Can. J. Chem. Downloaded from www.nrcresearchpress.com by UNIV OF SOUTHERN CALIFORNIA on 11/09/14
For personal use only.

THE SYNTHESIS OF SOME STEREOISOMERIC DERIVATIVES OF DECAHYDRONAPHTHALENE[1]

By A. Zlatkis[2] and E. A. Smith

Abstract

Both racemic forms of *trans* 2-chlorodecalin have been prepared and separated in pure form. The reaction between these chlorodecalins and ethylmagnesium bromide has been studied and two racemates of *trans* 2-ethyl decalin have been isolated. Some progress has been made in the preparation of the 9-chlorodecalins. A new method for converting *cis* decalin to *trans* decalin rapidly in high yield using tertiary butyl chloride and anhydrous aluminum chloride is indicated.

Introduction

The preparation of the monoalkyl derivatives of decahydronaphthalene (decalin) has not been extensively investigated. One approach to the synthesis of this group of hydrocarbons has been the hydrogenation of the corresponding naphthalene derivative. Three isomers of 1-methyldecalin have been prepared in this manner (9).

The present work describes a new route by way of the reaction of the monochlorodecalins with ethylmagnesium bromide. The two racemic forms of *trans* 2-ethyldecalin have been prepared from the corresponding chlorodecalins.

Experimental*

Preparation of trans Decalin

Commercial decalin (Eastman Kodak Co.) (500 ml.) was treated twice with 200 ml. of concentrated sulphuric acid with vigorous agitation. The purified product was then dried for 24 hr. over sodium hydroxide pellets. Refractometric measurements indicated that the decalin contained 70% of the *cis* isomer and 30% of the *trans* isomer (8).

The conversion of *cis* to *trans* decalin in the presence of anhydrous aluminum chloride has been reported by Zelinsky (10), who obtained low yields. It was found since by the author that by using a 10% catalytic mixture of 3:1 anhydrous ferric chloride and anhydrous aluminum chloride, complete isomerization could be effected in three hours (11). Final purification of the *trans* decalin was accomplished by vacuum distillation at 10 mm. pressure through a Stedman column. The physical constants of the resultant product were: b.p.$_{10}$ 63.7°C., n_D^{20} 1.4696, d_4^{20} 0.8699. These agreed closely with those reported in the literature by Seyer and Walker (8): b.p.$_{10}$ 63.7°C., n_D^{20} 1.4697, d_4^{20} 0.8695.

---

[1] *Manuscript received in original form November 8, 1949, and, as revised, November 7, 1950.*
Contribution from the Department of Chemical Engineering, University of Toronto, Toronto, Ontario.

[2] *Present address: Dept. of Chemistry, Wayne University, Detroit, Michigan.*

* *All boiling points are uncorrected.*

Can. J. Chem. Downloaded from www.nrcresearchpress.com by UNIV OF SOUTHERN CALIFORNIA on 11/09/14
For personal use only.

The Chlorination of trans Decalin

The procedures of Gysin (5) and Borsche and Lange (2) have been modified as follows to give higher yields.

The reaction vessel consisted of a one-liter three-necked flask. Chlorine, previously moistened by passing through a wash bottle containing water, was passed in through a tube which was pulled out to a capillary. A dropping funnel at the center of the flask permitted decalin to be dropped in slowly. The capillary part of the chlorine tube was placed 1/2 in. from the end of the dropping funnel so that an atomizing effect could be produced when the decalin and chlorine met. A glass tube extending to the bottom of the vessel and leading to a receiver, at a level below the reaction flask, acted as a siphon and captured the product.

The decalin was sprayed in the form of a fine mist, with chlorine under pressure, against the walls of the reaction vessel which was immersed in an ice–salt bath. The system was kept slightly below atmospheric pressure to prevent the escape of chlorine, and to facilitate removal of the product from the reaction vessel to the receiver. Decalin was passed through the apparatus at the rate of 100 ml. per min. The chlorinated product was recycled until the desired degree of chlorination, as determined by checks on the specific gravity, was obtained. The reaction was stopped when the specific gravity of the chlorinated product reached unity. As a rule, seven to nine cycles were required. The crude chlorodecalin was washed first with 15% sodium carbonate solution, then with water. This was dried over calcium chloride and finally distilled. Five hundred milliliters of decalin could be fully treated in one hour using this atomizing procedure, with an over-all yield of 80% or better.

The following conditions appeared to be most favorable for the reaction:
(*a*) Intimate mixture of the chlorine with the decalin,
(*b*) The use of a small amount of iodine (1/2%) as a catalyst,
(*c*) Moistening the chlorine before passing it into the reaction chamber,
(*d*) The use of a strong light source to catalyze the reaction,
(*e*) Stopping the reaction before appreciable dichlorination set in.

Distillation of the halogen products was carried out in a large fiber glass packed fractionating column (3 ft. by 1 in.) under vacuum. The still was tested at total reflux at atmospheric pressure, and gave a result of 20 theoretical plates. Several distillations were necessary to obtain the isomers in their pure forms. Table I shows the properties found for these chlorodecalins. The *trans* isomer

TABLE I

Property	*trans* 2-chlorodecalin A	*trans* 2-chlorodecalin B
b.p.$_{15}$, °C.	115	117
n_D^{20}	1.4946	1.4970
d_4^{20}	1.0234	1.0377
% C : H : Cl calc.	69.56 : 9.86 : 20.58	69.56 : 9.86 : 20.58
% C : H : Cl found	69.62 : 9.88 : 20.50	69.48 : 9.92 : 20.60

Can. J. Chem. Downloaded from www.nrcresearchpress.com by UNIV OF SOUTHERN CALIFORNIA on 11/09/14
For personal use only.

of 2-chlorodecalin corresponding to the chlorodecalin derivable from 2-decalol (m.p. 75°C.) (4) has been designated as *trans* 2-chlorodecalin A, the one derivable from 2-decalol (m.p. 53°C.) *trans* 2-chlorodecalin B.

The values found compare favorably with those of the literature (4, 6). The chlorodecalins are colorless, but turn light yellow on standing.

Twenty milliliters of *trans* 2-chlorodecalin A was heated for six hours in 25 ml. of diethyl ether in the presence of 5 gm. of magnesium, resulting in the decalylmagnesium chloride. The latter, on treatment with oxygen at 0°C. and followed by decomposition with water, resulted in the decalol m.p. 74°C. The same procedure with *trans* 2-chlorodecalin B produced the decalol m.p. 53.5°C.

Synthesis of the 9-Chlorodecalins

Bartlett's work (1) on the catalyzed exchange of hydrogen and halogen offered a convenient method of preparing a pure 9-chlorodecalin. Pure isomers of decalin were used to facilitate identification of the products.

Three hundred milliliters (1.89 moles) of pure *trans* decalin was mixed with 115 ml. (1.05 moles) of tertiary butyl chloride in a two-liter separatory funnel. To this was added 15 gm. of anhydrous aluminum chloride, and the mixture was then shaken for a period of 30 sec. A reaction took place as soon as the aluminum chloride came in contact with the solution. The solution turned dark amber in color and the sides of the vessel became black. On quenching the reaction with three times the volume of water, two layers were formed. The top oily, amber layer was washed with water and dried with phosphoric anhydride. This solution now had a blue fluorescence and on distillation gave a small yield (14%) of a 9-chlorodecalin: b.p.$_7$ 83°C., n_D^{20} 1.4937, d_4^{20} 1.0007. Calc. % Cl = 20.58. Found % Cl = 20.67.

The use of *cis* decalin in a similar procedure produced a more violent reaction and the 9-chlorodecalin yield was greater (20%). During the course of the reaction (40 sec.), the *cis* decalin had almost completely isomerized to the *trans* form. This is rather remarkable in view of the authors' earlier experience in a study of this isomerization (11). The 9-chlorodecalin from this reaction had the following properties: b.p.$_7$ 85°C., n_D^{20} 1.4946, d_4^{20} 1.0645. Found % Cl = 20.60 This was probably a mixture of *cis* and *trans* 9-chlorodecalins due to the simultaneous occurrence of the isomerization.

Dehydrohalogenation with Pyridine

In order to identify the chlorinated product obtained with *trans* decalin, the corresponding 9, 10 octalin was prepared: 20 ml. of the chlorodecalin n_D^{20} 1.4937 was refluxed in an equal volume of dry pyridine for three hours, at the end of which time a white precipitate of pyridine hydrochloride had formed. The red solution was decanted off, washed with water, then dried with phosphoric anhydride. The product was now colorless and had the following properties: b.p.$_{13}$ 74°C., n_D^{20} 1.4984. The literature reports (7) for 9, 10 octalin: b.p.$_{12}$ 75°C., n_D^{20} 1.4996. Three milliliters of the octalin was converted to the blue nitrosochloride. A solution consisting of the octalin, 10 ml. glacial acetic acid, and 6 ml. of isoamyl nitrite was cooled to −30°C. and then treated with 6 ml. of concentrated hydrochloric acid in a dropwise manner. The resulting blue precipitate was washed with acetone and had a melting point of 90–91°C. The melting point for 9, 10 octalin nitrosochloride is reported as 92°C. in the literature (3).

Synthesis of the trans 2-Ethyldecalins

Eighty-five milliliters (0.5 mole) of the colorless *trans* 2-chlorodecalin A was added to 0.75 mole of ethylmagnesium bromide in 100 ml. of isoamyl ether over a period of one hour. The Grignard reagent had been prepared in the usual manner. After refluxing for one hour, the solution was allowed to stand overnight. The reaction mixture was then poured into a beaker containing 300 ml. of 1:1 sulphuric acid solution and about 200 gm. of chopped ice. The ether layer was distilled in a fiber glass-packed column. Although the yield was low (10%) 5 ml. of a pure product was obtained: b.p.$_8$ 70°C., n_D^{20} 1.4716, d_4^{20} 0.8583. Calc.: C, 86.64, H, 13.36%. Found: C, 86.26; H, 13.53%.

A similar procedure was followed for the preparation of the other isomer of *trans* 2-ethyldecalin. In the latter case, *trans* 2-chlorodecalin B was used. The resulting product (5 ml.) showed the following characteristics: b.p.$_8$ 72°C., n_D^{20} 1.4809, d_4^{20} 0.8803. Calc.: C, 86.64; H, 13.36%. Found: C, 86.26; H, 13.52%.

Conclusions

While the Grignard reaction with the chlorodecalins has not produced good yields in the preparation of the *trans* 2-ethyldecalins, the racemic forms of the chlorodecalins isolated are of interest for further investigation. Particular significance may be attached to the isomerization occurring when *cis* decalin was treated with tertiary butyl chloride in the presence of anhydrous aluminum chloride. The catalyzed exchange of hydrogen and halogen offers a simple, convenient method for the conversion of *cis* decalin to *trans* decalin. Complete isomerization is effected in only 40 sec.

Acknowledgment

The authors express their appreciation of Mr. H. Shanfield and Dr. D. S. McArthur for their interest and assistance in this work.

References

1. BARTLETT, P. D., CONDON, F. E., and SCHNEIDER, A. J. Am. Chem. Soc. 66: 1538. 1944.
2. BORSCHE, W. and LANGE, E. Ann. 434: 134. 1923.
3. CAMPBELL, W. P. and HARRIS, G. C. J. Am. Chem. Soc. 63: 2725. 1941.
4. CAUQUIL, G. Compt. rend. 218: 463. 1944.
5. GYSIN, H. Helv. Chim. Acta, 9: 59. 1936.
6. LEVINA, R. YA. and KULIKOV, S. G. J. Gen. Chem. 10: 1189. 1940.
7. LINSTEAD, R. P. J. Chem. Soc. 1136. 1937.
8. SEYER, W. F. and WALKER, R. D. J. Am. Chem. Soc. 60: 2125. 1938.
9. SHANFIELD, H. and SMITH, E. A. Can. J. Research, B, 26: 763. 1948.
10. ZELINSKY, N. D. and TUROWA-POLLACK, M. B. Ber. 65B: 1299. 1932.
11. ZLATKIS, A. Thesis, University of Toronto. 1947.

Can. J. Chem. Downloaded from www.nrcresearchpress.com by UNIV OF SOUTHERN CALIFORNIA on 11/09/14
For personal use only.