tion afforded 12.56 g. (77%) of *trans*-4-*t*-butylcyclohexene oxide (IX), b.p. 51° (0.5 mm.), n_D^{25} 1.4601 (lit.[3] b.p. 96–97° at 10 mm., n_D^{20} 1.4623).

2ᵗ-Hydroxy-4ᶜ-t-butylcyclohexanol (X). The *trans,trans*-chlorohydrin (I) (5 g., 0.027 mole) was treated with 100 ml. of 5% potassium hydroxide in dry isopropyl alcohol at 55° under a nitrogen atmosphere for 2 hr.[4] The product was isolated as described above and 4.0 g. of a yellow oil was obtained. This oil solidified upon standing and was recrystallized from *n*-pentane, m.p. 141–142°. The mother liquor (2.0 g.) was distilled and 0.21 g. of the *trans*-oxide (IX) was isolated, n_D^{25} 1.4602. Approximately 1 g. more of the solid was obtained, yielding a total of 2.7 g. (51%) of 2ᵗ-hydroxy-4ᶜ-*t*-butylcyclohexanol (X). A mixed melting point with the diol obtained from the peracetic acid epoxidation of 4-*t*-butylcyclohexene showed no depression.

Anal. Calcd. for $C_{10}H_{20}O_2$: C, 69.78; H, 11.67. Found: C, 69.69; H, 11.74.

2ᵗ-Ethoxy-5ᵗ-t-butylcyclohexanol (XI). The *trans,trans*-chlorohydrin (I) (1 g., 0.006 mole) was heated at reflux temperature for 24 hr. with 125 ml. of a 5% solution of potassium hydroxide in absolute ethanol. After the reaction mixture was worked up, 1.03 g. (98%) of a white crystalline solid was obtained. An analytical sample was recrystallized from pentane and melted at 95–97°.

Anal. Calcd. for $C_{12}H_{24}O_2$: C, 71.95; H, 12.08. Found: C, 72.22; H, 12.08.

Reduction of trans-2-chloro-4-t-butylcyclohexanone. Ten grams (0.04 mole) of *trans*-2-chloro-4-*t*-butylcyclohexanone[5] was reduced with sodium borohydride by the procedure employed for the *cis*-chloro ketone. After distillation of the product, 9.5 g. of liquid which solidified immediately was obtained. Upon recrystallization from *n*-pentane 8.8 g. (87%) of crystalline 2ᶜ-chloro-4ᵗ-*t*-butylcyclohexanol (III), m.p. 76–77°, was recovered.

Anal. Calcd. for $C_{10}H_{19}OCl$: C, 62.97; H, 10.04; Cl, 18.60. Found: C, 62.71; H, 9.90; Cl, 18.48.

4-t-Butylcyclohexanone. A. Dehydrochlorination of II. The *cis,cis*-chlorohydrin (II) (1 g., 0.006 mole) was heated under reflux for 2 hr. with 125 ml. of a 5% solution of potassium hydroxide in methanol. The oil obtained on work-up was treated directly with an excess of 2,4-dinitrophenylhydrazine reagent. The precipitated hydrazone was purified by chromatography on alumina and elution with benzene. Pure 4-*t*-butylcyclohexanone 2,4-dinitrophenylhydrazone (1 g., 56%) was obtained and was recrystallized from 95% ethanol, m.p. 148.5–151.5°. A mixed melting point determination with an authentic sample (m.p. 151–152°) showed a m.p. of 149–152°.

B. Dehydrochlorination of III. By a procedure similar to that employed for the *cis,cis*-isomer (II) the *cis,trans*-chlorohydrin(III) (2.0 g. 0.01 mole) was converted to the 2,4-dinitrophenylhydrazone of 4-*t*-butylcyclohexanone, 3.1 g. (88%). After recrystallization from 95% ethanol, the derivative melted at 151–152° and showed no depression on admixture with an authentic sample.

2ᵗ-Acetoxy-5ᵗ-t-butylcyclohexanol (X. R = Ac). *trans*-4-*t*-Butylcyclohexene oxide (6.2 g., 0.04 mole) was treated with 50 ml. of glacial acetic acid and 2 drops of concd. sulfuric acid at 60° for 2 hr. The acidic reaction mixture was cooled, poured into 300 g. of crushed ice, and carefully neutralized with sodium carbonate. The product was extracted with ether, and the extracts were dried and concentrated. The crude residue, 8.9 g., show infrared absorption at 3510, 1740, and 1248 cm.$^{-1}$

2ᵗ-Acetoxy-5ᵗ-t-butylcyclohexyl tosylate. The crude hydroxy acetate (8.9 g.) was converted to the tosylate by way of the usual low temperature reaction with tosyl chloride and pyridine.[13] After workup, there was obtained 13 g. of a yellow oil. Trituration with pentane resulted in crystallization. The crystals were collected and washed several times with pentane to give 7.3 g. of acetoxy tosylate, m.p. 90–94°, infrared, 1740 and 1239 cm.$^{-1}$, no OH.

cis-4-t-Butylcyclohexene oxide (XII). 2ᵗ-Acetoxy-5ᵗ-*t*-butylcyclohexyl tosylate 6.75 g. (0.018 mole) was heated under reflux for 3 hr. with 50 ml. of a 2.5% solution of potassium hydroxide in absolute methanol.[14] After dilution of the reaction mixture with cold dilute hydrochloric acid, the product was extracted with pentane. The extract was washed, dried and concentrated and the concentrate was cooled. Approximately 0.30 g. of a solid, m.p. 150.5–151.5° was obtained. No attempt was made to identify this compound. The pentane filtrate was further concentrated and 2.25 g. of a yellow oil remained. Distillation afforded 2.03 g. (33%)[15] of *cis*-epoxide (XII), b.p. 58–59° (2.5 mm.), $n_D^{22.9}$ 1.4589 (lit.[3] b.p. 85° at 11 mm., n_D^{22} 1.4608).

2ᵗ-Chloro-4ᶜ-t-butylcyclohexanol (IV). A solution of 1.5 g. (0.009 mole) of the *cis*-epoxide (XII) in 225 ml. of anhydrous chloroform was saturated with dry hydrogen chloride. The mixture was allowed to stand for 24 hr. Cold water was added and the chloroform layer was separated and washed with sodium bicarbonate solution. The organic layer was dried and concentrated to give 1.9 g. of a crude yellow oil which solidified. Recrystallization from pentane afforded 1.75 g. (94%) of IV, m.p. 75–76°.

Anal. Calcd. for $C_{10}H_{19}OCl$: C, 62.97; H, 10.04; Cl, 18.60. Found: C, 62.86; H, 10.03; Cl, 18.60.

Chlorohydrin tosylates. Employing the usual procedure, 15 g. (0.08 mole) of the chlorohydrin II was converted to its tosylate (29.8 g.). Recrystallization from 95% ethanol produced 20.2 g. (74%) of 2ᶜ-chloro-4ᶜ-*t*-butylcyclohexyl tosylate (VI), m.p. 94.5–95.5°.

Anal. Calcd. for $C_{17}H_{25}SO_3Cl$: C, 59.19; H, 7.31; Cl, 10.28. Found: C, 59.46; H, 7.37; Cl, 10.52.

2ᵗ-Chloro-4ᵗ-t-butylcyclohexyl tosylate (IV) was recrystallized from 95% ethanol, m.p. 88.5–89.5°.

Anal. Calcd. for $C_{17}H_{25}SO_3Cl$: C, 59.19; H, 7.31; Cl, 10.28. Found: C, 59.31; H, 7.35; Cl, 10.24.

2ᶜ-Chloro-4ᵗ-t-butylcyclohexyl tosylate (VII) was recrystallized from 95% ethanol, m.p. 109–110°.

Anal. Calcd. for $C_{17}H_{25}SO_3Cl$: C, 59.19; H, 7.31; S, 9.29. Found: C, 58.94; H, 7.56; S, 9.58.

2ᵗ-Chloro-4ᶜ-t-butylcyclohexyl tosylate (VIII) was recrystallized from 95% ethanol, m.p. 116.5–117.5°.

Anal. Calcd. for $C_{17}H_{25}SO_3Cl$: C, 59.19; H, 7.31; Cl, 10.28. Found: C, 58.99; H, 7.42; Cl, 10.39.

Department of Chemistry
Wayne State University
Detroit 2, Mich.

(13) E. L. Eliel and R. S. Ro, *J. Am. Chem. Soc.*, **79**, 5995 (1951).

(14) A. Furst and F. Koller, *Helv. Chim. Acta*, **30**, 1454 (1947).

(15) Yield based on *trans*-4-*t*-butylcyclohexene oxide.

Preparation of Alkyl Chlorophosphines

Wm. A. Henderson, Jr., Sheldon A. Buckler, Nancy E. Day, and Martin Grayson

Received June 5, 1961

Because of our need for certain alkyl chlorophosphines, we have evaluated the reported methods for converting primary and secondary alkyl phosphines to these valuable intermediates. The substituted phosphines are readily available from free radical[1] and base-catalyzed[2] reactions of phosphine with olefins.

(1) A. R. Stiles, F. F. Rust, and W. E. Vaughn, *J. Am. Chem. Soc.*, **74**, 3282 (1952).

In our hands, treatment of phosphines with chlorine[3] led only to small and erratic yields of the desired halo derivatives. In contrast, phosgene proved to be an excellent reagent for direct chlorination. The only prior report of its use is that of Michaelis and Dittler,[4] who prepared phenyldichlorophosphine in unspecified yield by bubbling phosgene through the liquid phosphine.

$$C_6H_5PH_2 + 2\ COCl_2 \longrightarrow C_6H_5PCl_2 + 2\ CO + 4\ HCl$$

We have defined conditions for this reaction and extended it to the synthesis of several alkyl chlorophosphines. Primary phosphines are best treated by adding them slowly at low temperature to two or more equivalents of phosgene in an inert solvent. On slow warming of the reaction mixture, carbon monoxide and hydrogen chloride are evolved, the chlorinated phosphine remaining behind in solution. In the case of the more reactive secondary phosphines, addition of the phosgene to an equivalent amount of phosphine is necessary in order to prevent extensive chlorination of the initially formed product to the trihalide. Distillation of the reaction mixtures affords the chlorophosphines in yields of 70–90%, as shown in Table I.

TABLE I

CHLOROPHOSPHINES

Chlorophosphine	B.P.	Yield, %
i-$C_4H_9PCl_2$[a]	149–151[b]	72, 78
$CNCH_2CH_2PCl_2$[c]	103–108/12 mm.	75
cyclo-$C_6H_{11}PCl_2$[d]	40–41/10 mm.[e]	71, 76
n-$C_8H_{17}PCl_2$[f]	106–110/8 mm.	69
$(n$-$C_4H_9)_2PCl$	77–81/1.0 mm.[g]	89

[a] 98% pure, vapor phase chromatography. [b] Reported[5] b.p. 155–157°. [c] 96% pure, vapor phase chromatography. *Anal.* Calcd. for $C_3H_4PNCl_2$: C, 23.08; H, 2.58; N, 8.97. Found: C, 23.12; H, 2.85; N, 8.76. [d] 99% pure, vapor phase chromatography. [e] Reported[6] b.p. 98–99°/17 mm. [f] 97% pure, vapor phase chromatography. [g] Reported[6,7] b.p. 216–217, 120–125°/15 mm.

EXPERIMENTAL[8]

i-Butyldichlorophosphine. In a 250-ml. flask equipped with a dropping funnel, Dry Ice condenser, magnetic stirrer, and facility for maintaining a nitrogen atmosphere was put 50 ml. of chloroform. Phosgene (20 g., 0.2 mole) was condensed in the flask at −50°, after which the Dry Ice condenser was replaced by a water condenser. To the stirred solution was added dropwise at −50° 9 g. (0.1 mole) of *i*-butyl phosphine. Evolution of gas began during the addition and continued while the reaction mixture was allowed to reach ambient temperature. The solution, which was allowed to stand overnight, was stripped of solvent, and the residue distilled to yield 12.5 g. (78%) of *i*-butyldichlorophosphine, b.p. 147–151°.

Di-n-butylchlorophosphine. A solution of 29 g. (0.2 mole) of di-*n*-butylphosphine in 60 ml. of methylene chloride was placed in a 100-ml. flask fitted with a magnetic stirrer, ice condenser, and mercury trap, and cooled to −30°. Into the flask was distilled 19.8 g. (0.2 mole) of phosgene over the course of 1 hr., the temperature being maintained at −30°. The solution was then warmed to room temperature and allowed to stand overnight. The solvent was stripped, and the residue distilled to yield 32 g. (89%) of di-*n*-butylchlorophosphine, b.p. 77–81°/1.0 mm.

CHEMICAL RESEARCH DEPARTMENT
CENTRAL RESEARCH DIVISION
AMERICAN CYANAMID CO.
STAMFORD, CONN.

(2) M. M. Rauhut, I. Hechenbleikner, H. A. Currier, F. C. Schaefer, and V. P. Wystrach, *J. Am. Chem. Soc.*, **81**, 1103 (1959).

(3) C. Walling, U. S. Patents **2,437,796** (1948), **2,437,798** (1948).

(4) A. Michaelis and F. Dittler, *Ber.*, **12**, 338 (1879).

(5) F. Guichard, *Ber.*, **32**, 1572 (1899).

(6) K. Isslieb and W. Seidel, *Ber.*, **92**, 2681 (1959).

(7) V. M. Plets, dissertation, Kazan, 1938.

(8) All operations were carried out under nitrogen. Boiling points are uncorrected.