TABLE I

HYDROGENOLYSIS OF GRIGNARD REAGENTS[a]

Grignard	Hydrogenolysis (based on insoluble Mg), % 50°	75°	100°	125°	150°
CH_3MgCl	0	0	0	76	
C_2H_5MgCl	0	7, 14	100, 100	100	
C_2H_5MgBr		15	53	100	
C_2H_5MgI	10, 17	50, 60			
$(CH_3)_2CHMgCl$	80, 100	100	100	100	
$CH_2{=}CHCHMgBr$	10	89			
$CH_3CH_2CH_2CH_2MgCl$		0	85		
$CH_3CH_2CH(CH_3)MgCl$	0, 24[b]	79, 81	93	100	
$(CH_3)_3CMgCl$	0, 0	6, 13	47, 47	100	
$(CH_3)_3CCH_2MgCl$		0[c]	0[c]	60[c]	95[c]
C_6H_5MgCl			0[d]	44[d]	100[d]
C_6H_5MgBr		0	0, 15	53, 67	100
$C_6H_5CH_2MgCl$		0	0		

[a] 150 ml. of 2 *M* solutions in ether were used except where noted. Reactions were run 12 hr. at 5000-p.s.i.g. hydrogen. [b] Temperature rose to 70° momentarily. [c] Concentration was 1 *M*. [d] Concentration was 1.3 *M*.

superiority of argon or helium over nitrogen was demonstrated by Owens, *et al.*[1]

Usually the reaction was initiated by simply warming a concentrated ether solution of halide in the presence of magnesium. Once the reaction started, more ether was added, after which a 50% halide solution in ether was added dropwise over a period of several hours. The neopentyl Grignard could not be initiated in this manner but addition of 1 ml. of ethyl bromide led to quick initiation.

Phenylmagnesium chloride was prepared by refluxing a mixture of 40 g. of magnesium, 400 ml. of chlorobenzene, and 1 g. of aluminum chloride overnight. A high speed stirrer was used to agitate the refluxing mixture. Excess chlorobenzene was removed by vacuum pumping at 130°. The residue was washed thoroughly with hexane and filtered in a nitrogen box. Ether was added to the dried residue, and this mixture was then filtered. The filtrate was 2 *M* in phenylmagnesium chloride.

Both methyl chloride and ethyl chloride were used as ether solutions. In order to prevent loss of halide from these solutions by evaporation, a Dry Ice condenser was simply placed on top of the addition funnel. The Grignard preparation proceeded in the normal manner.

Standardization.—All Grignard reagents were filtered in a nitrogen box and then standardized. Initially, the method of Gilman[2] was used; later on, most of the magnesium analyses were done by Versene titration. Halogen was determined by the Volhard method. In most cases the magnesium and halogen analyses agreed to within 1%. Where appreciable Wurtz coupling occurred, notably with the allyl and *t*-butyl Grignard reagents, excess magnesium halide was present.

Hydrogenolysis Procedure.—In general the standardized Grignard solution was diluted with ether to a concentration of 2.00 *M*. A 150-ml. aliquot was charged into a 250-ml. Magne-Dash autoclave. This mixture was heated at 50, 75, 100, 125, or 150° for 12 hr. under 5000-p.s.i.g. hydrogen.

After the reaction mixture had been cooled and vented, it was filtered in a nitrogen box. Both precipitate and filtrate were analyzed for magnesium by Versene titration, for halide by the Volhard method, and by gas evolution, where applicable, by measuring the gas evolved upon hydrolysis of a weighed sample. The vent gas, where applicable, was analyzed by a mass spectrometer. The per cent hydrogenolysis was calculated on the basis of the magnesium present in the precipitate. In the case of the bromides and iodides the precipitate was predominantly magnesium hydride but did contain a small amount of halide. In the case of the reaction product from ethylmagnesium bromide, for example, the amount of halogen present was 11.6 wt. %. This was reduced to 4.1% by extraction with tetrahydrofuran overnight. The purity of the magnesium hydride is thus 95 wt. %, or 99.8 mole %.

For chlorides a mixture of magnesium chloride and magnesium hydride was obtained. The product from the hydrogenolysis of ethylmagnesium chloride at 100° was extracted with tetrahydrofuran. The magnesium chloride was extracted out, leaving the insoluble magnesium hydride in the precipitate.

Acknowledgment.—The support of the Advance Research Projects Agency, Department of Defense, under whose sponsorship this work was conducted, is gratefully acknowledged.

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[1] F. H. Owens, R. P. Fellman, and F. E. Zimmerman, *J. Org. Chem.*, **25**, 1808 (1960).

[2] H. Gilman, E. A. Zoellner, and J. B. Dickey, *J. Am. Chem. Soc.*, **51**, 1576 (1929).

A Convenient Laboratory Preparation of Pure $\Delta^{9,10}$-Octalin

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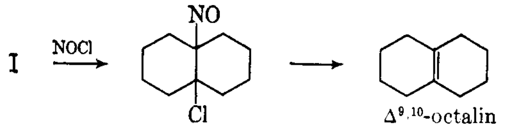
Numerous preparations for $\Delta^{9,10}$-octalin have been described.[1] It generally seems conceded[2,3] that the best method for making the pure compound involves the following four-step sequence.

$$\text{2-Naphthol} \xrightarrow[\text{cat.}]{H_2} \text{2-decalol} \xrightarrow[\Delta]{H^+} \text{octalin mixture (I)}$$



While purity of product by this method is excellent, some of the steps are tedious.[4] An optimistic estimate of over-all yield would be 50% based on 2-naphthol.

We demonstrated earlier[5] that lithium dissolved in methylamine effectively reduces naphthalene to a

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[1] See Elsevier ["Encyclopedia of Organic Chemistry," Vol. 12, Elsevier Publishing Co., Houston, Tex., 1948, p. 76] for a compilation of these methods.

[2] W. G. Dauben, E. C. Martin, and G. J. Fonken, *J. Org. Chem.*, **23**, 1205 (1958).

[3] A. S. Hussey, J. F. Sauvage, and R. H. Baker, *ibid.*, **26**, 256 (1961).

[4] For example, high pressure hydrogenation equipment has been used in the first step [see W. P. Campbell and G. C. Harris, *J. Am. Chem. Soc.*, **63**, 2721 (1941)]. A hydrogen pressure of 2000 p.s.i. and temperatures of 150-170° are recommended.

[5] R. A. Benkeser, R. E. Robinson, D. M. Sauve, and O. H. Thomas, *J. Am. Chem. Soc.*, **77**, 3230 (1955).

mixture of octalins. More recently we have found[6] that the addition of certain secondary amines to such reduction mixtures greatly increases the selectivity of the reducing system.

In extending this work we have found that, by carrying out the reduction of naphthalene with lithium in a solvent consisting of ethylamine and dimethylamine, a mixture composed of 80% $\Delta^{9,10}$-octalin and 20% $\Delta^{1,9}$-octalin can be obtained in one convenient step. The purification of this mixture also has been modified to avoid the troublesome nitrosyl chloride treatment.[7]

It has been shown[8] that bis-3-methyl-2-butylborane, because of its high steric requirements, adds quite selectively to hindered carbon–carbon double bonds. We have found this reagent very effective in removing the 20% impurity of $\Delta^{1,9}$-octalin from the original mixture. Presumably it adds preferentially to the less hindered (relative to the $\Delta^{9,10}$) $\Delta^{1,9}$ isomer. Upon oxidation with hydrogen peroxide the adduct is presumably converted to an alcohol,[9] which permits a facile separation from the $\Delta^{9,10}$-octalin.

Our two-step preparation of $\Delta^{9,10}$-octalin proceeds in an over-all 50–54% yield, based on the starting naphthalene.

Experimental

Reduction of Naphthalene.—A mixture containing 25.6 g. (0.2 mole) of naphthalene and 250 ml. *each* of anhydrous ethylamine and dimethylamine was placed in a 1-l. three-necked round bottom flask fitted with a mechanical stirrer and a Dry Ice condenser. After this was stirred briefly, 11.55 g. (1.65 g.-atoms) of lithium wire cut into 0.5-cm. pieces was added all at once. After the mixture was stirred for 14 hr., the Dry Ice condenser was replaced by a water condenser and the solvent was allowed to evaporate. Anhydrous conditions were maintained during this process by having a drying tube attached to the condenser. The flask was then placed in an ice bath and the grayish white residue was decomposed by the dropwise addition of about 100 ml. of water (*Caution!*) accompanied by occasional slow stirring. The mixture was filtered under aspirator vacuum, and the precipitate was washed four times with 25–30-ml. portions of diethyl ether. The ether layer was separated and the aqueous layer was extracted several more times with 25-ml. portions of diethyl ether. The combined ether extracts were dried over anhydrous calcium sulfate. The solvent was removed and the residual liquid was distilled. A 19–20-g. fraction (75–80%), boiling at 72–77° at 14 mm., was collected. Analysis by vapor phase chromatography (Apiezon L column, 148°, 25-p.s.i. helium pressure) showed that the product contained 80% $\Delta^{9,10}$-octalin and 20% $\Delta^{1,9}$-octalin.

Purification of $\Delta^{9,10}$- and $\Delta^{1,9}$-Octalin Mixture.—In a 1-l. three-necked round-bottom flask equipped with a magnetic stirrer, dropping funnel, and a reflux condenser attached to a mercury trap was placed 4.7 g. (0.125 mole) of sodium borohydride, 23.1 g. (0.33 mole) of 2-methyl-2-butene, and 100 ml. of anhydrous tetrahydrofuran. This mixture was stirred for 15 min., and then 23.5 g. (0.165 mole) of boron trifluoride etherate dissolved in 22 ml. of anhydrous tetrahydrofuran was added dropwise over a 45-min. period. The rate of the addition was initially slow, but could be increased gradually. The octalin mixture prepared above was then added dropwise over a 10-min. period. After the mixture was stirred for 3.5 hr., 50 ml. of water was added dropwise with slow stirring. Thirty-five milliliters of 3 *N* sodium hydroxide was next added dropwise over a 10-min. period, followed by 35 ml. of 30% hydrogen peroxide over a 45-min. period. After stirring for 5 hr. at 44–45°, the mixture was cooled and the layers were separated. The ether layer was washed several times with 30-ml. portions of water and was then dried over calcium sulfate. After ether removal, the residual liquid was distilled under a nitrogen atmosphere. The fraction (12–13 g.) boiling at 75–77° at 14 mm. was collected, representing a yield of 50–54% based on naphthalene. Analysis of this material by v.p.c. indicated it was 99% pure $\Delta^{9,10}$-octalin[10], $n^{20}\mathrm{D}$ 1.4990.

Acknowledgment.—The authors are grateful to the National Science Foundation for financial assistance which made this work possible.

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[6] R. A. Benkeser, R. K. Agnihotri, and M. L. Burrous, *Tetrahedron Letters*, **No. 16**, 1 (1960).

[7] Since the same 80:20 ratio was obtained (ref. 3) using the four-step reaction sequence, undoubtedly the nitrosyl chloride purification method described in ref. 3 would also be successful with our mixture.

[8] H. C. Brown and G. Zweifel, *J. Am. Chem. Soc.*, **83**, 1241 (1961).

[9] H. C. Brown, "Hydroboration," W. A. Benjamin Inc., New York, N. Y., 1962, p. 69.

[10] The identity of the $\Delta^{9,10}$-octalin was readily established by its n.m.r. spectrum which showed a complete lack of vinyl hydrogens., characteristic of the other octalin isomers. Likewise the v.p.c. retention time relative to *trans*-decalin agreed well with that reported [J. W. Powell and M. C. Whiting, *Tetrahedron*, **12**, 163 (1961)].

The Solvent Sensitivity of the Charge-Transfer Band of Tropylium Iodide

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Solutions of tropylium iodide in nonpolar solvents are quite sensitive to air and light. A simple apparatus (Fig. 1) permits the preparation of such solutions with the exclusion of light and air. The solvent sensitivity of the charge-transfer band can then be measured. Conventional technique in the preparation of solutions in nucleophilic, polar solvents is used since an acidic medium is required. The transition energies for the charge-transfer band in different solvents (eq. 1) show a good linear correlation with the solvent polarity values, *Z*[2], with a slope somewhat greater than unity.

(1)

The colors of tropylium halides have been attributed to the occurrence of charge-transfer transitions,[3] and the position of the charge-transfer band in methylene chloride has been measured.[4]

Tropylium iodide was prepared by adding excess concentrated hydriodic acid to hot ethanolic tropylium fluoborate, cooling, rapidly filtering, and drying the crystals on a high-vacuum line. The crystals were bright red, m.p. *ca.* 125° dec. Solvents (methylene chloride, acetonitrile, isopropyl alcohol, acetone) were spectrophotometric grade and were degassed before distillation into the reservoir of the apparatus (Fig. 1). Mixing was effected immediately before measurement of the spectra with a Cary Model 14 spectrophotometer. The low rate of solution[4] observed for tropylium iodide in all but the most polar solvents along with a decrease in the intensity of the charge-transfer band dependent on the solvent, light, oxygen, and impurities forced us to focus our attention exclusively on the position of the maximum rather than the intensity

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[1] Alfred P. Sloan Fellow, 1960–1964.

[2] E. M. Kosower: (a) paper presented at a Symposium on Molecular Interactions in Liquid Solution, Société de Chimie Physique, June 4–8, 1963, Paris; (b) *J. Am. Chem. Soc.*, **80**, 3253 (1958).

[3] (a) E. M. Kosower and P. E. Klinedinst, Jr., *ibid.*, **78**, 3493 (1956); (b) W. v. E. Doering and H. Krauch, *Angew. Chem.*, **68**, 661 (1956).

[4] K. M. Harmon, F. E. Cummings, D. A. Davis, and D. J. Diestler, *J. Am. Chem. Soc.*, **84**, 3349 (1962).