

This article was downloaded by:

On: 29 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>

Preparation, Reactions, and NMR Studies of 4-Methyl-4-Phosphatetracyclo [3.3.0.0^{2,8}.0^{3,8}] Octane 4-Oxide and Derivatives

S. E. Cremer^a; J. M. Cowles^a; F. R. Farr^a; P. W. Kremer^a; H. Hwang^a; A. C. Peterson^a

^a Dept. of Chemistry, Marquette University, Milwaukee, WI

To cite this Article Cremer, S. E. , Cowles, J. M. , Farr, F. R. , Kremer, P. W. , Hwang, H. and Peterson, A. C.(1990) 'Preparation, Reactions, and NMR Studies of 4-Methyl-4-Phosphatetracyclo [3.3.0.0^{2,8}.0^{3,8}] Octane 4-Oxide and Derivatives', *Phosphorus, Sulfur, and Silicon and the Related Elements*, 51: 1, 192

To link to this Article: DOI: 10.1080/10426509008040726

URL: <http://dx.doi.org/10.1080/10426509008040726>

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.

PREPARATION, REACTIONS, AND NMR STUDIES OF 4-METHYL-4-PHOSPHATETRACYCLO [3.3.0.0^{2,9}.0^{3,8}] OCTANE 4-OXIDE AND DERIVATIVES

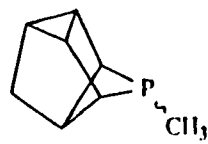
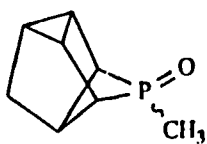
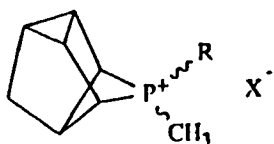
S.E. Cremer, J.M. Cowles, F.R. Farr, P.W. Kremer, H. Hwang and A.C. Peterson
 Marquette University, Dept. of Chemistry, Milwaukee, WI 53233

The title compound which we¹ and others² have previously synthesized has now been extensively investigated. The tetracyclic phosphonium chloride **1** was prepared by treatment of norbornadiene with CH_3PCl_2 at 65-80°C for one week. Treatment of **1** with $\text{AlCl}_3/\text{CH}_2\text{Cl}_2$ gave **2**. Direct or "inverse" addition of water to **2** dictated the stereochemistry of the oxide **3**. Stereoassignments of **3** were made based on lanthanide shift -- ^1H and ^{13}C nmr studies. Extensive 2-D nmr studies (HETCOR, COSY) and triple irradiation experiments enabled chemical shift and coupling constant assignments.

The stereochemistry of conversion of **3** to **4** can be controlled by selection of the reducing reagent. Various derivatives of **4** (sulfide, selenide and salts) were then prepared.

An extensive low-temperature ^{31}P nmr study was made by treatment of the salt **5** with CH_3Li at -70°C. The initial phosphorane (P^+) intermediate (^{31}P = -100 ppm) gave rise to several ring-opened species as the temperature was increased. Structures consistent with these results are proposed.

Detailed ^1H , ^{13}C , and ^{31}P nmr data as well as studies of ring opening reactions will be presented.



- 1** R=Cl, X=Cl
2 R=Cl, X=AlCl₄
5 R=CH₃, X=Br

3

4

- 1) S.E. Cremer et al., *J.C.S. Chem. Commun.*, 374 (1974)
 2) M. Green, *J. Chem. Soc.*, 541 (1965)