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REGIOSELECTIVE PREPARATION OF VINYL CHLORIDES FROM 2-METHYLCYCLOHEXANONE

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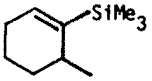
Abstract: Treatment of 2-methylcyclohexanone with PCl_5 in hexane at reflux gives predominantly 2-chloro-3-methylcyclohexene (**3**). On the other hand, treatment with catechyl phosphorus trichloride followed by alcoholic KOH gives predominantly the isomeric vinyl chloride, 1-chloro-2-methylcyclohexene (**4**).

In connection with other projects we needed vinylsilanes 1 and 2. Cyclic vinylsilanes of this type are generally prepared by silylation of the corresponding vinylmetallic reagents,[1] which are most often generated from the corresponding vinyl halides.[5] An attractive and inexpensive method to prepare vinylsilanes is the reaction of the corresponding vinyl halides with sodium and Me_3SiCl, sometimes called the Wurtz-Fittig reaction.[6] We have therefore investigated the preparation of vinyl halides 3 and **4**.



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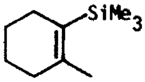

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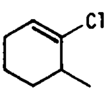
The classic method for preparing cyclic vinyl chlorides is the reaction of ketones with PCl_5.[7-10] Under the usual conditions, mixtures of isomers are formed from unsymmetrical ketones. More recently, additional reagents have been shown to convert ketones to vinyl chlorides: $Cl_2CHOMe/ZnCl_2$,[11] Ph_3PCl_2,[12] Ph_3P/CCl_4,[13] catechyl phosphorus trichloride,[14,15] and a polymer-supported phosphine dichloride.[16] In most cases these reagents have not been tested on unsymmetrical ketones where mixtures of isomers would be possible. We have investigated the reactions of 2-methylcyclohexanone with PCl_5 and with catechyl phosphorus trichloride and have found conditions under which either of the isomeric vinyl chlorides 3 or **4** can be made to predominate.

RESULTS

Reactions of 2-methylcyclohexanone with PCl_5[9] were investigated in several different solvents. The rate of reaction depended on the solvent[17] but the ratio of products appeared to depend more on temperature than on the nature of the solvent.[18] At room temperature, in every case a mixture of vinyl chlorides 3 and **4** and dichloride 5 was obtained. Reactions carried out in CH_2Cl_2 (10 min), CCl_4 (1 hr), petroleum ether (2 hr), or diethyl ether (18 hr) gave similar mixtures, containing about 50% of 3 by VPC. At higher temperatures,[19] the proportion of 3 increased, rising to about 90% in hexane at reflux. On a preparative scale, vinyl chloride 3[9d] was obtained in 52% yield and 92% isomeric purity.



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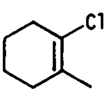

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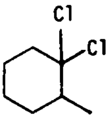

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In order to prepare vinyl chloride **4**, we sought conditions to favor formation of **4** and/or dichloride **5**. We had previously observed that a mixture of **3**, **4**, and **5** (3:2:3 ratio by VPC) could be converted to a mixture of vinyl chlorides **3** and **4** (3:5 ratio by VPC) by treatment with alcoholic KOH, suggesting that dehydrohalogenation of dichloride **5** gave almost entirely the more substituted vinyl chloride isomer **4**.[20] We found that treatment of 2-methylcyclohexanone with catechyl phosphorus trichloride[14] in CH_2Cl_2, initially at -78°, then warmed to room temperature, produced a mixture of **3**, **4**, and **5** in a ratio of 1:6:2. In a preparative scale reaction, the crude product was treated with ethanolic KOH to produce vinyl chloride **4**[9,21] in 46% overall yield and 89% isomeric purity.

CONCLUSION

Treatment of 2-methylcyclohexanone with PCl_5 in hexane at reflux gives mainly **3**, whereas treatment with catechyl phosphorus trichloride followed by alcoholic KOH gives predominantly **4**. To our knowledge this is the first example where the regioselectivity of the reactions of ketones with PCl_5 and related reagents can be controlled.

EXPERIMENTAL

2-Chloro-3-methylcyclohexene (3). To a solution of 8.33 g (40 mmol) of PCl_5 in 75 ml of hexanes heated at reflux was added dropwise (over 10 min) a solution of 3.584 g (32 mmol) of 2-methylcyclohexanone in 10 ml of hexane. The resulting solution was heated at reflux for 15 min, cooled, and gradually poured into an ice-cooled solution of 100 ml of 40% aqueous NaOH overlaid with 50 ml of petroleum ether. The resulting mixture was stirred for 20 min, the layers were separated, and the organic layer was washed with two portions of saturated $NaHCO_3$ followed by two portions of water, dried ($MgSO_4$), and concentrated. VPC analysis[22] (82°) showed peaks at 5.2 min (88%, **3**), 6.0 min (8%, **4**), and 11.1 min (4%, **5**). Distillation produced 2.15 g (52%) of **3** as a colorless liquid: bp 75-77° (41 mm) (lit.[9d] bp 72-73° (40 mm)); IR (film) 1650 cm^{-1}; NMR ($CDCl_3$) δ 5.77 (m). VPC analysis[22] (82°, $C_{10}H_{22}$ = 7.3 min) showed the major peaks (>98% of peak area) at 5.2 min (**3**) and 6.0 min (**4**) in a ratio of 92:8, and a small peak (1% of peak area) at 11.1 min (**5**).

1-Chloro-2-methylcyclohexene (4). A mixture of 9.76 g (40 mmol) of catechyl phosphorus trichloride[14] in 50 ml of methylene chloride under nitrogen was cooled in Dry Ice - acetone, and a solution of 2.24 g (20 mmol) of 2-methylcyclohexanone in 5 ml of methylene chloride was added. The resulting mixture was stirred at -78° for 1 hr, and then allowed to warm to room temperature overnight. Aqueous workup as described above gave 2.5 g of crude product. VPC analysis[22] (100°, $C_{10}H_{22}$ = 5.1 min) showed the major peaks at 4.0 min (13%, **3**), 4.7 min (65%, **4**), and 8.2 min (22%, **5**). The IR and NMR spectra of the crude product were consistent with the VPC analysis.

To 50 ml of 20% KOH in ethanol (w/v) under nitrogen was added a solution of the above crude product in 2 ml of ethanol, and the resulting mixture was heated at reflux overnight (∿18 hr). The reaction mixture was cooled, diluted with water, and extracted with three portions of pentane. The combined organic layers were washed with saturated $NaHCO_3$ followed by water, dried ($MgSO_4$), concentrated, and distilled bulb-to-bulb (oven temperature 40-45°, oil pump vacuum) (lit. bp 76-77° (40 mm)[9d]), giving 1.27 g (49% from 2-methylcyclohexanone) of **4**[9,21] as a colorless liquid. The IR and NMR spectra were in agreement with reported values.[9c] VPC analysis[22] (112°, $C_{10}H_{22}$ = 3.0 min) showed the major peaks at 2.4 min (**3**) and 2.8 min (**4**) in a ratio of 11:89.

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17. Newman has previously observed that reactions of ketones with PCl_5 are faster in CH_2Cl_2 than in CCl_4,[10] CH_3CN,[10b] or nitroethane.[10b]

18. Some previous studies of solvent effects were complicated by the fact that reaction temperatures were also changed.[10c]

19. The reaction of cyclohexanone with PCl_5 is reported to give higher yields of 1,1-dichlorocyclohexane at low temperatures.[8b] Reactions of ketones with PCl_5 are reported to give chlorinated by-products at higher temperatures.[7a,8j,10] Our attempts to obtain a higher proportion of vinyl chloride 3 by carrying our the reactions in toluene or dioxane at reflux gave mixtures containing unidentified by-products.

20. We subsequently discovered that a similar observation had been made by Domnin in 1940.[9a]

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22. Vapor phase chromatographic (VPC) analyses were performed on a Varian Aerograph model 90-P instrument using a 10 ft x 0.25 in. column packed with 10% SE-30 on Chromosorb W; in some cases the retention time of a hydrocarbon standard under the given conditions is included.