76-4; *trans*-3,4-dimethylcyclohexanone, 28023-45-2; *cis*-3,4-dimethylcyclohexanone, 27922-05-0.

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Effects of Base Association upon Geometrical Orientation in Elimination from 1-Phenyl-2-propyl Chloride in Potassium *tert*-Butoxide–*tert*-Butyl Alcohol

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Base association was clearly shown to exert a strong influence upon positional and geometrical orientation in base-promoted anti β-eliminations from 2-alkyl halides and arenesulfonates in t-BuOH.[1] Regarding geometrical orientation it was observed that base association is responsible for the generally low trans:cis 2-alkene ratios found for the reaction of these substrates with t-BuOK. Accordingly, the trans:cis 2-alkene ratios were found to significantly increase when the reaction is carried out in the presence of crown ethers which are able to convert contact ion pairs or ion pair aggregates into separated ions. This trend was suggested to be originated by the larger steric requirements of the associated base.

Interestingly, low trans:cis olefin ratios in t-BuOK–t-BuOH (especially with respect to those in EtO^-–EtOH and MeO^-–MeOH) are considered as the "normal pattern" of β-elimination reactions which proceed *via* an anti mechanism, since, by this mechanism, contact ions are expected to lead to preferential formation of cis olefin.[2] Deviations from this pattern are considered highly indicative of the intervention of a syn mode of β-elimination, since it is well known[2c] that syn elimination leads nearly exclusively to the trans olefin and is favored by base association.

We wish now to report that similar conclusions do not apply to the elimination reactions of β-phenyl activated systems. We have studied the β-elimination reactions of 1-phenyl-2-propyl chloride in t-BuOK–t-BuOH and found (see Table I) that the *trans*- to *cis*-1-phenylpropene ratio is significantly larger than those in EtONa–EtOH and MeONa–MeOH; a significant decrease of this ratio is obtained using t-BuON–n-Bu_4 or crown ether complexed t-BuOK. Clearly, base association plays an important role in determining the trans:cis olefin ratios also in the elimination reactions of 1-phenyl-2-propyl halides; however, the pattern is exactly the opposite of that found for the elimination reactions of nonactivated alkyl halides. This striking difference cannot be attributed to the intervention of a syn mechanism of elimination in the phenyl activated series, since we have evidence that this reaction path is of very little importance in the case of 1-phenyl-2-propyl chloride;[3] it results therefore that the geometrical orientation in the anti eliminations from β-phenyl activated substrates is influenced by steric effects and/or basicity in a different way from the anti eliminations of nonactivated substrates.

Table I
Trans:Cis Olefin Ratios in the E2 Eliminations from 1-Phenyl-2-propyl Chloride in Various Solvent–Base Systems at 60° [a]

Solvent–Base	*trans*- to *cis*-1-Phenylpropene
MeOH–MeONa [b]	23.5 ± 0.1
EtOH–EtONa [c]	25.0 ± 0.1
t-BuOH–t-BuOK [d]	72 ± 5
t-BuOH–t-BuOK [e]	45 ± 1
t-BuOH–t-BuON–n-Bu_4 [f]	37.7 ± 0.1

[a] Determined by glpc. Each value is the average of at least three determinations. The initial concentration of 1-phenyl-2-propyl chloride was ~0.02 M. According to blank experiments the trans:cis ratios are not significantly affected by the isomerization reactions of allylbenzene (formed in a very little amount) and of *cis*- and *trans*-1-phenylpropene. [b] [MeONa] = 2.3 M. Reaction time 15 hr. In the absence of MeONa no production of chloride ions was observed after 70 hr. [c] S. Alunni and E. Baciocchi, *Tetrahedron Lett.*, 205 (1973). With EtOK the trans:cis ratio is 28. [d] [t-BuOK] = 0.2–0.8 M. Reaction time 50–210 min. No appreciable variation of the trans:cis ratio with t-BuOK concentration was observed. [e] In the presence of dicyclohexyl-18-crown-6. [t-BuOK] = 0.17 M. Reaction time 5–15 min. [f] Prepared by mixing 0.3–0.5 M t-BuOK–t-BuOH with appropriate amounts of n-Bu_4NBr. Reaction time 30–75 min.

At present, we have no explanation of this phenomenon, even though it may be recalled that in the eliminations from β-phenyl activated substrates the trans/cis ratios derive from differences in the conjugation extent of the phenyl group with the developing negative charge at the β carbon in addition to differences in the nonbonded interactions at C_α and C_β, as it occurs in the resulting olefins. However, it seems important to point out, in the light of this result and the recent data on the leaving group effects,[5] that considerable caution must be exerted in applying conclusions reached from studies of elimination reactions of β-phenyl activated substrates to the elimination reactions of nonactivated substrates and vice versa.

Experimental Section

Materials. 1-Phenyl-2-chloropropane. A solution of 29 g of thionyl chloride in 125 ml of anhydrous benzene was added at 0° and under stirring to a solution of 25 g of 1-phenyl-2-propanol (Fluka) and 4 g of pyridine in 420 ml of anhydrous benzene. After standing overnight the mixture was refluxed for 3 hr. The mixture was then cooled and washed with cold water, diluted sulfuric acid, 10% solution of sodium bicarbonate, and a solution of sodium thiosulfate. After the mixture was dried on sodium sulfate and the solvent was removed, distillation at reduced pressure gave 16.4 g (55% yield) of 1-phenyl-2-chloropropane, bp 100° (30 mm). *Anal.* Calcd for $C_9H_{11}Cl$: Cl, 22,9. Found: Cl, 22,6.

***cis*-1-Phenylpropene** was prepared by decarboxylation of α-metylcinnamic acid, according to a procedure described in the literature,[6] and purified by fractional distillation on a Todd column, bp 65° (12 mm), $n^{22.5}D$ 1.5415 (lit.[6] $n^{20}D$ 1.5430). Its purity (>99.5%) was checked by glpc.

***trans*-1-Phenylpropene** and **allylbenzene** were commercial products (Fluka) purified by distillation. Their purity (glpc) was 99%.

Dicyclohexyl-18-crown-6 ether was prepared according to the procedure described by Pedersen.[7]

Base–Solvent Solution. Methanol was refluxed with magnesium and resublimed iodine and fractionally distilled. Absolute ethanol was refluxed with sodium and diethyl phthlate and fractionally distilled. t-Butylalcohol was distilled after treatment with potassium metal. Solutions of alkoxide were obtained by reactions,

under nitrogen, of freshly cut sodium and potassium metal with the appropriate alcohol.

Procedure for Product Studies. A known amount of the halogeno derivative was added, under strong stirring, to a solution of alkoxide in alcohol placed in a flask surrounded by a jacket for the circulation of a thermostating liquid. After a variable time (depending on the reactivity of the substrate and the concentration of alkoxide), the reaction mixture was poured into water and extracted several times with pentane. After the mixture was dried, most of pentane was removed and the resulting solution (~2 ml) was analyzed by glpc.

Glpc Analysis of Reaction Products. These analyses were performed on a Model GI, Carlo Erba gas chromatograph, equipped with a flame ionization detector and using nitrogen as a carrier gas. The olefins were nicely separated on a 3.2 × 0.002 m column packed with 20% LAC-728 on 60–80 mesh Chromosorb W, at 70°. The retention times were as follows: allylbenzene, 1350 sec; *cis*-1-phenylpropene, 1980 sec; *trans*-1-phenylpropene, 3100 sec.

For the quantitative analysis of *cis*- and *trans*-1-phenylpropene it was necessary to use different attenuations of the detector signal owing to the large trans:cis olefin ratios generally observed in the present work. The molar response of the trans olefin with respect to the cis olefin was 1.14.

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Registry No.—1-Phenyl-2-propyl chloride, 10304-81-1; *trans*-1-phenylpropene, 873-66-5; *cis*-1-phenylpropene, 766-90-5.

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(4) To investigate the influence of the nucleophile basicity on the trans/cis ratios we attempted to study the eliminations from 1-phenyl-2-propyl chloride induced by potassium phenoxide in *t*-BuOH; however, this reaction resulted too slow to be conveniently studied.
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Trimethyl Phosphite Displacement on Mucochloryl Chloride

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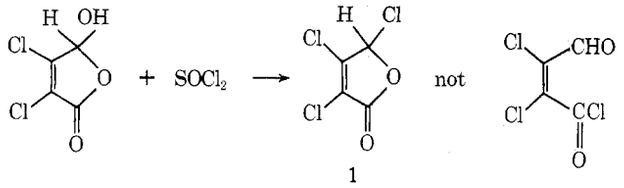
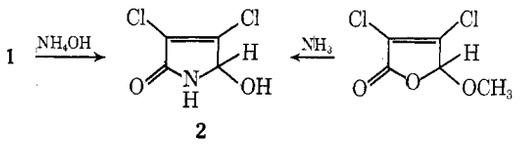
Mucochloryl chloride (**1**), derived from mucochloric acid and thionyl chloride, is a masked acid chloride in that it exists in the 5*H*-2-furanone ring structure.[1] This "pseudo



1

acid chloride" possesses three potentially reactive halogens. Nevertheless, mucochloryl chloride reacts with ammonium hydroxide to produce the corresponding 5-hydroxy-3,4-dichloropyrrolin-2-one (**2**).[2] The corresponding methyl ester of mucochloric acid upon treatment with ammonia gave the same compound **2**.[3] Consequently the vinylic chloride atoms have not been displaced.



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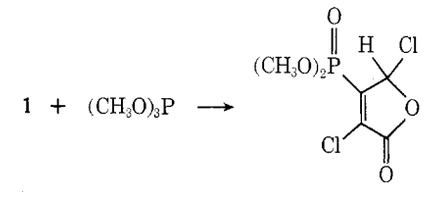
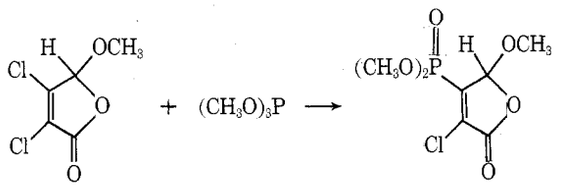
We wish to report a surprising result observed in an attempted reaction of mucochloryl chloride with trimethyl phosphite. The product of this reaction results from phosphite displacement of the 4-chlorine rather than the 5-chlorine, and is 3,5-dichloro-4-dimethoxyphosphinyl-2,5-dihydrofuran-2-one (**3**). The identity of **3** was established



3

by its infrared spectrum and comparison of its hydrogen decoupled ^{13}C nmr spectrum[4] with 5-methoxy-4-dimethoxyphosphinyl-3-chloro-2,5-dihydrofuran-2-one[5] (**4**). The sp^3 methine carbon for **3** could easily be observed and the ^{13}C–C–P coupling of 12 cps compared favorably to that of **4** where J = 16 cps. A model for one bond ^{13}C–P coupling, *N*-phosphonomethylglycine,[6] showed $J_{^{13}C-P}$ to be much higher, *i.e.*, 160 cps. The product **3** exhibits a normal lactone carbonyl at 1787 cm^{-1}. This eliminates the possibility of the tautomeric furan structure and confirms a 2-furanone structure. Dimethyl phosphite reacts with 5-methoxy-3,4-dichloro-2,5-dihydrofuran-2-one to produce **4**.[5] By



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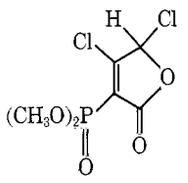
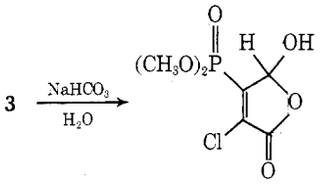
comparison the reaction of **1** with trimethyl phosphite would produce **3** rather than the positional isomer **5**. Hy-



5

drolysis of **3** gave 5-hydroxy-4-dimethoxyphosphinyl-3-chloro-2,5-dihydrofuran-2-one (**6**).[7] Comparison of the H′



6

nmr spectra of **3**, **4**, and **6** showed an identical $J_{P-C-C-H}$ coupling constant of 2 cps. This supports the structures given since coupling constants of the P–C–H type are usually much larger.[8]

Carbanion delocalization in the intermediate formed by addition of trimethyl phosphite to C-4 of mucochloryl chloride is undoubtedly a factor in the preference of the reactants for this reaction pathway. Facile reversal to eliminate