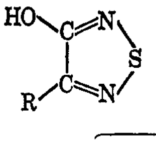
Table I



| Compd | R | Yield pure, % | Mp, °C | Formula | Calcd, % C | H | N | Found, % C | H | N | p$K_a'$ |
|---|---|---|---|---|---|---|---|---|---|---|---|
| VIII | $CH_2{=}CH$ | 54 | 92–94 | $C_4H_4N_2OS$ | 37.48 | 3.14 | 21.86 | 37.30 | 3.24 | 20.98 | 6.80 |
| IX | $CH_3SCH_2CH_2$ | 57 | 65 | $C_5H_8N_2OS_2$ | 34.07 | 4.57 | 15.89 | 33.85 | 4.60 | 15.94 | 7.0 |
| X | $CH_3$ | 22 | 146 | $C_3H_4N_2OS$ | 31.02 | 3.47 |  | 31.21 | 3.23 |  | 7.10 |
| XI | $(CH_3)_2CH$ | 42 | 84–85 | $C_5H_8N_2OS$ | 41.64 | 5.59 | 19.43 | 41.86 | 5.79 | 19.67 | 7.25 |
| XII | $C_6H_4$ | 56 | 165–166 | $C_8H_6N_2OS$ | 53.91 | 3.39 | 15.72 | 54.23 | 3.78 | 15.68 | 6.98 |
| XIII | $C_6H_4CH_2$ | 45 | 139–140 | $C_9H_8N_2OS$ | 56.22 | 4.19 |  | 56.02 | 4.35 |  | 7.1 |

Methioninamide methylsulfonium chloride hydrochloride (VII) was allowed to react with thionyl chloride in chloroform. The resulting product was 3-hydroxy-4-vinyl-1,2,5-thiadiazole, dimethyl sulfide having been eliminated during the reaction. Methioninamide hydrochloride yielded the expected methylmercaptoethylhydroxythiadiazole without complication.

### Experimental Section[14]

**3-Hydroxy-4-methyl-1,2,5-thiadiazole (X). Method A.**—To 10 g of alaninamide hydrochloride[13] suspended in 200 ml of chloroform was added 150 ml of thionyl chloride. The well-stirred reaction mixture was heated to reflux for 48 hr. The reaction was concentrated *in vacuo* to a brown solid, which was then taken up in 600 ml of chloroform. The solution was washed with two 150-ml portions of water and extracted with two 150-ml portions of 10% sodium hydroxide solution. The basic extracts were cooled to 0°, made acidic with concentrated hydrochloric acid, and extracted with four 200-ml portions of chloroform. The latter solution was washed with water, followed by brine, dried over magnesium sulfate, and concentrated *in vacuo*. A yield of 150 mg (1.2%) of product was obtained as a yellow solid. It was sublimed at 75° (0.3 mm), mp 143°.

**Method B.**—To 22 g of alaninamide, free base, suspended in 1500 ml of dry pyridine was added 121 g of thionylaniline.[12] The well-stirred reaction mixture was kept under a nitrogen atmosphere while being heated at 90° for 16 hr. The reaction was worked up as in the method A to yield 8.6 g of a rust-colored solid. The compound was purified by chromatography on silicic acid and Supercel: 6.56 g (22% yield), mp 144–146°, p$K_a'$ = 7.10, mol wt 120 (calcd 116.1).

**Methioninamide methylsulfonium chloride hydrochloride** (VII) was obtained as a by-product, in about 30% yield, during the preparation of methioninamide (VIII), mp 168–172° from ethanol.

*Anal.* Calcd for $C_5H_{16}Cl_2N_2OS$: C, 30.63; H, 6.80; Cl, 30.12; N, 11.91; S, 13.61. Found: C, 30.56; H, 7.00; Cl, 29.88; N, 11.87; S, 13.80.

**3-Hydroxy-4-Substituted 1,2,5-Thiadiazoles (Table I).**—Compounds IX–XIII were prepared from thionylaniline and the appropriate α-amino acid amide. The 4-vinyl compound (VIII) was obtained as the only product isolated from the reaction starting with methioninamide methylsulfonium chloride hydrochloride (VII) and thionyl chloride. The molecular weight of each of the compounds in Table I was determined from the electrometric titration curve. The values found agreed with those calculated within the limits of experimental error.

**Acknowledgment.**—We are indebted to Messrs. W. L. Brown, G. M. Maciak, H. L. Hunter, A. Brown, D. Cline, and C. W. Ashbrook for elemental analyses and Mr. L. A. White for large-scale preparations of starting materials. In addition, we wish to thank Dr. H. Boaz and his group for the physicochemical measurements: Messrs. H. Howard and L. Huckstep. ultraviolet spectra; Mr. L. Spangle, titration; Messrs, P. Landis and J. Klemm, nmr; and Mr. D. Woolf and Miss M. Hofmann, infrared spectra.

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[14] All melting points are corrected. Ultraviolet, infrared, and nmr spectra were obtained in ethanol, chloroform, and deuteriochloroform, respectively. Titrations were carried out in a 66% aqueous dimethylformamide system.

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## Dehydration of the Four Stereoisomers of 1-Decalol over Thoria, Silica–Alumina, and Silico–Phosphoric Catalysts[1]

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In the preceding paper of this series it was shown that the dehydration of 1-decalols over aluminas takes place preferentially through a *trans*-elimination reaction. Thus *cis,cis*-1-decalol formed about 89% 1,9-octalin and only 5% *cis*-1,2-octalin, while *cis,trans*-1-decalol yielded 4% of 1,9-octalin and 92% *cis*-1,2-octalin. A similar trend was obtained with *trans,cis*- and *trans,trans*-1-decalol.[1]

The present paper reports the dehydration of the four stereoisomers of 1-decalol over thoria and over acidic type catalysts, namely, silica–alumina and silico–phosphoric acid. The experiments were made in a micropulse reactor.[1]

**Thoria.**—Two sets of experiments were made, one using 30 mg and the other 500 mg of thoria (Table I). With the lesser amount of catalyst only *ca.* 3–13% of the decalols underwent dehydration to octalins, while with the 500 mg of thoria the dehydration amounted to from 26 to 61%, depending on the decalol used. The most resistant toward dehydration was the *trans,trans*-1-decalol, which is in agreement with a previous observation.[1] Part of the decalols underwent epimerization and dehydrogenation to *cis*- and *trans*-decalones.

The dehydration seems to proceed mainly *via* a *trans*-elimination reaction as evidenced by the formation of 1,9-octalin as the principal product from the dehydration of the *cis,cis*-1-decalol, and *cis*-1,2-octalin as the main olefin from the *cis,trans*-1-decalol. The stereospecificity of the dehydration of decalols in the presence of thoria was not so great, however, as in the

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[1] Paper IX in the series of Dehydration of Alcohols. For the previous paper, see F. G. Schappell and H. Pines, *J. Org. Chem.*, **31**, 1735 (1966).

[2] Taken from a Ph.D. dissertation submitted to the Graduate School, June 1965. Monsanto Co. Fellow, 1963–1964.

TABLE I

COMPOSITION OF THE PRODUCTS FROM DEHYDRATION OF 1-DECALOLS OVER THORIA AT 350°

| Products | Thoria, mg[b] | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| | *c,c*-1-OH[a] | | *c,t*-1-OH[a] | | *t,c*-1-OH[a] | | *t,t*-1-OH[a] | |
| | 30 | 500 | 30 | 500 | 30 | 500 | 30 | 500 |
| Octalins, mole % | 8.4 | 51.4 | 13.3 | 61.0 | 4.6 | 39.7 | 3.4 | 26.3 |
| *t,c*-1-OH | 3.0 | 10.1 | 2.1 | 3.8 | 88.9 | 33.0 | 0.7 | 2.4 |
| *t,t*-1-OH | 0.7 | 10.1 | | 1.2 | 2.6 | 11.5 | 95.9 | 53.8 |
| *c,t*-1-OH | | 1.2 | 83.3 | 28.6 | 0.5 | | | |
| *c,c*-1-OH | 84.7 | 10.7 | | | 0.5 | | | |
| *t*-1-one[c] | 2.4 | 12.7 | 1.3 | 3.9 | 2.5 | 14.2 | | 13.6 |
| *c*-1-one[c] | 0.8 | 3.8 | | 1.5 | 0.4 | 1.5 | | 3.9 |
| Octalins, % | | | | | | | | |
| *trans*-1,2- | | 5.3 | 15.8 | 14.4 | 12.7 | 13.3 | 17.6 | 16.3 |
| *trans*-2,3- | | 4.1 | | 5.3 | | 5.8 | 8.6 | 9.8 |
| 1,9- | 62.0 | 45.1 | 19.5 | 14.5 | 56.7 | 44.8 | 53.9 | 36.8 |
| *cis*-1,2- | 17.8 | 18.7 | 40.6 | 34.5 | | 8.5 | | 12.2 |
| 9,10- | 20.2 | 26.8 | 24.1 | 18.7 | 30.6 | 27.6 | 19.9 | 24.9 |

[a] *c,c*-1-OH corresponds to *cis,cis*-1-decalol; *c,t*-1-OH to *cis,trans*-1-decalol; *t,c*-1-OH to *trans,cis*-1-decalol; *t,t*-1-OH to *trans,trans*-1-decalol. For structures of these alcohols see ref 1. All of the decalols were 10% solutions in *t*-butyl alcohol. [b] In runs where 500 mg of catalyst was used only about 50% of material balanced was maintained. [c] *t*-1-one corresponds to *trans*-1-decalone; *c*-1-one to *cis*-1-decalone.

TABLE II

COMPOSITION OF PRODUCTS FROM THE DEHYDRATION OF 1-DECALOL OVER SILICA-ALUMINA AND SILICO-PHOSPHORIC ACID CATALYSTS

| Alcohol[a] | Temp, °C | Products formed, mole % | | | C-omposition of octalins, % | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | | Low boiling | Octalins | Higher boiling | *trans*-1,2 | *trans*-2,3 | 1,9 | *cis*-1,2 | 9,10 |
| | | | | Silica-Alumina | | | | | |
| *c,c*-1-OH | 250 | 2.9 | 50.6 | 3.7 | 6.3 | | 22.9 | 5.2 | 65.5 |
| *c,c*-1-OH | 350 | 1.1 | 51.7 | 5.2 | 3.6 | 2.0 | 25.9 | 7.6 | 59.0 |
| *c,t*-1-OH | 250 | 0.8 | 52.5 | 1.4 | 5.5 | | 15.8 | 26.3 | 52.3 |
| *c,t*-1-OH | 350 | 1.2 | 47.4 | 6.1 | 4.2 | 5.6 | 22.0 | 14.6 | 53.6 |
| *t,c*-1-OH | 250 | 2.5 | 48.4 | 3.4 | 3.7 | 4.1 | 24.4 | | 67.8 |
| *t,c*-1-OH | 350 | 0.9 | 51.1 | 3.8 | 6.1 | 4.6 | 29.0 | | 60.3 |
| *t,t*-1-OH | 250 | 1.8 | 45.5 | | 6.5 | 6.5 | 21.9 | | 65.1 |
| *t,t*-1-OH | 350 | 1.2 | 51.7 | | 6.1 | 6.1 | 27.6 | | 60.2 |
| | | | | Silico-Phosphoric Acid | | | | | |
| *c,c*-1-OH | 250 | | 44.3 | | Trace | Trace | 38.6 | 9.0 | 52.4 |
| *c,c*-1-OH | 350 | | 68.6 | | 0.5 | 0.5 | 32.0 | 15.4 | 51.6 |
| *c,t*-1-OH | 250 | | 30.2 | | 5.0 | | 17.6 | 31.2 | 46.2 |
| *c,t*-1-OH | 350 | | 51.2 | | 3.8 | | 19.4 | 37.9 | 38.9 |
| *t,c*-1-OH | 250 | | 36.3 | | 3.6 | 2.9 | 27.6 | | 65.9 |
| *t,c*-1-OH | 350 | | 57.7 | | 7.8 | 3.3 | 36.3 | | 52.6 |
| *t,t*-1-OH | 250 | | 26.2 | | 7.3 | 6.4 | 24.4 | | 61.9 |
| *t,t*-1-OH | 350 | | 40.6 | | 12.2 | 7.8 | 27.8 | | 52.2 |

[a] See footnote *a* in Table I.

case of the alumina catalysts; this may be due in part to the ease of dehydrogenation of decalols to decalones, with a consequent epimerization of the alcohols.

**Silica-Alumina and Silico-Phosphoric Acid.**—The experiments were made with both catalysts at 250 and 350° (Table II). The dehydration reaction was apparently accompanied by an extensive double-bond migration as evidenced by the large amounts of 9,10-octalins in the product. The dehydration occurred only to a small extent through a *trans* elimination, as indicated by the presence in the olefins of 26–31% of *cis*-1,2-octalin from *cis,cis*-1-decalol; *cis,trans*-1-decalol under similar conditions produced only 5–9% of the *cis*-1,2-octalin. The major part of the dehydration reaction seems to proceed *via* a cationic mechanism.

**Conclusion.**—The acidic type catalysts such as silica-alumina and silico-phosphoric acid dehydrate 1-decalols. The reaction is not very stereospecific and only part of the dehydration occurred *via* a *trans*-elimination reaction. Extensive isomerization of 1,9- to 9,10-octalin took place.

Thoria is a more stereospecific catalyst for the dehydration of 1-decalols than are the acid catalysts. Its activity and selectivity, however, is not so great as that of the alumina catalysts.[1]

## Experimental Section

The apparatus, which consisted of a pulse microreactor, and the procedure used were the same as described previously.[1]

**Thoria** was prepared by heating 10 g of thorium oxalate in a vertical furnace at 400° for 4 hr under a stream of nitrogen. The thoria thus produced was compressed at 38,000 psi, crushed, and sieved to 20–40 mesh.

**Silica-alumina** was the commercial cracking catalyst, type S-45, manufactured by Houdry Process Corp., Philadelphia, Pa. The catalyst was sieved to 20–40 mesh.

**Silico-phosphoric acid** was obtained from Universal Oil Products Co., Des Plaines, Ill. The catalyst which can be prepared by calcining Kieselguhr with phosphoric acid[3,4] was ground to 20–40 mesh size.

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(3) V. N. Ipatieff, U. S. Patents 1,993,512, 1,993,513, 2,018,065, 2,018,066, 2,020,649 (1935).

(4) F. G. Ciapetta and C. J. Plank, *Catalysis*, **1**, 344 (1954).