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A Study of the Preparation of Δ^9-Octalin

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In the course of an investigation of the stereochemistry of 9-substituted decalins,[1] the need arose for considerable quantities of pure Δ^9-octalin. Of the numerous preparations of this compound,[2] the one of choice is that described by Campbell and Harris[3] and which is a modification of the procedure of Linstead, Wang, Williams, and Errington.[4] This method involves the dehydration of 2-decalol, obtained by hydrogenation of 2-naphthol, with phosphoric acid and phosphorus pentoxide to yield a mixture of isomeric octalins which, in turn, are treated with phosphorus pentoxide to bring about conversion of the mixture to a practically pure Δ^9-octalin. Recently, Cope, Cotter, and Pike[5] have described a simplification which utilizes boric acid[6] for the initial dehydration step. Following this modification, in combination with the final phosphorus pentoxide treatment, the octalins obtained varied in refractive indices from run to run and the infrared spectrum of each preparation possessed a band at 3020 cm.$^{-1}$, an absorption characteristic of olefinic hydrogens. The nuclear magnetic resonance spectra of such preparations also displayed bands due to vinyl proton absorption.[7] From these latter spectra, it could be estimated that the Δ^9-octalin obtained by this method possessed 15–30% of other isomeric octalins, depending on whether the impurity was considered as a di- or a trisubstituted olefinic linkage.

It has been found, however, that purification of the mixed octalins *via* the blue nitrose chloride derivative, a derivative which can be prepared in 60% yield, does yield a pure Δ^9-octalin. The nuclear magnetic resonance spectrum of such a material showed the complete absence of any vinyl hydrogens. When this pure isomer was allowed to react with phosphorus pentoxide it was transformed into a mixture of octalins containing 10–20% of isomers with vinyl hydrogen atoms. Such a result clearly indicates, as might be expected, that phosphorus pentoxide treatment simply equilibrates the octalins and from such a procedure pure Δ^9-octalin cannot be obtained.

Recently, it has been reported that reduction of tetralin with lithium in either ethylamine[8] or ethylenediamine[9] yields practically pure Δ^9-octalin. When a procedure involving the dissolution of lithium in ethylenediamine prior to the addition of the tetralin was used, the reaction was erratic and the formation of the lithium derivative of the amine often resulted. It was found that by adding the lithium to a solution of tetralin in ethylenediamine, the reaction was reproducible and octalin was isolated in 70% yield. The nuclear magnetic resonance spectrum of the product, however, showed it to be a mixture of isomers containing 10–20% of material with di- or trisubstituted double bonds. It would thus appear that this method of preparation, as well as the phosphorus pentoxide method, yields an equilibrium mixture of octalins.

During the course of this work, the preparation of $\Delta^{1(9)}$-10-amino-octalin was attempted following the published procedure which allows the blue nitroso chloride to react with zinc and hydrochloric acid in ether.[10] In our hands, only a small yield of the amine was obtained, the principal product being Δ^9-octalin. This method of regeneration of pure octalin gives yields comparable to the normal sodium methoxide procedure.

EXPERIMENTAL

Preparation of octalins. (A) From 2-decalol. A mixture of 154 g. of isomeric decalols, prepared by hydrogenation of 2-naphthol, and 62 g. of boric acid was placed in a 500 ml. round-bottomed flask which was attached to a 5″-column packed with glass helices and the system arranged for distillation. The mixture was immersed in a bath at 170° and the bath temperature was allowed to gradually rise to 350° and the distillation of octalin and water had practically ceased. After cooling the distillation residue slightly, the system was evacuated to water aspirator vacuum and the distillation continued until no further product was obtained

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[1] W. G. Dauben, R. C. Tweit, and R. L. MacLean, *J. Am. Chem. Soc.*, **77**, 48 (1955).

[2] For a complete bibliography see Elsevier, *Encyclopedia of Organic Chemistry*, Elsevier Publishing Co., Houston, Tex., 1948, Vol. 12, p. 76.

[3] W. P. Campbell and G. C. Harris, *J. Am. Chem. Soc.*, **63**, 2721 (1941).

[4] R. P. Linstead, A. B. Wang, J. H. Williams, and K. D. Errington, *J. Chem. Soc.*, 1136 (1937).

[5] A. C. Cope, R. J. Cotter, and R. A. Pike, private communication.

[6] W. Brandenberg and A. Galat, *J. Am. Chem. Soc.*, **72**, 3275 (1950).

[7] These spectra were kindly determined by Dr. James N. Schoolery, Varian Associates, Palo Alto, Calif.

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

[9] L. Reggel, R. A. Friedel, and I. Wender, *J. Org. Chem.*, **22**, 891 (1957).

[10] W. Hückel and M. Blohm, *Ann.*, **502**, 114 (1933).

The total distillate was dissolved in ether, the water separated, the ethereal layer dried, and the solvent evaporated. The crude octalin was distilled at atmospheric pressure, b.p. 189–193°, n_{D}^{25} 1.4890–1.4950, yield 110–130 g. (80–95%).

A mixture of three parts of octalin and one part of phosphorus pentoxide was heated at 140° for 3 hr. and processed in the usual manner.[3] The product was distilled at atmospheric pressure through an 18″ column packed with Podbielniak tantalum Heli-pak: fraction 1, b.p. 191–193°, n_{D}^{25} 1.4920–1.4940; fraction 2, b.p. 192–194°, n_{D}^{25} 1.4940–1.4970. Fraction 1 usually amounted to a 25% yield and fraction 2 to a 60% yield.

(*B*) *From tetralin.* In a three-necked, round-bottomed flask fitted with a glass stopper, a sealed all-glass stirrer and a reflux condenser closed with a calcium chloride tube were placed 500 ml. of ethylenediamine (distilled from sodium hydroxide pellets before use) and 66.1 g. (0.5 mole) of tetralin. Clean lithium wire (21 g., 3 moles) was cut into short pieces and a 5 g. portion was added to the reaction flask. Stirring was commenced and in about 20 min. the lithium began to dissolve and heat was evolved. When the bulk of the initial lithium had dissolved, the remainder of the lithium was added in portions of about 3 g. over a period of about 15 min. Near the end of the addition of lithium, the solution developed a blue color. Stirring was continued for an additional 30 min. during which time the blue coloration faded to a slate-gray color.

The reaction mixture was decomposed by the addition of 200 ml. of ethanol over a period of 20 min. and the solution then poured into 2 l. of ice water. The mixture was extracted with several portions of benzene, the benzene solutions washed with 5% sulfuric acid and water. The solvent was removed and the product distilled at atmospheric pressure through a 20″ column, b.p. 194–196°, n_{D}^{25} 1.4950–1.4970, yield 48 g. (71%).

9-Nitroso-10-chlorodecalin. A solution of 45 g. (0.33 mole) of mixed octalins, prepared above, and 75 g. (1 mole) of ethyl nitrite in 100 ml. of glacial acetic acid was allowed to react with 75 ml. of concentrated hydrochloric acid at −15° in the usual manner and after 2 hr. the blue crystalline solid was removed by filtration. The solid was recrystallized from acetone twice to yield 35–40 g. (50–60%), m.p. 91–92° (lit.[2] 92°).

The yield of this derivative when pure Δ^9-octalin was employed was 77%.

Δ^9-Octalin. In an all-glass apparatus were placed 30 g. (0.46 mole) of zinc dust and a solution of 35 g. (0.17 mole) of 9-nitroso-10-chlorodecalin in 300 ml. of dry ether and to the stirred mixture was added 6 ml. of concentrated hydrochloric acid over the period of 10 min. The stirring was continued for 12 hr., then an additional 30 g. portion of zinc dust and 6 ml. of hydrochloric acid was added. The mixture was allowed to stir for an additional 24 hr., the zinc dust removed by filtration and washed with ether. The combined filtrate and washing were washed with sodium bicarbonate and water and then dried. After removal of the solvent, the Δ^9-octalin was distilled at atmospheric pressure, b.p. 194–196°, n_{D}^{25} 1.4971, yield 13.8 g. (59%).

When 9.8 g. of the purified material was heated with 5 g. of phosphorus pentoxide under the usual conditions and the product distilled, the following fractions were obtained: (1) b.p. 193–194°, n_{D}^{25} 1.4910, yield 1.7 g.; (2) b.p. 194–195°, n_{D}^{25} 1.4930, yield 0.6 g.; (3) b.p. 195.0–195.5°, n_{D}^{25} 1.4960, yield 7.8 g.; (4) b.p. 195.5–196.0°, n_{D}^{25} 1.4965, yield 2.3 g.

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Crystallizable Polystyrene. III. A Comparison of Crystallinities of Polystyrenes Prepared Using Various Catalysts

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In preceding publications,[1-3] crystallizable polystyrene was prepared by the use of Alfin catalysts and alkali-metal derivatives of arylmethanes. It is the purpose of this paper to demonstrate the difference in crystallizability between polystyrenes made using Alfin-type catalysts and arylmethane–alkali-metal catalysts, and those prepared using a Ziegler-type polymerization system.

The isotactic polystyrenes, prepared using various catalysts, are listed in Table I in the order of increasing crystallizability. X-ray diffraction photographs of these polymers are presented in Fig. 1.

TABLE I

CRYSTALLINITY OF ISOTACTIC POLYSTYRENES

Catalyst	(η)	Yield, %	Figure Number
Alfin catalyst	2.98	77.0	1
Triphenylmethyl potassium	1.58	11.1	2
Modified Ziegler, Run 1 system	1.14	0.13	
Modified Ziegler, Run 2 system	4.42	72.0	3

The most striking difference between polystyrenes obtained from organo-alkali-metal catalysts and those obtained from a Ziegler-type catalyst, is the higher degree of crystallinity obtained in the latter case. The order of increasing crystallizability was found to be the following: Alfin, triphenylmethylpotassium, and Ziegler-catalyzed polystyrene. Although only very low yields were obtained at first, using the Ziegler system, it was discovered that, by modification of the Ziegler system, high yields of isotactic polystyrene were obtained. In attempts to repeat the method described in the Ziegler Australian Patent No. **14116**, it was expedient to substitute trimethylaluminum for triethylaluminum. It was also necessary to run the reactions under atmospheric pressure. By employing these two changes, the catalyst prepared according to the reaction sequences described by Ziegler gave

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(1) J. L. R. Williams, J. VanDenBerghe, W. J. Dulmage, and K. R. Dunham, *J. Am. Chem. Soc.*, **78**, 1260 (1956).

(2) J. L. R. Williams, J. VanDenBerghe, K. R. Dunham, and W. J. Dulmage, *J. Am. Chem. Soc.*, **79**, 1716 (1957).

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