Tetrahedron Vol. 26, pp. 4277 to 4286. Pergamon Press 1970 Printed in Great Britain

ELIMINATION REACTIONS IN THE 1,2-DIPHENYL-2-PROPYL SYSTEM

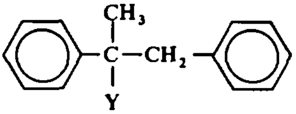
I. Ho and J. G. Smith
University of Waterloo, Department of Chemistry, Waterloo, Ontario

(*Received in the USA 7 March* 1970; *Received in the UK for publication 7 May* 1970)

Abstract—Elimination reactions of 2-substituted-1,2-diphenylpropanes are described. It is shown that dehydrations, dehydrohalogenations and deaminations of the appropriate compound produce alkene mixtures containing 45–55% of α-benzylstyrene. This alkene is shown to be the least stable of the isomeric trio α-benzylstyrene, *cis* and *trans*-α-methylstilbene by isomerization studies.

Studies of the dehydration include the 1-phenyl-2-(*p*-substituted phenyl)-2-propanols which show the same characteristics as the unsubstituted alcohol. On the basis of the effect of substituents on the rate of dehydration, it is suggested that these eliminations proceed through a carbonium ion like transition state. The composition of the initially formed alkene is then determined by the steric size of the groups attached to the reaction centre.

Elimination reactions of 2-substituted-1,2-diphenyl-propane (1) can produce three isomeric alkenes, *cis*- and *trans*-α-methylstilbene and α-benzylstyrene. Our study of these reactions was stimulated by the chance observation that the acid-catalyzed dehydration of 1,2-diphenyl-2-propanol (1, Y = OH) produced an alkene mixture surprisingly rich in α-benzylstyrene. This contrasted with earlier reports[1, 2] of the dehydration and with the naive expectation that the double bond should be formed in conjugation with both aromatic rings.



1

In seeking an explanation of the conflict between our observations and those previously recorded, a study of this dehydration as a function of time was undertaken. The results, which are summarized in Fig 1, show that the alkene composition formed during dehydration (the kinetic product) is approximately 1:1 *trans*-α-methylstilbene: α-benzylstyrene. It is only *after* the dehydration is complete that a slow isomerization of the alkene mixture to its equilibrium composition occurs. The earlier dehydrations of this alcohol undoubtedly were effected under conditions which generated this equilibrium mixture.

From a preparative viewpoint, α-benzylstyrene can be synthesized in approximately 90% isomeric purity by suitable control of the dehydration conditions followed by crystallization of the co-product, *trans*-α-methylstilbene; however, further purification required careful distillation[3] or preparative vapour phase chromatography. More conveniently, reference samples were prepared by the interaction of benzyne

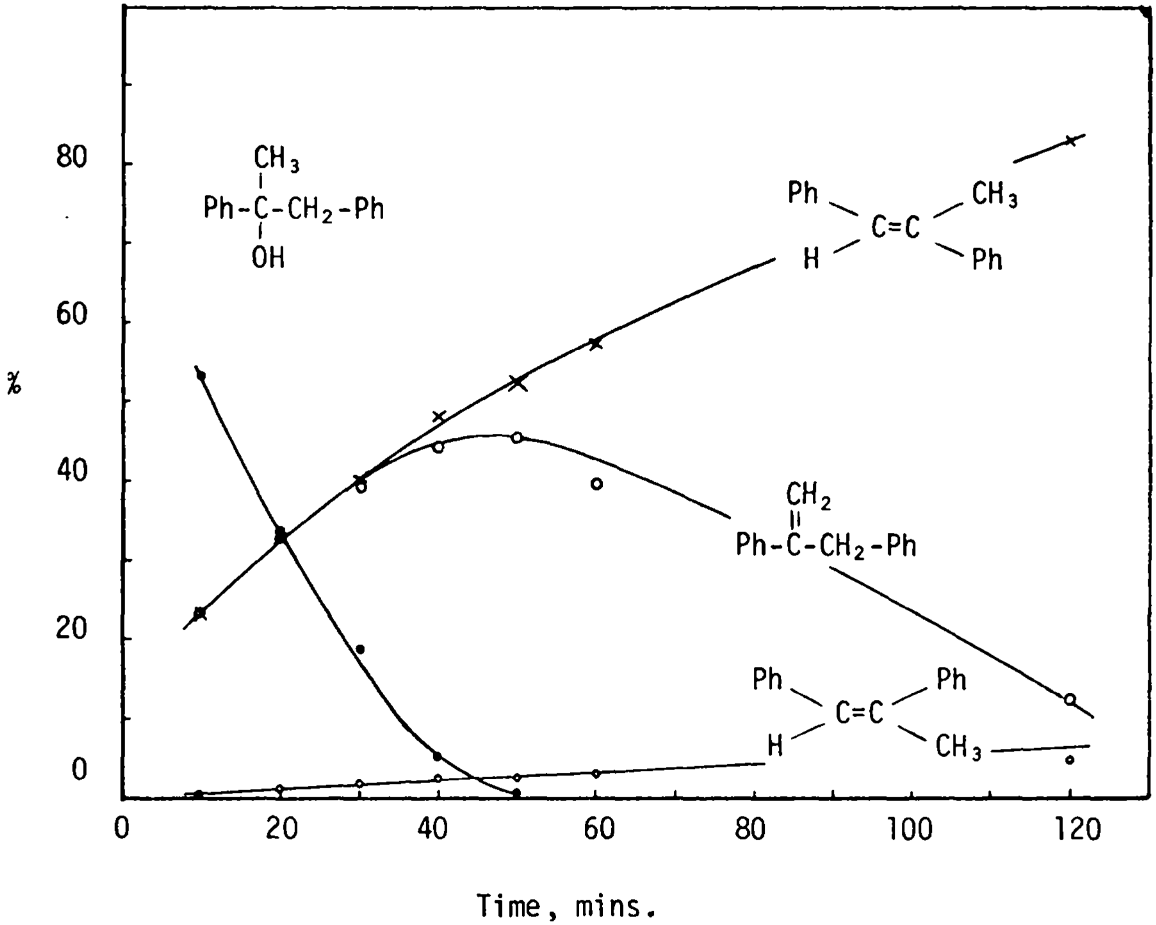


Fig. 1

Table 1. Equilibrium composition of 1,2-diphenylpropenes

Composition			Comments
%α	%*cis*	%*trans*	
0·6	18·6	81·0[a]	from *cis*, $T_{1/2}^{b}$ = 80 min
0·7	18·1	81·2[a]	from *trans*, $T_{1/2}$ = 240 min
0·7	18·2	81·1[a]	from α, $T_{1/2}$ < 5 min
2	19	79	75° in t-BuOH, KOt-Bu catalyzed[3]
3	21	76	116° in HOAc, TsOH catalyzed[3]
2·4	21	76·6	139° in Xylene, KOt-Bu catalyzed[5]

[a] 70° in benzene, TsOH catalyzed

[b] the time required for the alkene to reach a point mid-way between its initial composition and the equilibrium composition

and α-methylstyrene,[4] a reaction which produced by-products readily removed by column chromatography.

The equilibrium composition of the "1,2-diphenylpropenes" was established by isomerization of the three possible isomers under the conditions used in the dehydration. This composition is quite similar to equilibrium compositions previously reported but generated under different conditions and these are summarized in Table 1.

One observation made during these isomerizations seemed in conflict with the results obtained during dehydration. As shown in Table 1 by the $T_{\frac{1}{2}}$ values, isomerization of α-benzylstyrene occurred much more rapidly than either of the other two isomers. However, under the conditions of dehydration the α-benzylstyrene, once formed, appeared reasonably stable. This difference was traced to the water formed during dehydration which, separating as a second phase removed the acid catalyst and protected the alkene. Thus, these particular dehydration conditions permitted the detection and isolation of the kinetic product rather than the thermodynamic one.

TABLE 2. COMPOSITION OF ELIMINATION PRODUCTS

Y	Conditions	%Alkene	%*cis*	%α	%*trans*
—OH	TsOH, benzene, 70°	100	2	46	52
	TsOH, CH_3CN, 70°	100	2	43	55
	TsCl, pyridine, reflux	42	5	53	42
	$POCl_3$, pyridine	100	2	46	52
—OCH_3	TsOH, CH_3CN, 50°	100	1	45	53
—Cl	Pyridine, 70°	100	2	49	49
—NH_2	$NaNO_2$, aqu. H_2SO_4	3	*ca* 10	*ca* 55	*ca* 35
	i-AmONO, C_6H_6-AcOH, 80°	72	17	55	28
	i-AmONO, C_6H_6, 80°	90	12	55	33
$-\overset{+}{N}(CH_3)_3$	KNH_2, NH_3	61	9[a]	2	89
			7[b]	1	92

[a] Before acid extraction; 39% amine by-product formed

[b] After acid extraction

Other elimination reactions of the 2-substituted-1,2-diphenylpropyl system were also studied. Here, the production of α-benzylstyrene as a function of the leaving group was examined and the results are summarized in Table 2.

The synthesis of the required intermediates followed conventional procedures and these are detailed in the experimental section. Two different methods of dehydration were included in the hopes of changing the mechanism of dehydration. The $POCl_3$-pyridine procedure has been reported to proceed by an E2 mechanism.[6, 7]* Unfortunately, a *p*-toluenesulfonate could not be prepared so that an *in situ* generation and decomposition was employed.

The base catalyzed decomposition of the ammonium salt had been examined by Hauser[9] and found to be accompanied by an amine co-product. The alkene composition was determined both before and after removal of this amine by acid extraction

---

* However see Ref 8, in which rearrangements, attributed to a carbonium ion intermediate, were observed.

to ensure that no isomerization of the alkenes had occurred. Diazotization of the 2-amino compound was carried out under conditions adapted from Friedman's studies[10] in order to avoid the large amount of alcohol which was the major product of diazotization in aqueous media.

The results show that the alkenes formed in these various reactions almost invariably contain approximately 50% α-benzylstyrene and is largely independent of the leaving group. The sole exception to this is the base catalyzed elimination of the quaternary ammonium salt. Some dependence of the *cis/trans* ratio of α-methylstilbene can be seen in the diazotization of the 2-amino compound.

DISCUSSION

If an elimination reaction proceeds by the central transition state of an E2 elimination,[11] the product composition is determined by a combination of electromeric and inductive effects of the substituent groups. In the case of the system examined here, 2-substituted-1,2-diphenylpropane, these substituents are primarily aromatic in nature. Data is relatively meagre for such groups (compared to saturated alkyl groups) but Ingold[12] has shown that both an α- and a β-phenyl group increased the rate of formation of the double bond. Ingold[12, 13] and Bunnett[11] point out that a β-aryl group directs the formation of the unsaturation into conjugation. The presence of both an α- and a β-phenyl group should exert a strong directing force on the developing double bond bringing it into conjugation with both aryl groups and so produce largely α-methylstilbene. For the most part (Table 2) this is not the case in these eliminations.

Alternatively, a carbonium ion mechanism might be considered. Bunnett[11] states that an α-aryl and an α-alkyl group shift the transition state from the central position in an "E-1 like" direction. However, a β-phenyl substituent has the opposite effect.

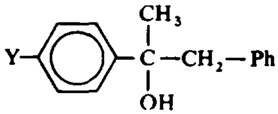
It appears that an "E-1 like" mechanism is a reasonable possibility and indeed other evidence supports this. Noyce[14, 15] has demonstrated a carbonium ion intermediate in the dehydration of the closely related alcohol 1,2-diphenylethanol. Bunnett[16] has proposed an E1-like transition state for the dehydrohalogenation of 2-chloro-1-phenyl-2-methylpropane.

In an attempt to provide more direct evidence for an "E-1 like" transition state in the dehydration of the alcohol, the effect of para-substituents on the rate of dehydration was examined. The kinetics of the dehydration measured in acetonitrile using *p*-toluenesulfonic acid as catalyst is somewhat complicated by a second-order dependence on the alcohol concentration under certain reaction conditions. A complete report on this is under preparation.

The pseudo first-order rate constants of the *para*-substituted alcohols are shown in Table 3. The value for the *p*-methoxy alcohol at 50° was obtained by extrapolation from lower temperatures but the others were directly measured. It is readily seen that electron donating substituents have a marked accelerating affect. Indeed, a Hammett ρ-σ plot using the rate constants at 50° is linear when σ^+ constants[17] are employed with a ρ value of $-3{\cdot}92$. Such a behavior reflects considerable charge separation in the transition state and confirms an E-1 like (or E1) mechanism.

While the product composition from such a reaction should be (and is) relatively independent of the leaving group, the factors controlling the alkene composition are in dispute. In the case of alkyl groups, Ingold[13] suggests that "hyper-conjugation and

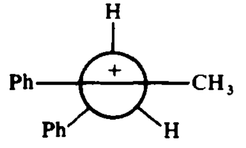
TABLE 3. DEHYDRATION OF



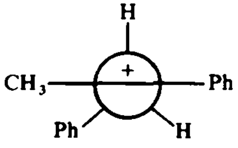
Y	Temp °C	Rate constant, min^{-1}
Cl	70	$9{\cdot}83 \times 10^{-3}$
	60	$8{\cdot}13 \times 10^{-3}$
	50	$3{\cdot}95 \times 10^{-3}$
H	70	$8{\cdot}81 \times 10^{-2}$
	60	$3{\cdot}77 \times 10^{-2}$
	50	$1{\cdot}16 \times 10^{-2}$
CH_3	50	$2{\cdot}50 \times 10^{-1}$
	40	$7{\cdot}44 \times 10^{-2}$
	30	$2{\cdot}03 \times 10^{-2}$
OCH_3	50	11·48 (extrapolated)
	25	$3{\cdot}92 \times 10^{-1}$
	20	$2{\cdot}21 \times 10^{-1}$
	13·5	$8{\cdot}32 \times 10^{-2}$

the Saytzeff rule will dominate when the whole of an electron is transferred to the leaving group . . . as in any E1 elimination". Brown[18–20] has demonstrated that steric factors can play a role in product determination and shift the alkene composition away from that expected.

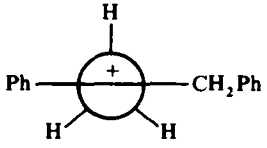
The Newman projection formulae for the intermediate carbonium ion viewed down the bond connecting the carbons bearing the aromatic groups are represented in 2 and 3 while the same intermediate viewed down the C—CH_3 bond is shown in 4.



2



3



4

If one considers the loss of a proton from the rear carbon of these formulae, it is evident that there is a greater increase in steric interaction with formation of the double bond in 2 and 3 than in 4. Loss of a proton from the benzylic carbon atom (i.e. from 2 or 3) is less favourable than loss of a proton from the methyl group (i.e. from 4). The conjugative influence of the phenyl groups is counteracted (at least partially) by this steric effect and the formation of α-benzylstyrene (the Hoffman product)* is favoured at the expense of the α-methylstilbenes (the Saytzeff product).*

---

* While the Hoffman and Saytzeff rules were originally applied to saturated alkyl groups, the terms are used here in the sense suggested by Bunnett[11] as describing the direction which the new double bond takes relative to a β-substituent.

The ratio of *trans* to *cis*-α-methylstilbene might be due to the relative population of 2 and 3, the former producing the *cis*-isomer and the latter the *trans*. However, the observed ratio of *trans*- to *cis*-alkene is approximately 50 to 1 and it seems unlikely that the amounts of the two conformational isomers 2 and 3 would be this different.

As the Curtin–Hammett principle would indicate, it is more likely that the factor responsible for the observed isomer ratio in the α-methylstilbenes is the relative energies of the transition states leading to these alkenes. As the proton is eliminated from the rear carbon of conformations 2 and 3, the groups attached to the developing double bond become coplanar. It is evident that the increase in steric interaction resulting from deprotonation of 2 (phenyl-phenyl interaction) is greater than that resulting from deprotonation of 3 (phenyl-methyl interaction). This difference is reflected in the much smaller amount of *cis*-α-methylstilbene formed than *trans* in the kinetically controlled product.

Not surprisingly, the presence of a para-aromatic substituent had little effect on the composition of the products. Both the kinetic products (Table 6, Experimental) and thermodynamic products (Table 7, Experimental) are essentially independent of this substituent since it has little effect on the steric size of the groups in the vicinity of the reaction centre. The differences noted in the ratio of *trans*-α-methylstilbene to α-benzylstyrene reflect the ease of isomerization of the α-alkene to the equilibrium composition.

The single exception to the product pattern shown in Table 2 is the elimination of the $(CH_3)_3$ N-group effected by a strong base. It is possible that a change in transition state is occurring but a control run showed that α-benzylstyrene is rapidly isomerized under the reaction conditions to a product similar to that isolated. Consequently, no conclusion can be based on this particular observation.

EXPERIMENTAL

M.ps are uncorrected and were determined on a Mel-temp apparatus using open capillaries. The NMR spectra were recorded on a Varian T-60 spectrometer using 10–15% solns of the compound in $CDCl_3$ with TMS as an internal standard. Line positions are reported in ppm downfield from this standard. IR spectra were recorded on a Beckman IR-10 spectrometer. Microanalyses were carried out by A. B. Gygli, Toronto.

All VPC analyses were performed on a Varian-Aerograph model 1520 gas chromatograph equipped with flame ionization detectors. Peak areas were measured by a Disc integrator and corrected using response factors obtained with standard mixtures of the pure compounds. Generally, a 5 ft by $\frac{1}{8}$ inch column packed with 10% Carbowax 20M on Chrom W 80/100 mesh was used to effect separation of the components. The column was operated at 165° with the injector at 175°, detector at 255° and a helium flow rate of 30–35 ml/min. In the case of 1-phenyl-2-(*p*-chlorophenyl)-2-propanol, a column temp of 180° was used. The more sensitive alcohol, 1-phenyl-2-(*p*-methoxyphenyl)-2-propanol, required the same column treated with potassium hydroxide to prevent on-column dehydration.

Isomeric 1,2-diphenylpropenes. cis-α-Methylstilbene was prepared by the reduction of *cis*-α-phenylcinnamic acid[21] with LAH-$AlCl_3$[22] in 35% yield; m.p. 47–48°. The NMR spectrum showed CH_3 at 2·17 (doublet, J = 1·4 c/s, 3H), the vinyl H at 6·60 (quartet, 1H) and the aromatic H in a complex band 6·9–7·1 (10H). Analysis by VPC showed the material to be free of the other two isomers.

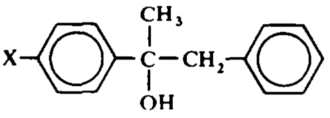
trans-α-Methylstilbene was prepared by the acid-catalyzed dehydration of 1,2-diphenyl-2-propanol under equilibrating conditions. The NMR spectrum showed the CH_3 at 2·26 (doublet, J = 1·4 c/s, 3H) the vinyl H at 6·81 (quartet, J = 1·4 c/s, 1H) and the aromatic H as a broad singlet at 7·3 (10H).

α-Benzylstyrene was prepared[4] by the reaction of benzyne with α-methylstyrene in 30% yield, b.p. 104–108° at 0·6–0·7 mm. The NMR spectrum showed the CH_2 as a broad singlet at 3·43 (2H), the two vinylic H as broad singlets at 4·97 and 5·43 (1H each) and the aromatic H in a broad band 7·0–7·5 (10H).

Preparation of 2-substituted-1,2-diarylpropanes. The required alcohols were prepared by the interaction of substituted acetophenones with benzylmagnesium chloride. The results and properties of the products are summarized in Table 4. NMR data are recorded in Table 5 together with that of the other compounds prepared.

2-Chloro-1,2-diphenylpropane. 1,2-Diphenyl-2-propanol was converted to the corresponding chloride in 90% yield using the procedure described.[22]

TABLE 4. PREPARATION OF

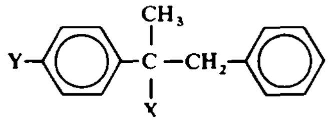


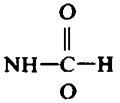
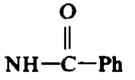
X	% Yield	m.p.	b.p. (mm Hg)	Theory		Found	
				%C	%H	%C	%H
H	84	48–49	134 (1·5)	—	—	—	—
Cl	81	56·5–58	148–150 (0·9)	73·01	6·13[a]	73·10	6·25[a]
CH_3	76	—	138–140 (1·2)	84·92	8·02	85·31	7·84
OCH_3	82	—	156–157 (0·8)[b]	79·32	7·49	79·12	7·43

[a] %Cl: Calc 14·37; Found, 14·36%.

[b] Distilled in the presence of a little Na_2CO_3 to avoid dehydration by traces of acid.

TABLE 5. NMR DATA OF COMPOUNDS PREPARED



X	Y	δCH_3	δCH_2	δ other
OH	H	1·50	3·03	
OH	OCH_3	1·42	2·95	3·61, OCH_3
OH	CH_3	1·42	2·95	2·25, aromatic CH_3
OH	Cl	1·50	3·00	
OCH_3	H	1·40	2·94	2·98, OCH_3
Cl	H	1·89	3·35	
NH_2	H	1·38	2·90	[a]—NH_2
$N(CH_3)_2$	H	1·19	2·95	2·20, $N(CH_3)_2$
 $\mathrm{NH{-}\overset{\overset{O}{\|}}{C}{-}H}$	H	see Experimental		
 $\mathrm{NH{-}\overset{\overset{O}{\|}}{C}{-}Ph}$	H	1·79	3·22, 3·60[b]	

[a] Several hours were required to observe exchange with D_2O.

[b] AB quartet, $J = 13$ c/s.

Preparation of 2-methoxy-1,2-diphenylpropane. 1,2-Diphenyl-2-propanol (21·2 g, 0·1 mole) in 100 ml MeOH containing *p*-toluenesulfonic acid (0·5 g, 0·00263 mole) was refluxed for 5·5 hr. The MeOH was removed under reduced press and the residue dissolved in 75 ml ether. The soln was washed with water, dried (Na_2CO_3) and evaporated to give 21·2 g crude residue which on analysis (VPC) was found to contain

2-methoxy-1,2-diphenylpropane 93·4%, 1,2-diphenyl-2-propanol 1·1%, *trans*-α-methylstilbene 2·2%, α-benzylstyrene 3·3%, and a trace of *cis*-α-methylstilbene. The crude residue was dissolved in a small amount of hexane and chromatographed on a column of silica gel. Elution with hexane gave 17·5 g (77·4% yield) 2-methoxy-1,2-diphenylpropane; b.p. 92–94° (0·1 mm). (Found: C, 84·82; H, 8·05. Calc for $C_{16}H_{18}O$: C, 84·92; H, 8·02%).

2-Dimethylamino-1,2-diphenylpropane. 2-Dimethylamino-1,2-diphenylpropane was prepared in the manner described by Hauser[9, 23, 24] in 75% yield, b.p. 122–123° at 0·8 mm.

Preparation of 2-amino-1,2-diphenylpropane. It was found necessary to modify the preparation described.[25] KCN (39 g, 0·6 mole) and 1,2-diphenyl-2-propanol (42·4 g, 0·2 mole) were suspended in 120 ml dibutyl ether and conc H_2SO_4 (80 ml) was added at such a rate that the temp did not rise above 70°. After addition was complete, the reaction was stirred a further 2 hr at 50–60° then cooled, made basic (20% NaOH) and extracted with ether. After removal of the solvent, the residue was recrystallized from EtOH to give 47·8 g (63% yield) of 2-formamido-1,2-diphenylpropane, m.p. 108·5–110·5°. (Found: C, 80·59; H, 7·31; N, 5·88. Calc for $C_{16}H_{17}NO$: C, 80·30; H, 7·16; N, 5·85%).

The NMR spectrum was a superposition of the spectra from two isomers due to restricted rotation about the amide C—N bond. Integration allowed the following assignments; Isomer A (60%) showed a CH_3 singlet at 1·67, the CH_2 as an AB quartet at 3·12 and 3·45 (J = 14 c/s) aromatics 6·8–7·3 and $\overset{\text{O}}{\overset{\|}{\text{C}}}\text{-}\underline{\text{H}}$ as a doublet at 8·00 (J = 8 c/s). Isomer B (40%) showed a CH_3 singlet at 1·70 the CH_2 as a singlet at 3·10, the aromatics 6·8–7·3 and $\text{—}\overset{\text{O}}{\overset{\|}{\text{C}}}\text{—}\underline{\text{H}}$ as a doublet at 8·12 (J = 3 c/s).

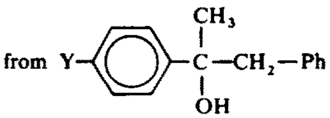
The 2-formamido derivative (10 g, 0·042 mole) was hydrolyzed by refluxing under N_2 in 100 ml 6N HCl. On cooling, partial precipitation of the amine salt occurred. The mixture was made basic with 20% NaOH and the product isolated by ether extraction. After drying ($MgSO_4$) and removal of the solvent, the residual oil was distilled to give 6·0 g (71% yield) 2-amino-1,2-diphenylpropane, b.p. 124–125° at 1 mm. (Found: C, 85·38; H, 8·26; N, 6·76. Calc for $C_{15}H_{17}N$: C, 85·25; H, 8·11; N, 6·63%).

Acid-catalyzed dehydration of 1,2-diphenyl-2-propanol. The alcohol (0·0071 mole, 1·50 g) was placed in a flask equipped with a reflux condenser and mechanical stirrer operating through it and immersed in a Tamson constant temp bath controlled at 50·0 ± 0·1°. The solvent, 15·0 g of anhyd acetonitrile, was measured in through a side neck and the soln allowed to equilibrate. The catalyst, *p*-toluenesulfonic acid (0·075 g, $3{\cdot}41 \times 10^{-4}$ mole) was measured in as a freshly prepared soln in acetonitrile.

Periodically, approximately 0·5 ml samples of the mixture were withdrawn, quenched by adding to anhyd Na_2CO_3 and analyzed by VPC.

The first-order rate constants obtained for the disappearance of the alcohol are summarized in Table 3. In addition, the composition of the alkenes formed at 10% and 25% reaction are summarized below in Table 6. This same procedure was used for dehydrations in benzene (temp = 70°) although no attempt at

TABLE 6. INITIALLY FORMED ALKENE COMPOSITION

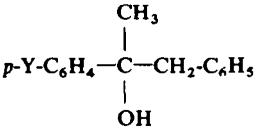


Y	Temp.,°C	Alkene ratio at 10% reaction	%*trans*-α-methylstilbene[a] %α-benzylstyrene at 25% reaction
H	50	1·14	1·20
Cl	50	1·28	1·40
CH_3	30	1·22	1·27
OCH_3	13·5	1·38	1·36

[a] *cis*-α-methylstilbene was too small to measure accurately.

studying the kinetics was attempted because of the non-homogeneity of the system. By continuing the reaction until the alkene composition became constant over a 24 hr period, the equilibrium composition of the alkene mixture was obtained and is summarized in Table 7.

TABLE 7. EQUILIBRIUM ALKENE COMPOSITION

Starting alcohol  $p\text{-Y-}C_6H_4\text{—}C(CH_3)(OH)\text{—}CH_2\text{-}C_6H_5$	Alkene composition, 70° in benzene		
	%α	%*cis*	%*trans*
Y = H	0·7	18·2	81·1
Y = OCH_3	0·4	18·6	80·1
Y = CH_3	0·6	18·2	81·3
Y = Cl	0·6	17·8	80·0

For the case of Y = H, the individual alkenes were isomerized at 70° in benzene with *p*-toluenesulfonic acid catalyst. Here the soln was homogeneous and the equilibrium compositions as well as an estimate of the rate of isomerization ($T_{\frac{1}{2}}$) was obtained.

The results are summarized in Table 1. In the case of α-benzylstyrene, the alkene was 90% isomerized before the first sample (10 min) was taken. Consequently, this $T_{\frac{1}{2}}$ value was approximated.

Dehydration of 1,2-*diphenyl*-2-*propanol with* $POCl_3$-*pyridine*. A stirred soln of 1,2-diphenyl-2-propanol, 9·0 g (0·043 mole) in 37·5 ml in pyridine was treated with 7·0 ml (0·075 mole) $POCl_3$ added dropwise over 30 min. The temp rose to 42° and was maintained at 45° for 48 hr. Periodically, small samples were withdrawn, extracted with ether, washed with water, dried (Na_2SO_4), and analyzed by VPC. The composition shown in Table 2 was unchanged over a 24 hr period.

Dehydration of 1,2-*diphenyl*-2-*propanol with* p-*toluenesulfonyl chloride and pyridine*. A mixture of 2·12 g (0·01 mole) 1,2-diphenyl-2-propanol, 1·9 g (0·01 mole) *p*-toluenesulfonyl chloride and 20 ml pyridine was refluxed under N_2 for 20 hr. The product was isolated by ether extraction of the soln after dilution with water and analyzed by VPC. The product composition is shown in Table 2.

α-Benzylstyrene and trans-*α-methylstilbene via dehydration of* 1,2-*diphenyl*-2-*propanol*. To a soln of 2·50 g p-toluenesulfonic acid in 500 ml benzene at 70°, 50·0 g (0·236 mole), 1,2-diphenyl-2-propanol was added with stirring. The progress of the reaction was followed by means of the IR spectra of samples withdrawn at intervals. After 3·5 hr, the OH band of the alcohol had disappeared. The reaction mixture was cooled, treated with anhyd Na_2CO_3, filtered and concentrated under reduced press to about 100 ml. The solid which separated was filtered off and recrystallized from EtOH to give 21·0 g (45·0% yield) *trans*-α-methylstilbene, m.p. 79–80°. Analysis by VPC showed one component.

The benzene filtrate was concentrated further and any residual alcohol was removed by chromatographing on a column of alumina with light petroleum (30–60°) as eluant. There was obtained, after vacuum distillation of the effluent, 17·2 g (37·5%) of olefins; b.p. 126–130° at 1·7 mm. Analysis by VPC indicated the presence of 3·7% *cis*-α-methylstilbene, 89·6% of α-benzylstyrene, and 6·7% *trans*-α-methylstilbene. Further purification of the α-benzylstyrene was effected by preparative gas chromatography using a 10 ft by $\frac{3}{8}$ inch column packed with 20% Apiezon J on Chrom W 60/80 mesh, operated at 165°.

Dehydrohalogenation of 2-*chloro*-1,2-*diphenylpropane*. The 2-chloro-1,2-diphenylpropane (2·30 g, 0·01 mole) was dissolved in 20·0 ml pyridine and the soln placed under N_2 in a constant temp bath at 70°. The reaction was monitored by following the disappearance of the Me absorption of the chloro compound in the NMR spectrum of the soln. After 24 hr, the chloro compound had disappeared and the soln was subjected to VPC analysis at this time and 24 hr later. No difference was observed in the two analyses the average of which is shown in Table 2.

Preparation and reaction of 2-(1,2-*diphenylpropyl*)*trimethylammonium iodide*. The procedure described[9] was used to prepare 2-(1,2-diphenylpropyl)trimethylammonium iodide. The quaternary ammonium salt (0·025 mole) was added to 0·07 mole potassium amide in 300 ml liquid ammonia. The mixture turned dark after 30 min and was stirred for 2 hr. Ether was added and the ammonia allowed to evaporate. A sample was withdrawn, diluted with 20 ml ether, washed with water, dried and analyzed by VPC.

The remaining soln was treated with 60 ml 2N HCl and extracted with ether. After washing with water and drying, this extract was analyzed by VPC. Both results are shown in Table 2.

Isomerization of α-benzylstyrene by potassium amide in liquid ammonia. α-Benzylstyrene (1·94 g, 0·01 mole) was added to a stirred suspension of 0·05 mole potassium amide in liquid ammonia and stirred for 3 hr. The product was then isolated as described above. The alkene mixture consisted of 91·0% *trans*-α-methylstilbene, 7·6% *cis*-α-methylstilbene and 1·3% α-benzylstyrene by VPC analysis.

Elimination of 2-amino-1,2-diphenylpropane with isoamyl nitrite. The procedure described[10] was followed. The amine (11·2 g, 0·053 mole), dissolved in anhyd benzene (20 ml), with or without glacial AcOH (0·10 mole) added, was treated with isoamyl nitrite[26] (1·29 g, 0·011 mole) with stirring and heating in an 80° oil bath. Samples were withdrawn at regular intervals with a syringe, quenched on anhyd Na_2CO_3 and analyzed by VPC. After 10 hr the reaction attained the constant composition shown in Table 2.

Acknowledgement—The authors are grateful for financial support from the Department of University Affairs of Ontario and for a Province of Ontario fellowship awarded to one of us (I.H.). Funds from the National Research Council of Canada for the purchase of the gas chromatographic equipment are also gratefully acknowledged.

REFERENCES

[1] M. Juot and M. Guyard, *Bull. Soc. Chim. Fr.* 1086 (1947)
[2] C. F. Koelsch and R. V. White, *J. Org. Chem.* **6**, 602 (1941)
[3] D. H. Hunter and D. J. Cram, *J. Am. Chem. Soc.* **86**, 5478 (1964)
[4] E. Wolthius and W. Cady, *Angew. Chem.* Int. Ed. **6**, 555 (1967)
[5] A. Zwierzak and H. Pines, *J. Org. Chem.* **27**, 4084 (1962)
[6] D. H. R. Barton, A. da S. Campos-Neves and R. C. Cookson, *J. Chem. Soc.* 3500 (1956)
[7] R. R. Sauers, *J. Am. Chem. Soc.* **81**, 4873 (1959)
[8] R. R. Sauers and J. M. Landesberg, *J. Org. Chem.* **26**, 964 (1961)
[9] H. M. Taylor and C. F. Hauser, *J. Am. Chem. Soc.* **82**, 1960 (1960)
[10] L. Friedman and J. H. Bayless, *Ibid.* **91**, 1790, 1795, 1800, 1803 (1969)
[11] J. F. Bunnett, *Angew. Chem.* Int. Ed. **1**, 225 (1962)
[12] C. K. Ingold, *Structure and Mechanism in Organic Chemistry* (2nd Edition), p. 678–680. Cornell University Press (1969)
[13] C. K. Ingold· *Proc. Chem. Soc.* 265 (1962)
[14] D. S. Noyce, D. R. Hartter and R. M. Pollack, *J. Am. Chem. Soc.* **90**, 3791, 3794 (1968)
[15] G. M. Loudon and D. S. Noyce, *Ibid.* **91**, 1433 (1969)
[16] J. F. Bunnett, G. T. Davis and H. Tanida, *Ibid.* **84**, 1606 (1962)
[17] H. C. Brown and Y. Okamoto, *Ibid.* **80**, 4979 (1958)
[18] H. C. Brown and I. Moritani, *Ibid.* **77**, 3607, 3623 (1955)
[19] H. C. Brown and M. Nakagawa, *Ibid.* **77**, 3610, 3614 (1955)
[20] H. C. Brown and Y. Okamoto, *Ibid.* **77**, 3619 (1955)
[21] L. F. Fieser, *Experiments in Organic Chemistry* (3rd Edition), pp. 184–185. Heath, Boston (1955)
[22] J. H. Brewster and H. O. Bayer, *J. Org. Chem.* **29**, 110 (1964)
[23] C. R. Hauser and T. M. Harris, *J. Am. Chem. Soc.* **80**, 6360 (1958)
[24] C. R. Hauser, H. M. Taylor and T. G. Ledford, *Ibid.* **82**, 1786 (1960)
[25] H. Cristol, A. Laurent and G. Solladie, *Bull. Soc. Chim. Fr.* **4**, 877 (1963)
[26] *Organic Syntheses* Coll. Vol. 2, p. 108