through a Nester-Faust spinning band column to yield 9.0 g. of diethyl methylmalonate (40%), b.p. 43–54° (0.8 mm), and 11.0 g. of diethyl dichloromethylmethylmalonate (33%), b.p. 73–75° (0.5 mm.). A dark pot residue remained (4.0 g.). The infrared spectrum of the dichloro fraction was identical in all respects to that of the fraction formed in the sodium trichloroacetate run listed above.

Reaction of Diethyl Methylsodiomalonate with Bromoform.—The reaction was performed as in the chloroform run listed above. Sodium (2.0 g., 0.09 g.-atom), 100 ml. of anhydrous diethyl ether, and 17.0 g. (0.10 mole) of diethyl methylmalonate were utilized. On removal of the ether, bromoform (33.0 g., 0.13 mole) was added and on gentle warming a vigorous exothermic reaction occurred. The mixture was refluxed for 1 hr. and then filtered from the solid which separated. The mixture was concentrated under reduced pressure and distilled through the spinning band column to yield 8.0 g. of bromoform (26% recovery), b.p. 25–36° (3.5 mm.); 5.0 g. diethyl methylmalonate (30%), b.p. 57–65° (2.5 mm.); and 6.0 g. (20%) of diethyl dibromomethylmethylmalonate, b.p. 105–107° (2 mm.). A redistilled fraction had b.p. 105–107° (2 mm.). A dark pot residue remained.

Anal. Calcd. for $C_9H_{14}O_4Br_2$: C, 31.06; H, 4.05. Found: C, 31.40; H, 4.37.

Saponification of Diethyl Dichloromethylmethylmalonate.—Diethyl dichloromethylmethylmalonate (II) (9.0 g., 0.035 mole) was added to a potassium hydroxide (7.0 g., 0.125 mole) solution in 60 ml. of 95% ethanol and 20 ml. of water. The solution was allowed to reflux overnight. The ethanol and water were removed by distillation under reduced pressure and the pasty solid which resulted was extracted once with ether. The residue was dissolved in ice water and acidified with dilute sulfuric acid. A solid precipitated which was filtered and dried. The solid was dissolved in hot acetonitrile and was filtered to remove insoluble salts. On cooling in the freezer (−20°), 3.0 g. (71%) of *trans*-β-chloromethacrylic acid was obtained of m.p. 57–58°, lit. m.p. 57–58°.[9]

Anal. Calcd. for $C_4H_5O_2Cl$: C, 39.85; H, 4.18; Cl, 29.42. Found: C, 39.99; H, 3.85; Cl, 29.47.

The infrared spectrum and mixed melting point were identical to those of an authentic sample of *trans*-β-chloromethacrylic acid prepared according to the procedure described by Bieber.[10]

Saponification of Diethyl Dibromomethylmethylmalonate.—The reaction was run as in the saponification above. A 63% yield of *trans*-β-bromomethacrylic acid was obtained of m.p. 63.0–64.0°, lit. m.p. 64.5–65.0°.[10] The infrared spectrum and the mixed melting point were identical to those of an authentic sample of this acid prepared according to Bieber's procedure.[10] The analytical sample was crystallized from acetonitrile.

Anal. Calcd. for $C_4H_5O_2Br$: C, 29.12; H, 3.05; Br, 48.44. Found: C, 29.44; H, 3.28; Br, 48.27.

Acknowledgment.—This investigation was supported by USPHS Grant No. RG-8241. We also express our appreciation to Dr. I. Starer (American Cyanamid Co., Bound Brook, New Jersey) for discussions during the course of this work.

Dehydration of Alcohols in Dimethyl Sulfoxide[1,2]

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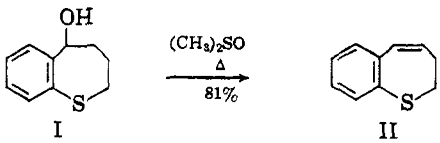
When *sec*- and *tert*-benzylic alcohols or *tert*-aliphatic alcohols were heated in dimethyl sulfoxide at 160–185° for nine to sixteen hours, dehydration produced olefins in 70–85% yield. The direction and stereochemistry of this elimination are reported, and based on these data a mechanism is offered. In general the suggested path involves carbonium ions.

In recent years several interesting reports have appeared in the literature describing new reactions and applications of dimethyl sulfoxide.[4] Among these was a paper by Searles and Hays[5] in which they describe the formation of simple sulfoxides by heating the corresponding sulfide in dimethyl sulfoxide. When 5-hydroxy-2,3,4,5-tetrahydrobenzo[*b*]thiepin (I) was treated under these conditions, instead of a sulfoxide 2,3-dihydrobenzo[*b*]thiepin (II) was formed. In this report we wish to describe a number of examples of this dehydration and comment on the course of this reaction.



I II

The general experimental conditions involved heating one mole of the alcohol in four to eight moles of dimethyl sulfoxide at 160–185° for nine to sixteen hours. When low boiling olefins were products, these distilled during the reaction and were collected in an appropriate trap, while the high boiling olefins were conveniently isolated by dilution of the reaction mixture with water, extraction with petroleum ether followed by distillation. In addition to compound I, the other alcohols dehydrated by this procedure are listed in Table I. The resulting olefins were identified by physical constants, infrared spectra, and in some cases by conversion to solid dibromides.

The dehydration of α-phenethyl alcohol in dimethyl sulfoxide gave styrene which under the

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[1] Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for partial support of this research.

[2] Presented in part at the 138th Meeting of the American Chemical Society at New York City, New York, in September, 1960.

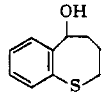
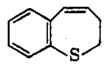
[3] Smith, Kline and French Foundation Fellow, 1959–1960.

[4] For a review of the literature see "Technical Information on Dimethyl Sulfoxide" issued by Crown Zellerback Corp.

[5] S. Searles, Jr., and H. R. Hays, *J. Org. Chem.*, **23**, 2028 (1958).

TABLE I

DEHYDRATION OF ALCOHOLS IN DIMETHYL SULFOXIDE

Alcohol	Alkene	% Yield	
		$(CH_3)_2SO$	Neat[a]
$C_6H_5\overset{OH}{C}HCH_3$	$C_6H_5CH{=}CH_2$	39[b]	0
$C_6H_5\overset{OH}{C}HCH_2CH_3$	$C_6H_5CH{=}CHCH_3$	79	<1
$C_6H_5\overset{OH}{C}(CH_3)_2$	$C_6H_5\overset{CH_3}{C}{=}CH_2$	75	...
$C_6H_5\overset{OH}{C}(CH_2CH_3)_2$	$C_6H_5\overset{CH_2CH_3}{C}{=}CHCH_3$	77	40
		81	0
$(CH_3)_2\overset{OH}{C}CH_2CH_3$	$CH_2{=}\overset{CH_3}{C}{-}CH_2CH_3$ (41)[c] $(CH_3)_2C{=}CHCH_3$ (59)[c]	70	0
$(CH_3)_2\overset{OH}{C}CH_2CH_3$[d]	$CH_2{=}\overset{CH_3}{C}{-}CH_2CH_3$ (39)[c] $(CH_3)_2C{=}CHCH_3$ (61)[c]	79	
$(CH_3)_2\overset{OH}{C}(CH_2)_3CH_3$	$CH_2{=}\overset{CH_3}{C}(CH_2)_3CH_3$ (46)[c] $(CH_3)_2C{=}CHCH_2CH_2CH_3$ (54)[c]	87	8
$(CH_3)_2\overset{OH}{C}(CH_2)_3CH_3$[d]	$CH_2{=}\overset{CH_3}{C}(CH_2)_3CH_3$ (41)[c] $(CH_3)_2C{=}CHCH_2CH_2CH_3$ (59)[c]	93	
$(CH_3CH_2)_3COH$	$(CH_3CH_2)_2C{=}CHCH_3$	78	26
$(CH_3CH_2CH_2CH_2)_3COH$	$(CH_3CH_2CH_2CH_2)_2C{=}CHCH_2CH_2CH_3$	75	0

[a] Pure alcohol alone was subjected to reaction temperature and time. [b] This yield of pure styrene was obtained when 20% by weight of *m*-dinitrobenzene was added to the reaction. [c] Per cent of olefin as determined by vapor phase chromatography. [d] This reaction was carried out in the presence of 0.1 g. of sulfuric acid.

reaction conditions polymerized to polystyrene. When pure styrene and dimethyl sulfoxide were heated at 160° for five hours, polystyrene formed in 90% yield; however, when the experiment was repeated in the presence of 20% by weight of *m*-dinitrobenzene, the yield of polystyrene was reduced to 5% and 65% pure styrene was recovered by distillation. Thus the addition of 20% *m*-dinitrobenzene to the α-phenethyl alcohol dehydration afforded pure styrene in 39% yield. Therefore, in application of this method to the preparation of sensitive olefins, polymerization inhibitors may be necessary.

When 1-pentanol and β-phenethyl alcohol, both primary alcohols, and cyclohexanol, 3-methyl-2-butanol, and 1-phenyl-2-propanol (all secondary alcohols) were subjected to the dehydration conditions in dimethyl sulfoxide; no olefin was isolated; and unchanged starting alcohols were recovered in good yield. In view of the above results and those listed in Table I, the structural requirement for successful dehydration appears to be a benzylic alcohol (either secondary or tertiary) or a tertiary aliphatic alcohol. One exception to this generalization is *t*-butyl alcohol, which failed to produce any isobutylene.

In the consideration of various mechanisms for this dehydration one must exclude a simple thermal elimination of water since the pure alcohols were subjected to the reaction conditions and produced little or no olefins (Table I). Thus dimethyl sulfoxide or perhaps some trace impurity facilitate this dehydration. Precautions were taken to exclude acidic contamination (by exposing the dimethyl sulfoxide to sodium hydroxide) and other contaminants (by careful fractional distillation). However, on prolonged heating at the temperatures used in these reactions, dimethyl sulfoxide undergoes some decomposition and this complicates the attempt to exclude impurities.

A series of experiments were performed with *t*-pentyl alcohol, 2-methyl-2-hexanol, and *erythro*- and *threo*-1,2-diphenyl-1-propanol[6] to study the direction and stereochemistry of this elimination. Table I records the amounts of 2-olefin and 1-olefin formed in the dehydration of *t*-pentyl alcohol and 2-methyl-2-hexanol. These two alcohols gave comparable ratios of 2- and 1-olefins and it is interesting to note that addition of small amounts of sulfuric acid to the dimethyl sulfoxide dehydration showed no appreciable change in these ratios. However,

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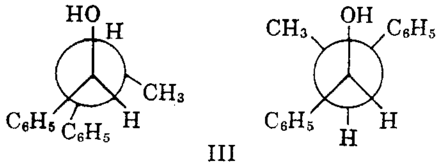
[6] D. J. Cram and F. A. A. Elhafez, *J. Am. Chem. Soc.*, **74**, 5829 (1952). According to the definitions of *erythro* and *threo* described in this paper, *erythro* refers to that diastereomer of such configuration that one of its three eclipsed conformations has at least two sets of substituents of identical or like composition side by side. The term *threo* refers to the other diastereomer.

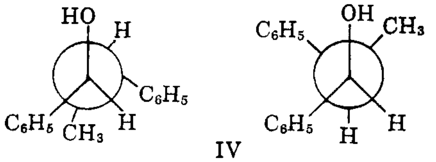
the dehydration of *t*-pentyl alcohol in aqueous sulfuric acid according to the procedure of Norris and Joubert[7] gave an olefin mixture with 10.5% 2-methyl-1-butene and 89.5% 2-methyl-2-butene. Under similar conditions 2-methyl-2-hexanol produced 19% 2-methyl-1-hexene and 81% 2-methyl-2-hexene. These latter results are readily explained by a carbonium ion mechanism and are in general agreement with other eliminations in the *t*-pentyl system which proceed *via* carbonium ions—namely, solvolysis of *t*-pentyl halides and *t*-pentyl dimethyl sulfonium salts,[8] and the dehydration of *t*-pentyl alcohol and 2-methyl-2-pentanol by iodine or *p*-toluenesulfonic acid.[9]

The larger amount of 1-olefin present (41–46%) in the dimethyl sulfoxide dehydration may lead one to question a carbonium ion mechanism in this case; however, two recent reports[8,10] invoke carbonium ions for reactions in *t*-pentyl systems which give better than 60% of 2-methyl-1-butene. These reactions are the nitrous acid deamination of *t*-pentylamine[8] and the deoxideation of *t*-pentyl alcohol.[10] Thus from our data on the direction of elimination for the dehydration of alcohols in dimethyl sulfoxide, one is not presented with any strong evidence on the basis of which any particular mechanistic possibility could be favored.

A study of the stereochemistry of elimination with *erythro*- and *threo*-1,2-diphenyl-1-propanol did provide useful information about the path of this dehydration. In a preliminary experiment *threo*-1,2-diphenyl-1-propanol(III) was heated in dimethyl sulfoxide at 160–170° for sixteen hours and after separation of components by chromatography on alumina gave 22% *cis*-methylstilbene, 25% *trans*-methylstilbene, 8% of an unidentified solid and oil, 7% 1,2-diphenylpropanone-1, and 30% III. When III alone was subjected to reaction conditions only 7% *cis*- and 1% *trans*-methylstilbene were formed. The other products with amounts are listed in the Experimental.



III
threo



IV
erythro

A more detailed study of the olefin fraction from both erythro (IV) and *threo* alcohols (III) was made and the results are recorded in Table II. The olefins were separated from the other products by chromatography on alumina and the *cis*-*trans* composition determined by ultraviolet spectroscopy, vapor phase chromatography, or by isolation from column chromatography. The results of these dehydrations were somewhat complicated by the fact that isomerization of *cis*- and *trans*-methylstilbene occurs in dimethyl sulfoxide under the experimental conditions for dehydration. Thus a study of this isomerization was undertaken and is summarized in Table III. It is interesting to note that appreciable isomerization of *trans*- to *cis*-methylstilbene occurs and at what appears to be equilibrium (*ca.* 175° these experiments were not performed in a thermostated bath) about 26% *cis*-methylstilbene is present.[11] A third component was formed in these isomerizations, the nature of which is currently under investigation. Table III also reveals that addition of *m*-dinitrobenzene inhibits somewhat the isomerization of *cis*- to *trans*-methylstilbene. Thus the dimethyl sulfoxide dehydration of III and IV in the presence of *m*-dinitrobenzene was also undertaken with the results reported in Table II. The absence of reaction between both 1,2-diphenyl-1-propanols and *m*-dinitrobenzene was

TABLE II

DEHYDRATION OF *threo*- AND *erythro*-1,2-DIPHENYL-1-PROPANOL IN DIMETHYL SULFOXIDE AT 175° FOR 9 HOURS

Alc., mole	DMSO,[a] mole	*m*-DNB,[b] mole	% yield methyl-stilbenes	% *cis*	% *trans*
		threo alcohol			
0.0188	0.151	...	44	54	41[c]
0.0118	0.094	...	71.5	40.5	59.5[d]
0.0071	0.057	...	70.5	50	50[d]
0.0118	0.094	0.0024	60	60	40[c]
0.0118	0.094	0.0024	67	60	40[e]
				59.5	40.5[d]
0.0071	0.057	0.0014	67.3	61.5	38.5[d]
0.094	...	...	3		
		erythro alcohol			
0.0094	0.075	...	41	39	61[c]
0.0068	0.054	...	73.5	37	63[e]
				40	60[d]
0.0071	0.056	...	47.7	50	50[d]
0.0113	0.090	0.0023	24	57	43[e]
0.0094	0.076	0.0019	24	57.5	42.5[e]

[a] DMSO is dimethyl sulfoxide. [b] DNB is dinitrobenzene. [c] Mixture analyzed by isolation from column chromatography. [d] Mixture analyzed by vapor phase chromatography using an Aerograph A-90 P instrument; column, silicone QF-1 on firebrick (60–80 mesh); temp., 220° and 60 ml. helium/min. [e] Mixture analyzed by ultraviolet absorption spectrum.

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(7) J. F. Norris and J. M. Joubert, *J. Am. Chem. Soc.*, **49**, 873 (1927).

(8) M. S. Silver, *ibid.*, **83**, 3484 (1961). The results of several investigators who used different *t*-pentyl halides and dimethyl sulfonium salts in different solvents are summarized in tabular form. The amount of 2-methyl-2-butene ranged from 69% to 87%, and 2-methyl-1-butene, 13–31%.

(9) In a preliminary report P. F. G. Praill and B. Saville, *Chem. Ind.* (London) 495 (1960), claim that regardless of the catalyst employed three to four parts of 2-olefin and one part of 1-olefin were formed in the dehydration of the alcohols cited above.

(10) P. S. Skell and I. Starer, *J. Am. Chem. Soc.*, **81**, 4117 (1959).

(11) The isomerization of *cis* to *trans*-methylstilbene in glacial acetic acid at 75° with *p*-toluenesulfonic acid produced 98% *trans*- and 2% *cis*-methylstilbene. D. J. Cram, F. D. Greene, and C. H. Depuy, *ibid.*, **78**, 795 (1956).

TABLE III

ISOMERIZATION OF METHYLSTILBENES IN DIMETHYL SULFOXIDE AT 175°

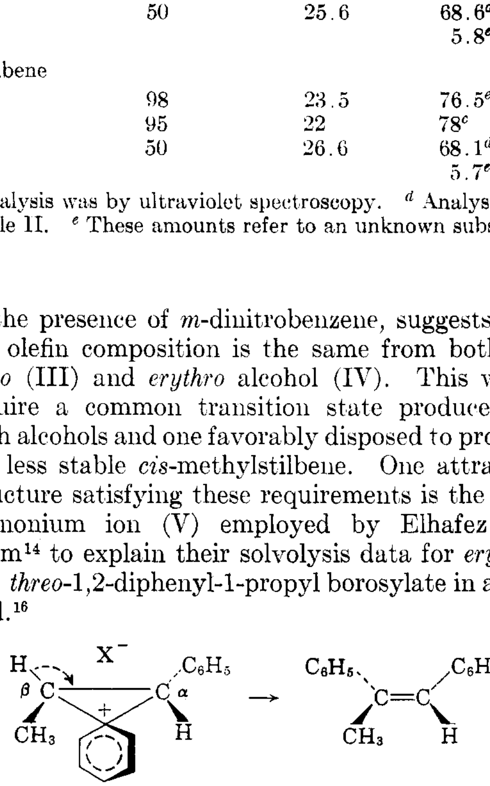
Olefin, mmole	DMSO,[a] mmole	*m*-DNB,[b] mmole	Time, hr.	% recovery olefins	% *cis*	% *trans*
			cis-Methylstilbene			
2.56	23	...	9	95	35	65[c]
2.06	23	0.4	9	98	51	49[c]
1.03	11.5	...	45	50	25.6	68.6[d]
						5.8[e]
			trans-Methylstilbene			
2.56	29	...	9	98	23.5	76.5[e]
2.56	29	0.5	9	95	22	78[c]
1.03	11.5	...	45	50	26.6	68.1[d]
						5.7[e]

[a] DMSO is dimethyl sulfoxide. [b] DNB is dinitrobenzene. [c] Analysis was by ultraviolet spectroscopy. [d] Analysis was by vapor phase chromatography under conditions described in Table II. [e] These amounts refer to an unknown substance which is currently under investigation.

demonstrated by subjecting these materials in an inert solvent to the experimental conditions of dimethyl sulfoxide dehydration.

Cram and co-workers have studied the *threo*- and *erythro*-1,2-diphenyl-1-propyl system extensively. Their studies include the base induced elimination reactions of chlorides, bromides, iodides,[12,13] and trimethylammonium salts[13] which proceed by the *trans* coplanar E_2 mechanism; the Chugaev reaction with the alcohols[6] involving the cyclic six-membered transition state with *cis* elimination; and solvolysis reactions of the chlorides, bromides, and brosylates[14] with carbonium ion intermediates. Their reported results in the E_2 and *cis* cyclic Chugaev reactions are consistent with the geometric requirement for each. In the E_2 elimination the *threo* isomer gave *trans*-methylstilbene while the *erythro* isomer formed the *cis* olefin; for the Chugaev pyrolysis *threo* alcohol (III) produced *cis*-methylstilbene ande *rythro* alcohol (IV) gave the *trans* olefin. The results reported in Table II show that a large amount of *cis* olefin was formed in the dimethyl sulfoxide dehydration of both the *threo* and *erythro* alcohols, this quantity exceeding 50% when the dehydration was performed under conditions which reduce isomerization of *cis*- to *trans*-methylstilbene. On the basis of these results one is led to discard the E_2 and *cis* cyclic elimination mechanisms.[15]

The data in Table II, especially the dehydrations in the presence of *m*-dinitrobenzene, suggests that the olefin composition is the same from both the *threo* (III) and *erythro* alcohol (IV). This would require a common transition state produced by both alcohols and one favorably disposed to produce the less stable *cis*-methylstilbene. One attractive structure satisfying these requirements is the *trans* phenonium ion (V) employed by Elhafez and Cram[14] to explain their solvolysis data for *erythro*- and *threo*-1,2-diphenyl-1-propyl borosylate in acetic acid.[16]



V

The conversion of V to *cis*-methylstilbene can be rationalized if the electrons from the βC—H bond were to approach the α carbon-phenyl bond of the three-membered ring from the back side.

In order to generate V the 1,2-diphenyl-1-propanols must be converted to the corresponding carbonium ions. One can then utilize pathways similar to those described by Elhafez and Cram[14] in proceeding from the *erythro*- and *threo*-1,2-diphenyl-1-propyl cation to the *trans* phenonium ion V. The higher yields of olefin from the *threo* alcohol may be a reflection of the possible phenyl participation in the loss of the hydroxyl group to form V directly. The manner in which these carbonium ions may be produced is not clear. Since dimethyl sulfoxide undergoes decomposition upon prolonged heating (reaction conditions), there exists the possibility that trace impurities, perhaps acidic, may cause the production of these carbonium ions. Alternately some unusual interaction of alcohol and dimethyl sulfoxide may result in the formation of carbonium

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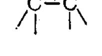
(12) D. J. Cram and F. A. A. Elhafez, *J. Am. Chem. Soc.*, **74**, 5851 (1952).

(13) D. J. Cram, F. D. Greene, and C. H. DePuy, *ibid.*, **78**, 790 (1956).

(14) F. A. A. Elhafez and D. J. Cram, *ibid.*, **75**, 339 (1953).

(15) The E_2 elimination path would require that the sulfoxide oxygen serve as a base to abstract the β-hydrogen with subsequent elimination of a hydroxide ion, while the cyclic six membered transition state would arise if a molecular association between the alcohol oxygen and sulfur of dimethyl sulfoxide (utilizing the vacant *d* orbitals of sulfur) resulted.



(16) In their experiments the solvolysis of the *erythro*- and *threo*-borosylates produced 63% and 70%, respectively, of the *threo*-acetate. A detailed analysis of the various ionizing possibilities and subsequent interactions was presented to rationalize these results; of particular interest here is the generation of the more stable *trans* phenonium ion (V) from the *erythro*-borosylate.

ions. These matters are currently under investigation.

Experimental

Dimethyl Sulfoxide.—Dimethyl sulfoxide as obtained from the Crown Zellerbach Co.[17] or Stepan Chemical Co. was allowed to stand over sodium hydroxide pellets and then distillation through a 45 × 1.6 cm. electrically heated column packed with $^1/_{16}$-in. glass helices and equipped with a variable take-off head gave pure dimethyl sulfoxide, b.p. 83° (17 mm.), $n^{20}\mathrm{D}$ 1.4795 [lit.,[18] b.p. 83° (17 mm.)]. An alternate purification procedure involved refluxing dimethyl sulfoxide over calcium hydride followed by distillation from calcium hydride.

Starting Alcohols.—The following available alcohols were distilled prior to use: *t*-butyl alcohol, *t*-pentyl alcohol, 1-pentanol, 3-methyl-2-butanol, 3-ethyl-3-pentanol, cyclohexanol, α-phenethyl alcohol, β-phenethyl alcohol, 1-phenyl-2-propanol, 2-methyl-2-hexanol, b.p. 138.5–139° (742 mm.), $n^{20}\mathrm{D}$ 1.4180 (lit., b.p. 143.0–143.2° (760 mm.),[19] $n^{20}\mathrm{D}$ 1.4186[20]) and 5-butyl-5-nonanol, b.p. 124° (14 mm.) [lit.,[21] b.p. 125° (15 mm.)].

5-Hydroxy-2,3,4,5-tetrahydrobenzo[*b*]thiepin.—Following the procedure described previously[22] 5-oxo-2,3,4,5-tetrahydrobenzo[*b*]thiepin (12.3 g., 0.069 mole) was converted by sodium borohydride (2.83 g., 0.075 mole) in 95% ethanol to 11.9 g. (96%) of the desired alcohol, m.p. 69–70.5° (lit.,[22] m.p. 70–71°).

1-Phenyl-1-propanol.—Propiophenone was reduced by sodium borohydride using the above procedure and the crude alcohol upon distillation from 2,4-dinitrophenylhydrazine gave pure (99.9% by vapor phase chromatography) 1-phenyl-1-propanol, b.p. 108° (16 mm.), $n^{20}\mathrm{D}$ 1.5215 (lit.,[23] b.p. 103°(14 mm.), $n^{20}\mathrm{D}$ 1.5257).

3-Phenyl-3-pentanol.—The Grignard reagent resulting from bromobenzene (31.4 g., 0.20 mole) and magnesium (4.62 g., 0.10 g.-atom) was treated with 3-pentanone (13.6 g., 0.16 mole) and then hydrolyzed with 10% sulfuric acid. The ether layer was separated, combined with an ether washing of the aqueous layer, and dried. Distillation gave 19.8 g., (76%) of 3-phenyl-3-pentanol, b.p. 113–115° (16 mm.), $n^{20}\mathrm{D}$ 1.5167 (lit.,[24] b.p. 111–113° (15 mm.), $n^{20}\mathrm{D}$ 1.5182).

2-Phenyl-2-propanol.—By a procedure[25] similar to that above, treatment of the Grignard reagent from bromobenzene (78.6 g., 0.50 mole) and magnesium (12.2 g., 0.50 g.-atom) with acetone (26.2 g., 0.45 mole) produced 41.9 g. (69%) of 2-phenyl-2-propanol, b.p. 98–106° (12 mm.), m.p. 29° (lit.,[25] b.p. 89–90° (10 mm.) m.p. 23°).

***threo*-1,2-Diphenyl-1-propanol.**—Using the method of Cram and Elhafez[6] a mixture of *threo*- and *erythro*-1,2-diphenyl-1-propanol, b.p. 125–130° (0.3–0.5 mm.), $n^{20}\mathrm{D}$ 1.5740, was obtained in 84% yield on a mole run.

A portion of this mixture was converted to the *p*-nitrobenzoate esters by action of *p*-nitrobenzoyl chloride and pyridine. Fractional crystallization from ethyl acetate gave a 53% yield of pure *threo*-1,2-diphenyl-1-propyl *p*-nitrobenzoate, m.p. 143–144° (lit.,[6] m.p. 143–144°).

Saponification of this ester by sodium hydroxide in methanol and water produced in 90% yield pure *threo*-1,2-diphenyl-1-propanol, b.p. 110–112° (0.1–0.15 mm.), $n^{20}\mathrm{D}$ 1.5737, $n^{27}\mathrm{D}$ 1.5710 (lit.,[6] b.p. 136–137° (1–2 mm.), $n^{25}\mathrm{D}$ 1.5718).

1,2-Diphenylpropanone-1.—A solution of 1,2-diphenyl-1-propanol (mixture of *erythro* and *threo*, 30.0 g. 0.41 mole) in 25 ml. of glacial acetic acid was added to a solution of chromium trioxide (25.0 g., 0.25 mole) in 300 ml. of acetic acid and 25 ml. of water. After the mixture was heated at 90° for 2 hr., the solution was cooled and diluted with water. The oil which separated, solidified upon scratching, and recrystallization of the solid from aqueous methanol gave 21 g. (70%) of 1,2-diphenylpropanone-1, m.p. 48.5–50° (lit.,[6] m.p. 50–52°).

***erythro*-1,2-Diphenyl-1-propanol.**—Employing the procedure of Cram and Elhafez,[6] the reaction of 1,2-diphenylpropanone-1 (24 g., 0.11 mole) and lithium aluminum hydride (2.0 g., 0.053 mole) gave 11.9 g. (49%) of *erythro*-1,2-diphenyl-1-propanol, m.p. 49–50° (lit.,[6] m.p. 50–51°).

Dehydration of Alcohols. General Procedure. Method A.—A solution of alcohol (1 mole) and dimethyl sulfoxide (4–8 moles) was heated in an oil bath at 160–185° under a reflux condenser for 14 to 16 hr., cooled, and diluted with water. The mixture was extracted with petroleum ether (b.p. 30–60°) and after the extract was dried, the olefin was isolated by distillation.

Method B.—This varies from the above procedure in that the reflux condenser was replaced by a Claisen head and the product (when b.p. <100°) was distilled during the reaction being collected in an appropriate receiver cooled in an ice bath or an acetone–Dry Ice bath.

The reaction conditions and identification of products are listed in Table IV while the olefin yields appear in Table I. In addition Table I contains the yields of olefins obtained when the individual alcohols, without solvent, were subjected to the experimental conditions (time and temperature) used in the corresponding dimethyl sulfoxide dehydration.

α-Phenethyl Alcohol.—When α-phenethyl alcohol and dimethyl sulfoxide were heated under the conditions in Table IV, the products were mainly polystyrene along with some styrene.

A solution of styrene (10 g., 0.096 mole) and dimethyl sulfoxide (30 g., 0.39 mole) was heated at 160° for 5 hr., poured into 5% hydrochloric acid, and extracted with benzene. After the benzene was dried and diluted with methanol, 9.0 g. (90%) of polystyrene was isolated.

When this experiment was repeated with the addition of *m*-dinitrobenzene (2.0 g., 0.012 mole), 6.5 g. (65% of styrene was recovered by distillation and about 5% polystyrene was found.

Thus the dehydration of α-phenethyl alcohol described in Table I was performed in the presence of *m*-dinitrobenzene in order to obtain styrene as the product.

***t*-Pentyl Alcohol.**—The olefin mixture (Table I) was analyzed by vapor phase chromatography:[31] column: $^1/_4$-in. o.d. × 10 ft. Ucon polar on fire brick (30–60 mesh); temp., 30° and helium flow rate 20 cc./min. These conditions were employed in all analyses of mixtures of 2-methyl-1-butene

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(17) The authors wish to thank the Crown Zellerbach Co. for making generous samples available for this work.

(18) Value determined from the equation reported by T. B. Douglas, *J. Am. Chem. Soc.*, **70**, 2001 (1948).

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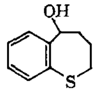
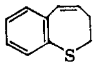
(31) An Aerograph Model A-90 instrument was employed. The composition of the mixture was determined from the individual peak areas which were measured with a planimeter. A mixture of authentic compounds was prepared and analyzed by vapor phase chromatography under identical conditions as used for the reaction mixture. Retention times of the individual components in each sample were identical and the area under each peak was proportional to the molar concentration of each component.

TABLE IV

REACTION CONDITIONS AND IDENTIFICATION OF PRODUCTS

Alc.	Moles	DMSO, moles	Temp.	Time, hr.	Method	Olefin	B.p., °C., $n^{20}D$	B.p., °C., lit. $n^{20}D$
$C_6H_5\overset{OH}{C}HCH_3$[a]	0.082	0.385	160	16	A	$C_6H_5CH{=}CH_2$[b]	34–37 (8 mm.) 1.5442[c]	p^f 36 (12 mm.) 1.5465[d]
$C_6H_5\overset{OH}{C}H{-}CH_2CH_3$	0.074	0.385	160	16	A	$C_6H_5CH{=}CHCH_3$[e]	62–64 (8 mm.) 1.5460[c]	61 (10 mm.) 1.5494[f]
$C_6H_5\overset{OH}{C}\,(CH_3)_2$	0.147	1.03	167	16	A	$C_6H_5\overset{CH_3}{C}{=}CH_2$	85–87 (42 mm.) 1.5376	68–69 (27 mm.)[g] 1.5363[g]
$C_6H_5\overset{OH}{C}\,(CH_2CH_3)_2$	0.061	0.385	160	16	A	$C_6H_5\overset{CH_2CH_3}{C}{=}CHCH_3$	80–84 (8 mm.) 1.5280	91–93 (18 mm.)[h] 1.5266[h,i]
	0.25	1.52	150–160	24	A		75 (0.4 mm.) 1.6465	95–96 (1.2 mm.)[j] 1.6470[j]
$(CH_3)_2\overset{OH}{C}CH_2CH_3$	0.10	0.70	185	14.5	B	$(CH_3)_2C{=}CHCH_3$ $CH_3CH_2\overset{CH_3}{C}{=}CH_2$	32–37	38.6[k] 31[k]
$(CH_3)_2\overset{OH}{C}CH_2CH_3$[l]	0.10	0.70	185	14	B	$(CH_3)_2C{=}CHCH_3$ $CH_3CH_2\overset{CH_3}{C}{=}CH_3$		
$(CH_3)_2\overset{OH}{C}(CH_2)_3CH_3$	0.10	0.70	185	14	B	$CH_2{=}\overset{CH_3}{C}(CH_2)_3CH_3$ $(CH_3)_2C{=}CH(CH_2)_2CH_3$	93–95 1.4130[n]	91[m] 1.4040[m] 94.5[m] 1.4075[m]
$(CH_3)_2\overset{OH}{C}(CH_2)_3CH_3$[l]	0.10	0.70	185	14	B	$CH_2{=}\overset{CH_3}{C}(CH_2)_4CH_3$ $(CH_3)_2C{=}CH(CH_2)_2CH_3$	93–95 1.4186[n]	
$(CH_3CH_2)_3COH$	0.10	0.70	185	15	B	$(CH_3CH_2)_2C{=}CHCH_3$	92–94 1.4160	95.2[o] 1.4139[o]
$[CH_3(CH_2)_3]_3C{-}OH$	0.10	0.70	185	16	A	$[CH_3(CH_2)_3]C{=}CH(CH_2)_2CH_3$	100–102 (17 mm.) 1.4394	98–99 (15 mm.)[p] 1.4415[p]

[a] The reaction was carried out in the presence of 2.0 g. (0.012 mole) of *m*-dinitrobenzene. [b] Also converted to its dibromide, m.p. 74–75° (lit.,[28] m.p. 74–75°). [c] $n^{25}D$. [d] See ref. 27. [e] Formed a dibromide, m.p. 66–67° (lit.,[28] m.p. 66–66.5°). [f] See ref. 27, p. 191. [g] See ref. 27, p. 192. [h] See ref. 27, p. 206. [i] $n^{15}D$. [j] See ref. 29. [k] See ref 30. [l] This reaction was carried out in the presence of 0.1 g. (0.001 mole) of sulfuric acid. [m] See ref. 30, p. 202 and 204. [n] Contaminated with dimethyl sulfide, $n^{20}D$ 1.43547. [o] See ref. 30, p. 207. [p] See ref. 30, p. 276.

(retention time 10.75 min.) and 2-methyl-2-butene (retention time 13.5 min.).

Alcohols Which Failed to Dehydrate.—Cyclohexanol (14.6 g., 0.146 mole), 3-methyl-2-butanol (8.8 g., 0.10 mole) and *t*-butyl alcohol (7.4 g., 0.10 mole) were dissolved in dimethyl sulfoxide (55 g., 0.7 mole) and placed in an oil bath at 185° for 16 hr., while β-phenethyl alcohol (5.0 g., 0.041 mole) and 1-phenyl-2-propanol (5.0 g., 0.037 mole) in dimethyl sulfoxide (23.0 g., 0.29 mole) were heated for 9 hr. in an oil bath at 175°. No olefinic products were found and the starting alcohols were recovered in 88, 90, 93, 78, and 75% yield, respectively. *n*-Amyl alcohol also failed to dehydrate under comparable conditions.

Sulfuric Acid Dehydrations. *t*-Pentyl Alcohol.—According to the procedure of Norris and Joubert;[7] the reaction of *t*-pentyl alcohol and sulfuric acid gave a mixture of olefins. Analysis by vapor phase chromatography[31] under conditions described above showed the mixture contained 10.5% 2-methyl-1-butene and 89.5% 2-methyl-2-butene.

2-Methyl-2-hexanol.—Using the above procedure, 2-methyl-2-hexanol and sulfuric acid produced a mixture of olefins, b.p. 93–96°, $n^{20}D$ 1.4080. Analysis by vapor phase chromatography[31]: column, 1/4-in. o.d. × 10 ft. Ucon polar on firebrick (30–60 mesh); temp., 65° and helium flow rate 20 cc./min. (these conditions were used for all analyses of the 2-methyl-1- and -2-hexenes) showed the presence of 19% 2-methyl-1-hexene (retention time 18 min.) and 81% 2-methyl-2-hexene (retention time 20.5 min.).

Dehydration of 1,2-Diphenyl-1-propanol in Dimethyl Sulfoxide *threo* Alcohol.—A solution of *threo*-1,2-diphenyl-1-propanol (4.24 g., 0.20 mole) in dimethyl sulfoxide (10.9 g., 0.140 mole) was heated at 160–170° for 16 hr. and processed according to method A. After the petroleum ether was removed the residue was purified by chromatography on 210 g. of Alcoa F-20 activated alumina. The first 1000 ml. of eluent (petroleum ether, b.p. 30–60°) contained *cis*- and *trans*-methylstilbene which was combined into two fractions 1.60 g. of a mixture and 0.30 g. of *trans*-methylstilbene, m.p. 78–80°. Rechromatography of the mixture produced 0.86 g. (22%) of *cis*-methylstilbene, m.p. 46–48° [recrystallization from methanol gave 0.80 g. (21%) of pure *cis* olefin, m.p. 47–48° (lit.,[6] m.p. 47–48°)] and 0.66 g. of *trans*-methylstilbene, m.p. 78–80° which gave a total yield of *trans* olefin 0.96 g. (25%). Recrystallization of the *trans* olefin from methanol produced 0.86 g. of pure product, m.p. 81–82° (lit.,[6] m.p. 81–82°). The second mixture of solid, m.p. 144–149°, and oil was eluted with 800 ml. of petroleum ether (b.p. 30–60°), 500 ml. 10% benzene in petroleum ether (b.p. 30–60°) and 500 ml. of 20% benzene in petroleum ether (b.p. 30–60°). These products remain to be identified. The next fraction was removed with benzene and was 0.28 g. (7%) of 1,2-diphenylpropanone-1, m.p. 43–47°. Recrystallization from methanol and water gave 0.25 g. of ketone, m.p. 48.5–49° (lit.,[6] m.p. 50–52°), a mixture melting point with an authentic sample was not depressed. The final fraction eluted with ether and methanol was 1.29 g. (30%) of unchanged *threo*-1,2-diphenyl-1-propanol.

When *threo*-1,2-diphenyl-1-propanol (3.0 g., 0.014 mole) was heated alone at 160–170° for 16 hr. and processed as above, the products were *cis*-methylstilbene (7%), *trans*-methylstilbene (1%), unknown solid and oil (34%), 1,2-diphenylpropanone-1 (4%), and *threo*-1,2-diphenyl-1-propanol (46%).

A series of dehydration experiments were performed at 175° for 9 hr. using pure *threo*- and pure *erythro*-1,2-diphenyl-1-propanol in the presence and absence of *m*-dinitrobenzene. The reaction was processed as above and the methylstilbenes were separated from the other products by chromatography. The olefin mixtures were analyzed by separation into pure components by column chromatography, by the ultraviolet spectroscopic procedure used by Kingsbury and Cram,[32] and by vapor phase chromatography.

The ultraviolet spectra were determined in 95% ethanol using a Beckman Model DU spectrophotometer and the mixture composition calculated from absorbancies at 260 mμ (λ_{max} for *cis*-methylstilbene) and 272 mμ (λ_{max} for *trans*-methylstilbene). The results of these studies are summarized in Table II.

Control Experiments. *m*-Dinitrobenzene plus *threo*- and *erythro*-1,2-Diphenyl-1-propanol.—A mixture of 1.00 g. (0.0047 mole) of alcohol, 0.19 g. (0.0094 mole) of *m*-dinitrobenzene and 4.90 g. (0.0376 mole) of *p*-cymene was heated at 175° for 9 hr. After the *p*-cymene was removed by distillation, chromatography on Alcoa F-20 activated alumina, showed the absence of methylstilbenes. The recovered alcohol was converted to the *p*-nitrobenzoates which was purified by chromatography on Alcoa F-20 activated alumina and recrystallization. When the *threo* alcohol was processed as described above, 1.00 g. (53%) of its *p*-nitrobenzoate, m.p. 141–143° (lit.,[6] m.p. 143–144°) was recovered; the *erythro* alcohol gave 1.10 g. (58%) of its *p*-nitrobenzoate, m.p. 102–106° (lit.,[6] m.p. 106–107°) and 0.08 g. of unchanged *erythro* alcohol, m.p. and mixture m.p. 47–48°, for a total recovery of 66%.

Isomerization of *cis*- and *trans*-Methylstilbenes in Dimethyl Sulfoxide.—Solutions of pure *cis*- and of pure *trans*-methylstilbene with and without *m*-dinitrobenzene were heated in dimethyl sulfoxide at 175° for 9 hr. or 45 hr. and processed according to method A. The methylstilbenes were separated from contaminants by chromatography on alumina and the mixture analyzed by the above spectroscopic method and by vapor phase chromatography. Table III lists the results of this study.

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Lithium Aluminum Hydride Reactions in Pyridine Solution. IV. Metalation of Di- and Triarylmethanes[1]

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Although fluorene, triphenylmethane, and related arenes are not metalated by lithium aluminum hydride in ethyl ether, the use of pyridine as solvent allows the metalation to proceed to an appreciable extent, particularly with fluorene. Carbanions generated in this way have been used in alkylation and carboxylation reactions. Fluorene gives 9,9-dibenzylfluorene, in addition to 9-benzylfluorene, in highest yield when carbanion solutions are slowly benzylated and unchanged lithium aluminum hydride is still present. Triphenylmethane is more acidic than 4-benzyl- and 2-benzylbiphenyl toward butyllithium in ether as well as lithium aluminum hydride in pyridine.

Hydrocarbons of the cyclopentadiene series are unusually acidic, since removal of a proton from the methylene group leads to a resonance-stabilized anion possessing an aromatic sextet.[3] Fluorene has been extensively studied and has been shown to be more acidic than triphenylmethane, which, in turn, is more acidic than diphenylmethane, etc.[4] Aldol-type condensations involving fluorene have generally been carried out in hydroxylic solvents, utilizing hydroxide or alkoxide as base, and in ether using organometallic bases or alkali amides as metalating agents.

A more facile method for carrying out aldol condensations, and also alkylations and ionic autoxidations, utilizing 9-fluorenyl anion, has been developed by Sprinzak and co-workers.[5] These investigators have shown that fluorene is extremely acidic toward Triton B in pyridine at room temperature,[5b] thus allowing the isolation of 9-(α-hydroxyalkyl)fluorenes,[5a] whereas dibenzofulvenes are usually obtained, as a result of dehydration of the above alcohols, when the aldol condensations are carried out in hydroxylic solvents at higher temperatures. Hydrogen-tritium exchange studies[5b] confirmed that carbanion formation was extremely rapid in pyridine solution, both 9-hydrogens of fluorene being completely exchanged in an hour at room temperature. Triphenylmethane shows no tendency to

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