

This article was downloaded by:

On: 28 January 2011

Access details: Access Details: Free Access

Publisher Taylor & Francis

Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



Phosphorus, Sulfur, and Silicon and the Related Elements

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title~content=t713618290>

Syntheses of Unique Bicyclop hostones and Unexpected Difference in the Reaction of Lawesson's Reagent vs. P_2S_5 with *Cis*-Bicyclop hostone (1)

Alexandre M. Polozov^a; Sheldon E. Cremer^a

^a Department of Chemistry, Marquette University, Milwaukee, WI, USA

To cite this Article Polozov, Alexandre M. and Cremer, Sheldon E.(1999) 'Syntheses of Unique Bicyclop hostones and Unexpected Difference in the Reaction of Lawesson's Reagent vs. P_2S_5 with *Cis*-Bicyclop hostone (1)', Phosphorus, Sulfur, and Silicon and the Related Elements, 147: 1, 335

To link to this Article: DOI: 10.1080/10426509908053647

URL: <http://dx.doi.org/10.1080/10426509908053647>

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: <http://www.informaworld.com/terms-and-conditions-of-access.pdf>

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

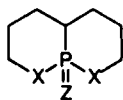
The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

Syntheses of Unique Bicyclop hostones and Unexpected Difference in the Reaction of Lawesson's Reagent vs. P_2S_5 with *Cis*-Bicyclop hostone (1)

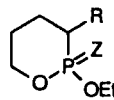
ALEXANDRE M. POLOZOV and SHELDON E. CREMER

Department of Chemistry, Marquette University, Milwaukee, WI. 53201-1881, USA

The purpose of this study was to synthesize *trans*-1 and determine the equilibrium constant with *cis*-1. Only the synthesis¹ and x-ray structure² of the *cis* isomer have been reported. Four prior synthetic routes to make the *trans* isomer³ gave only *cis* product. For example, intramolecular ring closure of the *cis* or *trans* isomers of 4 ($R = (CH_2)_3OH$) with LiH or thermal closure of the *cis* or *trans* 4 ($R = (CH_2)_3I$) gave only *cis*-1. Since both isomers of 1,8-dioxabicyclo[4.4.0] decane are known and readily equilibrate (57% *cis* and 43% *trans*), the apparent inaccessibility of *trans*-1 attracted our attention. The preparation of *trans*-1 was achieved by treatment of *cis*-1 with Lawesson's reagent (LR) to provide *cis*-2, followed by oxidation with *m*-chloroperbenzoic acid/trifluoroacetic acid to give a 5:1 mixture of *cis:trans* 1, respectively. An unexpected formation of the sulfur analogue of 1 was observed on treatment of *cis*-1 with P_2S_5 /pyridine at reflux temperatures to give a 1.6:1 mixture of *cis:trans* 3, respectively. Thermal equilibration of 1 at 204 °C provided an equilibrium ratio of 99.5% *cis* and 0.5% of the *trans* isomer. However, equilibration of 3 at 250 °C led to 82.2:17.8 ratio in favor of the *cis* isomer. These results are consistent with semiempirical MO calculations. The stereochemical outcome on treatment of 4 with LR was also investigated. X-ray structures for six compounds: *trans*-1, *cis*-2, *cis* and *trans*-3; *cis*-4 ($R=Ph$), and *cis*-5, ($R = Ph$) were determined.



1. $X = Z = O$
2. $X = O; Z = S$
3. $X = Z = S$



4. $Z = O$
5. $Z = S$
- $R = Ph, alkyl$

References

- [1] Whitham, G.H. personal communication (1989).
- [2] Bellard, S., Postle, S., and Sheldrick, G.M. *Acta Cryst B*, **34**, 1032 (1978).
- [3] Oscar Rodriguez, Ph.D. thesis Marquette University (1995).