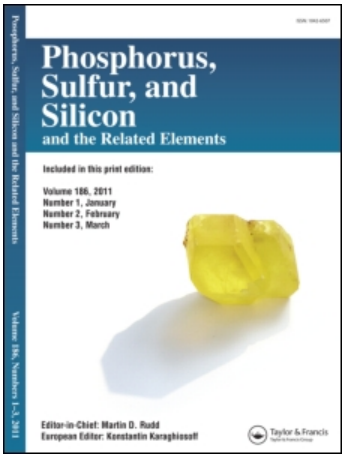


Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

TWO STEP SYNTHESIS OF 3,7,7-TRIMETHYL-1,3,5-CYCLOHEPTATRIENE FROM Δ³-CARENE

G. Déléris[a]; A. Gadras[b]; J. Dunoguès[c]
[a] Laboratoire de Chimie Bioorganique, Université de Bordeaux 2, Bordeaux, France [b] Rhône-Poulenc Agrochimie, Centre de Recherches de la Dargoire, Lyon, France [c] Laboratoire de Chimie Organique et Organométallique CNRS URA 35, Talence, France

To cite this Article Déléris, G. , Gadras, A. and Dunoguès, J.(1995) 'TWO STEP SYNTHESIS OF 3,7,7-TRIMETHYL-1,3,5-CYCLOHEPTATRIENE FROM Δ³-CARENE', Phosphorus, Sulfur, and Silicon and the Related Elements, 101: 1, 287 — 289
To link to this Article: DOI: 10.1080/10426509508042529
URL: http://dx.doi.org/10.1080/10426509508042529

Phosphorus, Sulfur, and Silicon, 1995, Vol. 101, pp. 287–289
Reprints available directly from the publisher
Photocopying permitted by license only

Communication

TWO STEP SYNTHESIS OF 3,7,7-TRIMETHYL-1,3,5-CYCLOHEPTATRIENE FROM Δ^3-CARENE

G. DÉLÉRIS
Laboratoire de Chimie Bioorganique, Université de Bordeaux 2, F-33076 Bordeaux, France

and

A. GADRAS
Rhône-Poulenc Agrochimie, Centre de Recherches de la Dargoire, F-69009 Lyon, France

and

J. DUNOGUÈS
Laboratoire de Chimie Organique et Organométallique CNRS URA 35, Université de Bordeaux 1, F-33405 Talence, France

(Received May 18, 1994; in final form July 18, 1994)

3,7,7-trimethyl-1,3,5-cycloheptatriene was obtained in 74% overall yield when adducts from ene reaction between Δ^3-carene and N-sulphinyl arenesulphonamides are reacted with hexamethyl disilazane at 80°C.

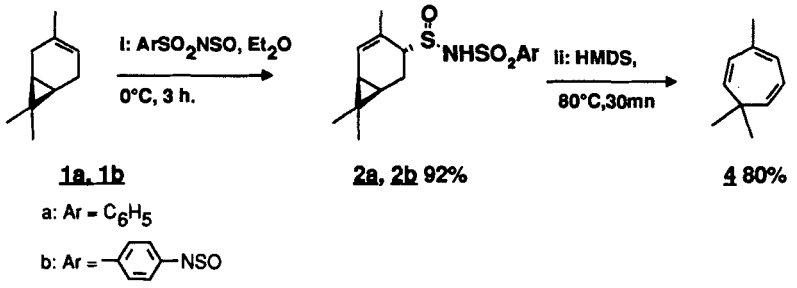
Key words: Ene reaction, N-sulphinyl arenesulphonamides, hexamethyl disilazane, Δ-3 carene.

We previously pointed out that pericyclic reactions involving readily available N-sulphinyl arenesulphonamides were a convenient way to introduce at allylic positions various functions such as thiols[1] or silyl groups[2,3] from which ketones, nitriles, etc., could be obtained. This scheme enabled us to alkylate or isomerize terpenes[4] or to synthesize alkylation derivatives.[5,6]

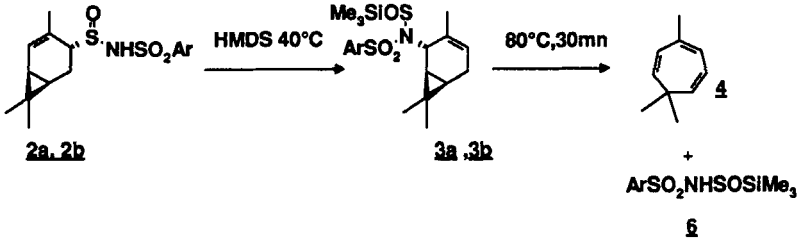
Recently, we have shown[7,8] that ene adducts **2** react with hexamethyldisilazane (HMDS) to yield allylic amines, protected as sulphonamides. These reactions, when carried out with Δ-3 carene, required a careful control of the reaction temperature conditions, i.e. 40°C in this case.

Here we report that ene reaction of Δ^3-carene with N-sulphinyl sulphonamides followed by treatment with HMDS at 80°C for 30 minutes promptly yielded 3,7,7-trimethyl-1,3,5-cycloheptatriene[9] **4** (Scheme I).

Compound **4** is a natural product isolated from *Pinus sylvestris*.[10] This hydrocarbon has been extensively studied for its spectroscopic[11] and chemical[12] properties relevant to the cycloheptatriene to norcaradiene conversion. Its first syntheses have



SCHEME I

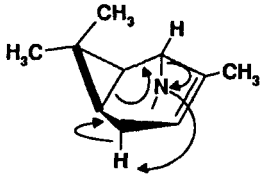


SCHEME II

been described by Corey[13] and by Campbell.[14] They required acidic isomerization of carvone and subsequent reduction to eucarvol which was then dehydrated (H^+, 120°C, 20 min) to provide **4** (26% overall yield).

In order to examine whether this reaction follows the same pathway as our previous amination reaction, we reacted **2a** or **2b** with HMDS at 40°C, and **3a** or **3b** (from which allylic sulphonamides can be obtained after hydrolysis[7,8]) were obtained as previously described. However when **3a** or **3b** were heated at 80°C for 30 min, they afforded **4** (74% yield from **1**) along with **6** (Scheme II).

The driving force for this apparently facile rearrangement might well be the release of steric compression due to the disappearance of 1,4-cis proton-nitrogen pseudo diaxial interaction in the "inverted boat" conformation of **3**.



3: Conformation

This new ring-enlargement appears to be competitive for the synthesis of 3,7,7-trimethyl-1,3,5-cycloheptatriene from Δ^3-carene, the major component of Indian pine tree (*Pinus longifolia*) turpentine. Work dealing with the application of this reaction to the synthesis of more sophisticated natural compounds is in progress.

ACKNOWLEDGEMENTS

Rhône-Poulenc is acknowlédged for financial support and we especially thank Dr. F. Gobert, Centre de Recherches des Carrières, Rhône-Poulenc, for valuable help in NMR structural study.

REFERENCES AND NOTES

1. A. Gadras, J. Dunoguès, R. Calas and G. Déléris, *J. Org. Chem.*, **49,** 442 (1984).
2. G. Déléris, J. Kowalski, J. Dunoguès and R. Calas, *Tetrahedron Lett.*, 4211 (1977).
3. J. P. Pillot, G. Déléris, J. Dunoguès and R. Calas, *J. Org. Chem.*, **44,** 3397 (1979).
4. G. Déléris, J. Dunoguès and R. Calas, *Tetrahedron Lett.*, 4835 (1979).
5. G. Déléris, J. Dunoguès and A. Gadras, *Tetrahedron Lett.*, **25,** 2135 (1984).
6. S. Géhanne, F. Raynaud, A. Gadras and G. Déléris, *Tetrahedron*, **48,** 6043 (1992).
7. G. Déléris, J. Dunoguès and A. Gadras, *Tetrahedron*, **44,** 4243 (1988).
8. G. Déléris, A. Gadras and J. Dunoguès, *Tetrahedron*, **46,** 5999 (1990).
9. In a typical experiment, **2a** or **2b** (40 mmol, prepared as reported in References 7 and 8) was dissolved in 1,2-dichlorethane (30 ml) in the presence of HMDS (25 ml) and heated at 80°C for 30 mn. The reaction mixture was then concentrated under reduced pressure (10 Torr) until only a brown solid remained. The liquid phase was then trapped with acetone/dry ice and distilled to yield **4** (4.3 g, 32 mol, 80% yield). Bp/27 torr = 67°C, ^{1}H NMR ($CDCl_3$, TMS ref, BRUKER WM 360) spectrum in full accordance with the one described in Reference 2; ^{13}C NMR ($CDCl_3$, TMS ref, BRUKER WH 90) δ ppm: 127.1 C_1 or C_6; 127.3 C_1 or C_6; 132 C_2 or C_5; 133.4 C_2 or C_5; 124, C_3; 138.1 C_4; 26.15 C_7 or C_8; 34.7, C_9; 24.3, C_{10}. Mass spectrometry (EI): m/z 134 (14.8) M^+, 119 (100) M—CH_3, 91 (32.2) tropylium, 77 C_6H_6+.
10. E. N. Manukov, V. A. Chuiko and P. V. Kuz'michkin, *Khim. Prir. Soedin*, **6,** 783 (1979).
11. a) H. Günther, M. Görtlitz and H. Meisenheimer, *Org. Magn. Resonance*, **6,** 388 (1974); b) M. Yamamoto, K. Nishikawa and S. Aono, *Bull. Chem. Soc. Jap.*, **58,** 3176 (1985).
12. K. Alder, K. Kaiser and M. Schumacher, *Ann. Chem.*, **602,** 80 (1957); E. J. Morriconi and C. F. Hummel, *J. Org. Chem.*, **41,** (3583 (1976).
13. E. J. Corey, J. H. Burke and W. A. Remers, *J. Am. Chem. Soc.*, **78,** 180 (1956).
14. J. R. B. Campbell, A. M. Islam and R. A. Raphael, *J. Chem. Soc.*, 4096 (1956).