the catalyst.

In a similar dehydration, cyclopentanone (XIII) yielded cyclopentene and 2-cyclopentenone (XIV) in yields of 11 and 5%, respectively. On the basis of reactions similar to those given above for the dehydration of cyclohexanone, these products should have been obtained in equal molar amounts.



XIII XIV

Inasmuch as a considerable quantity of higher boiling material, which could not be fractionated into clear cut fractions, was obtained in this dehydration, it seems likely that self-condensation products of XIV account for the low yield of that compound.

2-Pentanone passed over P at 450° produced 33% pentenes and a high boiling mixture containing carbonyl compounds. Under the same conditions diisopropyl ketone was not dehydrated.

Ipatieff[11] has assumed that alumina forms a

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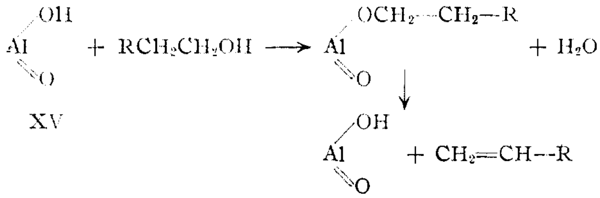
[9] L. W. Newton and E. R. Coburn, *Org. Syntheses*, **22**, 40 (1942).

[10] G. A. Hill and E. W. Flosdorf, "Organic Syntheses," Coll. Vol. I, John Wiley and Sons, Inc., New York, N. Y., 1941, p. 462.

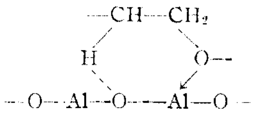
[11] V. N. Ipatieff, "Catalytic Reactions at High Pressures and Temperatures," The Macmillan Co., Inc., New York, N. Y., 1936, p. 541.

hydrate XV (an aluminic acid) and that the dehydration of alcohols occurs through the formation and decomposition of unstable esters according to the following scheme.



However, this theory does not account for the reactions of certain non-hydroxylic compounds over alumina, *e.g.*, the dehydration of ethers.[6,12]

It seems likely that alumina adsorbs these oxygen compounds by coördination of the electron deficient aluminum atom with the oxygen with a resultant change of adjacent bond energies to permit cleavage of that bond. It is possible that during coördination hydrogen bonding may occur between the hydrogen in the β-position to the coördinated atom and an oxygen of the alumina to such a complex.



The adsorption can take place at low temperatures as evidenced by the separation of compounds of different polarity by chromatographic adsorption on alumina. At room temperature the energy imparted to the bond in question is not sufficient for cleavage but as the temperature is rasied a point is finally reached where bond cleavage will occur.

It is thought that the increased activity of the alkoxide catalysts as compared with H is due to the greater aprotic acidity of the alkoxide catalysts. Such a conclusion seems justified in view of the fact that these catalysts adsorb such weak bases as the alkenes and cause their rearrangement to a much greater extent than does H.

Experimental

Apparatus.—The dehydration chamber consisted of a $^{13}/_{16}$ inch steel conduit tube bent in the shape of a U 9 inches in height and connected by means of standard union connections to an inlet and an outlet sidearm. The chamber was heated by a sodium nitrate–potassium nitrate bath controlled to constant temperature by a Leeds Northrup micromax. The inlet side of the U-tube was filled with $^3/_{16}$ inch steel balls to act as a baffle and vaporize the incoming material. The outlet side was filled with the catalyst to within approximately one inch of the nitrate bath level and a few steel balls placed on top.

The material to be dehydrated was pushed through the reaction tube by a Universal Oil Products bellows type pump. The use of a pump of this type was the most expedient means by which a quantity of liquid could be passed over the catalyst at a constant rate. With this instrument uniform flow of material up to 10 cc. per minute over the catalyst was maintained. Exit vapors from the reaction chamber were cooled by a 9-inch water cooled condenser and then passed to a series of three receivers consisting of 1.5 × 12 inch test-tubes. The first receiver was immersed in an ice–water-bath, while the second and third were surrounded by Dry Ice in methyl alcohol. The third receiver was connected through a manometer to a water pump for obtaining reduced pressure and as a means for cleaning the catalyst.

For dehydrations at reduced pressures a similar chamber was used but the union type connection was replaced by two flat discs 2.5 inches in diameter at each joint, which were connected through a gasket of equal diameter and held together by four bolts. The system was completed by connecting the reservoir of the pump to the outlet side of the third receiver through a barostat to maintain constant pressure.

Catalysts.—The commercial catalyst was purchased from the Harshaw Chemical Co., Cleveland, Ohio.

The aluminum alkoxides, from which the alkoxide aluminas were derived, were prepared by established procedures.[13-16] The quantity of aluminum alkoxide prepared from 100 g. of aluminum was added with vigorous stirring to 3-l. of water in a 4-l. beaker. The methoxide and *t*-butoxide were added as powder and the ethoxide and isopropoxide were added in the liquid form. The mixture was then heated to just below boiling for eight hours with vigorous stirring by a Hershberg stirrer to prevent bumping. The precipitate of aluminum hydroxide was allowed to settle overnight, the liquid decanted, and the hydroxide dried to a thick paste and pressed into a tablet mold making pellets $^3/_{16}$ inch in diameter and $^1/_8$ inch thick before drying. The pellets were dried at 100° for two hours yielding 130–140 g. of hard white tablets approximately one-half of mold size; 75 cc. of these pellets weighed 55–60 g. Just before use the hydrated alumina was completely dried and activated by heating in the reaction chamber to 350° for 12 hours.

Materials.—1-Hexanol, cyclohexanone, cyclopentanone, diisopropyl ketone, 2-pentanone and anhydrous pinacol were purchased from the Eastman Kodak Company. 2-Hydroxycyclohexanone was prepared by Dr. Jacob Szmuszkovicz in this Laboratory according to the procedure of Bartlett and Woods.[8] Pinacol hexahydrate, prepared by standard procedures, was purified by recrystallization from water. *trans*-1,2-Cyclohexandiol (III) was prepared by the method of Adkins and Roebuck[7] except that the crude material obtained was purified by crystallization from dioxane instead of by distillation. The yield of III, m.p. 99–102°, from 164 g. of cyclohexene was 187 g. (81%).

General Dehydration Procedure.—It was found in exploratory experiments that better yields and material balances were obtained if the catalyst employed had been conditioned by use in a previous dehydration. Therefore, the dehydrations discussed here were carried out over a used catalyst. A clean catalyst was conditioned by passing about 25 cc. of the compound to be dehydrated over it, if sufficient of the compound were available, or if not available, by passing 40–50 cc. of ethanol over the catalyst followed by 25–50 cc. of water to sweep the ethanol and its products from the reaction chamber. Then the material to be dehydrated was pumped through the tube at a constant rate and finally pushed over by 25 cc. of water.

The condensed material was collected from the receivers, the water layer separated and saturated with potassium carbonate. The organic layers were combined, dried over Drierite and fractionated through a 9-inch column packed with wire gauze saddles. The products were identified by their boiling points and refractive indexes, and, in any case of doubt, by derivatives. The compensator readings (*Z*) on the refractometer were also valuable for the identification of unsaturated compounds. For the refractometer used certain structures were associated with the following *Z* values: one double bond, *Z*, 18; two double bonds not conjugated, *Z*, 20; two double bonds conjugated, *Z*, 22; a benzenoid nucleus, *Z*, 25.

The catalyst could be cleaned by passing a stream of air over it at 400° for two to three hours.

Comparison of Catalysts.—These dehydrations were carried out by passing 102 g. (1 mole) portions of 1-hexanol over 75 cc. of the catalyst heated to 450°. Each portion was passed over at a different rate starting with the slowest feed velocity. Each series of runs was then repeated in the re-

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[12] R. N. Pease and C. C. Yung, This Journal, **46**, 390 (1924).

[13] W. Chalmers, "Organic Syntheses," Coll. Vol. II, John Wiley and Sons, Inc., New York, N. Y., 1947, p. 599.

[14] L. F. Fieser, "Experiments in Organic Chemistry," D. C. Heath and Co., Boston, Mass., 1941, 2nd ed., p. 445.

[15] S. M. McElvain and J. T. Venerable, This Journal, **72**, 1668 (1950).

[16] W. G. Young, W. H. Hartung and F. S. Crossley, *ibid.*, **58**, 101 (1936).

verse order, *i.e.* starting with the fastest feed velocity, without cleaning the catalyst. Upon fractionation the fractions boiling 61–65°, $n^{25}\mathrm{D}$ 1.3855–1.3860, *Z*, 18, from the dehydrations over H and 62–70°, $n^{25}\mathrm{D}$ 1.3870–1.3890, *Z*, 18, from the dehydrations over the alkoxide aluminas were collected as hexene.

Dehydration of 2-Hydroxycyclohexanone (I).—Dehydration of 25 g. (0.22 mole) of I dissolved in 275 g. of water by 75 cc. of P held at 310° resulted only in the production of phenol and cyclohexanone which were salted out of the aqueous solution by sodium chloride and fractionated. No 2-cyclohexenone (II) was detected. Recovered material corresponded to approximately 50% of the starting material.

For the dehydration of I over H, 75 cc. of the catalyst was placed in a combustion tube one inch in diameter clamped in a vertical position and heated by an electric furnace. The lower end of the tube was drawn to a diameter of 8 mm. and to such a length as to extend through a one-hole rubber stopper to within one-half inch of the bottom of a 250-cc. filter flask surrounded by an ice-salt mixture. Into the top of the tube there was fitted a one-hole rubber stopper holding a 50-cc. dropping funnel. The temperature was measured by an iron–constantan thermocouple at the center of the catalyst bed and connected to a Leeds–Northrup Micromax.

The temperature of the catalyst was raised to 350°, 26.5 g. (0.23 mole) of molten I was placed in the dropping funnel and the stopcock adjusted to deliver approximately 2 g./min. After the material had been added, the reaction chamber was swept by a slow stream of air for 15 minutes. The receiver was disconnected, 75 cc. of ether added to the products to break the emulsion, the water layer separated and the ether solution dried over anhydrous magnesium sulfate. After removing the ether by distillation, the residual material was fractionated through a 12 inch Podbielniak column into two fractions; (1) 6.2 g., b.p. 41.5° (8 mm.), $n^{25}\mathrm{D}$ 1.4749; (2) 2.7 g., b.p. 41.5–78° (8 mm.); 7.5 g. of tarry residue remained. Fraction (1) showed a maximum adsorption at 225 mμ and an $E_{\max}$ of 6920. Comparison of this fraction with a sample of II,[17] $n^{25}\mathrm{D}$ 1.4850, $\lambda_{\max}$ 225 mμ, $E_{\max}$ 10,200, indicated that it contained 72% of II based on refractive index calculations, assuming cyclohexanone, $n^{25}\mathrm{D}$ 1.4483, as the only other component, or 68% based on calculations using adsorption data. Therefore, fraction (1) contained approximately 4.4 g. of II and 1.8 g. of cyclohexanone corresponding to 20 and 8% conversions, respectively, of the amount of I subjected to dehydration. Fraction (2) treated with an aqueous solution of bromine and potassium bromide gave 3.8 g. of tribromophenol, m.p. 93–94°, corresponding to 1.4 g. (6.4%) of phenol based on a yield of 2.8 g. of tribromophenol prepared from 1.0 g. of pure phenol by the same procedure. No tribromophenol could be isolated from the residue after treatment with bromine.

Dehydration of *trans*-**1,2-Cyclohexanediol** (III).—This diol, dissolved in water in a molar ratio of 1:10, was passed at a rate of 4–5 g./min. over P heated to 340°. Upon fractionation of the material collected from 174 g. (1.5 mole) of III there were obtained 31.9 g. (29%) of 1,3-cyclohexadiene (V), b.p. 80°, $n^{25}\mathrm{D}$ 1.4668–1.4678, *Z*, 22; maleic anhydride adduct,[18] m.p. 145–147°; and 24.4 g. of cyclopentyl formaldehyde (IV), b.p. 134–139°, $n^{25}\mathrm{D}$ 1.4417–1.4450, *Z*, 18; semicarbazone, m.p. 123–124° (air dried) 139–140° (drying at 1 mm. for 12 hours). The melting point reported in the literature[19,20] for the semicarbazone of cyclopentyl formaldehyde is 123–124°.

Anal. Calcd. for $C_7H_{13}N_3O$: C, 54.17; H, 8.44. Found: C, 54.29; H, 8.18.

Oxidation of IV by silver oxide produced an acid from which was formed an amide, m.p. 174–176°. The melting point of the amide of cyclopentanoic acid as reported[21] is 178°. The melting point of 139–140° for the semicarbazone of IV was later checked by Dr. Jack L. Williams[22] of this Laboratory using a sample of the aldehyde prepared from cyclopentene by hydroformylation. Lowering the temperature to 325° did not alter the relative yields of IV and V obtained.

Very little dehydration was observed when 58 g. (0.5 mole) of III was passed at 4.5 g./min. over H at 325° as in the above procedure. At 350° and otherwise duplicating conditions there were obtained 2 g. (5%) of V, an odor of IV and 10.8 g. (22%) of 2-cyclohexenol (VI), b.p. 159–163°, 69–70° (18 mm.), $n^{25}\mathrm{D}$ 1.4661–1.4670; phenylurethan,[23] m.p. 103–104.5°. Upon passing 50 g. of III in 90 g. of water over H at 375° there were obtained 3.6 g. (10%) of V, 11.2 g. (27%) of IV and 10.0 g. (24%) of VI.

Dehydration of Pinacol–Pinacol Hexahydrate (VII).—The reaction chamber containing 50 cc. of P was heated to 310° and 100 cc. of ethyl alcohol passed over the catalyst followed by 50 cc. of boiling water to heat the reservoir and inlet tubes and to sweep the reaction tube free of ethanol and its dehydration products. While the reservoir was still hot, 130 g. (1 mole) of the eutectic mixture of pinacol-pinacol hexahydrate, m.p. 29°, previously heated to 70–80° was introduced into the reservoir and pumped through the dehydration tube at a rate of 6–8 g./min. Upon fractionation a small forerun (1–2 g.) came over first followed by 8.9–9.9 g. of 2,3-dimethyl-1,3-butadiene (IX), b.p. 68–72°, $n^{25}\mathrm{D}$ 1.4320–1.4350, *Z*, 22; and 85–87 g. (85–87%) of pinacolone (VIII), b.p. 101–105°, $n^{25}\mathrm{D}$ 1.3950. Comparable results were obtained using pinacol hexahydrate, but difficulty was encountered in preventing the pinacol hexahydrate from solidifying in the pumping apparatus. From 255 g. of pinacol hexahydrate, dehydrated at 450°, 35 g. (43%) of IX and 32 g. (31%) of VIII were produced.

Using the same procedure with 60 cc. of H at 325°, 3.3 g. (8%) of IX and 29 g. (58%) of VIII were obtained from 65 g. of VII. Raising the temperature to 375° changed the yields to 6.2 g. (15%) of IX and 40 g. (80%) of VIII.

Dehydration of Ketones (a) Pinacolone.—This ketone was dehydrated over various catalysts using different conditions. The data pertinent to those dehydrations and the yields of IX are shown in Table II.

TABLE II

DEHYDRATION OF PINACOLONE TO 2,3-DIMETHYLBUTADIENE (IX)

Catalyst	Cc. of cat.	*T*, °C.	Rate, g./min.	Press., mm.	Yield (%) of IX
H	300	450	1.9	100	67
H	300	350	1.9	100	12
H	100	450	2.5	100	67
H	50	450	2.8	Atm.	10
P	50	450	4.0	Atm.	67
P	50	450	5.5	100	63
P	50	400	3.9	Atm.	42
P	75	450	3.5	Atm.	57–71
M	75	450	3.5	Atm.	64–78

(b) **Cyclohexanone** (**X**).—This ketone was passed at a feed velocity of 4.2 g./min. over 50 cc. of P heated to 450°. The products from 294 g. (3.0 mole) of X were fractionated and found to consist of 75.1 g. of cyclohexene (XI), b.p. 82–85°, $n^{25}\mathrm{D}$ 1.4451–1.4456, *Z*, 18; 85.3 g. of cyclohexanone (X); and 43.4 g. of impure phenol (XII), b.p. 81–86° (17 mm.), $n^{25}\mathrm{D}$ 1.5211–1.5306, *Z*, 24.5; *p*-nitrobenzoate, m.p. 127–129°; tribromophenol, m.p. 93–94.5°. A mixed melting point of the tribromophenol with an authentic sample of this compound showed no depression. The amount of XII (37.1 g.) contained in this fraction was determined by comparison of the yields of tribromophenol obtained from it with that obtained from pure phenol. The yields of XI and XII corresponded to 44 and 19%, respectively, based on unrecovered ketone.

(c) **Cyclopentanone** (**XIII**).—The dehydration of XIII was accomplished by the same procedure as described above for X except that a feed velocity of 2 g./min. was used. From 235 g. (2.8 mole) of XIII, b.p. 128–130°, $n^{25}\mathrm{D}$ 1.4340, there were obtained 10.6 g. (11%) of cyclopentene, b.p. 41–42°, $n^{25}\mathrm{D}$ 1.4190, *Z*, 18; 125 g. of recovered XIII; 5.7 g. (5%) of 2-cyclopentenone (XIV), b.p. 39.5–41° (8 mm.),

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(17) Prepared in this Laboratory by the pyrolysis of 2-acetoxycyclohexanone; W. S. Johnson and J. Szmuszkovicz, unpublished observations.

(18) O. Diels and K. Alder, *Ann.*, **460**, 115 (1928).

(19) O. Wallach, *ibid.*, **347**, 326 (1906).

(20) M. Urion, *Ann. chim.*, [11] **1**, 44 (1934).

(21) C. D. Nenitzescu, *et al.*, *Ber.*, **71B**, 2056 (1938).

(22) H. Adkins and J. L. Williams, unpublished data, University of Wisconsin.

(23) R. Criegee, *Ann.*, **481**, 285 (1930), reported for VI, b.p. 164°, 63-65° (12 mm.); phenylurethan, m.p. 105°.

n^{25}D 1.4780, Z, 21.7, $\lambda_{max.}$ 218 mμ, $E_{max.}$ 10,250; 2,4-dinitrophenylhydrazone, m.p. 169–169.5°; 20.8 g. of material was in the intermediate fractions and the undistillable residue amounted to 35.5 g.

(d) **2-Pentanone.**—For this dehydration 258 g. (3.0 moles) of 2-pentanone, n^{25}D 1.3878, was passed over P heated to 450° to produce 19.4 g. (33%) pentenes, b.p. 30–34°, n^{25}D 1.3751–1.3757, Z, 18; dibromopentane, b.p. 78–80° (25 mm.); and 42.2 g. of high boiling material, which gave a positive carbonyl test when treated with 2,4-dinitrophenylhydrazine reagent. The yield is based on unrecovered starting material.

(e) **Diisopropyl Ketone.**—Under the same conditions as described above for 2-pentanone, only starting material was recovered after passing 180 g. (1.5 mole) of diisopropyl ketone over P.

MADISON 6, WIS. RECEIVED NOVEMBER 18, 1950

[CONTRIBUTION FROM THE CONVERSE MEMORIAL LABORATORY OF HARVARD UNIVERSITY]

The Course and Kinetics of the Acid–Base-Catalyzed Rearrangements of 11-Hydroxytetrahydrocarbazolenine[1]

BY BERNHARD WITKOP AND J. B. PATRICK

11-Hydroxytetrahydrocarbazolenine (III) was prepared (a) by catalytic oxidation of tetrahydrocarbazole in ethyl acetate with platinum catalyst and subsequent gentle hydrogenation, (b) by the action of ethereal hydrogen peroxide on tetrahydrocarbazole. The compound III is remarkable for the ease with which it undergoes rearrangements under the influence of acid, base, heat, refluxing solvents and acetic anhydride. The rearrangement product in all cases was *spiro*-[cyclopentane-1,2′-ψ-indoxyl] (IV), m.p. 79°, which, in the presence of acid, easily added to III yielding Compound A, $C_{24}H_{26}N_2O_2$, m.p. 138–141°, which in turn easily lost water to give Compound B, $C_{24}H_{24}N_2O$, m.p. 227–229°; finally Compound C, $C_{24}H_{22}N_2$, m.p. 255 and 315° (dec.), was formed as a by-product in all rearrangements of III involving acid catalysis, possibly by an independent route.

The acid-catalyzed Wagner–Meerwein rearrangement leading from III to IV (and subsequently to Compounds A, B and C) was measured spectrophotometrically and found to be first order with regard to III and with respect to acid. The rearrangement of III in base, formally analogous to a benzilic acid type of reaction, was first order with respect to III and to base. Further reactions are discussed and a revision of some derivatives of tetrahydrocarbazole is given.

The investigation of the mechanism of oxidation of indole compounds[2] made it necessary to prepare a derivative of a hydroxyindolenine.[3] It was previously shown that the "11-hydroxytetrahydrocarbazolenine" of the literature[4] is in reality *spiro*-[cyclopentane-1,2′-ψ-indoxyl] (Chart II).[5,6] In this paper we describe the preparation of authentic 11-hydroxytetrahydrocarbazolenine,[7] some of its remarkable chemical features, as well as some kinetic observations.

Tetrahydrocarbazole (I) in ethyl acetate over platinum took up one mole of oxygen to yield the peroxide (II) first mentioned in the literature by Robertson, *et al.*[8] In the preparation of 11-hydroxytetrahydrocarbazolenine (III) it was unnecessary to isolate the intermediary II. After the catalytic oxidation the material was hydrogenated and one mole of hydrogen was taken up; III was obtained in beautiful crystals from ethyl acetate in 75% yield. Any other oxidation of tetrahydrocarbazole, *e.g.*, the reaction with absolute ethereal hydrogen peroxide[9] for several days gave much smaller yields (*cf.* Method B, Experimental part). The initial slow uptake of oxygen in the catalytic oxidation of tetrahydrocarbazole seemed to indicate an induction period as is frequently observed in (aut)oxidations.[10] However, this initial delay in oxygen uptake seems to be due to changes occurring at the surface of the catalyst when the freshly reduced platinum catalyst comes into contact with oxygen.[11] Indeed, a steady curve of oxygen uptake was obtained when the catalyst was shaken with oxygen before the solution of tetrahydrocarbazole was added. The well-known 1,3-relationship for indoles, or 9,11-tautomerism of tetrahydrocarbazole, encountered in so many ionic reactions, is demonstrated here in a radical type of reaction. The radical (Ia) produced from I reacts with oxygen rather in the form (Ib)[12] to give a peroxide radical intermediate which reacts with a further molecule of tetrahydrocarbazole to yield 11-hydroperoxytetrahydrocarbazolenine (II) and a new radical (Ia↔Ib). There is no reason to depart from this generally accepted picture of oxidation[13] and to assume, for instance, the formation of a four-membered peroxide ring.[8,14,15]

The structure of III was proven by gentle hydrogenation to 11-hydroxy-1,2,3,4,10,11-hexahydrocarbazole (V). The reduction of indolenines under more vigorous conditions to give dihydroindolenines is known.[16] V is only stable in the

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(2) Witkop, THIS JOURNAL, **72**, 1428 (1950).

(3) Witkop and Patrick, *Experientia*, **6**, 183 (1950).

(4) Perkin and Plant, *J. Chem. Soc.*, **123**, 688 (1923).

(5) Witkop, THIS JOURNAL, **72**, 614 (1950).

(6) Plant and Robinson, *Nature*, **165**, 36 (1950), and (added in proof) *ibid.*, **165**, 928 (1950); *J. Chem. Soc.*, 2127 (1950).

(7) Adumbrated in a Communication to the Editor, THIS JOURNAL, **72**, 633 (1950).

(8) Beer, McGrath, Robertson and Woodier, *Nature*, **164**, 362 (1949), and (added in proof) *J. Chem. Soc.*, 2118, 3283 (1950).

(9) Criegee and Richter, *Ann.*, **522**, 94 (1936).

(10) *Cf.* Frank, *Chem. Revs.*, **46**, 156 (1950).

(11) A comprehensive account of such displacement and reorientation reactions occurring at the surface of noble metal catalysts is given by Bacaredda in Schwab, "Handbuch der Katalyse," Vol. VI, Springer, Vienna, 1943, p. 234.

(12) We are at present engaged in an investigation of nitrogenous peroxides. So far, we have not encountered a single case of an >N–O–O– type of organic peroxide. As we shall show in a subsequent paper (*cf. Experientia*, **6**, 461 (1950)) the size of the isocyclic ring C changes the nature and stability of the peroxide and the preceding radical intermediate.

(13) Farmer, Koch and Sutton, *J. Chem. Soc.*, 541 (1943); Cullis and Hinshelwood, *Discussions of the Faraday Society*, **2**, 117 (1947).

(14) Hilditch, *J. Chem. Soc.*, 1022 (1946).

(15) Hilditch, *J. Oil & Colour Chemists' Assoc.*, **30**, 1 (1947).

(16) Ciamician and Plancher, *Ber.*, **29**, 2476 (1896): sodium in ethyl or amyl alcohol Brunner, *Monatsh.*, **16**, 864 (1895); **18**, 115 (1897); zinc and acetic acid, Plancher and Ghigi, *Gazz. chim. ital.*, **59**, 339 (1929). Another method to arrive at indolines from indolenines was shown by Leuchs, Heller and Hoffmann, *Ber.*, **62**, 871 (1929).