

As expected, the isomerization increases with contact time on the acidic alumina (expt. 1, 2 and 3 of Table II).

The Effect of Regeneration of Catalysts.—It was observed that all catalyst preparations increased in acidity on regeneration in air at 500°. This effect on the B2 alumina can be seen by comparing experiments 18, 19 and 20 (Table II) which were conducted after 0, 1 and 2 regenerations in air at 500° for 16 hr. This increase in acidity can be so great that after several regenerations, exposure to ammonia has little effect in suppressing isomerization (see Expt. 11, 12 and 15 which were

conducted after 0, 3 and 7 regenerations, respectively). Evidently during regeneration new strong acid sites are being formed. Ammonia is not strong enough to neutralize these acid sites. The stronger bases, trimethylamine and piperidine, are more effective (see Expt. 12, 13 and 14).

The increase in acidity during regeneration can be somewhat corrected by carrying out the process at as low a temperature as possible by diluting the air with nitrogen. However, for synthetic purposes, where secondary reactions are to be avoided, it is best to use non-regenerated alumina.

[CONTRIBUTION FROM THE IPATIEFF HIGH PRESSURE AND CATALYTIC LABORATORY, DEPARTMENT OF CHEMISTRY, NORTHWESTERN UNIVERSITY, EVANSTON, ILL.]

Alumina: Catalyst and Support. XI.¹ Mechanism of Dehydration of Aliphatic Alcohols and the Formation of Cyclopropanes during Dehydration²

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The dehydration of several aliphatic alcohols over weakly acidic alumina catalysts were studied. It was found that the dehydration of neopentyl-type alcohols is usually accompanied by rearrangement and that during rearrangement the double bond is formed in preference between the 2- and 3-carbon atoms with respect to the original position of the hydroxyl group. The direction of elimination shifted from Saytzeff to Hofmann as the alcohol became highly branched. Primary and secondary neopentyl-type alcohols gave small amounts of cyclopropanes on dehydration. Possible mechanisms of these reactions are discussed.

In earlier papers of these series,^{1,4} the dehydration of certain aliphatic and cyclic alcohols over various aluminas was reported. It was shown that secondary isomerizations accompanying dehydration could be avoided by using aluminas containing only relatively weak acid sites. Modification of alumina by the use of organic bases was found to be the most practical method for obtaining such catalysts.

The products of dehydration corresponded to *trans* elimination of the elements of water.¹ Simple alcohols like 2-butanol and 2-pentanol dehydrated to form more of the internal olefins than of the terminal olefins (Saytzeff elimination).⁴ When the internal olefins were formed, the thermodynamically less stable *cis*-olefin was formed in preference to the *trans*.

In the present paper, the dehydration of several aliphatic alcohols, including neopentyl-type alcohols, is discussed.

Experimental Part

The catalysts were prepared as described before.¹ The reactions were carried out in the apparatus previously described. Where piperidine was used to modify the alumina, it was mixed with the alcohol feed, usually 10% by weight of the alcohol.

Pinacolyl alcohol was prepared by the reduction of pinacolone over a nickel catalyst at 100° and an initial hydrogen pressure of 100 atmospheres; b.p. 120–122°, n_D^{20} 1.4160.

(1) For part X of these series, see H. Pines and C. N. Pillai, *J. Am. Chem. Soc.*, **83**, 3270 (1961).

(2) Paper IV of the series: Dehydration of Alcohols; for paper III, see ref. 1.

(3) Taken in part from the Ph.D. thesis of C. N. Pillai, Northwestern University, 1960. Grateful acknowledgment is made to the donors of the Petroleum Research Fund for the support of this research.

(4) H. Pines and W. O. Haag, *J. Am. Chem. Soc.*, **83**, 2847 (1961).

Neopentyl alcohol was prepared by the reduction of trimethylacetic acid⁵ by lithium aluminum hydride⁶; b.p. 112–114°.

2,3-Dimethyl-2-butanol was prepared by Grignard reaction from 3-methyl-2-butanone and methyl iodide; b.p. 120–121°, n_D^{20} 1.4176.

3,3-Dimethyl-2-pentanol was prepared by Grignard synthesis from *t*-amyl chloride and acetaldehyde. By distillation of the crude product on a semi-micro spinning band column, pure 3,3-dimethyl-2-pentanol, b.p. 146.8–147.2° at 750 mm., n_D^{20} 1.4301, was obtained in 15% yield; reported⁷ b.p. 147–148°.

2,3-Dimethyl-2-pentanol was similarly prepared from *sec*-butyl bromide and acetone. After distillation, 2,3-dimethyl-2-pentanol, b.p. 139.9–140° at 750 mm., n_D^{20} 1.4268, was obtained in 22% yield; reported⁷ b.p. 129–130.5°.

2,3,3-Trimethyl-2-butanol was prepared by the reaction of acetone with *t*-butylmagnesium chloride and the crude hydrate was purified by sublimation to obtain crystals melting at 82°, reported⁷ m.p. 80°.

1,1,2-Trimethylcyclopropane.—A mixture of 21 g. of zinc-copper couple,⁸ 54 g. (0.2 mole) of methylene iodide, 21 g. (0.3 mole) of 2-methyl-2-butene, a crystal of iodine and 80 ml. of anhydrous ether was stirred and refluxed under anhydrous conditions for 30 hours. At the end of this time, gas chromatographic analysis of the reaction product showed that 1,1,2-trimethylcyclopropane had formed in 41% yield based on methylene iodide. The mixture was filtered free of solids, washed with 5% HCl, 5% sodium bicarbonate and water and dried over MgSO₄. By distillation on a semi-micro spinning band column, 3.1 g. of pure 1,1,2-trimethylcyclopropane, b.p. 50.8–51.1° at 738 mm., n_D^{20} 1.3831, was obtained; reported⁹ b.p. 52.6°, n_D^{20} 1.3834.

(5) S. V. Puntambeker and E. A. Zoellner, "Organic Syntheses," Coll. Vol. I, John Wiley and Sons, Inc., New York, N. Y., 1941, p. 524.

(6) R. F. Nystrom and W. G. Brown, *J. Am. Chem. Soc.*, **69**, 2548 (1947).

(7) G. Edgar, G. Calingaert and R. E. Marker, *ibid.*, **51**, 1483 (1929).

(8) H. E. Simmons and R. D. Smith, *ibid.*, **81**, 1256 (1959).

cis-1,2-Dimethyl-1-ethylcyclopropane.—A mixture of 17.5 g. (0.21 mole) of *cis*-3-methyl-2-pentene, 53 g. (0.2 mole) of methylene iodide, 22 g. of zinc-copper couple⁸ and a crystal of iodine in 60 cc. of anhydrous ether was refluxed with stirring for 24 hours and worked up as before to obtain 4.2 g. (21%) of *cis*-1,2-dimethyl-1-ethylcyclopropane, b.p. 83.8–84.5° (740 mm.), n_D^{20} 1.4023. Assignment of configuration is based on the assumption that the reaction is stereospecific.⁸

1,1-Dimethylcyclopropane was obtained from 1,3-dibromo-2,2-dimethylpropane by the procedure described in the literature.¹⁰ The crude product was used without purification for identification purposes.

Analysis of Products.—The dehydration products were identified and quantitatively analyzed by gas chromatography. The columns used and relative retention times are given in Table I.

TABLE I

Component	RELATIVE RETENTION TIMES OF DEHYDRATION PRODUCTS ^a		
	Col. A ^b	Col. B ^c	Col. C ^d
1,1-Dimethylcyclopropane	0.39	0.29	0.44
2-Methyl-1-butene	.69	1.89	.75
3,3-Dimethyl-1-butene	.75	1.94	.69
2-Methyl-2-butene	.94	1.00	1.00
1,1,2-Trimethylcyclopropane	.94	0.43	0.95
2,3-Dimethyl-1-butene	1.28	2.23	1.25
<i>n</i> -Hexane	1.00
2-Methyl-1-pentene	1.62
2-Methyl-2-pentene	1.93
3,3-Dimethyl-1-pentene	2.25
2,3,3-Trimethyl-1-butene	2.54
<i>cis</i> -1,2-Dimethyl-1-ethylcyclopropane	2.5	1.27	..
<i>trans</i> -1,2-Dimethyl-1-ethylcyclopropane(?) ^e	2.6
2,3-Dimethyl-2-butene	2.70	1.55	2.41
2,3-Dimethyl-1-pentene	2.95
3-Methyl-2-ethyl-1-butene	3.25
2,3-Dimethyl-3-pentene(?) ^f	3.77, 3.94
2,3-Dimethyl-2-pentene	5.54

^a Data relative to *n*-hexane for column A and to 2-methyl-2-butene for columns B and C. ^b Dimethyl sulfolane, 33% by weight on 100–120 mesh Celite, 10 ft., 31°, He flow 80 ml./min. This column was prepared by Mr. Signmund Csicsery. A detailed list of retention times of hydrocarbons on this column will be published later. ^c Silver nitrate in diethylene glycol (19% solution) deposited on 30–60 mesh Celite, 17% by weight, 5 ft., 30°, He flow 40 ml./min. ^d β,β -Oxydipropionitrile, 20% in 20–40 mesh firebrick, 40 ft., 30°, He flow 65 ml./min. ^e Not confirmed by comparison with authentic sample; overlaps with the *cis* isomer. ^f Two overlapping peaks, probably *cis* and *trans* isomers; not confirmed by comparison with authentic samples.

The presence of the cyclopropanes in the dehydration products was confirmed by comparison of the retention time of the suspected component with that of the synthetic sample on the different column. The cyclopropanes were further confirmed by hydrogenation of the dehydration products over a palladium-on-charcoal catalyst at 1 atmosphere pressure, under which conditions the olefins were converted to saturated products, but the peaks due to the cyclopropanes remained unchanged.

Results and Discussion

The results of the dehydration of 3,3-dimethyl-2-butanol, 2,3-dimethyl-2-butanol, neopentyl alcohol, *t*-amyl alcohol, 2-butanol, 2-pentanol, 3-pentanol, 3,3-dimethyl-2-pentanol and 2,3-

dimethyl-2-pentanol are given in Tables II–V. In addition to these, 2,3,3-trimethyl-2-butanol and *n*-propyl alcohol also were dehydrated over alumina modified by piperidine. These yielded 2,3,3-trimethyl-1-butene and propylene, respectively, as the sole dehydration products. No cyclopropanes were formed from these alcohols.

The dehydration of some of these alcohols (pinacolyl alcohol, 2-butanol, 2-pentanol and 3-pentanol) on relatively more acidic aluminas was reported before.⁴ It appears that the product distribution at low conversions (primary dehydration products) is essentially the same on the different types of aluminas.

The four neopentyl-type alcohols studied are 2,2-dimethyl-1-propanol (neopentyl alcohol), 3,3-dimethyl-2-butanol (pinacolyl alcohol), 3,3-dimethyl-2-pentanol and 2,3,3-trimethyl-2-butanol. The first one obviously cannot be dehydrated to an olefin without rearrangement. The last one will give the same product by normal dehydration and by dehydration accompanied by methyl migration. The other two should lead to 3,3-dimethyl-1-butene and 3,3-dimethyl-1-pentene, respectively, by a simple 1,2-elimination of the elements of water. Examination of Tables II and V show that these are the major products. However, products of rearrangement having 2,3-dimethylbutane and 2,3-dimethylpentane skeleton, respectively, are formed in all cases. In the presence of piperidine the product distribution is essentially constant at different contact times. It was also shown that the catalysts modified by piperidine are incapable of isomerizing the free olefins under the conditions of the reaction. Hence these products having rearranged carbon skeletons are primary dehydration products.

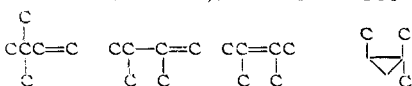
From 3,3-dimethyl-2-butanol, the major product of rearrangement is 2,3-dimethyl-1-butene. The distribution of the primary dehydration products is far from equilibrium. The maximum ratio of 2,3-dimethyl-1-butene to 2,3-dimethyl-2-butene is about 10. This is higher than that to be expected if a proton is removed from the 2,3-dimethyl-2-butyl carbonium ion in a statistical manner. However, elimination of a proton from this carbonium ion probably does not take place in the statistical manner. The maximum ratio of 2,3-dimethyl-1-butene to 2,3-dimethyl-2-butene obtained from 2,3-dimethyl-2-butanol is also about 10 (see Expts. 8–13, Table II). Hence it can be argued that the high yield of 2,3-dimethyl-1-butene from pinacolyl alcohol does not necessarily rule out a classical carbonium ion reaction. The results from neopentyl alcohol are more revealing (Table III). This alcohol yields 2-methyl-1-butene and 2-methyl-2-butene in a maximum ratio of 3. However, 2-methyl-2-butanol yields these two olefins in a maximum ratio of only 1.4. Because of these facts, a simple carbonium ion mechanism as shown below is not adequate to explain the rearrangement taking place during the dehydration of neopentyl-type alcohols.

It was pointed out that anchimeric assistance may play an important role in the initial ionization during dehydration over a solid surface.⁴ As-

(9) R. G. Kelso, K. W. Greenlee, J. M. Derfer and C. E. Boord, *ibid.*, **74**, 287 (1952).

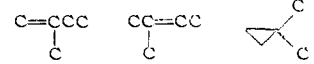
(10) R. W. Shortridge, R. A. Craig, K. W. Greenlee, J. M. Derfer and C. E. Boord, *ibid.*, **70**, 946 (1948).

TABLE II
 DEHYDRATION OF 3,3-DIMETHYL-2-BUTANOL AND 2,3-DIMETHYL-2-BUTANOL

Expt.	Catalyst ^a	Temp., °C.	HLSV ^b					Others	Dehydra- tion, %
				3,3-Dimethyl-2-butanol	2,3-Dimethyl-2-butanol	Others	Dehydra- tion, %		
1	A	280	1	11.7	29.5	58.4	0.05	0.41	100
2	A	280	4	67.4	24.5	7.5	0.56	0.07	100
3	A	280	8	70.3	25.6	2.8	1.45	0	83
4	A (10% pip.)	340	1	70.1	25.5	3.9	2.1	0.48	85
5	A (10% pip.)	340	4	76.4	18.3	1.7	2.4	.67	26
6	A (10% pip.)	340	8	78.1	17.3	1.6	2.1	.94	16
7	B2	290	1	50.1	40.8	6.7	2.4	0	4
2,3-Dimethyl-2-butanol									
8	A (10% pip.)	345	1	0.2	84.6	13.5	0	1.7	100
9	A (10% pip.)	345	4	0	88.4	9.9	0	1.7	97
10	A (10% pip.)	345	8	0	89.0	9.7	0	1.5	85
11	A (10% pip.)	275	1	0	89.2	9.4	0	1.3	60
12	A (10% pip.)	275	4	0.2	87.9	9.3	0.2	2.4	28
13	A (10% pip.)	275	8	0.3	87.1	9.0	0.3	3.2	18
Equilibrium ^c		327	4	44	52				

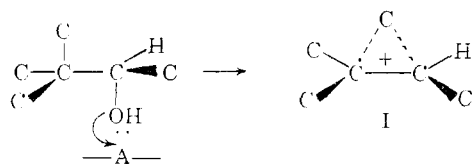
^a A refers to alumina prepared from aluminum isopropoxide.¹ A (10% pip.) refers to reaction on catalyst A where the alcohol feed was mixed with 10% by weight of piperidine. B2 refers to alumina prepared from sodium aluminate and washed twice. ^b Hourly liquid space velocity. ^c J. E. Kilpatrick, E. J. Prosen, K. S. Pitzer and F. D. Rossini, *J. Res. Natl. Bur. Standards*, **36**, 559 (1946).

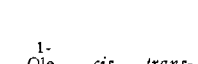
 TABLE III
 DEHYDRATION OF NEOPENTYL ALCOHOL AND *t*-AMYL ALCOHOL^a

Expt.	Temp., °C.	HLSV			Dehydra- tion, %	Ratio <i>cis</i> - 2-/ <i>trans</i> - 2-
			Neopentyl alcohol ^b	<i>t</i> -Amyl alcohol		
14	345	1	64.8	32.5	2.7	32
15	345	4	73.7	23.8	2.5	19
16	345	8	69.4	27.8	2.9	5
<i>t</i> -Amyl alcohol						
17	275	1	57.4	42.6	0	85
18	275	4	55.9	44.1	0	45
19	275	8	58.0	41.9	0	29
Equilibrium ^c		327°	33	66		

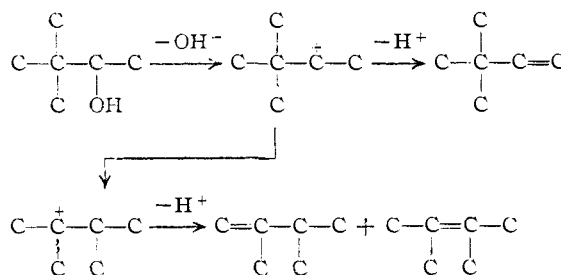
^a Catalyst: alumina from aluminum isopropoxide; the alcohol feed was mixed with 10% by weight of piperidine. ^b A 25% solution of neopentyl alcohol in ethylbenzene was used. ^c Footnote e, Table II.

istance by a methyl group in pinacolyl alcohol will lead to a non-classical carbonium ion I as


 TABLE IV
 DEHYDRATION OF 2-BUTANOL, 2-PENTANOL AND 3-PENTANOL^a

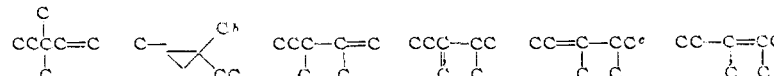
Expt.	Alcohol ^b	Temp., °C.	HLSV				Dehydra- tion, %	Ratio <i>cis</i> - 2-/ <i>trans</i> - 2-
				1-Olefin	<i>cis</i> -2	<i>trans</i> -2		
20	2-B	273	4	43.5	48.1	8.4	10	5.7
21	2-P	275	1	38.4	50.2	11.3	13	
22	2-P	275	4	40.7	47.0	12.3	8	3.9
23	3-P	300	1	0.75	70.8	28.5	88	
24	3-P	300	4	.68	70.6	28.7	63	
25	3-P	300	8	.50	70.6	28.9	36	2.4

^a Catalyst: alumina from aluminum isopropoxide with piperidine. ^b 2-B = 2-butanol; 2-P = 2-pentanol; 3-P = 3-pentanol.

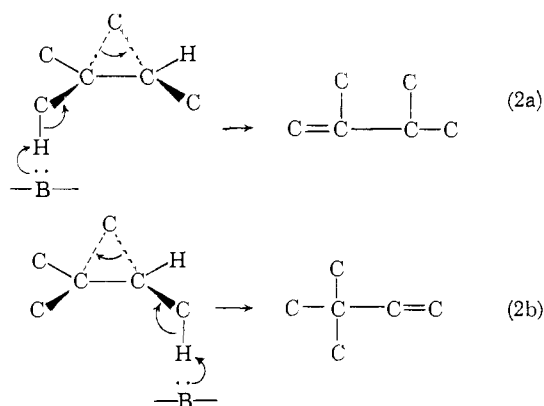


(1) This ion can now release a proton in one of two ways.

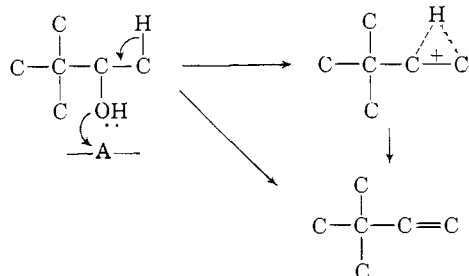
 TABLE V
 DEHYDRATION OF 3,3-DIMETHYL-2-PENTANOL AND 2,3-DIMETHYL-2-PENTANOL^a

Expt.	Alcohol	Dehydra- tion, %						
			3,3-DMP	2,3-DMP	Others	Dehydra- tion, %	Ratio <i>cis</i> - 2-/ <i>trans</i> - 2-	
26	3,3-DMP	14	77.8	2.0	5.0	6.7	7.2	1.4
27	3,3-DMP	10	79.0	2.05	4.9	6.3	6.7	1.1
28	3,3-DMP	3	75.9	2.3	5.0	6.9	8.4	1.6
29	2,3-DMP	100	0	0	92.1	0	0	7.9

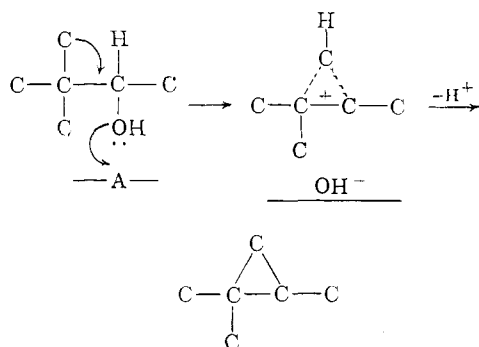
^a Temperature, 275°; catalyst, alumina from aluminum isopropoxide with piperidine. ^b Two unresolved peaks, probably *cis* and *trans*. This *cis* isomer was identified by comparison with authentic sample. ^c Two overlapping peaks, probably *cis* and *trans* isomers.



Whether 1 and 2a take place simultaneously or in two steps cannot be decided.¹¹ Steps 1 and 2b obviously cannot take place simultaneously. In fact, formation of the unrearranged product 3,3-dimethyl-1-butene probably takes place mostly by the *trans* elimination mechanism proposed earlier.¹



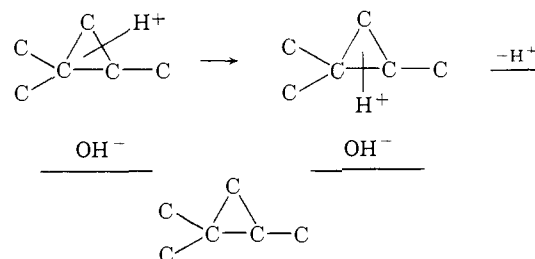
The three neopentyl-type alcohols, *viz.*, neopentyl alcohol, pinacolyl alcohol and 3,3-dimethyl-2-pentanol, gave small amounts of cyclopropane derivatives also on dehydration. An intermediate like I may be involved in the formation of these also. Here again, as in the proposed mechanism



for *trans* elimination in menthol,¹ the position in space of the basic site on the alumina which should accept the proton is obscure. It is attractive to suppose that the intermediate I is really a protonated cyclopropane and that the proton is mobile, so that it can be removed by the same planar surface that removed the OH group without the adsorbed

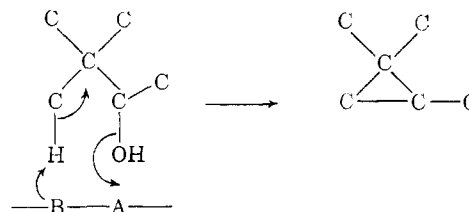
(11) In the preliminary communication¹² a concerted mechanism was proposed for these reactions. However, the arguments discussed in the present paper show that a concerted mechanism is not necessarily required to explain the products.

molecule having to turn around. The major objection to such a mechanism is that it has not



been possible to establish the existence of such protonated cyclopropane intermediates in other carbonium ion reactions.¹²

A concerted mechanism, which was tentatively proposed earlier,¹³ is free of this difficulty. Evi-



dence at this stage is insufficient to make a choice between the two mechanisms. Further studies are being made with alcohols where the H and the OH are fixed (bornyl and isobornyl systems) to learn more about this problem.

It should be pointed out that 1,1,2-trimethylcyclopropane itself is isomerized on the catalyst under the conditions of the reaction and the major product of isomerization is 2,3-dimethyl-1-butene (see Table VI). Because of this, the question may arise whether the cyclopropane is an intermediate in the rearrangement. However, this is not the case, since the percentage of the cyclopropane during dehydration is essentially unchanged when contact time is changed (see expts. 4-6, 14-16 and 26-28). Furthermore, methylpentenes, which are products of isomerization of 1,1,2-trimethylcyclopropane (see Table VI), were not detected during the dehydration reaction.

TABLE VI
ISOMERIZATION OF 1,1,2-TRIMETHYLCYCLOPROPANE OVER ALUMINA

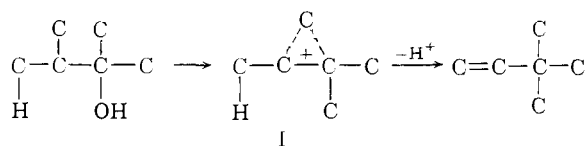
Catalyst, A(pip.); Temperature, 310°; HLSV, 1			
Composition of product, %			
1,1,2-Trimethylcyclopropane	58.3	2-Methyl-2-pentene	5.5
2,3-Dimethyl-1-butene	28.9	3,3-Dimethyl-1-butene	0.5
2,3-Dimethyl-2-butene	6.4	2-Methyl-1-pentene	0.3

An alcohol which is similar in some respects to 3,3-dimethyl-2-butanol is 2,3-dimethyl-2-butanol. The results obtained on the dehydration of this alcohol are given in Table II. The major product is the terminal olefin 2,3-dimethyl-1-butene. The maximum ratio 2,3-dimethyl-1-butene to 2,3-dimethyl-2-butene is about the same as that in the case of pinacolyl alcohol. However, it is not possible that the same intermediate, I, is involved

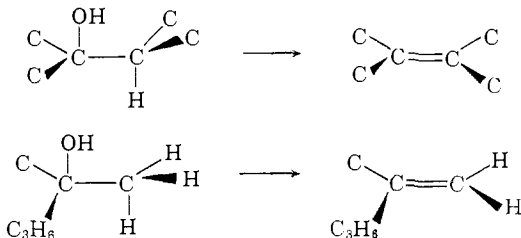
(12) G. J. Karabatos and J. D. Graham, *J. Am. Chem. Soc.*, **82**, 5250 (1960); P. S. Skell, I. Starer and A. P. Krapcho, *ibid.*, **82**, 5257 (1960).

(13) H. Pines and C. N. Pillai, *ibid.*, **82**, 2401 (1960).

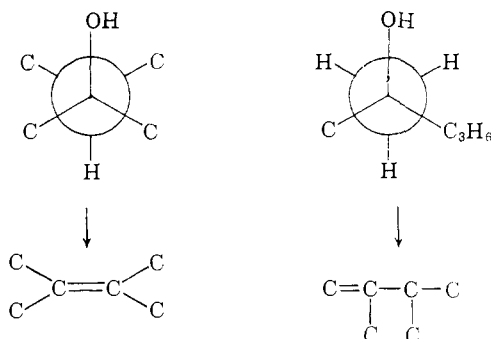
in both cases. If such were the case the former should have yielded significant quantities of 3,3-dimethyl-1-butene. However, the amount of this



olefin is negligibly small. Hence in the case of this alcohol, the simple *trans* elimination mechanism probably is operating. The preference



for the terminal olefin probably is due to the lack of steric hindrance in the transition state leading to this olefin. This can be seen clearly in the projection formulas



It is clear that regardless of whether the transition state more nearly resembles the alcohol or the olefin, there is less steric hindrance in the path leading to the terminal olefin. Partly this preference for terminal olefin also is due to the larger number (6) of terminal hydrogens than non-terminal hydrogen (1) available for elimination. Table V shows that 2,3-dimethyl-2-pentanol also leads to the terminal olefin in preference to the non-terminal olefin. When the alcohol is less heavily substituted as in the case of 2-butanol and 2-pentanol, the normal Saytzeff elimination product is formed in preference (see Table VII).

This problem of the direction of elimination during dehydration is quite interesting in view of the discussion in the recent literature regarding the interpretation of Hofmann and Saytzeff rules.¹⁴ In the case of dehydration reactions the leaving group probably is an oxonium ion, a positively charged group. One does not know whether the reaction is E_2 - or E_1 -type. It appears that on non-

(14) (a) H. C. Brown and I. Moritani, *J. Am. Chem. Soc.*, **78**, 2203 (1956); (b) C. K. Ingold, "Structure and Mechanism in Organic Chemistry," Cornell University Press, Ithaca, N. Y., 1953, pp. 419-472; (c) D. V. Banthorpe, E. D. Hughes and C. K. Ingold, *J. Chem. Soc.*, 4054 (1960).

TABLE VII
DIRECTION OF ELIMINATION IN ALIPHATIC ALCOHOLS

Alcohol	Ratio, 1-olefin/ 2-olefin ^a		Alcohol	Ratio, 1-olefin/2- olefin ^a	
	Obsd.	Cor. ^b		Obsd.	Cor. ^b
$\begin{array}{c} \text{C} & \text{C} \\ & \\ \text{C}-\text{C}-\text{C}-\text{C} \\ & \\ \text{H} & \text{OH} \end{array}$	0.78	0.52	$\begin{array}{c} \text{OH} \\ \\ \text{CC}-\text{CC} \\ & \\ \text{CC} & \text{C} \end{array}$	9.5	1.6
$\begin{array}{c} \text{C} & \text{C} & \text{C} \\ & & \\ \text{C}-\text{C}-\text{C}-\text{C}-\text{C} \\ & & \\ \text{OH} & & \end{array}$	0.69	.46	$\begin{array}{c} \text{OH} \\ \\ \text{CCC}-\text{CC} \\ & \\ \text{C} & \text{C} \end{array}$	11.7	1.9
$\begin{array}{c} \text{C} & \text{C} \\ & \\ \text{C}-\text{C}-\text{C}-\text{C} \\ & \\ \text{H} & \text{C} \end{array}$	1.4	.47			

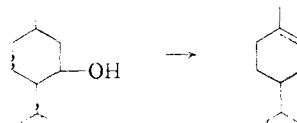
^a Maximum, from the various experiments. ^b Corrected for the number of hydrogens available.

acidic aluminas, there is a tendency toward the E_2 -type mechanism. It was shown that 2-butanol gave increasing amounts of 1-butene as the acidity of the alumina was decreased.⁴ This tendency toward Hofmann elimination becomes quite pronounced with heavily substituted alcohols (see Table VII). Thus it appears that steric factors are quite important in these reactions.

In the preceding sections it was shown that an alcohol $\text{HC}-\text{C}-\text{C}-\text{OH}$ can dehydrate by the mechanism (not necessarily in one step)



It was interesting to see whether, when $R = H$, by such a mechanism a 2,3-olefin (with respect to the original position of the hydroxyl group) is possible as a primary product. It should be recalled that from menthol, small amounts of 1-menthene could be obtained as a primary product.¹ Examination



of the data on 3-pentanol (Table III) and 2,3-dimethyl-2-pentanol (Table V) shows that at least in these cases, such a mechanism does not operate to any appreciable extent.

Conclusions

The general conclusion is that, normally, a simple 1,2-*trans* elimination is the preferred dehydration reaction, if such a reaction is possible. However, in neopentyl-type alcohols, rearrangement as a result of methyl group participation is also quite normal. When this takes place, olefins having double bond in the 2,3-position with respect to the leaving hydroxyl group are formed in preference. Cyclopropane derivatives also are formed under these conditions. When ionization becomes easy as with tertiary alcohols (e.g., 2,3,3-trimethyl-2-butanol), contribution due to this kind of participation becomes negligible and cyclopropane derivatives cannot be detected.

These rules are true only in the sense that they predict the most favored products. By no means are such products formed exclusively. Formation

of 2-methyl-2-butene from neopentyl alcohol, 2,3-dimethyl-2-butene from pinacolyl alcohol and 2,3-dimethyl-2-pentene and 2,3-dimethyl-1-pentene

from 3,3-dimethyl-2-pentanol can be explained only on the basis of classical carbonium ion rearrangements.

[CONTRIBUTION FROM THE CHEMICAL RESEARCH DEPARTMENT, CENTRAL RESEARCH DIVISION, AMERICAN CYANAMID CO., STAMFORD, CONN.]

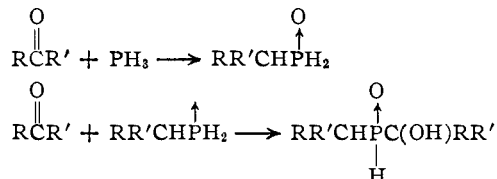
A Novel Phosphorus Heterocyclic System from the Reactions of Phosphine and Primary Phosphines with 2,4-Pentanedione

BY MARTIN EPSTEIN AND SHELDON A. BUCKLER

RECEIVED FEBRUARY 10, 1961

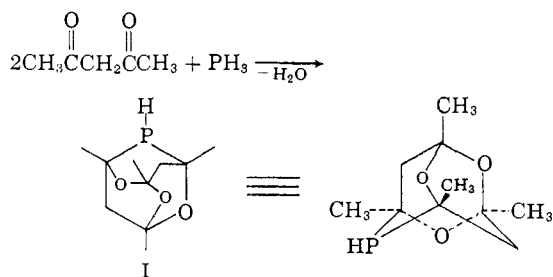
Reaction of phosphine with 2,4-pentanedione in aqueous acid solution gives a high yield of a product having the composition $C_{10}H_{17}O_3P$. On the basis of spectroscopic and chemical evidence, a cyclic acetal structure I is proposed for this substance which has the basic adamantane ring system. Similar materials (X–XII) are obtained from reactions of some primary phosphines with this diketone. In addition, compounds containing two and three phosphorus atoms have been isolated for which structures such as XIII–XV are suggested. Some reactions of these compounds are reported and a possible route for their formation is presented.

Previous reports from this Laboratory have described reactions of phosphine with a variety of aldehydes and ketones.^{1–3} The nature of the product varied considerably with structural changes in the carbonyl compound. With most ketones an "oxygen transfer" was observed resulting in the formation of a mixture of the primary phosphine oxide and hydroxy-substituted secondary phosphine oxide.¹

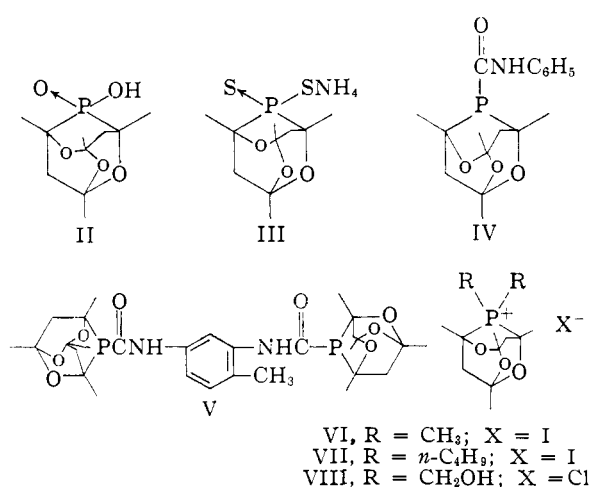


In extending this study, reactions of phosphine with a diketone, 2,4-pentanedione, have been attempted in the hope of producing a difunctional primary phosphine oxide or a four-membered ring. While the observed product was indeed heterocyclic, it was of an unexpected and unusual constitution.

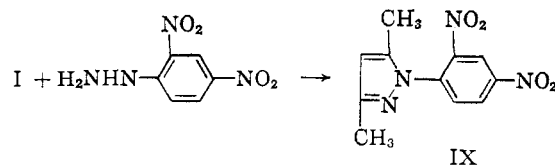
Solutions of 2,4-pentanedione in aqueous hydrochloric acid absorbed phosphine readily at room temperature and a white crystalline solid precipitated having the molecular formula $C_{10}H_{17}O_3P$. Chemical and spectroscopic evidence indicates that this material is 1,3,5,7-tetramethyl-2,4,8-trioxa-6-phosphaadamantane (I).



The chemical properties of I were typical of a secondary phosphine. Oxidation with hydrogen peroxide converted I to the phosphinic acid II and treatment with sulfur and ammonium hydroxide gave the ammonium salt of the dithiophosphinic acid III. Other derivatives which were prepared include the phenylcarbamoyl compound IV, the dicarbamoyl compound V, and the phosphonium salts VI–VIII.



That carbon skeleton rearrangement had not occurred in the formation of I was demonstrated by treatment with an acidic solution of 2,4-dinitrophenylhydrazine for an extended period of time, which produced a 59% yield of the 2,4-pentanedione derivative, pyrazole IX.⁴



The infrared spectrum of I exhibited P–H absorption at 2280 cm^{-1} which was shown to be due to a single P–H bond in the molecule by a 1:1 doublet

(1) S. A. Buckler and M. Epstein, *J. Am. Chem. Soc.*, **82**, 2076 (1960).

(2) S. A. Buckler, *ibid.*, **82**, 4215 (1960).

(3) S. A. Buckler and V. P. Wystrach, *ibid.*, **83**, 168 (1961).

(4) O. L. Brady, *J. Chem. Soc.*, 756 (1931).