2 (mp 145.5–146.5°) 139–149°. *Anal.* Calcd for $C_{16}H_{20}N_4O_9$: C, 46.61; H, 4.89; N, 13.59. Found: C, 46.90; H, 5.00; N, 13.44.

Conversion of 2-Chlorocyclohexanone to 2-Morpholinocyclohexanone.[6]—2-Chlorocyclohexanone (5 g, 0.038 mole) was reacted with morpholine (7 g, 0.081 mole) by the procedure of Mousseron[6] to give 9 as a light yellow oil; 1.45 g, 0.0079 mole, 21%, bp 85–86° (0.25 mm). The infrared spectrum of 9 thus obtained was nearly identical with that of 9 as formed above. This procedure is not recommended and should be improved by the use of a solvent.

Direct Conversion of Morpholinocyclohexene to 2-Morpholinocyclohexanone.—A solution of 1 (15 g, 0.090 mole) in tetrahydrofuran (150 ml) was treated with diborane from boron trifluoride etherate (0.136 mole) and lithium aluminum hydride (0.136 mole) as already described. A one-third aliquot was evaporated *in vacuo*, water (50 ml) was added, and then chromium trioxide (3.3 g, 0.033 mole) in water (25 ml)–sulfuric acid (5 ml) was added dropwise over 45 min with stirring and ice-bath cooling. The resultant mixture was stirred for 3 hr and a mixture of chromium trioxide (6.6 g, 0.066 mole) in water (12 ml)–sulfuric acid (10 ml) was added dropwise over 30 min at 0°. The resultant mixture was stirred for 2 hr, sodium bisulfite was added to reduce any chromium trioxide left, and the mixture was continuously extracted with ether for 12 hr. Distillation gave 9, 3.14 g, 57%, bp 96–97° (0.3 mm), with nearly identical infrared spectrum with that of 9 obtained from 2-chlorocyclohexanone.

Registry No.—2, 14909-79-6; picrate of 2, 14909-80-9; 4, 14909-81-0; 6a, 14909-82-1; 6b, 14909-83-2; 9, 14909-84-3; picrate of 9, 14909-85-4.

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A Useful Method for the Conversion of Alcohols into Iodides

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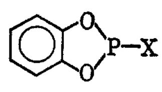
The standard methods for the preparation of iodides from alcohols and alcohol derivatives[2a] cannot be used effectively in certain cases because substitution is accompanied by complicating side reactions such as elimination and acid or base-catalyzed decomposition of sensitive functional groups. This Note reports a simple and convenient method for the formation of iodides under mild conditions which is especially valuable in systems which are prone to elimination.

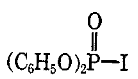
Forsman and Lipkin[2b] have reported that cyclohexyl iodide is formed upon treatment of cyclohexyl diphenyl phosphite (Ib) with iodine. In our experience the utility of this reaction for the conversion of alcohols into iodides is limited by the tendency of the required reagent, diphenyl phosphorochloridite (Ia), to disproportionate, by the necessity of purifying the intermediate phosphite (Ib) in order to obtain the iodide in good yield, and by the necessity of removing the difficultly hydrolyzable by-product, diphenyl iodophosphate (II), by ammonolysis. We have found that all of these problems can be avoided by employing the cyclic analog of Ia, *o*-phenylene phosphorochloridite (IIIa), a stable reagent which is easily prepared from catechol and phosphorus trichloride.[3] Reaction of IIIa in ether solution with an alcohol in the presence of pyridine affords, after removal of pyridine hydrochloride by filtration, a nearly quantitative yield of the corresponding phosphite IIIb sufficiently pure for use in the subsequent reaction. Treatment of a methylene chloride solution of the phosphite IIIb with iodine at 25° for 6 hr produces the desired iodide whose isolation is facilitated by the rapid base-catalyzed hydrolysis of the by-product, *o*-phenylene iodophosphate IV. The results for representative cases are summarized in Table I.

$(C_6H_5O)_2PX$

Ia, X = Cl
b, X = OR

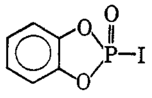


IIIa, X = Cl
b, X = OR



$(C_6H_5O)_2P(=O)\text{—}I$

II



IV

Experimental Section

All of the iodides in Table I were prepared by essentially the same procedure, illustrated by the following.

Preparation of Cyclohexyl *o*-Phenylene Phosphite.—A mixture of 10.12 g (58.0 mmole) of *o*-phenylene phosphorochloridite[3] and 4.6 g (58.0 mmole) of pyridine in 100 ml of diethyl ether was placed in a 250-ml flask and cooled to 0°. Cyclohexanol (5.85 g, 57.5 mmole) in 100 ml of ether was then added with stirring. The flask was stoppered, and the mixture was allowed to warm to 25°. After 12 hr the pyridine hydrochloride was filtered off and rinsed well with ether. Solvent was removed from the combined filtrate under reduced pressure to give 13.0 g (95.4%) of the phosphite as a colorless, mobile oil.

Distillation of a portion of the material gave phosphite: bp 103–105° (1.0 mm); infrared $\lambda_{\max}^{\text{neat}}$ 3.55 (w), 3.39 (s), 3.50 (m), 6.8 (s), 8.1 (s), 9.9 (s), 10.1–10.3 (s), 11.9–12.2 (s), 13.3–13.6 (s), 14.4 (m) μ; nmr (δ, $DCCl_3$) 1.0–1.8 (10 H) multiplet, 3.85 (1 H) multiplet, 6.96 (4 H) multiplet; $n^{25}D$ 1.5280.

Anal. Calcd for $C_{12}H_{15}O_3P$: C, 60.50; H, 6.35; P, 13.00. Found: C, 60.61; H, 6.43; P, 13.02.

Preparation of Cyclohexyl Iodide.—To a solution of 13.0 g (54.8 mmole) of crude cyclohexyl *o*-phenylene phosphite in 200 ml of methylene chloride was added 13.9 g (54.8 mmole) of iodine. After stirring for 6 hr at 25° the solution was extracted with 200 ml of 5% sodium hydroxide solution, then with 100 ml of 5% sodium hydrogen sulfite solution, and finally with 100 ml of a saturated solution of sodium chloride. After drying over anhydrous sodium sulfate, the solvent was removed at reduced pressure. Vacuum distillation of the residue afforded 10.0 g (87.4%; 83.2%, based on cyclohexanol) of cyclohexyl iodide: bp 78° (20 mm); $n^{20}D$ 1.5490 (lit.[4] $n^{20}D$ 1.54765).

Identification and Physical Properties. A. Phosphites IIIb.—The intermediate phosphites (IIIb) were examined spectroscopically to confirm their structures: (1) from *n*-heptanol, infrared maxima at 3.25 (w), 3.39 (s), 3.49 (m), 6.23 (w), 6.32 (w), 6.8 (s), 8.1 (s), 9.9 (s), 10.25 (m), 11.9–12.2 (s), 13.3–13.6 (s), and 14.4 (m) μ; nmr peaks (parts per million downfield from tetramethylsilane) at 0.83 (3 H), triplet, J = 5, 1.0–1.7 (10 H), 3.52 (2 H), quartet, J = 7, 6.97 (4 H), multiplet; (2) from 3-chloro-*n*-propanol, infrared maxima at 3.25 (w), 3.35 (m), 3.47 (w), 6.22 (w), 6.32 (w), 6.78 (s), 8.1 (s), 9.85 (s), 10.35 (s), 11.9–12.2 (s), 13.3–13.6 (s), and 14.3 (s) μ; nmr peaks

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[1] National Institutes of Health Predoctoral Fellow, 1965–1967.

[2] (a) For a review of the synthetic routes to alkyl iodides, see A. Roedig in "Methoden der Organischen Chemie" (Houben-Weyl), Vol. V/4, E. Müller, Ed., Georg Thieme Verlag, Stuttgart, 1960, pp 517–678; (b) J. P. Forsman and D. Lipkin, *J. Am. Chem. Soc.*, **75**, 3145 (1953).

[3] P. C. Crofts, J. H. H. Markes, and H. N. Rydon, *J. Chem. Soc.*, 4250 (1958).

[4] A. I. Vogel, *J. Chem. Soc.*, 1813 (1948).

TABLE I

SYNTHESIS OF *o*-PHENYLENE PHOSPHITES (IIIb) AND IODIDES

	IIIb		Iodide			
Alcohol	Reacn time, hr	Yield, %	Reacn time, hr	Yield, %	Bp, °C	$n^{20}\mathrm{D}$
Cyclohexyl	12	95.4	6	87.4	78 (20 mm)	1.5488
n-Heptyl	12	96.0	6	79.8	120–121 (65 mm)	1.4910
3-Chloro-*n*-propyl	3	97.5	6	61.1	70–72 (28 mm)	1.5481
3-Hydroxy-*n*-butyl	10	99.0	11	75.5[a]	72–73 (1 mm)	1.6147
trans-4-*t*-Butylcyclohexyl	10	91.6	11	72.0[b]	74–76 (0.55 mm)	1.5269

[a] Product, 1,3-diiodobutane. [b] 80% *cis*- and 20% *trans*-4-*t*-butylcyclohexyl iodide, as determined by vpc and nmr analysis.

(in parts per million) at 1.82 (2 H), quintet, $J = 7$, 3.48 (2 H), triplet, $J = 7$, 3.63 (2 H), quartet, $J = 7$, and 6.97 (4 H), multiplet; (3) from butane-1,3-diol, infrared maxima at 3.25 (w), 3.35 (w), 6.22 (w), 6.32 (w), 6,80 (s), 8.15 (s), 9.7–10.5 (s), 11.8–12.2 (s), 13.3–13.6 (s), and 14.3 (s) μ; nmr peaks (in parts per million) at 1.1 (3 H), doublet, $J = 7$, 1.5 (2 H), multiplet, 3.55 (2 H), quartet, $J = 7$, 4.0 (1 H), multiplet, and 7.0 (4 H) multiplet; (4) from *trans*-4-*t*-butylcyclohexanol, infrared maxima at 3.25 (w), 3.39 (s), 3.50 (w), 6.22 (w), 6.32 (w), 6.8 (s), 8.15 (s), 9.9 (s), 10.1 (s), 12.1 (s), 13.5 (s), and 14.4 (s) μ; nmr peaks (in parts per million) at 0.75 (9 H), singlet, 0.9–2.1 (9 H), 3.75 (1 H), multiplet, and 6.97 (4 H), multiplet. The infrared spectra were measured with neat liquids, and the nmr spectra were obtained using deuteriochloroform as the solvent.

B. Iodides.—1-Iodoheptane and 3-chloro-1-iodopropane were identified by comparison (using nmr) with authentic samples. The nmr spectrum (in $CDCl_3$) of 1,3-diiodobutane[5] confirmed its structure: doublet at 1.97 ppm (3 H), doublet, $J = 7$ cps, and multiplets at 2.17 ppm (2 H), 3.28 ppm (2 H), and 4.20 ppm (1 H). Vpc analysis of the 4-*t*-butylcyclohexyl iodides using a 15-ft 10% Carbowax column at 150° showed a 4:1 ratio of *cis* to *trans* iodides, with retention times of 10.8 and 12.2 min, respectively. This ratio was confirmed by an nmr analysis in which the signals for the isomers were for *cis*, 0.88 (9 H), singlet, 1.1–2.7 (9 H), 4.83 (1 H), multiplet; for *trans*, 0.83 (9 H), singlet, 1.1–2.7 (9 H), 4.1 ppm (1 H), broad multiplet.

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(5) F. Drahowzal and D. Klamann, *Monatsh.*, **82**, 970 (1951).