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-1phenylpropene, 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.

References and Notes

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- (3) From a study of the elimination reactions of *dl-erythro-* and *dl-threo-*1-phenyl-1-deuterio-2-chloropropane: to be published. (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



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.



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 5chlorine, and is 3,5-dichloro-4-dimethoxyphosphinyl-2,5dihydrofuran-2-one (3). The identity of 3 was established



by its infrared spectrum and comparison of its hydrogen decoupled ¹³C nmr spectrum⁴ with 5-methoxy-4-dimethoxyphosphinyl-3-chloro-2,5-dihydrofuran-2-one⁵ (4). The sp³ methine carbon for 3 could easily be observed and the ¹³C-C-P coupling of 12 cps compared favorably to that of 4 where J = 16 cps. A model for one bond ¹³C–P coupling, N-phosphonomethylglycine,⁶ showed $J_{^{13}\text{C-P}}$ 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



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



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



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 chloride from the above described intermediates, followed by dealkylation, produces the observed product. Ammonia, a much harder base than trimethyl phosphite.⁹ reacts more readily via alternative pathways not requiring intermediates stabilized by strong delocalization. Further developement of these ideas will be presented in future publications.

Experimental Section

3.4.5-Trichloro-2.5-dihydrofuran-2-one.10 Mucochloric acid (125 g, 0.74 mol) and 473 ml of thionyl chloride containing 2.0 ml of dimethylformamide were heated at 50° with stirring for 5 hr. The mixture was cooled and the excess thionyl chloride removed in vacuo. Distillation of the residual oil gave 117 g (84%) of product, bp 91- (6 mm), pmr spectrum (CDCl₃) δ 6.66 (s, 1 H, CH).

5-Hydroxy-3,4-dichloropyrrolin-2-one (2). An aqueous mixture of 13.7 ml of concd ammonium hydroxide, 10.6 g of sodium carbonate, and 100 ml of water was cooled in an ice bath to 0-5° and treated dropwise with 18.7 g (0.1 mol) of 3,4,5-trichloro-2,5dihydrofuran-2-one. The resultant mixture was stirred at room temperature overnight and the tan solid was filtered, washed with cold ethanol, and refluxed with ethyl acetate to give 14.1 g (84%) of product: mp 166–168°; pmr spectrum (D₃COD) δ 5.42 (s, 1 H, CH), 4.70 (s, 2 H, NH₂), (DMSO- d_6) 5.59 (d, J = 8 Hz, 1 H, OH), 6.92 (d, J = 8 Hz, 1 H, CH), 9.20 (s, 1 H, NH); ir spectrum (Nujol) 1689 cm⁻¹ (vs, carbonyl stretching). An identical material was obtained by the procedure of Hill, et al.³

3,5-Dichloro-4-dimethoxyphosphinyl-2,5-dihydrofuran-2one (3). Mucochloryl chloride (18.7 g, 0.1 mol) and trimethyl phosphite (12.4 g, 0.1 mol) were mixed and let stand overnight. Trimethylphosphite was removed under vacuum on the steam bath and the residue distilled at 87-130° (3 mm) to give 7.5 g (40%) of mucochloryl chloride. The dark pot residue crystallized on cooling. Recrystallization of the residue from chloroform-petroleum ether (bp 30-75°) gave 8.5 g (85%) of 3, mp 90-94°. A second recrystallization gave 6.5 g: mp 96–98°; pmr spectrum (CDCl₃) δ 4.0 (d, J = 12 Hz, 6 H, CH₃OP), 6.93 (d, J = 2 Hz, 1 H, CH); ir spectrum (CHCl₃) 1787 cm⁻¹ (vs, carbonyl stretching); ¹³C nmr spectrum relation to TMS (d_6 -acetone). δ 55.1 (s), 88.3 (d, J = 12 cps).

Anal. Calcd for C₆H₇Cl₂O₅P: C, 27.61; H, 2.70; Cl, 27.17; P, 11.87. Found: C, 27.41; H, 2.51; Cl, 26.98; P, 11.88.

5-Hydroxy-4-dimethoxyphosphinyl-3-chloro-2,5-dihydrofuran-2-one (6). To 17 g (0.2 mol) of sodium bicarbonate in 200 ml of water was added 26.1 g (0.1 mol) of 3,5-dichloro-4-dimethoxyphosphinyl-2,5-dihydrofuran-2-one. After stirring 1-2 hr, the mixture was acidified and the solid collected to give 26.0 g (77%) crude product. This solid was recrystallized from benzene and then water to give 5.0 g of product: mp 124-127°; pmr (CDCl₃) δ 3.95 (d, J = 12 Hz, 6 H, CH_3OP), 6.06 (br hump, 1 H, OH), 6.36 (3, J = 12Hz. 1 H. CH)

Anal. Calcd for C₆H₈ClO₆P: C, 29.69; H, 3.30. Found: C, 29.78; H. 3.36

5-Methoxy-4-dimethoxyphosphinyl-3-chloro-2,5-dihydro-

furan-2-one (4). The procedure of Malinowski, et al.,⁵ was followed to yield 38.0 g (75%) of product: bp 160-165° (1 mm); pmr $(\text{CDCl}_3) \delta 3.8 \text{ (d, } J = 12 \text{ Hz}, 6 \text{ H}, \text{CH}_3\text{OP}); 3.6 \text{ (s, } 3 \text{ H}, \text{CH}_3\text{O}), 6.0$ (d, J = 2 Hz, 1 H, CH).

Registry No.-1, 19714-00-2; 2, 52500-03-5; 3, 52500-04-6; 4, 37031-62-2; 6, 52500-05-7; mucochloric acid, 766-40-5; thionyl chloride, 7719-09-7; trimethyl phosphite, 121-45-9.

References and Notes

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