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139. Propellanes. L. Further Support for Control by Secondary Orbital Overlap During *Diels-Alder* Reactions of Certain Propellanes[1]

by **M. Kaftory, M. Peled** and **D. Ginsburg**

Department of Chemistry, Israel Institute of Technology, Haifa, Israel

Dedicated to Prof. Dr. h.c. *A. S. Dreiding* on the occasion of his 60th birthday

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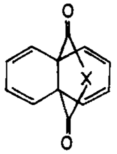
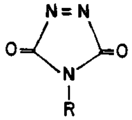
Summary

In contrast to the behavior of 4-substituted-1,2,4-triazoline-3,5-diones which add to the *syn*-face of the cyclohexadiene with respect to the hetero-ring in propellanes of type **1**, dienophiles containing a C,C double bond instead of an N,N double bond add exclusively to the *anti*-face of the same substrates. This supports our thesis that these reactions are controlled by secondary orbital interaction between the N,N dienophiles and the hetero-ring of the substrates, an interaction which cannot exist in the C,C dienophiles.

We have adduced a great deal of evidence for the interpretation that overwhelming *syn* attack of substrates of type **1** with dienophiles of type **2** occurs because of secondary orbital interaction between the CO π^* orbitals (LUMO) of **1** with the antisymmetrical n_- combination of lone pair orbitals. (HOMO) of **2** [1] [2]. One of the ways to test this hypothesis is to use dienophiles which cannot participate in such interaction, *e.g.* those which contain a C,C double bond rather than an N,N one, for the prosaic reason that there are no lone pairs on the pertinent carbon atoms. We have therefore chosen the mono-*Diels-Alder*-adducts of **1** (X=O and X=NMe) with N-phenylmaleimide which we view in this context as 4-phenyl-1,2,4-triazoline-3,5-dione in which $-\dot{N}=\dot{N}-$ is replaced by $-CH=CH-$. We shall not review here the manifold arguments as to the steric requirement of a hydrogen atom as compared to a lone pair orbital. The current view appears to be that, if anything, the steric requirement of the latter is somewhat larger.



1 X=O, NH, NR



2 R=Me, Ph

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[1] Part XLIX: see *P. Ashkenazi, M. Peled, E. Vogel & D. Ginsburg*, Tetrahedron, in press.

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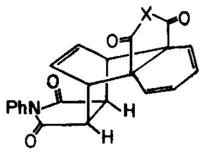
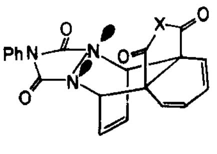


3 X=NMe
5 X=O



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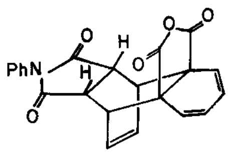

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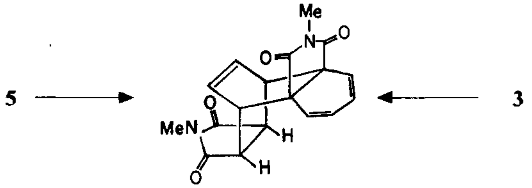
The *N*-phenylmaleimide attacks **1** (X=NMe) from the side *anti* to the methylimide ring and gives **3**, exclusively. The triazolinedione attacks the same propellane substrate exclusively from the side *syn* to the methylimide ring and gives **4**, exclusively.

In addition we have let to react **1** (X=O) in an NMR. tube, with *N*-phenylmaleimide in order to observe the chronology of the formation of the corresponding mono-adduct **5**. Does it form directly or perhaps the isomeric **6** forms first and then by equilibration **6** affords **5**? It is certain that if **6** does form, it is present in too low a concentration to be observed by NMR. Apparently **5** forms directly from the substrate but if **6** does form first, then **5** is the thermodynamically more stable isomer. We have shown that the only product obtained, **5**, has the structure shown by treating it with methylamine. We had hoped to convert the anhydride ring in **5** into the methylimide ring of **3** and thus inter-relate **5** to our crystallographically determined frame of reference. However, we obtained **7** rather than **3** and it was necessary to treat **3** as well with methylamine in order to achieve the desired chemical correlation. Both **3** and **5** afforded **7** whence the certainty that **5** has the same configuration as **3**. We thus have two examples to buttress our interpretation of control by secondary orbital interaction in the case of dienophiles of type **2**.



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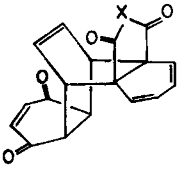
To widen the scope of this support we have let to react **1** (X=O) with *p*-benzoquinone and have determined the structure of the mono-adduct **8** by X-ray crystallography, as shown. Chemical correlation of the two adducts **8** and **9** by treatment with methylamine was not possible because of side reactions. We know



8 X=O
9 X=NMe

from experience that NMR. spectra of *syn*- and *anti*-monoadducts are quite different. The NMR. spectra of **8** and **9** are very similar yet this does not constitute *unequivocal* chemical proof that **9** is of the same configurational family as **8**.

Our interpretation is therefore that the hydrogen atoms on the C,C double bond evidently experience sufficient steric hindrance to make exclusive approach from the *anti*-side of the propellane hetero-ring the preferred mode of attack. And this despite the fact that the spatial requirement of these hydrogen atoms is smaller than that of the lone pairs on the $-\ddot{N}=\ddot{N}-$ groups in the dienophile component leading to **4**, the product of **1** (X=NMe) and **2** (R=Ph). Our results therefore provide significant support to the idea that there is an attractive interaction in the triazolinedione case, the secondary orbital interaction which has been our hobby-horse in recent years.

Thus, we have so far three certain examples to present to Professor *Dreiding* (as a birthday gift) and to others in support of the great efficacy of secondary orbital interaction in controlling the course of the pertinent *Diels-Alder* reactions. The ORTEP photographs of **3** and **8** appear in *Figures 1* and *2*, respectively.

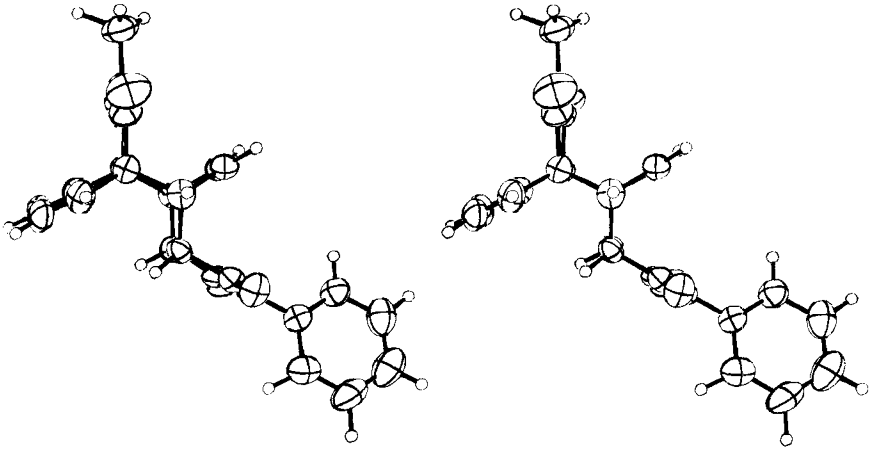


Fig. 1

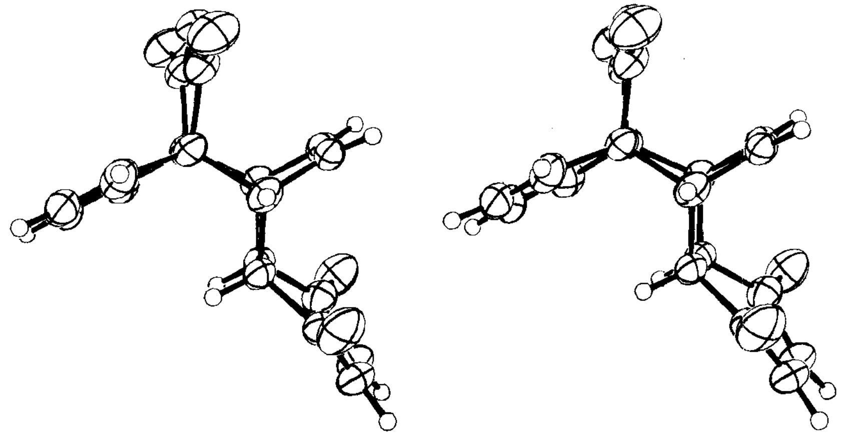


Fig. 2

Experimental Part

Preparation of **5**. A mixture of tetraenic anhydride (**1**, X=O; 210 mg) and *N*-phenylmaleimide (180 mg) in benzene (20 ml) was heated under reflux for 16 h. The solvent was removed and the residue was purified on a prep. silica plate (20×20 cm, *E. Merck*) using hexane/ethyl acetate. The mono-adduct **5** (330 mg; 85%) had m.p. 174-175° (benzene/hexane). (Found: N, 3,14; mol.-wt. 374.0983. $C_{22}H_{15}NO_5$ requires N, 3.75%; mol.-wt. 374.0943). - IR. (KBr): 3100-2900, 1730, 1500, 1400, 1200, 1000-900, 760-700 cm^{-1}. - NMR. (δ-values, $CDCl_3$): 7.4 (*m*, 5 arom. H); 6.7-5.5 (*m*, 6 vinylic H); 3.7 (*m*, 2 allylic H); 3.2 (*m*, 2 COCH). - MS. (*m/e*): 374 (2, M^+); 225 (39); 148 (15); 128 (10); 119 (100); 104 (37).

Preparation of **7**. a) The adduct **5** (330 mg) was heated under reflux with conc. aq. methylamine (10 ml) for 4 h. Evaporation afforded **7** (270 mg; 95%), m.p. 178-179° (benzene/hexane) identical in NMR. spectrum with **7** reported earlier [3] as having m.p. 192° (methylene chloride/ether).

b) Compound **3** [3] treated as above with aq. methylamine afforded **7** in 92% yield, m.p. 176-177° (benzene/hexane), mixed m.p. with product in part. a), 177-178°. The NMR. spectra were superimposable.

Preparation of **8**. A mixture of anhydride **1** (X=O, 200 mg) and *p*-benzoquinone (160 mg) in benzene (20 ml) was heated under reflux for 16 h. Evaporation of solvent afforded an aromatic product (by NMR.; 20 mg) and the mono-adduct **8** (300 mg; 68%) which is unstable on silica. It had m.p. 176-177° (CH_2Cl_2/benzene). (Found: mol.-wt. 308.0677. $C_{18}H_{12}O_5$ requires 308.0684). - IR. (KBr): 3000, 1800, 1780, 1680, 1220, 940 cm^{-1}. - NMR. (δ-values, $CDCl_3$): 6.7 (*s*, 2 COCH=); 6.5-5.6 (*m*, 4 dienic H+2 vinylic H); 3.7 (*m*, 2 allylic H); 3.1 (*m*, 2 COCH). - MS. (*m/e*): 308 (1, M^+); 160 (17); 158 (5); 128 (23).

Preparation of **9**. A mixture of methylimide **1** (X=NMe, 300 mg) and *p*-benzoquinone (155 mg) in benzene (20 ml) was heated under reflux for 16 h. Evaporation afforded **9** (400 mg; 88%), m.p. 192-193° (benzene). (Found: mol.-wt. 321.0991. $C_{19}H_{15}NO_4$ requires 321.1000). - IR. (KBr): 3000, 1780, 1700, 1680, 1430, 1300, 1270 cm^{-1}. - NMR. (δ-values, $CDCl_3$): 6.9 (*m*, 2 COCH=); 6.5-5.5 (*m*, 4 dienic H+2 vinylic H); 3.7 (*m*, 2 allylic H); 3.2 (*m*, 2 COCH); 2.9 (*s*, 3 NCH_3). - MS. (*m/e*): 321 (3, M^+); 162 (27); 161 (65); 160 (100); 131 (8); 128 (22).

REFERENCES

[1] *J. Kalo, E. Vogel & D. Ginsburg*, Tetrahedron *33*, 1177 (1977).
[2] *R. Gleiter & D. Ginsburg*, Pure appl. Chemistry in press and references cited therein.
[3] *M. Korat, D. Tatarsky & D. Ginsburg*, Tetrahedron *28*, 2315 (1972).