contained 2% of sodium. The mixture was stirred and heated to reflux. The dropwise addition of a solution of 92.6 g. (1.0 mole) of *tert*-butyl chloride[8] in 250 ml. of dry "unsaturate-free" *n*-pentane was then begun. After addition of about 5 ml. of the halide solution, the rate of reflux increased appreciably and the source of heat was removed. The remainder of the halide solution was then added over a 2.5-hr. period, at a rate such that sustained reflux was maintained throughout the addition. The reaction mixture was stirred for 0.5 hr. longer. The product solution was then filtered away from the residue of lithium chloride and excess metal through a sintered glass filter tube,[9] into a graduated dropping funnel (total volume, 589 ml.). Three-milliliter aliquots of the clear solution were then taken, hydrolyzed in flasks containing 10 ml. of standard 0.5*N* acid, and back-titrated with standard 0.1*N* base to a phenolphthalein end point. The yield of *tert*-butyllithium (based on *tert*-butyl chloride) was 89%.

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[7] The *n*-pentane was a 99 mole % (Phillips "Pure") grade which had been stirred with concd. sulfuric acid for 3 days, separated, washed with 5% sodium bicarbonate solution, washed with water, dried over calcium chloride (anhyd.) and, finally, dried over sodium ribbon.

[8] The *tert*-butyl chloride was obtained from Matheson, Coleman and Bell (purified grade); b.p. 51–52°, n_D^{20}, 1.3851.

[9] Ace Glass Co., Cat. No. 8575—porosity "E."

The Preparation of Grignard Reagents under Helium and Argon

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Grignard reagents prepared by conventional methods generally contain excess magnesium halide arising from a Wurtz-type reaction (Equation 1), and various preparative methods have been used to avoid this undesirable reaction.[1] Several investigators[2] have shown that the course of a Grignard

$$2RX + Mg \longrightarrow R{-}R + MgX_2 \qquad (1)$$

reaction can be altered by varying the amount of magnesium halide.

Recently we have found that the preparation of Grignard reagents under helium or argon, rather than the customary nitrogen or ether, consistently leads to higher yields and to smaller amounts of coupling products. The Grignard reagents listed in Table I were prepared by the dropwise addition of the organic halide to a 10% excess of magnesium metal in ether. The Grignard reagents prepared under helium or argon were clear, almost colorless solutions while those prepared under nitrogen or ether were cloudy, dark-colored solutions. One-milliliter samples were titrated with hydrochloric acid and with silver nitrate to determine the amount of excess halide. The values shown represent the average of several experiments in which the reproducibility was excellent.

TABLE I

GRIGNARD REAGENTS PREPARED UNDER HELIUM, ARGON, NITROGEN, AND ETHER

Halide	Prepared under	Yield,[a] %	Excess Halide,[b] %
n-Butyl chloride	Helium	99.0	0.0
n-Butyl chloride	Nitrogen	91.0	2.2
n-Butyl bromide	Helium	97.5	1.1
n-Butyl bromide	Argon	97.8	1.0
n-Butyl bromide	Nitrogen	80.1	15.2
n-Butyl bromide	Ether	89.0	7.7
Cyclohexyl bromide	Helium	68.3	38.5
Cyclohexyl bromide	Nitrogen	30.5	75.4
Bromobenzene	Helium	99.0	0.0
Bromobenzene	Argon	95.2	2.1
Bromobenzene	Nitrogen	85.0	8.0
Bromobenzene	Ether	88.3	5.7
Iodobenzene	Helium	81.0	10.2
Iodobenzene	Nitrogen	70.4	16.5
Benzyl bromide	Helium	91.3	7.6
Benzyl bromide	Nitrogen	62.2	20.3
Benzyl bromide	Ether	53.0	25.8

[a] Based on the acid titration. [b] The per cent excess halide is the quotient of the difference between the total base and halide titrations and the total base titration.

The principal advantages which accrue from this method are that (1) purification of the purging gas is unnecessary; (2) higher yields of the Grignard reagent are obtained; and (3) there is little or no contamination by coupling products. Furthermore, dilution of the halide with ether is not required so that concentrated solutions of the Grignard reagent are obtainable, and only 10% excess magnesium is used as compared with the one- to three-mole excess used in some preparations.[1]

EXPERIMENTAL

Magnesium. Domal High Purity, sublimed magnesium granules (Dominion Magnesium Co., Ltd., Haley, Ont.) was used.

Diethyl ether. Mallinckrodt analytical reagent ether containing 5 × 10^{-6} % sodium diethyldithiocarbamate was used without further treatment.

Organic halides were obtained from Distillation Products Industries and were dried over calcium chloride prior to use.

Nitrogen. Prepurified grade (Air Reduction Sales Co.) containing less than 0.002% oxygen and 0.0012% water was used without further treatment.

Helium was obtained from the Matheson Co., Inc. Minimum purity, 99.99%, used without further treatment.

Argon, obtained from the Matheson Co., Inc. Minimum purity, 99.998%, was used without further treatment.

Preparation of the Grignard reagents. The apparatus consisted of a three necked, round bottom flask equipped with a Dry Ice reflux condenser attached to a mercury bubbler,

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[1] M. S. Kharasch and O. Reinmuth, *Grignard Reactions of Nonmetallic Substances,* Prentice-Hall, Inc., New York, 1954, Chap. II.

[2] C. G. Swain and H. B. Boyles, *J. Am. Chem. Soc.,* **73,** 871 (1951); E. T. McBee, O. R. Pierce, and J. F. Higgins, *J. Am. Chem. Soc.,* **74,** 1736 (1952); A. C. Cope, *J. Am. Chem. Soc.,* **56,** 1578 (1934); R. C. Huston and A. H. Agett, *J. Org. Chem.,* **6,** 123 (1941).

a Teflon stirrer, and a pressure-equalizing dropping funnel. One neck of the flask was equipped with a rubber serum cap through which gas was admitted *via* a hypodermic needle which allowed the gas to pass over the mixture. When no purging gas was used, the Dry Ice condenser was replaced by an air-cooled condenser, and the ether was allowed to reflux so that a small amount constantly escaped from the top of the condenser which was protected from the atmosphere by a drying tube containing Drierite.

The Grignard reagents listed in Table I were prepared by the dropwise addition of the organic halide to a 10% excess of the magnesium metal in ether so that the final Grignard solution was approximately 2*N* in RMgX. When all of the halide had been added, the solution was heated under reflux from 2–3 hr., allowed to cool to room temperature, and was transferred to rubber serum-capped bottles by means of a hypodermic syringe. One-milliliter samples were titrated with 0.1*N* hydrochloric acid and with 0.1*N* silver nitrate using the Volhard method.[3]

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[3] W. Reiman, III, J. D. Neuss, and B. Naiman, *Quantitative Analysis*, McGraw-Hill Book Co., Inc., New York, 1951, p. 270.

A Test for Peroxides in Vinyl Ethers

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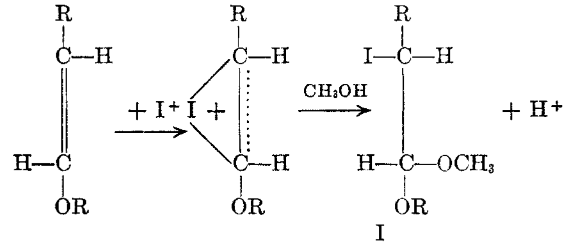
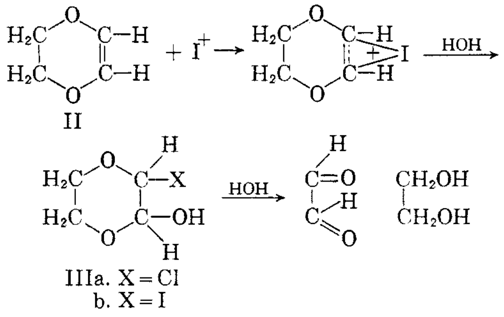
The hazards involved in evaporating or distilling ethers that contain peroxides are well recognized. In safety conscious laboratories a routine test is employed periodically to make certain that samples of ethers that have developed a dangerous peroxide content are discarded. The usual test[1] is to add acidified or neutral aqueous or alcoholic iodide to the suspected sample, or *vice versa* and a brown coloration is positive. The test is readily performed quantitatively.[2a,b] The purpose of this note is to point out that this test as usually performed is not valid in the presence of vinyl ethers and to suggest a modified procedure with which vinyl ethers do not interfere.

The reason for the failure of the usual form of the test is the immediate reaction of the liberated iodine with the vinyl ether. We became interested in the reaction when, during preliminary studies of the relative rates of iodine liberation by isomeric tetrachlorinated dioxanes,[3] we noticed that addition of water caused a rapid fading of the iodine color. Apparently the double bonded product from which vicinal halogens had just been removed by iodide ions was in turn adding back the iodine. The related parent compound, dioxene, was found to react with aqueous iodine as fast as mixing took place. It was then realized that a dioxene was a type of vinyl ether and that the observed reaction was closely related to the valuable quantitative method of Siggia and Edsberg[4] for determination of vinyl ethers by titration with aqueous methanolic iodine. These authors do not mention interference by peroxides, perhaps because it is so obvious, nor did they have occasion to point out the corollary: *that vinyl ethers would negate the usual peroxide test.* In view of the increasing commercial availability of vinyl ethers and the extreme hazards of handling ethers that contain peroxides, we think the corollary should be emphasized.

There is some evidence available concerning the course of these related reactions. Siggia and Edsberg[4] isolated an iodine-containing organic product from the reaction of methanolic iodine with butyl vinyl ethers, the analysis of which was consistent with the formula of an iodoacetal, I. The following mechanism explains this result:



In the case of our modified vinyl ether, II, the reaction would proceed further:



We have identified the glyoxal and the ethylene glycol by isolation of appropriate derivatives. The intermediate, IIIb, is the iodine analogue of one postulated by Salomaa.[5] To account for the first order kinetics of the hydrolysis of *trans*-2,3-dichloro-*p*-dioxane,[6] he proposed that the hydrolysis of IIIa was much more rapid than that of the parent dichloro compound. The iodine compound, IIIb, should hydrolyze even faster. There is no evidence for the formation of an intermediate diiodo

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[1] *Reagent Chemicals*, Am. Chem. Soc. Specifications (1955), American Chemical Society, Washington, D. C.

[2] (a) K. V. Kopatnur and M. Jelling, *J. Am. Chem. Soc.*, **63**, 1432 (1941).

(b) Union Carbide Chemical Co. *Ethers and Oxides* Booklet number 4764B (1957).

[3] A qualitative difference in rates was first observed by Milton Cooper, Ph.D. dissertation, Northwestern University, 1955.

[4] S. Siggia and R. L. Edsberg, *Anal. Chem.* **20**, 762 (1948).

[5] P. Salomaa, *Acta. Chem. Scand.*, **8**, 744 (1954).

[6] R. K. Summerbell and Hans E. Lunk, *J. Am. Chem. Soc.*, **79**, 4802 (1957).