Anal. Calcd for $C_{24}H_{32}O_7$: C, 66.64; H, 7.46. Found: C, 66.83; H, 7.61.

17,20α-Cyclocarbonyldioxy-11β,21-diacetoxypregn-4-en-3-one (23a) from 22a.—Treatment of 17,20α-cyclocarbonyldioxy-11β-acetoxy-21-hydroxypregn-4-en-3-one (20 mg) with acetic anhydride–pyridine for 2 hr and crystallization of the product from ethyl acetate gave 14 mg of prisms: mp 207.5–209.5°; $[\alpha]_{365}$ −141°, $[\alpha]_D$ 32.5°; λ_{max} 238 mμ (ε 16,600); ν_{max} 1805 and 782 (cyclic carbonate), 1738 and 1245 (very strong) cm^{-1} (acetate).

Anal. Calcd for $C_{26}H_{34}O_8$: C, 65.80; H, 7.22. Found: C, 65.80; H, 7.37.

23a from 2a.—To a solution of 17,20α-cyclocarbonyldioxy-21-acetoxy-11β-hydroxypregn-4-en-3-one (500 mg) in acetic acid (20 ml) and acetic anhydride (4 ml) was added *p*-TSA (400 mg). After 2 hr the product was recovered and chromatographed on a 25 × 760 mm silica gel column in ethyl acetate–isooctane (65:35), collecting 6 ml of effluent every 10 min. **Fractions 161–400** afforded prisms from ethyl acetate (335 mg, mp 206.5–209.5°; 37 mg, mp 199–202°) in a yield of 68%. The ir spectrum was identical with the acetylation product from **22a**.

17,20β-Cyclocarbonyldioxy-11β,21-diacetoxypregn-4-en-3-one (23b) from 22b.—Acetylation of 17,20β-cyclocarbonyldioxy-11β-acetoxy-21-hydroxypregn-4-en-3-one (20 mg) as in the preparation of **23a** from **22a** furnished 17 mg of prisms from ethyl acetate: mp 232–234°; $[\alpha]_{365}$ 120°, $[\alpha]_D$ 119°; λ_{max} 238 mμ (ε 16,200); ν_{max} 1805 and 778 (cyclic carbonate), 1740 and 1240 (very strong) cm^{-1} (acetate).

Anal. Calcd for $C_{26}H_{34}O_8$: C, 65.80; H, 7.22. Found: C, 65.83; H, 7.18.

23b from 2b.—A suspension of 17,20β-cyclocarbonyldioxy-21-acetoxy-11β-hydroxypregn-4-en-3-one (500 mg) in acetic acid (20 ml) and acetic anhydride (4 ml) containing *p*-TSA (400 mg) was stirred and warmed slightly to effect solution. After an additional hour at room temperature the product was recovered and crystallized from ethyl acetate (272 mg, mp 231.5–233.5°). The mother liquor was chromatographed on a 20 × 700 mm silica gel column in ethyl acetate–isooctane (3:2), collecting 4-ml fractions at 10-min intervals. From **fractions 166–350** was obtained an additional 96 mg of product, mp 230–232°, raising the yield to 67%. The ir spectrum was identical with that of the acetylation product from **22b**.

Registry No.—**2a**, 33537-28-9; **2b**, 33487-57-9; **3a**, 33487-58-0; **3b**, 33487-59-1; **4a**, 33487-60-4; **4b**, 33487-61-5; **5a**, 33537-24-5; **5b**, 33487-62-6; **6a**, 33608-34-3; **6b**, 33487-63-7; **7a**, 33487-64-8; **7b** 33487-65-9; **8a**, 33487-66-0; **8b**, 33487-67-1; **9a**, 33487-68-2; **9b**, 33487-69-3; **10a**, 33487-70-6; **10b**, 33487-71-7; **11a**, 33487-72-8; **11b**, 33487-73-9; **12a**, 33537-25-6; **12b**, 33487-74-0; **13a**, 33537-26-7; **14a**, 33487-75-1; **15a**, 33487-76-2; **15b**, 33487-77-3; **16a**, 33487-78-4; **16b**, 33487-79-5; **17a**, 33487-81-9; **17b**, 33487-80-8; **18a**, 33487-82-0; **18b**, 33487-83-1; **19a**, 33537-27-8; **19b**, 33487-84-2; **20a**, 33487-85-3; **20b**, 33487-86-4; **21a**, 33487-87-5; **21b**, 33487-88-6; **22a**, 33487-89-7; **22b**, 33487-90-0; **23a**, 33487-91-1; **23b**, 33487-92-2.

The Olefin Selectivity for the Dehydration of 2-Octanol by Alumina and Thoria

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The primary olefin distribution was determined for the dehydration of 2-octanol over several alumina and thoria catalysts. Rather than attempt the elimination of secondary reactions, the isomerization of a very similar olefin, 1-heptene, was used to determine the extent of isomerization of the primary olefin products. For acidic alumina the initial olefin products were 45% 1-octene, 5% *trans*-2-octene, and 50% *cis*-2-octene. The presence of alkali metals in the alumina to decrease acidity caused an increase in the amount of the trans isomer and a corresponding decrease in the 1 isomer.

The mechanism for alcohol dehydration has been widely studied. The results of an early kinetic study with ethanol were interpreted by Brey and Krieger[1] to favor a carbonium ion intermediate. More recent investigators have altered or abandoned a carbonium ion intermediate for secondary alcohols. For instance, Pines and coworkers[2] have expanded the idea of Schwab and coworkers[3] that dehydration occurred in the catalyst pores. Pines attributed a pseudosolvent character to alumina and thus explained dehydration as a typical concerted trans elimination reaction.[4]

A large portion of the data used for mechanism proof has been olefin product distributions. For this distribution to be meaningful one must use the primary olefin product distribution unaltered by later isomerization. Various means have been used to reduce isomerization: adding alkali metal ions to the catalyst, addition of nitrogen bases during the reaction, low conversion, etc. The use of these additives requires us to assume that the isomerization may be poisoned more easily than dehydration if both reactions occur on the same catalyst site or that dehydration and isomerization occur on different sites.

In the present study we have determined the olefin product distribution from 2-octanol dehydration using several alumina and thoria catalyst preparations. Rather than try to eliminate secondary isomerization reactions we have used the isomerization of a very similar olefin, 1-heptene added to the reactant, to determine the extent of isomerization of the olefin product during the dehydration of 2-octanol.

Results

In Table I the selectivity for olefin formation (1-, *trans*-2-, and *cis*-2-octene) from 2-octanol over several catalysts are presented with some results from the literature for other 2-ols. Our selectivity data are taken for the sample collected after about 150–200 min on stream. It is noted that there are two sets of selectivity: over acidic alumina where the amount of *trans*-2-octene is less than 10% of the total octenes and nonacidic alumina, chromia ,and molybdena catalysts where the trans isomer comprised 10–25% of the olefin products. Over all catalysts, including those from the

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[1] W. S. Brey, Jr., and K. A. Krieger, *J. Amer. Chem. Soc.*, **71**, 3637 (1949).

[2] E. J. Blanc and H. Pines, *J. Org. Chem.*, **33**, 2035 (1968), and references cited therein.

[3] G. M. Schwab and E. Schwab-Agallidis, *J. Amer. Chem. Soc.*, **71**, 1806 (1949).

[4] R. T. Morrison and R. N. Boyd, "Organic Chemistry," Allyn and Bacon, Boston, Mass., 1966.

literature, the amount of cis isomer is nearly 50% of the total olefins. In our runs with only 2-octanol, it was observed that at early time on stream the olefin distribution was different from that at later time on stream. Initially a large relative amount of *trans*-2-octene was formed but decreased to nearly a constant value at later times. The total conversion of 2-octanol usually decreased slowly as the catalyst aged with time on stream. The first sample is usually not representative, since a chromatographic effect allows the olefins to exit from the catalyst bed more rapidly than the alcohol.

To determine the amount of isomerization of the olefin product after desorption, we made runs in which 1-heptene was added to the 2-octanol charge. The added 1-heptene should undergo the same isomerization reactions as the olefin dehydration product (see isomerization paths 1 and 2 in the Discussion). As shown in Table II, the added 1-heptene underwent isomerization at early time on stream but the amount of isomerized heptene decreased to a very small amount at later times on stream. The decrease in 1-heptene isomerization parallels that of the decrease in *trans*-2-octene formation. Thus, isomerization of the octene product after desorption does not occur to a great extent at later time on stream.

TABLE I

CONVERSION OF 2 ALCOHOLS OVER ALUMINA CATALYSTS

Alcohol	Alumina	Temp, °C	Olefin distribution, %		
			1	t-2	c-2
2-Octanol	Al_2O_3–A[a]	180	43	9	48
2-Octanol	Al_2O_3 ex $AlCl_3$[a]	180	47	6	47
2-Octanol	Cr_2O_3–Al_2O_3[b]	250	38	18	47
2-Octanol	MoO_3–Al_2O_3[c]	180	42	11	47
2-Octanol	Al_2O_3–K (0.4%)[d]	250	41	13	47
2-Octanol	Al_2O_3–K (1.0%)[d]	250	37	19	44
2-Octanol	Al_2O_3–Li (5%)[d]	250	33	24	43
2-Octanol	Al_2O_3[e]	180	46	7	47
2-Octanol	Al_2O_3[f]	180	44	10	46
2-Butanol[g]	Al_2O_3–K	350	44	14	42
2-Pentanol[g]	Al_2O_3–K	350	34	13	54
2-Heptanol[h]	Al_2O_3	280; N_2[h]	34	16	50
		280; CO_2	36	16	48
		280, H_2	38	14	49
		280; NH_3	36	16	48

[a] Acidic alumina. [b] Chromia (16%) supported on nonacidic alumina. [c] Molybdena (10%) supported on nonacidic alumina. [d] Nonacidic alumina. [e] Acidic alumina prepared by hydrolysis of Al–Hg amalgam. [f] Commercial alumina from Continental Oil Co. [g] Results from H. Pines and J. Manassen, *Advan. Catal.*, 16, 49 (1966). [h] Results from M. Laroche, A. Pazdzerski, and B. Blouri, *Bull. Soc. Chim. Fr.*, 2541 (1968); the gas given under conditions was added during the run as a carrier gas.

TABLE II

CONVERSION OF 2-OCTANOL CONTAINING 1-HEPTENE OVER VARIOUS ALUMINA CATALYSTS (LHSV[a] 0.32, NO CARRIER GAS)

Catalyst	Temp, °C	Time, min	Conversion, %[b]	Octenes, %			Heptenes, %		
				1	t-2	c-2	1	t-2	c-2
Al_2O_3 from Al isopropoxide	180	87	85	43	24	33	63	26	11
		124	53	43	10	47	97	1.5	1.5
		167	39	42	10	48	97	1.5	1.5
		217	41	43	9.9	47	98	1	1
Al_2O_3–K (0.1% K)	250	60	95	40	30	30	59	25	17
		99	95	34	27	39	79	12	9.5
		186	95	34	25	41	86	7.2	8.6
		211	95	33	22	45	90	5	5
Al_2O_3–K (1.0% K)	250	66	45	36	29	35	85	9	6
		125	44	38	18	44	94	3	3
		195	39	39	18	43	93	3	3
		215	37	37	19	44	94	3	3
Al_2O_3–Li (5% Li)	250	50	29	34	27	37	97	1.8	1.7
		115	15	32	25	42	98	1	1
		165	15	35	23	42	99		
		225	15	33	24	43	99		
Al_2O_3 from Al chloride	180	88	96	46	21	33	68	18	14
		144	93	39	10	50	94	3	3
		208	89	38	10	52	98	1	1
		258	86	38	9.4	53	99		
		293	85	38	8.7	53	99		

[a] Liquid hourly space velocity. [b] Conversion is given for conversion to olefins plus other products.

2-Octanol, with 1-heptene added, was also converted over several thoria catalysts that had been found to be nonselective for α-olefin formation.[5] Over thoria there is little isomerization of the added 1-heptene even at early time on stream. However, the octene product contained large amounts of the *cis*- and *trans*-2-octene and in several runs the 2-octene isomers are the major product.

1-Heptanol with 1-octene added was also converted over thoria and alumina. The conversion of 1-heptanol is quite different over the two catalyst systems. 1-Heptene is the major olefin over alumina and approaches 100% at later time on stream. The isomerization of the added 1-octene parallels the formation of the *cis*- and *trans*-2-heptene. Also, diheptyl ether is formed over alumina and the amount even surpasses the amount of dehydration. In contrast, significant amounts of diheptyl ether do not form over thoria, but in some cases a large amount of the dihexyl ketone (identified by gc retention time) is formed by condensation of two alcohol molecules with the loss of CO or CO_2. Also, much more of the *cis*- and *trans*-2-heptenes are formed over these thoria samples than over alumina. The relative amount of the *cis*- and *trans*-2-heptene is larger than the corresponding isomerization of the added 1-octene. This is true even for low conversions;

(5) B. H. Davis and W. S. Brey, Jr., *J. Catal.*, in press.

TABLE III

CONVERSION OF 2-OCTANOL CONTAINING 1-HEPTENE OVER VARIOUS THORIUM OXIDE CATALYSTS

Catalyst[a]	Time, min	Conversion, %[b,c]	Octenes, % 1	Octenes, % t-2	Octenes, % c-2	Heptenes, % 1	Heptenes, % t-2	Heptenes, % c-2
25-Z	80	30	37	26	38	96	2	2
	135	16	35	24	41	99		
	200	8						
	250	9	39	23	38	99		
ThO_2 from $ThCl_4$	33	45	33	28	39	92	4	4
	89	66	29	32	39	97	1.5	1.5
	145	60	28	30	42	98	1	1
	205	52	28	30	42	98	1	1
	230	46	28	29	43	99		
ThO_2 (1.8 *M*)	80	44	50	26	25	93	3.5	3.5
	166	27	56	20	24	96	2	2
	205	17	58	20	22	99		
ThO_2 from thorium carbonate	63	88	51	26	23	58	23	19
	115	56	66	17	17	92	4	4
	175	64	68	16	16	92	4	4
	245	59	67	17	16	96	2	2

[a] All catalysts were pretreated at 600° for 4 hr in oxygen. [b] Conversion is for 2-octanol to octenes and 2-octanone. [c] Temperature was 250° except for ThO_2 from thorium chloride, where it was 190°.

TABLE IV

CONVERSION OF 1-HEPTANOL WITH ADDED 1-OCTENE OVER THORIA AND ALUMINA CATALYSTS

Catalyst[a]	Temp, °C	Time, min	Conversion, %[b]	Ether or[c] ketone, %	Heptenes 1	Heptenes t-2	Heptenes c-2	Octenes 1	Octenes t-2	Octenes c-2
ThO_2 (Cl)	240	50	100		40	39	21	61	27	13
		87	91	2.1	39	39	22	58	27	15
		141	68	1.3	41	38	21	63	21	17
		180	70	1.6	39	32	29	74	13	13
		205	70	1.4	40	32	28	73	15	12
ThO_2 (0.03 *M*)	380	60	21	1.1	67	13	20	93	3	4
		100	21	1.2	68	14	19	92	5	3
		170	26	3.3	68	14	18	92	5	3
		185	25	2.9	68	14	18	91	4	6
ThO_2 (25-Z)	360	65	80	10	46	31	23	68	18	13
		120	63	22	61	20	18	83	7.9	7.9
		175	60	23	59	21	20	84	9.1	7.3
		220	62	21	62	20	18	85	7	8
		260	60	26	64	17	19	85	7	8
ThO_2 (0.6 *M*)	400	80	74	23	68	16	17	80	10	10
		120	80	13	78	4.4	17	82	9	9
		190	70	12	76	5.1	18	95	2.5	2.5
		210	78	15	76	8.4	16	96	2	2
Al_2O_3–K (1% K)	330	95	57	30	92	2.4	6.1	90	4	6
		138	62	28	93	1.7	5	95	2.5	2.5
		188	56	27	93	1.8	5.4	93	3	4
Al_2O_3–A	220	40	90	25	63	26	10	79	12	9
		65	77	50	96	2	2	98	1	1
		125	74	51	98			98		
		225	74	50	98			98		
		270	78	52	98			98		

[a] Thoria and alumina catalysts were pretreated at 600° in flowing hydrogen for 3 hr before the run was started. [b] Conversion is the total alcohol conversion to heptenes and ketone or ether. [c] Over thoria this would be the dihexyl ketone; over alumina this would be diheptyl ether.

for example, over the thoria precipitated from 0.03 *M* thorium nitrate solution the amount of heptene formed is about the same as the amount of added octene, but the amount of 2-heptenes is greater than the amount of 2-octenes. Thus, if the olefins undergo an equal amount of isomerization from the gas phase olefins, some 1-heptene isomerization must occur before desorption. A comparison of the olefin isomerization for the runs with 1-heptanol and 2-octanol shows that more occurred over both catalysts in the 1-heptanol runs. This is probably due to the higher temperature required to obtain a similar conversion for 1-heptanol as for 2-octanol.

Discussion

The experimental olefin distribution may be altered by two reaction pathways (A, alcohol; E, initial olefin product; I, isomerized olefin; g, gas phase; ads, adsorbed phase).

$$\begin{tikzcd} (1) \quad A_{(g)} \arrow[r, shift left] & A_{(ads)} \arrow[l, shift left] \arrow[r] & E_{(ads)} \arrow[r] \arrow[dr] & E_{(g)} \\ & & & I_{(ads)} \arrow[r] & I_{(g)} \end{tikzcd}$$

$$\begin{tikzcd} (2) \quad A_{(g)} \arrow[r, shift left] & A_{(ads)} \arrow[l, shift left] \arrow[r] & E_{(ads)} \arrow[r] & E_{(g)} \arrow[r] & {} \\ & & & I_{(ads)} \arrow[r] & I_{(g)} \end{tikzcd}$$

In reaction pathway 1 the product distribution is determined by the adsorbed intermediate before desorption, and the addition of 1-heptene to the 2-octanol would not give a measure of the product isomerization, but in pathway 2 the olefin product desorbs to the gas phase and is isomerized only after readsorption. For 2 the addition of 1-heptene to 2-octanol would provide a measure of the influence of isomerization on the experimental olefin distribution.

Considering the data in Tables II, III, and IV, it appears that, at later time on stream, the octene isomer distribution is not being altered by pathway 2. Also, if the octene distribution is being altered by pathway 1, over acidic alumina the isomerization must be a selective one: 1-octene ⇄ *cis*-2-octene. Over nonacidic alumina we can eliminate pathway 2 for altering the octene distribution but not pathway 1. Over thoria, pathway 2 can make only a minor contribution to the olefin distribution. Thus, the larger amount of *trans*-2-octene formed over thoria cannot be accounted for by pathway 2.

To obtain more information about the contribution of pathway 1 on the olefin products, we converted a mixture of 1-heptanol and 1-octene over alumina and thoria. For pathway 1, presumably the only product of dehydration (1-heptene) would undergo isomerization to a similar extent as the 1-octene product from 2-octanol dehydration. For later time on stream, acidic alumina gave less than 5% isomerization and nonacidic alumina less than 10% isomerization of the 1-heptene product, but for thoria the isomerization of 1-heptene to 2-heptenes is considerably larger than the isomerization of the added 1-octene.

This would mean that over both aluminas isomerization by pathway 1, as well as 2, is small and the experimental octene distribution is very close to that obtained as primary products of the dehydration. Over thoria the olefin product distribution is not altered by pathway 2 but it is altered to a large extent by pathway 1 over some thoria samples. Thus we believe that the olefin distribution from 2-octanol dehydration may be summarized as shown in Table V.

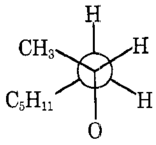
TABLE V

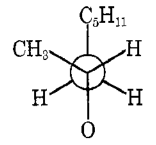
SUMMARY OF INITIAL OLEFIN PRODUCTS FROM 2-OCTANOL DEHYDRATION

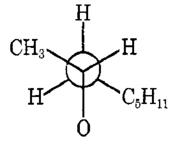
	Olefin distribution, %		
Catalyst	1-Octene	*trans*-2-Octene	*cis*-2-Octene
Acidic alumina	40–45	5–10	50
Nonacidic alumina	30–40	10–25	45–50
Thoria (selective)	100[a]		

[a] See ref 5 for octene distributions from several thoria samples. These show that 100% 1-octene is approached over some thoria preparations.

A trans elimination of water is the mechanism favored by most investigators for the dehydration of alcohols by alumina.[6,7] However, the present results can be explained by a cis elimination as well as by a trans elimination. If the alcohol is adsorbed on the catalyst surface by the OH group, three conformations are possible.


I


II


III

Adsorption by the OH group is probable, since both alumina and thoria are more selective dehydration catalysts when pretreated with hydrogen (and probably have an oxygen anion deficient surface) than when pretreated with oxygen.[5,8] If all three conformations are equally probable, a cis elimination would give about a 1:1 ratio of cis:trans isomer. Trans elimination should give a similar ratio, but alumina adsorbs olefins and may be used for gc columns to separate olefins or paraffins. For example, alkene retention times on alumina at 210° show that the free energy of adsorption is approximately -0.55 kcal/mol for each $-CH_2-$ group.[9] The adsorption would probably be weaker on hydrated alumina but would still be significant. This would mean that configurations similar to I and III would be favored, since they allow the C_5H_{11} alkyl group to be more easily adsorbed on the surface. The free energy of adsorption would be approximately -2.7 kcal/mol if all five $-CH_2-$ groups were adsorbed on dehydrated alumina. This should be sufficient to compensate for some increased conformational steric interaction in structures I and III and skew conformations similar to I and III. Thus, structures similar to I and III should predominate during dehydration reactions, but we would still obtain a 1:1 *cis*- to *trans*-2-octene ratio. However, the above conformations could determine the olefin selectivity provided I → *cis*-2-octene and III → 1-octene + *trans*-2-octene. Models of 2-octanol would suggest that, due to the C_5H_{11} alkyl group, the adsorption of the methyl group on the surface should be more difficult in conformation I than in III.

The dehydration using the nonacidic alumina yielded 2–4 times more *trans*-2-octene than acidic alumina. This could be due to the higher temperature required to obtain a given conversion over nonacidic alumina than was required for the acidic alumina. However, the small amount of 2-heptene from 1-heptanol dehydration would suggest that this is not the case. Another possibility is that the alkali metal, or the nitrogen base, added to decrease the acidity is responsible. This could be due to a decrease in the adsorption potential for the alkyl groups on a base-poisoned surface so that configuration II, which could yield all three isomers, contributes more over these catalyst. Another possibility is that the base is present close enough to the dehydration site so that it alters the bond angles in conformations I and III sufficiently to effect the formation of larger amounts of the trans isomer.

The deuterium tracer study of acyclic alcohol dehydration by Lundeen and Van Hoozer[10] provides convincing evidence for a cis elimination mechanism over thoria catalysts. The present olefin distribution can be accounted for by a cis mechanism. A cis elimination mechanism would mean that a single mechanism would be sufficient to describe the dehydration of secondary acyclic alcohols over both thoria and alumina.

Catalysts. **Al_2O_3–A** was prepared by the hydrolysis of aluminum isopropoxide (1 kg/3 l. isopropyl alcohol) with water.[11]

Al_2O_3–K.—Alcoa alumina (99.99%) was dissolved in potassium hydroxide. Alumina was precipitated by the addition of CO_2.[11] The precipitate was washed with water; the amount of washing determined the final potassium content.

Al_2O_3–Li.—Alcoa aluminum was added to a lithium hydroxide solution. The lithium aluminate precipitate was washed with water to reduce the Li to 5% in the calcined (600°) catalyst.

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[6] H. Pines and J. Manassen, *Advan. Catal.*, **16**, 49 (1966).

[7] K. Narayana and C. N. Pillai, *Indian J. Chem.*, **7**, 409 (1969).

[8] B. H. Davis, unpublished work.

[9] R. M. Lane, B. C. Lane, and C. S. G. Phillips, *J. Catal.*, **18**, 281 (1971).

[10] A. J. Lundeen and R. Van Hoozer, *J. Org. Chem.*, **32**, 3386 (1967).

[11] H. Pines and W. O. Haag, *J. Amer. Chem. Soc.*, **82**, 2471 (1960).

MoO_3–Al_2O_3.—Al_2O_3–K (1% K) was impregnated with aqueous ammonium molybdate to give 10 wt % MoO_3.

Cr_2O_3–Al_2O_3.—Al_2O_3–K (0.1% K) was impregnated with chromic acid solution to give 13 wt % Cr.

Al_2O_3–B.—Alcoa aluminum was hydrolyzed by forming the mercury amalgam using mercuric chloride.

Al_2O_3–C.—Ammonium hydroxide was added to aluminum chloride (2 *M*) to form the hydroxide; the precipitate was washed with water until a negative test for chloride in the wash was obtained with $AgNO_3$.

Thoria.—25-Z was prepared by the thermal decomposition of thorium nitrate hydrate; the heating program was similar to 25-H in reference 12. ThO_2 (1.8 *M*): thorium hydroxide was precipitated from a 1.8 *M* thorium nitrate solution (or other concentration if given) and washed to give high surface area thoria.[13] ThO_2–Cl: the hydroxide was precipitated from 1 *M* thorium chloride solution with ammonium hydroxide and washed to a negative Cl test.[12] ThO_2–C: thorium carbonate was heated to 600° in air.

Dehydration Procedure.—The catalyst was heated in hydrogen or oxygen *in situ* for 4 hr at 600°. 2-Octanol was fed by a displacement pump (LHSV 0.3) and the liquid products were collected after passing through a water-cooled condensor. The 2-octanol contained about 1.8% 2-octanone. The samples were analyzed for conversion by temperature-programmed gc using a Carbowax 20M column. The octene isomers and heptene isomers (1-, *trans*-2-, and *cis*-2-olefin) were analyzed using the same column isothermally at 60°. These three isomers could be determined quantitatively in the *absence* of the 3 and 4 isomers. For several runs, the octene isomer peaks were trapped and no 3 or 4 isomers were detected by ir. The presence of large amounts of the 3- and 4-octene isomers could be detected by gc because of peak broadening and retention time changes, even though a complete separation of all octene isomers were not possible.

Registry No.—2-Octanol, 123-96-6; 1-heptene, 592 76-7; 1-heptanol, 111-70-6; 1-octene, 111-66-0; Al_2O_3, 1344-28-1; ThO_2, 1314-20-1.

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Metal Nitrides in Organic Reactions. II. Reactions of Lithium Nitride with Aromatic Aldehydes[1a-c]

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Aromatic aldehydes react with lithium nitride (Li_3N) in refluxing carbon tetrachloride to give numerous products, which have resulted from a combination of diverse reactions. Benzaldehyde gives primarily Tishchenko or Cannizzaro reaction products, as well as 2,4,5-triphenylimidazole, *cis*-*N*-(2-benzamido-1,2-diphenylethenyl)benzamide, and *threo*-1,2-diphenyl-2-benzamidoethanol. The isolation and structure determination of the various products will be discussed.

Early reports indicated that nitride (N^{-3}) failed to react with alkyl halides,[2] acid chlorides,[3] and other compounds.[2-4] However, nitrides with acid anhydrides have been reported to give nitriles[2] or imides,[5] and more recently nitrides with acid chlorides afforded amides[1a,b] and cyclic imides.[6] Various other diverse reactions of ionic nitrides have been observed.[1b] In this paper, we describe the assorted reactions of aromatic aldehydes with lithium nitride.

Results and Discussion

When benzaldehyde was allowed to react with lithium nitride in refluxing carbon tetrachloride under nitrogen, the following products were isolated (Table I): benzyl benzoate (**2a**), benzoic acid (**3a**), benzyl alcohol (**4a**), benzamide (**5a**), benzonitrile (**6a**), *cis*-*N*-(2-benzamido-1,2-diphenylethenyl)benzamide (**7a**), 2,4,5-triphenylimidazole (**8a**), and *threo*-1,2-diphenyl-2-benzamidoethanol (**9a**).

Non-nitrogen-Containing Products.—Benzyl benzoate (2a) is the major product (60%) of the reaction arising by either a Cannizzaro or Tishchenko reaction. It has been well established that benzaldehyde gives exclusively the Cannizzaro reaction products (benzyl alcohol and benzoic acid) when treated with either strong sodium hydroxide or other strong bases,[7] while under aprotic basic reaction conditions, using most commonly aluminum ethoxide[8] or sodium in tetrahydrofuran,[9] the Tishchenko reaction product (benzyl benzoate) is formed.[10] However, either reaction mechanism involves an oxidation–reduction sequence, which produces an adduct that transfers a hydride ion to another molecule of aldehyde. Since both hydride

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