Pergamon

Tetrahedron Letters, Vol. 35, No. 48, pp. 8935-8938, 1994
Elsevier Science Ltd
Printed in Great Britain
0040-4039/94 $7.00+0.00

0040-4039(94)01958-4

(Z)- AND *(E)*-1,2-DI(1-ADAMANTYL)ETHENE

Alan P. Marchand*, Dongxia Xing, and Simon G. Bott*
Department of Chemistry, University of North Texas, Denton, Texas 76203-0068
Keiichiro Ogawa* and Jun Harada
Department of Chemistry, College of Arts and Sciences, The University of Tokyo,
Komaba, Meguro-ku, Tokyo 153, Japan

Abstract. A highly stereoselective four-step synthesis of (*Z*)-1,2-di(1-adamantyl)ethene (**1a**, overall yield 64%) which employs methyl 1-adamantanecarboxylate (**2**) as starting material is described. Compound **1a** is isomerized quantitatively to the corresponding *E*- isomer (**1b**) by reaction with molecular iodine. Some features of the X-ray crystal structures of **1a** and **1b** are described.

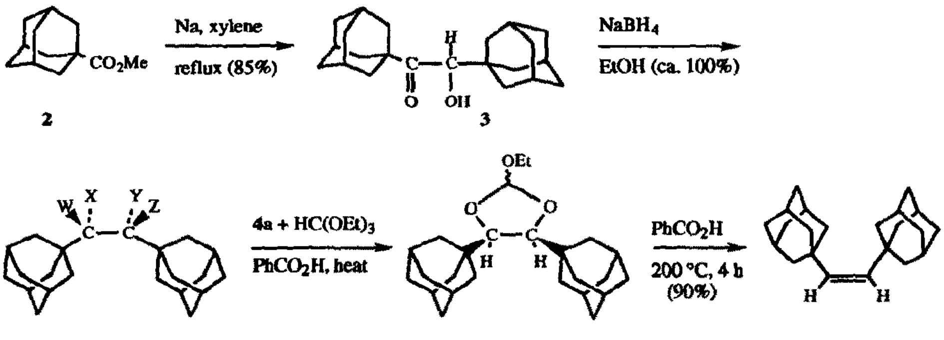
Introduction. There is considerable current interest in the synthesis, structure, and chemistry of sterically congested alkenes.[1,2] Sterically congested 1,2-dialkylated ethylenes might relieve strain caused by nonbonded interactions between the bulky alkyl groups via, e.g., pyramidalization, twisting, and/or stretching of the carbon-carbon double bond.[1,2] Another, less energetic alternative involves in-plane bond angle deformation.[1b] In an effort to further explore the effects of steric crowding on the structure and reactivity of the carbon-carbon double bond in 1,2-disubstituted ethylenes, we have synthesized *(Z)*- and *(E)*-1,2-di(1-adamantyl)ethenes (**1a** and **1b**, respectively).

Syntheses of 1a and 1b. The method employed to synthesize **1a** is shown in Scheme 1. Thus, sodium promoted acyloin condensation of methyl 1-adamantanecarboxylate (**2**) afforded **3**, mp 224-225 °C (lit.[3] mp 224-225 °C) in 85% yield. Sodium borohydride promoted reduction of **3** afforded a mixture of the corresponding *meso* and *d,l* pinacols (**4a** and **4b**, respectively) in essentially quantitative yield. Integration of the ^{1}H NMR spectrum of this mixture revealed the product ratio to be **4a**:**4b** = 15:1. Pure **4a**, mp 273-274 °C,[4] was isolated from this mixture in 93% yield via column chromatography on silica gel by using 2% EtOAc-hexane as eluent.

Conversion of the major product, **4a**, into **1a** was performed via application of the Crank-Eastwood elimination reaction sequence.[5] First, **4a** was reacted with triethyl orthoformate to afford the corresponding cyclic orthoformate ester, **5**, as a mixture of diastereoisomers. Subsequent stereoselctive *cis* cycloelimination[5] was performed by heating **5** with benzoic acid at 200 °C for 4 h, thereby affording **1a**, mp 139.5-140.0 °C,[4] in 90% yield (from **4a**). The structure of **1a** was established unequivocally via single crystal X-ray structural analysis (*vide infra*).

The impressively high degree of stereoselectivity which accompanies $NaBH_4$ promoted reduction of the acyloin (**3**) merits comment. It was suspected that intramolecular hydrogen bonding in **3** might be the primary factor which is responsible for this result. Further evidence to support this suggestion has been obtained via a study of the corresponding reduction of AdC(O)-CH(OAc)Ad (**6**, Ad = 1-adamantyl), which was obtained as a colorless microcrystalline solid, mp 129-130 °C (85%)[4] via reaction of **3** with Ac_2O-dimethylaminopyridine. Since this compound lacks a free hydroxyl group, intramolecular hydrogen bonding cannot influence the preferred ground state conformation of **6**. Unlike $NaBH_4$ promoted reduction of **3**, the corresponding reduction of **6** proceeds with low stereoselectivity, thereby affording a 60:40 mixture of *erythro*- and *threo*- AdCH(OH)-CH(OAc)Ad [**7a** (mp 187.0-187.5 °C)[4] and **7b** (mp 195.5-196.5 °C),[4] respectively; see Scheme 2) in 80% yield. Unequivocal assignment of the structure of **7b** was secured via X-ray structural analysis[6] of a crystalline derivative, AdCH(OH)-CH(OAr)Ad, (Ar = 3,5-dinitrobenzoyl; mp 195-196 °C).[4]

Scheme 1



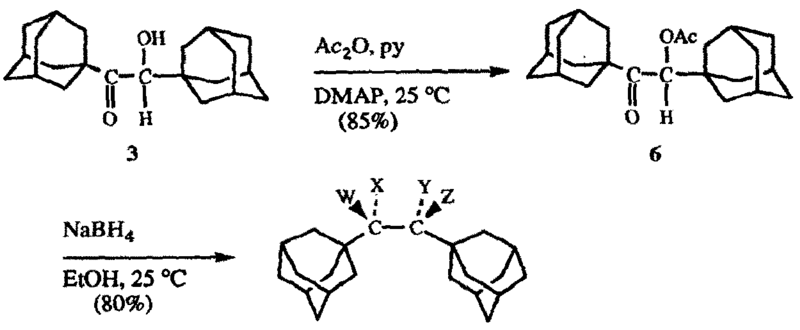
2 **3**

4a: W = Z = OH; X = Y = H *(meso)*
4b: W = Y = OH; X = Z = H *(d,l)*
(product ratio 4a:4b = 15:1)

5 (mixture of diastereoisomers)

1a

Scheme 2

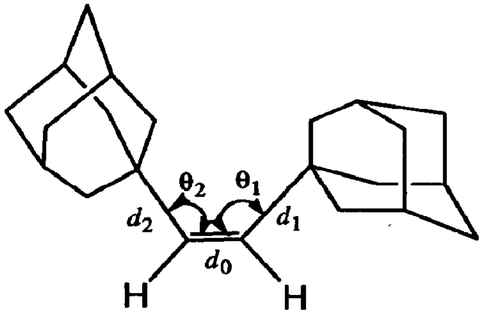


3 **6**

7a: W = OH; X = Y = H; Z = OAc *(erythro)*
7b: W = OH; X = Z = H; Y = OAc *(threo)*
(product ratio 7a:7b = 1.5:1)

Iodine promoted isomerization of **1a**[7] afforded the corresponding *E*-isomer, **1b**, mp >278 °C (dec.)[4] [lit.[2a] mp >260 °C (subl.)], in essentially quantitative yield. Its structure was verified via single crystal X-ray structural analysis (*vide infra*). The driving force for the isomerization of **1a** to **1b** most likely is thermodynamic in origin (i.e., relief of steric strain arising via nonbonded interaction between the *cis* 1-adamantyl moieites in **1a**). This suggestion receives support from the calculated heats of formation of **1a** and **1b**.[8,9]

Some Features of the X-ray Structures of 1a and 1b. Salient features of the X-ray structures of **1a** and **1b** are summarized in Figures 1 and 2, respectively. The *Z*- isomer (**1a**) contains a symmetry plane on which the ethylene moiety rides. The fact that the C=C double bond in **1a** is perfectly planar, irrespective of the severe steric congestion presented by the bulky *cis* 1-adamantyl moities, is probably a consequence of crystal-lographic symmetry constraints. Steric congestion in **1a** is effectively released by widening of the C=C-C bond angles. A similar effect has been observed previously in the X-ray structure of *(Z)*-2,2,5,5-tetramethyl-3,4-diphenyl-3-hexene.[2c] The remarkably large C=C-C bond angles observed in the X-ray structure of **1a** are well reproduced by the results of MM3 calculations[10] which were performed by using the observed molecular struc-ture as the starting structure. The MM3 method also well reproduces the observed length of the "normal" C=C carbon-carbon double bond in **1a**.

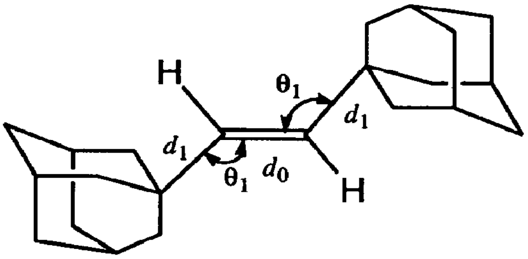


	Observed (X-ray)	Calculated (MM3)[10]
d_0	1.34 (1) Å	1.345 Å
d_1	1.49 (1) Å	1.518 Å
d_2	1.50 (1) Å	1.529 Å
θ_1	139 (1) °	140.1 °
θ_2	138 (1) °	137.7 °

Figure 1. Selected X-ray structure data for **1a**.

The *E*- isomer contains (i) a symmetry plane on which the ethylene moiety rides and (ii) an inversion center in the middle of the ethylene C=C double bond. The C=C-C bond angles are essentially normal, in contrast with those observed for the corresponding bond angles in the X-ray crystal structure of the *Z*- isomer (**1a**).

The length of the ethylene C=C double bond in **1b** is slightly shorter than that which is predicted by the results of MM3 calculations (i.e., 1.314 (5) Å vs. 1.342 Å). This shortening of the C=C double bond is most likely an artifact due to an unresolved disorder in the crystal and/or to a bond vibration which is similar to that reported for (*E*)-stilbenes (for which unusually short C=C bond lengths have been reported in crystals).[11]



	Observed (X-ray)	Calculated (MM3)[10]
d_0	1.314 (5) Å	1.342 Å
d_1	1.500 (4) Å	1.515 Å
θ_1	128.2 (4) °	127.1 °

Figure 2. Selected X-ray structure data for **1b**.

Complete X-ray structural information for **1a** and **1b** will be presented and discussed in the full paper. In addition, the results of studies (currently in progress) of the mechanism of addition of uni- and biparticulate electrophiles to **1a** and **1b** will be reported.

Acknowledgment. Financial support of this study by the Robert A. Welch Foundation [Grants B-963 (A. P. M.) and B-1202 (S. G. B.)], the Office of Naval Research [Grant N00014-94-1-1029] and the Department of the Air Force [Contract F29601-92-K-0018 (A. P. M.)] is gratefully acknowledged.

References and Footnotes

1. *Methods in Stereochemical Analysis, Vol. 3: Stereochemistry and Reactivity of Systems Containing π–Electrons*; Watson, W. H., Ed.; Verlag Chemie International: Deerfield Beach, FL, 1983; 439 pp.

2. (a) Adam, W.; Martinez, G.; Thompson, J.; Yany, F. *J. Org. Chem.* **1981**, *46*, 3359. (b) Gano, J. E.; Park, B. S.; Pinkerton, A. A.; Lenoir, D. *J. Org. Chem.* **1990**, *55*, 2688. (c) Gano, J. E.; Park, B.-S.; Subramaniam, G.; Lenoir, D.; Gleiter, R. *J. Org. Chem.* **1991**, *56*, 4806. (d) Brooks, P. R.; R. Bishop; Craig, D. C.; Scudder, M. L.; Counter, J. A. *J. Org. Chem.* **1993**, *58*, 5900 and references cited therein. (e) Columbus, I.; Biali, S. E. *J. Org. Chem.* **1994**, *59*, 3402.

3. Stetter, H.; Rauscher, E. *Chem. Ber.* **1960**, *93*, 1161.

4. Satisfactory microanalytical data was obtained for all new compounds reported herein. Elemental microanalyses were performed by M-H-W Laboratories, Phoenix, AZ.

5. (a) Crank, G.; Eastwood, F. W. *Aust. J. Chem.* **1964**, 17, 1392. (b) Block, E. In: *Organic Reactions*, Dauben, W. G., Ed., John Wiley & Sons: New York, **1984**, Vol. 30, *pp.* 457-482.

6. Complete X-ray crystallagraphic data for **7b** (S. G. B.) will be given in the full paper.

7. Deter, D. F.; Chu, Y. W. *J. Am. Chem. Soc.* **1955**, *77*, 4410.

8. MOPAC,[9] AM1 Hamiltonian; $(\Delta H_f)_{calcd}$ = -48.8 and -57.1 kcal/mol, for **1a** and **1b** respectively.

9. (a) Dewar, M. J. S.; Zoebisch, E. G.; Healy, E. F.; Stewart, J. J. P. *J. Am. Chem. Soc.* **1985**, *107*, 3902. (b) Stewart, J. J. P. *MOPAC. A General Molecular Orbital Package*, Version 6.0, 1990; QCPE Program No. 455.

10. (a) Allinger, N. L.; Yuh, Y. H.; Lii, J.-H. *J. Am. Chem. Soc.* **1989**, *111*, 8551 8566, 8576. (b) Allinger, N. L.; Li, F.; Yan, L. *J. Comput. Chem.* **1990**, *11*, 848.

11. (a) Ogawa, K.; Sano, T.; Yoshimura, S.; Takeuchi, Y.; Toriumi, K. *J. Am. Chem. Soc.* **1992**, *114*, 1041. (b) Ogawa, K.; Harada, J.; Tomoda, S. *Acta Crystallogr., Sect. B* In press.

(*Received in USA* 26 *July* 1994; *revised* 28 *September* 1994; *accepted* 3 *October* 1994)