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.

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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).

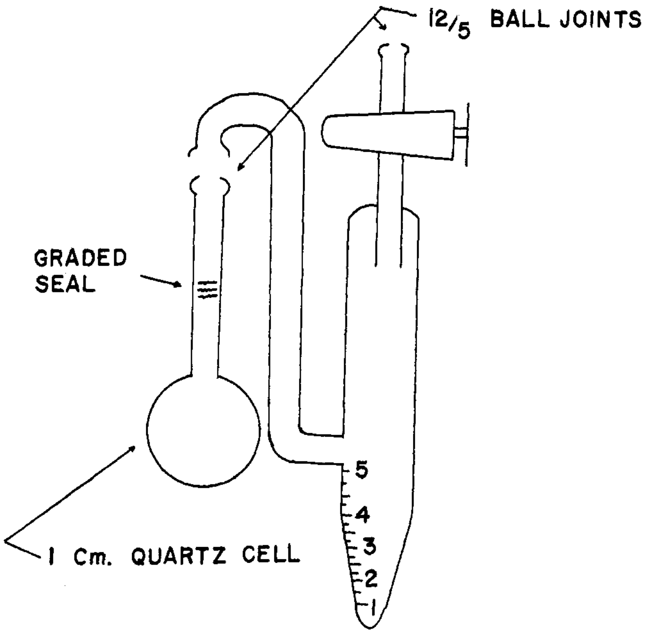

Fig. 1.—Apparatus for the preparation of solutions in degassed solvents. The sample is weighed directly into the quartz cell. After evacuation and flushing with solvent vapor, solvent is distilled into the graduated reservoir (3.5–4.0 ml.). Mixing may be effected immediately before the spectrum is measured. A black-painted wooden piece is used to enlarge the working space in the Cary 14 sample compartment.

of the absorption. No effect of concentration on the position of the maximum was *noted.* The charge-transfer band disappeared in carefully degassed acetone with unusual celerity, but the reaction responsible for the disappearance was not investigated.

The tropylium iodide was weighed directly into the quartz cell, either that of Fig. 1 or a 1-cm. stoppered cell. The polar solvents, water, methanol, and ethanol, were nitrogen-saturated and contained *ca.* 0.05 N hydriodic acid. Some five to ten minutes were required before a stable maximum was obtained in these solvents, and the steady decrease in the intensity of the charge-transfer band obviated accurate measurement of the maxima. The maximum in water was duplicated when sulfuric acid (0.1 N) was used; the latter solution was not particularly sensitive to light. Fourteen hours exposure to a 100-watt light led to the disappearance of both the charge-transfer band and absorption due to iodide ion (at 2260 Å.).

The data for tropylium iodide are summarized in Table I, and the correlation with Z is shown in Fig. 2. The fact of the correlation and the magnitude of its slope suggests that the previously proposed theoretical analysis is reasonable, *i.e.*, that the stabilization of the ion-pair ground state by solvent is equal to the destabilization of the excited state in comparison to the same states in a nonpolar medium.[2b,5] Attempts to calculate the ground state interaction energy in a solvent like acetonitrile by considering reasonable models for the structure of the *cybotactic region*[2b] lead to quantities which are somewhat too large. This is not surprising since the desired interaction energy represents the difference between a large attraction and large repulsion. Although the detailed energetics of the excited state are ignored in this approach, it would seem like a reasonable way to evaluate the ground state interactions derived from the spectroscopic data.

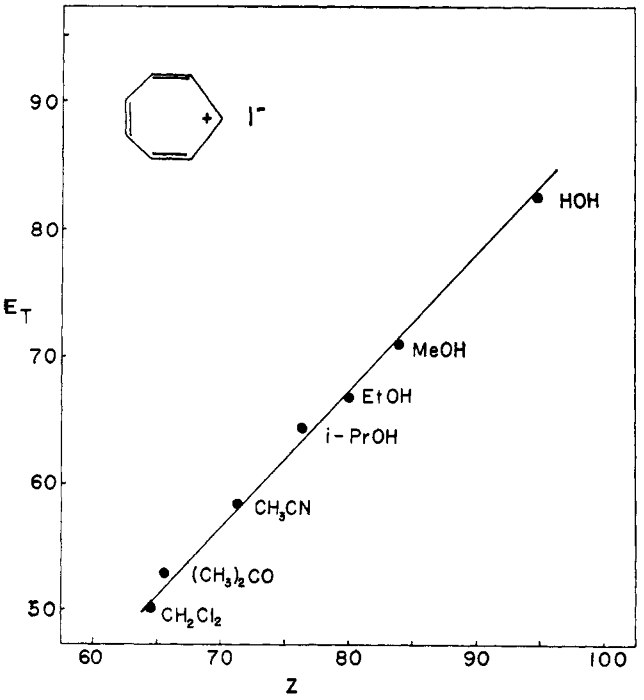

Fig. 2.—A plot of the transition energies for the charge-transfer band of tropylium iodide against the Z values for the solvents used (ref. 2b).

Table I

Charge-Transfer Band Maxima of Tropylium Iodide

Solvent (Z^a)	λ_{max}, Å.	$E_T{}^b$	Comment
Water (94.6)[c]	3457	82.7	I^- (0.1 N H_2SO_4) had no absorption between 3000 and 4000 Å., I_3^- had λ_{max} 3514 Å.
Methanol (83.9)[c,d]	4035	70.9	Charge-transfer band disappeared at moderate rate
Ethanol (80.0)[c,d]	4295	66.6	Charge-transfer band disappeared at moderate rate
Isopropyl alcohol (76.3)[c]	4432	64.5	Solubility low
Acetonitrile (71.3)	4905	58.3	Second maximum at 3300 Å.[e,f]
Acetone (65.7)	5390	53.0	Fast scan necessary since charge-transfer band disappears rapidly ($t_{0.5}$ *ca.* 14 min.)
Methylene chloride (64.5)	5715[g]	50.0	
	4090	69.9	Second maximum[g,h]

[a] Ref. 2b. [b] In kcal./mole. [c] Contained *ca.* 0.05 N HI. [d] Z-values corrected for water content. [e] The second band was only visible in the most dilute solutions. Its shape is *not* that of a charge-transfer band. [f] Exposure to light produced triiodide ion, λ_{max} 3610 Å. [g] Previously reported at 575 and 422 mμ (ref. 3). [h] ΔTE 19.9 kcal./mole [theoretical for $^2P_{1.5}$–$^2P_{0.5}$ 21.7 kcal./mole, *cf.* E. M. Kosower, *et al.*, *J. Am. Chem. Soc.*, **82**, 2188 (1960)].

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(5) An analysis of this type was originally proposed for halide ions. L. Pauling, *Phys. Rev.*, **34**, 954 (1929).