7b and **10** appears in Table IV. Principal nmr absorptions for **5a**, **5b**, **6**, **7b**, and **10** are given in Table III.

Condensations of Trisodio Salt 3′ with Aromatic Aldehydes.—To a stirred suspension of 0.02 mole of trisodio salt **3′** in 300 ml of liquid ammonia was added 0.02–0.022 mole of the appropriate aldehyde in 30 ml of anhydrous ether. The reaction mixture was allowed to stir for 0.5–1.0 min, neutralized inversely with ammonium chloride, and processed as described for condensations of **3′** with aromatic ketones. In the condensation of **3′** with *p*-dimethylaminobenzaldehyde, the product isolated from the reaction mixture was found to be unsaturated imide **12b**, rather than the expected hydroxy imide.

The infrared spectra of **11a–c** and **12b** had absorption at 2.8–3.1 (NH and OH) and 5.8–6.2 μ (C=O). Analytical data and yields for hydroxy imides **11a–c** are presented in Table II. Similar data for unsaturated imide **12b** may be found in Table IV. Nmr data for these compounds appears in Table III.

Dehydration of Hydroxy Imides 5a, 6, and 11a to Form Unsaturated Imides 7a, 8, and 12a.—A 1.0–2.0-g sample of the appropriate hydroxy imide was refluxed with 25–40 ml of benzene containing a few crystals of *p*-toluenesulfonic acid for 1–12 hr. The resulting solution was cooled to precipitate the desired products which were recrystallized from appropriate solvents. The infrared spectra of these compounds had absorption at 2.8–3.1 (NH and OH) and 5.8–6.2 μ (C=O). Yields and analytical data for **7a**, **8**, and **12a** are given in Table IV. Important nmr peaks are presented in Table III.

Aroylation of Triosodio Salt 3′ with Methyl Benzoate.—To a suspension of 0.02 mole of trisodio salt **3′** in 300 ml of liquid ammonia was added 3.0 g (0.02 mole) of methyl benzoate in 20 ml of dry ether. The resulting mixture was stirred for 2 hr and the ammonia was evaporated (steam bath) as an equal volume of ether was added. The ethereal suspension was poured onto 300 g of crushed ice. The two layers were separated, the ethereal layer was discarded, and the aqueous layer was washed with 50 ml of ether which was also discarded. The aqueous layer was filtered and the dark residue was washed with water. The combined aqueous filtrate was cooled in an ice bath and acidified with 12 *N* hydrochloric acid to precipitate 2.42 g (43%) of N-salicyloyl-α-benzoylacetamide (**13**) as colorless needles, mp 167–168°, after two recrystallizations from 95% ethanol: nmr peaks (DMSO-d_6) at δ 7.42 (9 H multiplet, aromatic) and 4.58 ppm (2 H singlet, $-COCH_2CO$); infrared absorption at 2.9–3.1 (NH and OH) and 5.8–6.2 μ (C=O).

Anal. Calcd for $C_{16}H_{13}NO_4$: C, 67.84; H, 4.63; N, 4.95. Found: C, 68.05; H, 4.67; N, 5.04.

Hydrolysis of 13.—A 1.0-g sample of **13** was refluxed with 40 ml of 6 *N* hydrochloric acid for 5 hr. The resulting mixture was processed in the manner described for the acidic hydrolysis of alkylation products of **3′** to give 0.42 g (68%) of salicylic acid and 0.325 g (75%) of aceophenone, which was identified by comparison of its infrared spectrum with that of an authentic sample.

Registry No.—**3′**, 14001-88-8; **4a**, 13942-90-0; **4b**, 13942-91-1; **4c**, 13942-92-2; **4d**, 13942-93-3; **4e**, 13942-94-4; **5a**, 13942-95-5; **5b**, 13942-96-6; **6**, 14054-27-4; **7a**, 14001-89-9; **7b**, 13942-97-7; **8**, 14001-90-2; **9**, 13942-98-8; **10**, 14001-91-3; **11a**, 14001-92-4; **11b**, 14001-93-5; **11c**, 13942-99-9; **12a**, 13943-00-5; **12b**, 13943-01-6; **13**, 14001-94-6.

Selective Catalytic Dehydration. Thoria-Catalyzed Dehydration of Alcohols

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Thoria-catalyzed dehydration of secondary alcohols involves stereospecific *cis* elimination of water. Products from secondary 2-alkanols are largely (*ca.* 95%) 1-olefins. The major products from other secondary alkanols are the less substituted olefins. This is a general reaction of value in the preparation of alkenes of known structure. Thoria-catalyzed dehydration of tertiary alkanols is not selective.

Dehydration of alcohols over a metal oxide catalyst to form olefins has been extensively studied, particularly with low molecular weight alcohols and alumina catalysts. Recent reviews have summarized general dehydration literature[1] and progress in alumina-catalyzed dehydration of alcohols.[2] The extensive work of Pines and co-workers provides evidence that initial products of alumina-catalyzed dehydrations of primary and secondary alcohols arise from concerted *trans* elimination. Participation of two catalyst surfaces was proposed to achieve the required steric arrangement.[2,3] A parallel was noted between elimination reactions in solution and dehydration of alcohols catalyzed by alumina.

Differences in dehydration catalyzed by thoria and alumina have been discussed by Winfield.[1] Butadiene was the major product of thoria-catalyzed dehydration of 2,3-butanediol[4] but methyl ethyl ketone was the major product with alumina catalysis. Formation of 1-alkenes as major products from thoria-catalyzed dehydration of secondary 2-alkanols was recently shown to be a general reaction.[5] Alumina-catalyzed dehydration of 2-alkanols, however, results in formation of 2-alkenes as major products.[6] Alumina, but not thoria, catalyzes formation of diethyl ether from ethanol.[1]

Thoria-catalyzed dehydration of secondary 2-alkanols is an excellent synthetic method for preparing 1-alkenes of known structure. The present report describes this reaction in some detail and presents evidence that this dehydration involves stereospecific *cis* elimination of water.

Results

Dehydration of Secondary Alcohols.—Thoria and other oxides of actinide, lanthanide, and group IIIB elements catalyze the dehydration of secondary 2-alkanols to yield 1-alkenes as major products. Representative examples are summarized in Table I.

Dehydrations were conducted in a flow system with contact times of 0.1–0.5 sec, temperatures in the range of 330–420° and pressures of 10 mm to 1 atm.

The composition of olefins formed by thoria-catalyzed dehydration did not change significantly with temperature. The catalyst was remarkably stable and could be used to treat large quantities of alcohol, particularly when dehydrations were carried out at reduced pressure. Initially, about 5% of the product was ketone. This

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[1] M. E. Winfield, *Catalysis*, **7**, 93.

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

[3] F. G. Schappell and H. Pines, *J. Org. Chem.*, **31**, 1735 (1966).

[4] M. E. Winfield, *J. Council Sci. Ind. Res.*, **18**, 412 (1945).

[5] A. J. Lundeen and R. Van Hoozer, *J. Am. Chem. Soc.*, **85**, 2180 (1963).

[6] H. Pines and W. O. Hoag, *ibid.*, **83**, 2847 (1961).

Table I

Thoria-Catalyzed Dehydration of Secondary 2-Alkanols

Alcohol	Products, %[a] 1-Alkene	2-Alkene	Ratio, *trans/cis*
2-Butanol	93–94	6–7	1.1
2-Hexanol	95–97	3–5	...
2-Octanol	95–97	3–5	...
4-Methyl-2-pentanol	96–98	2–4	5.0
1-Cyclohexyl-1-ethanol	96–98	2–4	...

[a] These values do not include 1-2% ketone formed by competing dehydrogenation.

decreased rapidly to a constant value of *ca.* 1%. Results described in Table II serve to illustrate some preparative aspects of thoria-catalyzed dehydration of secondary 2-alkanols.

Table II

Thoria-Catalyzed Dehydration of 4-Methyl-2-pentanol

Temp, °C	HLSV[a]	Conversion, %	Products, % 1-Alkene	2-Alkene
335	9.4	*Ca.* 5	98.0	2.0
356	27.8	18	97.0	3.0
360	10.0	55	98.0	2.0
387[b]	20.5	87	97.0	3.0
399	26.0	87	97.5	2.5
415	37.2	43	96.5	3.5

[a] HLSV, hourly liquid space velocity, is the volume of liquid (milliliters) per weight (grams) of catalyst per hour. [b] Alcohol (27 moles) and thoria (6 g) were used. In all other experiments, 1 mole of alcohol and 3 g of thoria were used. Products were isolated by distillation. All dehydrations were at 100 mm.

The relative reactivity of isomeric hexanols in dehydration and dehydrogenation over thoria was studied in a micro flow system.[7] From the results presented in Table III, we see that 2-alkanols were dehydrated much faster than 3-alkanols by thoria but the rate of dehydrogenation remained essentially constant. Relative rates of dehydration cannot be readily obtained from these values because water formed retards the reaction.[8]

Table III

Thoria-Catalyzed Dehydration of Isomeric Secondary Hexanols

Alcohol	% conversion to, Olefin	Ketone
2-Hexanol	80	4.0
4-Methyl-2-pentanol	75	3.5
3-Hexanol	10	5.0
2-Methyl-3-pentanol	3	4.0

Stereochemistry of Thoria-Catalyzed Dehydration.—Reduction of *cis*-2,3-epoxy-4-methylpentane with lithium aluminum deuteride resulted in a mixture of alcohols containing 96% *threo*-2-methyl-4-deuterio-3-pentanol (I) (Scheme I). Similar reduction of *trans*-2,3-epoxy-4-methylpentane was slower and gave a mixture of alcohols containing 73% *erythro*-2-methyl-4-deuterio-3-pentanol (II). Alcohols I and II were obtained 99+% pure by preparative gas chromatography using a 4-in.-diameter column of Apiezon supported on Celite.[9] These alcohols were characterized by nuclear magnetic resonance (nmr) spectra shown in Figure 1.[10,11]

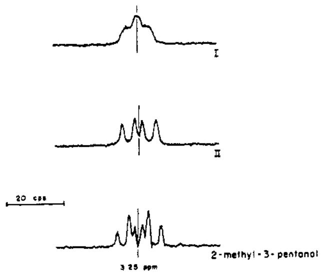
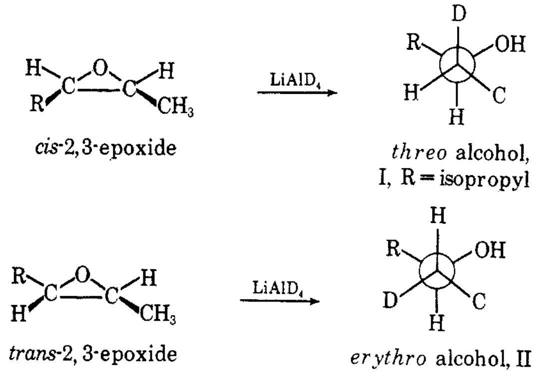


Figure 1.—Partial nmr spectra (C*H*OH) of 2-methyl-3-pentanols.

Scheme I



The stereochemistry of thoria-catalyzed dehydration was investigated by dehydrating *threo*- and *erythro*-2-methyl-4-deuterio-3-pentanols at 350°.

The olefin fraction was separated into pure components by gas–liquid partition chromatography (silver nitrate–tetraethylene glycol) and analyzed by mass spectrometry for deuterium. From these results (Table IV) and correlation with the related conformations of alcohols I and II, it is evident that most of each olefin was formed by stereospecific *cis* dehydration. However, a significant contribution arises from another path. This will be discussed in a later section.

Table IV

Thoria-Catalyzed Dehydration of 2-Methyl-3-pentanol

Alcohol	Olefin composition, % 2-Methyl-2-pentene	4-Methyl-2-pentene *cis*	*trans*	Monodeuterated 4-methyl-2-pentene *cis*, %	*trans*, %
I	11 ± 1	25 ± 2	64 ± 2	90	13
II	12	20	68	13	77
Undeuterated	12	22	66	..	..

Dehydration of Tertiary Alcohols.—In contrast to the dehydration of secondary 2-alkanols, product distribution from dehydration of *t*-amyl alcohol over thoria is temperature dependent and not selective. The selectivity for 1-alkene approaches that predicted statistically only at low temperature and conversion (Table V).

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[7] These experiments differ from larger scale dehydrations in that the small amount of alcohol used (0.5 ml) did not allow attainment of steady-state conditions. The only effect on product composition was the relatively large amount of ketone formed. All small-scale dehydrations (Tables III and IV) were at 350°.

[8] M. E. Winfield, *Australian J. Sci. Res.*, **A3**, 290 (1950).

[9] A. B. Carel and G. Perkins, Jr., *Anal. Chim. Acta*, **34**, 83 (1966).

[10] Nmr splitting patterns support assigned structures of the deuterio alcohols and indicate that the methyl and isopropyl groups prefer a *trans* conformation. P. W. Flanagan and A. J. Lundeen, unpublished results.

[11] C. A. Kingsbury and W. B. Thornton, *J. Org. Chem.*, **31**, 1000 (1966).

TABLE V

THORIA-CATALYZED DEHYDRATION OF *t*-AMYL ALCOHOL

Temp, °C	HLSV	Conversion, %	1-Alkene, %	2-Alkene, %
339	39	100	41	59
316	35	10	52	48
306	36	5	73	27

Other Oxides as Catalysts.—Several other oxides, chosen from group IIIB, including the lanthanides and actinides, were briefly examined as selective dehydration catalysts. From results (Table VI), all are seen to be highly selective dehydration catalysts.

TABLE VI

DEHYDRATION OF 4-METHYL-2-PENTANOL AND OTHER OXIDES

Oxide	Temp, °C	HLSV	Conversion to olefin, %	Olefin products, %: 1-Alkene	Olefin products, %: 2-Alkene
Sc_2O_3[a]	407	28	5	95	5
Y_2O_3[a]	412	26	63	96	4
La_2O_3[b]	414	55	39	96	4
CeO_2[b]	350	50	14	86	14
Pr_6O_{11}[b]	424	55	11	92	8
N_2O_3[b]	418	55	25	94	6
Sm_2O_3[b]	415	52	24	94	6
Eu_2O_3[a]	427	46	10	95	5
Gd_2O_3[b]	423	48	23	94	6
Tb_4O_7[a]	427	16	2	90	10
Dy_2O_3[a]	404	45	6	97	3
Ho_2O_3[b]	411	52	47	97	3
Er_2O_3[a]	403	45	6	97	3
Tm_2O_3[a]	403	60	6	95	5
Yb_2O_3[b]	403	50	42	97	3
UO_2[c]	417	44	49	81	19

[a] Oxides from Michigan Chemical were used as received. [b] Oxalates from K & K Chemical were calcined 16 hr at 400°. [c] Oxalate prepared from nitrate was calcined 16 hr at 400°.

Discussion

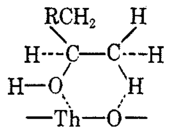
The relative ease of dehydration of isomeric hexanols by thoria suggests that most dehydration sites have rather special steric limitations. Dehydrogenation, however, is essentially constant in this series (Table III). Previous work has shown that the rate of dehydration of ethanol catalyzed by thoria increased rapidly as the surface area of the catalyst increased. Dehydration was believed to occur on interior surfaces or pore walls of the oxide which were not present in low surface materials.[12,13]

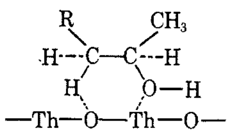
Thoria-catalyzed dehydrations of the 2-methyl-4-deuterio-3-pentanols demonstrate that *cis*- and *trans*-4-methyl-2-pentenes are formed largely by stereospecific *cis* elimination. This alcohol was the least reactive to dehydration by thoria of the alcohols studied. It is probable that the decline in rate of dehydration observed in Table III is due to a decline in rate of selective dehydration and that random dehydration processes are essentially constant. Thoria-catalyzed dehydration of secondary 2-alkanols therefore appears to be essentially entirely a stereospecific *cis*-elimination reaction. This view is consistent with the high selectivity for 1-alkene in the dehydration of secondary 2-alkanols and the more random distribution of olefins from 2-methyl-3-pentanol.[14]

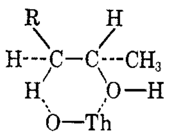
Pyrolysis of acetates is representative of several pyrolytic *cis*-elimination reaction.[15,16] Butenes resulting from pyrolysis of *sec*-butyl acetate are of a nearly statistical composition based on loss of adjacent hydrogens. Thoria-catalyzed dehydration of 2-butanol, however, is similar to the pyrolysis of trimethyl-*sec*-butylammonium hydroxide in composition of butenes formed.[17]

In contrast to pyrolytic *cis* eliminations[3] and quaternary ammonium hydroxide pyrolysis,[18] thoria-catalyzed dehydrations of secondary 2-alkanols appears to have a very small (or zero) deuterium isotope effect, as evidenced by data in Table IV. The stereospecific nature of the reaction, however, requires participation in the transition state of the β hydrogen eliminated.[19]

To accommodate these observations, we suggest that an essential feature of thoria-catalyzed dehydration of alcohols is chemisorption of the alcohol on the catalyst with bonds to oxygen and hydrogen on an adjacent carbon. Possible transition states for alkene formation are shown in III–V. Structures IV and V involve more eclipsing strain than III. However, differences in products when R is methyl and isopropyl are relatively small (Table I). Eclipsing interactions of this type are not sufficiently large to explain the preferential formation of 1-alkenes observed in thoria-catalyzed dehydrations.


III


IV


V

A source of larger differences between these transition states may arise from nonbonded interactions between the chemisorbed alcohol and the catalyst surface. Transition states for 2-alkene formation (IV and V) require a larger part of the alcohol molecule to be closer to the catalyst surface than the transition state for 1-alkene formation (III). An additional alkyl–catalyst interaction in IV and V not present in III results from the bonding of methylene rather than a methyl hydrogen to the catalyst. This interaction could be large if hydrogen–catalyst bonds involve sites buried in the catalyst surface.

Oxides found to be selective dehydration catalysts (Table VI) are trivalent or tetravalent and represent several crystal structures. However, ionic radii of the metals are similar and many of their chemical properties are similar. Chemisorption of alcohols on these oxides with bonds to hydroxyl oxygen and methyl or methylene hydrogen will depend on the chemical prop-

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[12] W. S. Brey, Jr., B. H. Davis, P. G. Schmidt, and C. G. Moreland, *J. Catalysis*, **3**, 303 (1964).

[13] In a study of dehydrogenation and dehydration of alcohols by alumina, dehydrogenation was considered to occur on and dehydration within the catalyst surface: G. M. Schwab and E. Schwab-Agallidis, *J. Am. Chem. Soc.*, **71**, 1806 (1949).

[14] Thoria-catalyzed dehydration of 2-methyl-3-pentanol yields 88% of the less substituted olefin and is less selective in this sense than thoria-catalyzed dehydration of secondary 2-alkanols which typically yield above 95% of the less substituted olefin.

[15] P. S. Skell and W. L. Hall, *J. Am. Chem. Soc.*, **86**, 1557 (1964).

[16] C. H. DePuy and R. W. King, *Chem. Rev.*, **60**, 431 (1960).

[17] A. C. Cope, N. A. LeBel, H. H. Lee, and W. R. Moore, *J. Am. Chem. Soc.*, **79**, 4720 (1957).

[18] V. J. Shiner, Jr., and M. L. Smith, *ibid.*, **80**, 4095 (1958).

[19] For a discussion of small deuterium isotope effects, see F. H. Westheimer, *Chem. Rev.*, **61**, 265 (1961).

erties of the oxide and should be similar through the series. Steric hindrance around the catalyst–hydrogen bond will be significant if the formation of this bond requires that the methyl or methylene involved become very close to the catalyst surface and does not presuppose any special surface features.

The greater acidity of methyl hydrogens will also favor participation of methyl rather than methylene hydrogens in this elimination if the carbon losing hydrogen develops carbanionic character in the transition state. The relative importance of steric and electronic factors cannot be assigned at this time.

The dehydration of tertiary 2-alkanols over thoria is not selective. The more facile cleavage of the carbon–oxygen bond probably results in a transition state in which this bond is largely broken but carbon–hydrogen cleavage is not well developed. Following elimination of hydroxyl, an adjacent proton is eliminated in a statistical manner.[20]

The most active and selective thoria catalysts were prepared by calcining thorium oxalate in air.[4] Less active although equally selective catalysts were prepared by calcining thorium acetate and carbonate. Thoria prepared by calcining thorium hydroxide was recently reported to be a selective dehydration catalyst.[21]

Experimental Section

Catalyst Preparation.—Catalysts were prepared by heating oxalates,[4] acetates, or carbonates in air at 400° for 16 hr. For large experiments (Tables I and II) the catalyst powder (3.0 g) was coated on small glass beads[22] (50 g) by wetting the beads with 0.5 ml of alcohol and mixing in a small flask. Small dehydrations (Tables III and IV) were made using 0.2 g of catalyst supported on 20 g of 3-mm-diameter glass beads.

General Dehydration Procedure.—All dehydrations were carried out in Pyrex flow systems consisting of a vaporizer, catalyst bed, and trap system. In large runs, alcohols were metered into a vaporizer which consisted of a heated bed of 50 g (3-mm diameter) of glass beads.[23] Products were collected in a series of three cold traps. Most dehydrations were conducted at reduced pressure (100 mm) to facilitate vaporization of the alcohol.

Dehydrations were conducted on a microscale using 0.5 ml of alcohol with a small reactor. A nitrogen flow of 45-cc/min was maintained over the catalyst. Samples were introduced by vaporizing from a chamber maintained at 90° in the nitrogen stream (Table III) or 65° (Table IV). Products were condensed in a spiral trap cooled with Dry Ice.

Analysis of Products.—Total reaction products were analyzed by gas chromatography (Silicone SE-30 on Chromosorb-G or Resoflex on Celite) to determine conversion. Olefins from large runs were isolated by distillation. Analysis of olefins was by gas chromatography using silver nitrate–tetraethylene glycol[24] and Resoflex columns. Compositions assigned by glpc were confirmed by infrared and (except for butenes) nmr spectroscopy. Small runs were analyzed by glpc and mass spectrometry.

2-Methyl-4-deuterio-3-pentanols.—*cis*- and *trans*[25]-2,3-epoxy-4-methylpentanes were prepared from corresponding olefins (Phillips 99% min) and *m*-chloroperbenzoic acid. Each epoxide was obtained 99+% pure. *cis*-2,3-Epoxy-4-methylpentane (bp 99–100°) gave expected nmr and infrared spectra.

Anal. Calcd for $C_6H_{12}O$: H, 12.08. Found: H, 12.20.

Reduction of the *trans*-epoxide with $LiAlD_4$ (10 ml of oxide, 1 g of $LiAlD_4$ in ether) resulted in a mixture of pentanols (73% 2-methyl-3-pentanol and 27% 4-methyl-2-pentanol) and unreacted epoxide. By preparative glpc[9] 4.0 g of *erythro*-2-methyl-4-deuterio-3-pentanol was isolated.

Reduction of the *cis*-epoxide was more rapid (12 ml of oxide, 1 g of $LiAlD_4$ in ether) and resulted in a mixture of pentanols (96% 2-methyl-3-pentanol and 4% 4-methyl-2-pentanol) from which was isolated 5.5 g of *threo*-2-methyl-4-deuterio-3-pentanol as described above.

The deuterio alcohols were characterized by nmr spectra (Figure 1) which were determined at 60 Mc on a Varian Associates HR-60 spectrometer. The methyne–methylene region had 1.0 fewer protons for the deuterio alcohols than forun deuterated 2-methyl-3-pentanol.

Registry No.—*threo*-2-Methyl-4-deuterio-3-pentanol (I), 13976-09-5; *erythro*-2-methyl-4-deuterio-3-pentanol (II), 13976-10-8; thoria, 13976-11-9; 2-butanol, 78-92-2; 2-hexanol, 626-93-7; 2-octanol, 123-96-6; 4-methyl-2-pentanol, 108-11-2; 1-cyclohexyl-1-ethanol, 1193-81-3; 3-hexanol, 623-37-0; 2-methyl-3-pentanol, 565-67-3; *t*-amyl alcohol, 75-85-4; CeO_2, 13940-82-4; UO_2, 7543-50-2.

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(20) The tendency to form a larger amount of the more substituted olefin at higher temperatures than is predicted by statistical elimination may be the result of isomerization of initial products.

(21) J. W. Legg, Ph.D. Thesis, University of Florida, Tallahassee, Fla., 1964.

(22) The average diameter of the microbeads (3M Co.) was 0.57 mm.

(23) A Beckman Solution Metering pump or a Sigmamotor pump was used. Catalyst bed and vaporizer were heated electrically and maintained at constant temperature (±2°) by a temperature controller. Temperature was measured by an iron–constantan thermocouple in the center of the catalyst bed.

(24) A. C. Cope and E. M. Acton, *J. Am. Chem. Soc.*, **80**, 355 (1958).

(25) A. T. Boltini, R. L. Van Etten, and A. J. Davidson, *ibid.*, **87**, 755 (1965).