273. Propellanes

Part LXXI

Confirmation of Predicted Regiospecificity in *Diels-Alder* Reactions of Certain Propellanes with 4-Phenyl-1,2,4-triazoline-3,5-dione [1])

by **Pnina Ashkenazi**[a]), **Menachem Kaftory**[a]), **Tuğmaç Sayraç**[b]), **Günther Maier**[c]), and **David Ginsburg***

[a]) Department of Chemistry, Israel Institute of Technology, Haifa, Israel

[b]) Middle East Technical University, Ankara, Turkey

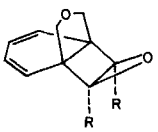
[c]) Institut für Organische Chemie der Universität, Giessen, BRD

(30.IX.83)

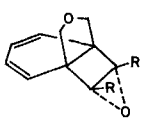
Summary

Two isomeric propellane epoxides **1a** and **1b** containing a cyclohexadiene ring are attacked by the title dienophile as predicted, *syn* to the five-membered ether ring whose α-hydrogens exert less repulsion than the α-epoxy hydrogens or the epoxide oxygen, respectively, of the cyclobutane ring.

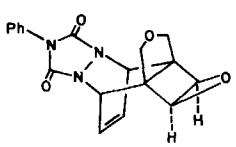
Several propellane substrates prepared by *Maier et al.* [2] could be used to modulate the competition between various rings in exerting larger (or smaller) steric repulsion for the approach of 4-substituted 1,2,4-triazoline-3,5-diones which undergo a *Diels-Alder* reaction with a hexadiene ring. We have studied this problem in many propellanes [3a] and have shown that larger repulsion is exerted, for example, by a cyclopropane ring than by a cyclobutane, a cyclopentane, or a cyclohexane ring in the same propelladiene molecule [3b], by a tetrahydrofuran ring than by a tetrahydrothiophane ring in the same propelladiene [3c], by a cyclobutane ring rather than a 6-membered ring in various oxidation states in the same propelladiene [3d]. From several substrates (compounds **5**–**8** in [2]) that would have been useful for such a competitive study, both configurational isomers of the epoxides were still available (**7b** and **7a** in [2]), herein called *syn*- and *anti*-**1**, respectively, the latter prefixes in keeping with our previous papers [3]. These were treated



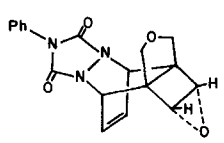
1a R = H
3a R = Me



1b
3b



2a

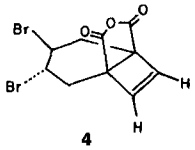


2b

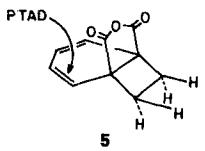
[1]) Part LXX: [1].

with 4-phenyl-1,2,4-triazoline-3,5-dione (PTAD) and suitable crystals were prepared for X-ray structural analysis. ORTEP projections of the PTAD respective derivatives **2a** and **2b** of the *syn*- and *anti*-epoxides **1a** and **1b** are shown (the tetrahydrofuran (THF) ring is our configurational frame of reference). These structures indicate that the substituents on the cyclobutane ring of the propellane whether they be H-atoms or an epoxide ring, exert greater steric repulsion (perhaps electronic repulsion also operates in the *anti*-epoxide **1b**) than does the set of H-atoms in α-position of the O-atom of THF, facing the *syn*-face of the cyclohexadiene ring. It is probably more fortunate that **1a** and **1b** were available rather than the corresponding dimethyl derivatives **3a** and **3b** (**8a** and **8b** in [2]). One may argue that if in **1a** the H-atoms *anti*- to the THF-ring cause PTAD to attack the *syn*-face of the cyclohexadiene ring, the more so in **3a** in which the *anti*-methyl groups would exert *larger* steric repulsion upon the approaching dienophile molecule. Similarly in **3b**, any electronic repulsion by the epoxide O-atom would be greater in **3b** than in **1b** owing to the inductive effect of the methyl groups. We are less certain about the steric portion of such repulsion because we cannot be sure about the overall molecular geometry owing to the angle between the cyclobutane and epoxide planes in **1b** as compared to **3b**. Thus it seems worthwhile to prove this experimentally for the corresponding PTAD derivatives of **3a** and **3b** as well.

If compound **4** (**11**, R = H in [2]) had been reduced and dehydrobrominated to afford **5** we have no doubt that attack by PTAD would occur all the more on the cyclohexadiene face *syn* to the anhydride ring, owing to the attractive secondary orbital interaction operating between the π* carbonyl orbitals (LUMO) and the n_--antisymmetric orbitals of the nitrogen lone pairs (HOMO) in the dienophile [3a, e]. This attractive effect would be buttressed by the steric repulsion of the cyclobutane *endo*-H-atoms upon the dienophile attempting to attack the *anti*-face of the diene [3d].



4



5

We dare make the above prediction in view of experience in this field and success in correctly predicting direction of attack in several additional cases [2] [4].

The X-ray structural parameters will be published elsewhere [5] ORTEP projections of **2a** and **2b** are shown *(Figure)* [2]).

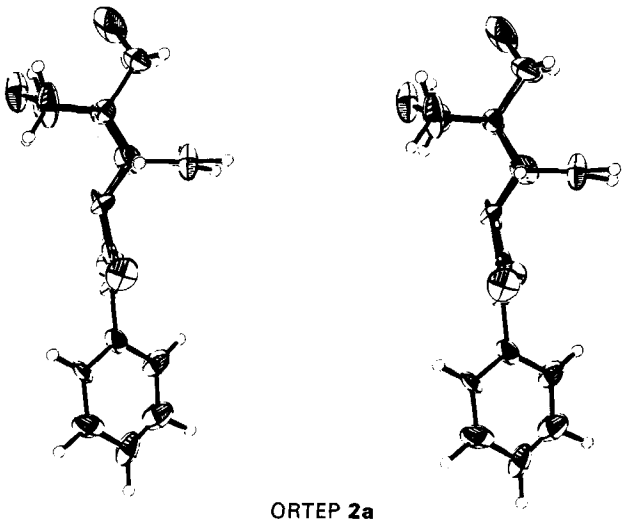
Experimental. – Compounds **2a** and **2b** were prepared in the usual way [2] [2]), had m.p. 222–223° (EtOAc) and 198–200° (EtOAc), respectively. Crystals suitable for X-ray structural determination were also obtained from this solvent.

2a. IR ($CHCl_3$): 1770, 1710, 1410, 1160. ^{1}H-NMR ($CDCl_3$): 7.40 (*s*, 5H, C_6H_5); 6.45 (*t*, 2 vinylic H); 4.95 (*t*, 2H, CHN); 4.10 (*AB*, 4 CH_2O); 3.90 (*s*, 2 epoxide H). MS: 337(15, M^+); 222(12); 177(64); 162(100). M.W.: Calc. 337.1062, Found 337.1017.

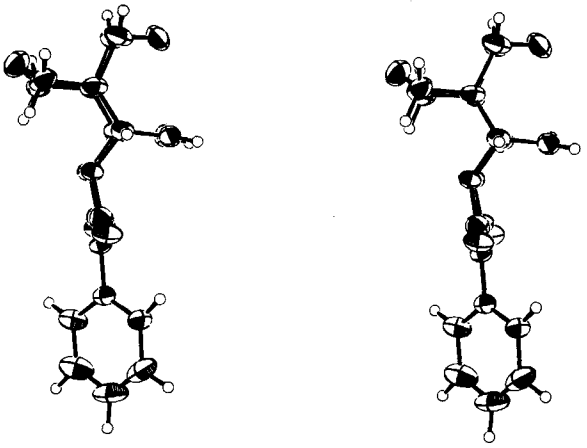
2b. Required purification on prep. SiO_2 plate, $CHCl_3$ eluent, before crystallization. IR ($CHCl_3$): 1770, 1715, 1410, 1150. ^{1}H-NMR ($CDCl_3$): 7.40 (*s*, 5H, C_6H_5); 6.60 (*t*, 2 vinylic H); 5.00 (*t*, 2H, CHN); 3.90 (*s*, 4 CH_2O); 3.60 (*s*, 2 epoxide H). MS: 337(100, M^+); 227(30). M.W.: Calc. 337.1062, Found 337.1070.

---

[2]) The X-ray structures of **2a** and **2b** require reversal of the configurational assignments for the epoxides **7a** and **7b** in [2]. **7a** is the *exo*-epoxide, herein *syn* and **7b** is its *endo*-isomer, herein *anti*.



ORTEP **2a**



ORTEP **2b**

Figure. *ORTEP Projections of* **2a** *and* **2b**

REFERENCES

[1] *S. Bhanumati, P. Ashkenazi & D. Ginsburg*, Helv. Chim. Acta *66*, 2707 (1983).

[2] *G. Maier, T. Sayraç & H.P. Reisenauer*, Chem. Ber. *115*, 2202 (1982).

[3] a) *R. Gleiter & D. Ginsburg*, Pure Appl. Chem. *51*, 1301 (1979); b) *P. Ashkenazi, M. Kaftory, W. Grimme, K. Heger, E. Vogel & D. Ginsburg*, Bull. Soc. Chim. Belg. *88*, 841 (1979); c) *P. Ashkenazi, J. Oliker & D. Ginsburg*, Tetrahedron *34*, 2171 (1978); d) *J. Kalo, J.M. Photis, L.A. Paquette, E. Vogel & D. Ginsburg*, Tetrahedron *32*, 1013 (1976); e) *D. Ginsburg*, Tetrahedron *39*, 2095 (1983).

[4] *K. Kurosawa & J.F.W. McOmie*, Bull. Chem. Soc. Jpn. *54*, 3877 (1981), *cf.* [6].

[5] *M. Kaftory*, unpublished results.

[6] *P. Ashkenazi, M. Kaftory & D. Ginsburg*, Helv. Chim. Acta, in press.