

Notes

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Direct Preparation of Vinyllithium¹

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Received October 4, 1960

The useful intermediate vinyllithium can be prepared by cleavage of tetravinylltin 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 esti-

mated 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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(7) Technical Bulletin No. 312-360, Lithium Corp. of America, Inc., Minneapolis, Minn., 1960.

(8) H. Normant, *Compt. rend.*, **240**, 316 (1955).

Relative Stabilities of *cis* and *trans* Isomers.

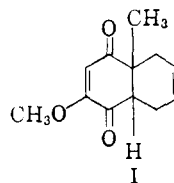
XI. The 9-Methyldecalins¹

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Received August 9, 1960

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* ⇌ *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 Turner⁴ who predicted that the *trans* would have a lower enthalpy by 0.8 kcal./mole. Recently⁵

(1) This research was supported by a grant from the Atomic Energy Commission.

(2) D. Seyierth 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.

(1) Paper X, N. L. Allinger and R. J. Curby, *J. Org. Chem.*, **26**, 933 (1961).

(2) R. B. Woodward, F. Sondheimer, D. Taub, K. Heusler, and M. W. McLamore, *J. Am. Chem. Soc.*, **74**, 4223 (1952).

(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).

(4) R. B. Turner, *J. Am. Chem. Soc.*, **74**, 2118 (1952).

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