Notes A department for short papers of immediate interest.

Direct Preparation of Vinyllithium[1]

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The useful intermediate vinyllithium can be prepared by cleavage of tetravinyltin with phenyllithium.[2] The direct preparation of vinyllithium from vinyl halides and lithium metal at very low temperatures has been reported,[3] but the yields are low and erratic.[4]

In these laboratories we have been unsuccessful in all attempts to prepare vinyllithium from vinyl chloride or bromide and ordinary lithium metal containing about 0.02% sodium, in various solvents. Recently the presence of sodium in the lithium metal used has been found to have a pronounced catalytic effect on the ease of preparation of certain organolithium compounds.[5] This observation prompted us to study the effect of sodium on the preparation of vinyllithium. We find that vinyllithium can be readily prepared in tetrahydrofuran from vinyl chloride and a lithium dispersion containing about 2% sodium.[6] This procedure should provide a highly convenient method for the preparation of vinyllithium reagent solutions. Satisfactory yields are obtained at 25°, but the preferred temperature for the reaction is 0-10°.

EXPERIMENTAL

Vinyl chloride (Matheson Co.) from a cylinder was condensed into a calibrated trap. Six grams (0.10 mole) of the chloride was entrained in a stream of argon and bubbled into a stirred flask containing 1.5 g. of lithium −2% sodium dispersion in 250 ml. of tetrahydrofuran under an argon atmosphere. A reaction commenced after about one-fourth of the vinyl chloride had been added, and the remainder of the addition was carried out at 0–10°. After addition the mixture was stirred for 2 hr. at 0° and then allowed to warm to room temperature with stirring. Filtration in an argon atmosphere gave a clear colorless solution of vinyllithium in tetrahydrofuran. The yield of vinyllithium was 60–65% as estimated by titration with base and by reaction with vanadium pentoxide followed by titration with standard permanganate solution.[7] A derivative from acetone yielded approximately 20% of dimethylvinylcarbinol, b.p. 97–99°, n_D^{25} 1.4178.[8]

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[1] This research was supported by a grant from the Atomic Energy Commission.

[2] D. Seyferth and M. A. Weiner, *Chem. & Ind.*, 402 (1959).

[3] B. Bartocha, C. M. Douglas, and M. Y. Gray, *Z. Naturforsch.*, **14b**, 809 (1959).

[4] Private communication, B. Bartocha.

[5] C. W. Kamienski and D. L. Esmay, *J. Org. Chem.*, **25**, 1807 (1960); T. A. Beel, W. G. Koch, G. E. Tomasi, D. E. Hermansen, and P. Fleetwood, *J. Org. Chem.*, **24**, 2036 (1959); M. Stiles and R. P. Mayer, *J. Am. Chem. Soc.*, **81**, 1497 (1959) ref. 38b.

[6] Supplied by the Lithium Corp. of America, Inc., through the courtesy of Dr. Donald L. Esmay.

[7] Technical Bulletin No. 312-360, Lithium Corp. of America, Inc., Minneapolis, Minn., 1960.

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Relative Stabilities of *cis* and *trans* Isomers. XI. The 9-Methyldecalins[1]

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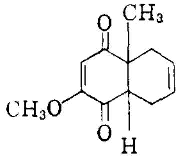
The 9-methyldecalin system occurs widely in nature, and the relative stabilities of the *cis* and *trans* isomers have been of considerable interest. The thermodynamic quantities for the reaction *cis*$\rightleftharpoons$*trans* 9-methyldecalin are reported in this paper.

The *cis*- and *trans*-9-methyldecalins are known compounds, and the assignment of their stereochemistry is based on the fact that I (*cis*-form) results from the Diels-Alder addition of butadiene to the appropriate quinone,[2] while the *trans* form is obtained by treating the Diels-Alder adduct with base.[3] That the energies (enthalpies) of the isomeric 9-methyldecalins would be more similar to one another than is found with the decalins themselves was recognized some years ago by Turner[4] who predicted that the *trans* would have a lower enthalpy by 0.8 kcal./mole. Recently[5]



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[3] For a complete discussion of the stereochemistry of the compounds and references, see W. G. Dauben, J. B. Rogan, and E. J. Blanz, Jr., *J. Am. Chem. Soc.*, **76**, 6384 (1954).

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[5] W. G. Dauben, O. Rohr, A. Labbauf, and F. D. Rossini, *J. Phys. Chem.*, **64**, 283 (1960).

the heats of combustion have been measured for the compounds, and the enthalpy of the *trans* isomer was found to be less than that of the *cis* by 1.39 ± 0.64 kcal./mole (liquid phase, 298° K.).

The present work was undertaken to obtain values of ΔF, ΔH, and ΔS for the isomerization of 9-methyldecalin in the liquid phase. The method employed, which has previously been described in detail,[6] involves equilibrating small samples of the isomers at several different known temperatures. With hydrocarbons a palladium on carbon catalyst has usually been suitable. The present work was carried out over the temperature range 557-611° K. At still lower temperatures the equilibration is very slow, while at higher temperatures excessive decomposition sets in. The equilibrated samples were analyzed by gas phase analysis, the equilibrium constant was calculated at each temperature, and from a plot of ln K against 1/ T the thermodynamic constants for the reaction *cis*- $\rightleftharpoons$ *trans*-9-methyldecalin were found to be $\Delta H_{584} = -0.55 \pm 0.28$ kcal./mole, and $\Delta S_{584} = -0.5 \pm 0.5$ e.u. These values were not as accurate as those usually obtained by this method,[6] due partly to the somewhat restricted temperature range that was conveniently available and partly to the fact that the isomers are not easily separable by vapor phase chromatography. Under the best conditions found, the separation was still not complete, and the composition of a given sample could be determined only with an accuracy of ± 0.24%.

The value for ΔH found in the present work is in good agreement with both the theoretical value,[4] and with the value determined from the heat of combustion measurements.[5]

The entropy change expected for the reaction can be predicted by noting that both isomers have symmetry numbers of 1, and the *cis* is *dl* while the *trans* is *meso*. The calculated (gas phase) value is $\Delta S = -1.4$ e.u. The experimental value is correct in sign but smaller than this in magnitude. The same situation was noted with the unsubstituted decalins,[7-9] and is not completely understood. In that case the experimental gas phase values were in better agreement with theory than were the liquid phase values, and the same may be true here.

It can be seen (Table I) that the equilibrium composition of the 9-methyldecalins is essentially independent of temperature, 55 ± 1% over the range studied. The difference in energy between the isomers is sufficiently small that in substituted systems the position of the *cis-trans* equilibrium will be determined to an important extent by the nature of the substituents.

TABLE I

EQUILIBRATION DATA FOR THE REACTION *cis*-9-METHYLDECALIN $\rightleftharpoons$ *trans*-9-METHYLDECALIN

T° K	Starting Isomer	Eq. % *trans*
557	*cis*	55.98
557	*trans*	56.56
572	*cis*	56.21
580	*trans*	55.99
583	*cis*	55.70
597	*cis*	55.14
597	*trans*	55.27
611	*trans*	55.21

EXPERIMENTAL

The compounds used in the present work were samples prepared earlier by Dauben, Rogan, and Blanz.[3] Equilibrium was established by heating the compound (100 mg.) with palladium on carbon (10%, 50 mg.) in a small sealed tube as previously described.[6] The times used for the equilibrations varied from 350 hr. at 577° K., to 46 hr. at 611° K. The equilibration was quenched and the sample was analyzed as described earlier. The column used for the analysis and which gave the best separation of the many columns tried was 14.5 feet long, and was packed with 9.5 g. of γ-methyl-γ-nitropimelonitrile on 33 g. of 60-80 mesh firebrick. The analyses were carried out at 95°. The ratio of the isomers in the mixture was taken as equal to the ratio of the products of the band heights and the half-band widths as determined graphically. Each sample was analyzed at least three times and the average deviation for all duplicate analyses was ±0.24%. The results are summarized in Table I. The calculation of the thermodynamic quantities from the data was carried out as described earlier.[6]

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Preparation of Sodium 2,2-Dimethyl-2-silapentane-5-sulfonate, a Useful Internal Reference for N.S.R. Spectroscopy in Aqueous and Ionic Solutions

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Recently a study has been made[1] to develop, in so far as possible, an adequate internal referencing technique for nuclear spin resonance (N.S.R.)