Tetrahedron Letters,Vol.24,No.43,pp 4747-4750,1983 0040-4039/83 $3.00 + .00
Printed in Great Britain

"Π-TILTING" IN BRIDGED POLYCYCLIC COMPOUNDS

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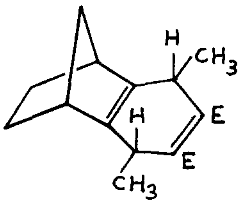
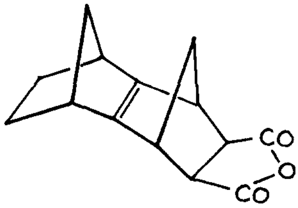
Summary: X-ray analysis reveals non-planarity around the common π-bond in each stereoisomer of a fused norbornene-norcarene system. Products of acid- and of base hydrolysis of halogenated norcarenes with relevance to the occurrence of benzocyclopropenes, are discussed.

Interest in the occurrence,[1,2] magnitude[2] and origins[3] of "π-tilting" in compounds (e.g. **1**)[2] containing a fused bicyclic ring sharing a common double-bond, and similar to that in syn-sesquinorbornene **2**,[1a] with the relevance it has to the phenomena of π-orbital extension, and exo-selectivity in reactions of norbornenes,[4] prompts us to report contrasting results of X-ray crystal structure analysis of two isomeric compounds each having this same structural element but within a different stereochemical environment.

Heating an equimolar mixture of 2,3-bismethylenenorbornene and perchlorocyclopropene ($CC\ell_4$/sealed tube/135°/17-24 hr.) gives a 1:1 cycloaddition product (A) m.p. 85-88° in 71% purified yield.[5] The product is not readily resolved by analytical or preparative TLC; it slowly decomposes at 20-25° leaving a tarry residue from which a single 1:1 cyclo-adduct, **3**[6] m.p. 100-102°, and a 10,11-$HC\ell$ adduct of **3** and/or **4** m.p. 184-186° are isolable.[7] ^{13}C n.m.r. spectroscopic features of product (A) which due to co-incident signals appeared inconsistent with a 1:1 mixture of stereoisomers **3** and **4**, prompted derivatisation as the tetrachlorocyclopentadienone dimethyl acetal adduct for further characterisation. A 92% overall yield of two crystalline 1:1 adducts was obtained, manual separation giving each isomer[8] in a form suitable for X-ray crystal structure analysis: **5**, needles, m.p. 224-225° (and identical to the product of similar cycloaddition with compound **3**) and **6**, diamonds, m.p. 236-238°. Diffraction data are as follows:



1 E = CO_2Me



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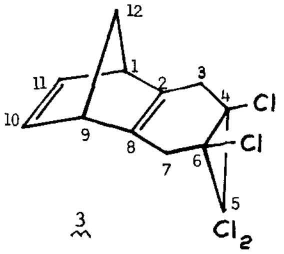

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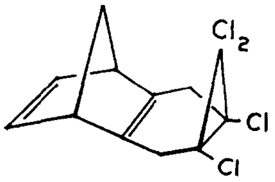


4

$C_{19}H_{16}Cl_8O_2$, F.Wt.560.0. **5**, triclinic, a = 8.045(1), b = 9.572(1), c = 15.705(2)Å, α = 71.40(1), β = 79.39(1), γ = 78.21(1)°. **6**, triclinic, a = 9.601(1), b = 11.104(1), c = 13.027(2)Å, α = 63.69(2), β = 63.94(1), γ = 74.07(1)°. Both **5** and **6** belong to space group P$\bar{1}$ with Z = 2, D_c = 1.671 g cm^{-3}, and V = 1113Å^3. Data were measured and the structures solved by standard methods.[9] R = 0.034 for 3203 data (**5**) and 0.048 for 2722 data (**6**) using full matrix least squares.

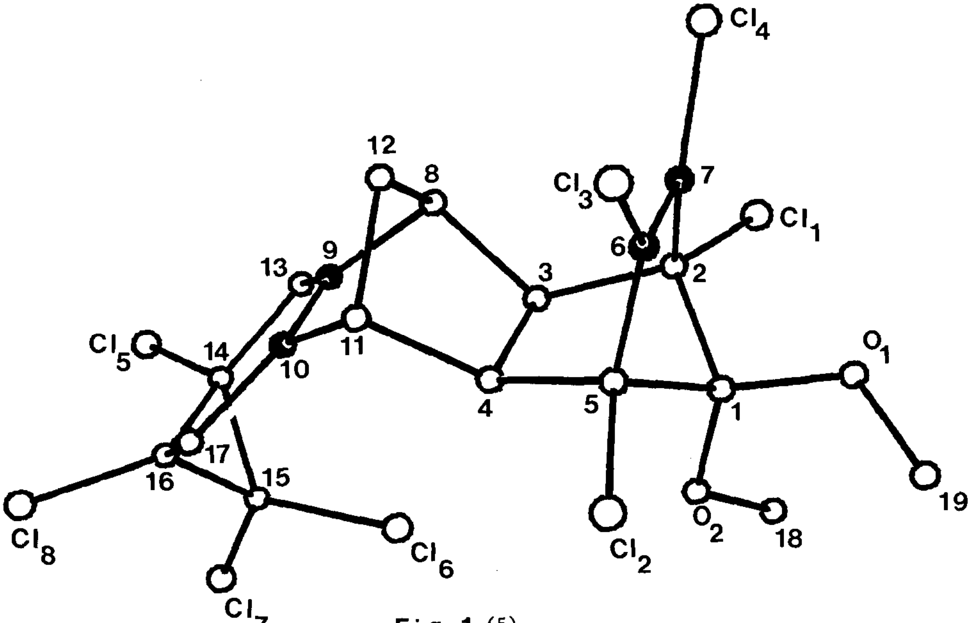


Fig.1 (**5**)

● Denotes olefinic carbon.

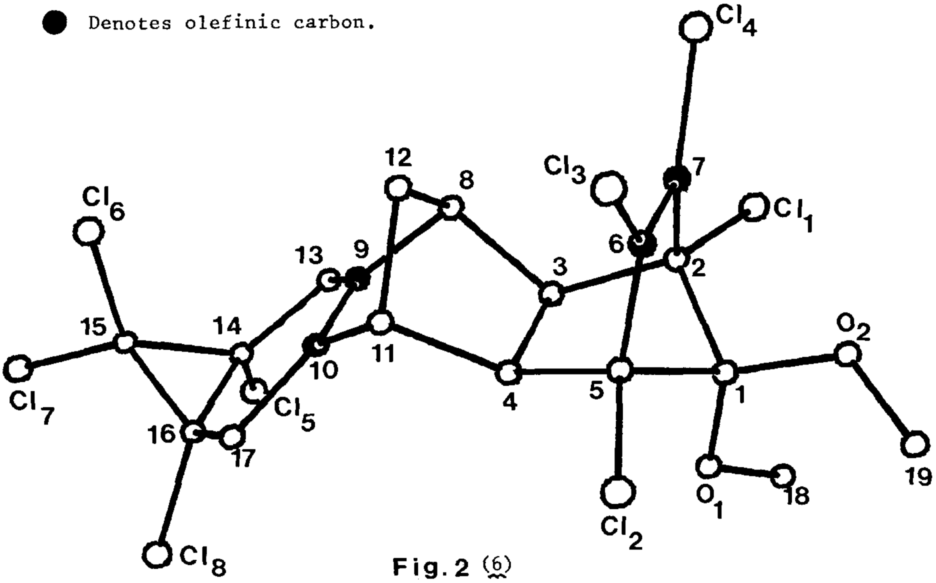
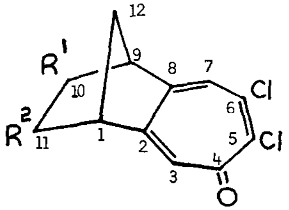


Fig.2 (**6**)

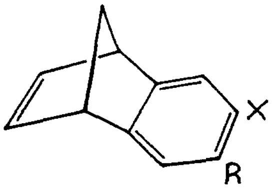
The two structures are illustrated in Figs. 1 and 2. Each molecule is nearly mirror symmetric (excluding the OMe groups), relative dispositions of the two norbornenyl skeletons being identical in the two compounds. Corresponding molecular parameters agree extremely well: bond-lengths to within 0.03 Å and bond angles to within 3°. Torsion angles also correspond, to within 4°, except C(8)-C(9)-C(13)-C(14) and C(11)-C(10)-C(17)-C(16); these are 179° and 180° in compound 6 but each is reduced to 167° in isomer 5. In both compounds the cyclohexene ring is folded about the C(13)-C(17) axis - by 4.2° towards the endo face in 5, and by 7.1° in the opposite direction in 6. Significantly both 5 and 6 exhibit deformation of the C(9)-C(10) double-bond geometry; the dihedral angles between the planes C(8)-C(9)-C(10)-C(11) and C(13)-C(9)-C(10)-C(17) are respectively 7.8° and 6.3°, in each case the "tilt" carrying C(13) and C(17) towards the endo face, and comparable in magnitude to that found for compound 1.[2]

It has been postulated that the "π-tilt" phenomenon is due to consequent reduction of destabilising (closed-shell) interaction between σ-framework and π-bond.[3b] The present instances, where the deformation effect is unambiguously divorced from bridge-CH_2/CCl_2 proximity effects, also supports an electronic explanation.

Acid treatment of product (A) ($^1H_2SO_4$ and $^2H_2SO_4$) gives two minor products, 7 m.p. 93-95° (11%) and 8 m.p. 163-165° (6.6%), the major product being dichlorotropone derivative 9 m.p. 125-127° (37%).[10] For the corresponding deuteriated compounds ^1H/^2H n.m.r. indicates each minor product is specifically mono-deuteriated (∿50% ^2H in each norbornane CH_2 group) with partial vinylic incorporation (55-70% ^2H at C-3,7). Only fractional but methylene-specific deuteriation of the norbornane ring is seen in the major product 9, with significantly reduced vinylic incorporation (∿30% ^2H-C=). Carbocation rearrangement pathways which may account for these facts can be constructed which imply that the minor products derive by initial protonation at the "external" π-face but that the major product results from exo-protonation at the "internal" π-site as the initiation step.



7 R^1=Cℓ R^2=H
8 R^1=H R^2=Cℓ
9 R^1=R^2=H



10 X=CO_2Bu^t R=H
11 X=Cℓ R=CHO

The reactions of 1,6,7,7-tetrahalonorcar-3-enes with alkoxide bases in aprotic media have excited much attention since halogenated benzocyclopropenes can be isolated[11] and are sometimes hydrolysed to alkyl benzoates.[12] Concordantly product (A), treated with $KOBu^t$/DMSO (0.5 hr. 20°), gives ester 10 (35%) and the corresponding methyl thiomethyl ester (2.2%) derived by Pummerer reaction.[13] By contrast, heating (A) with $KOBu^t$/^tBuOH (18 hr. ∿80°) gives chloroaldehyde 11 (5%) as the only isolated neutral product. In our view, this compound must result from base-catalysed elimination in adducts 3 and 4, the bridging $CCℓ_2$ acting as anti-periplanar leaving group from an appropriate boat conformation of the cyclohexene ring or from the near-planar arrangement of the solid state, giving intermediately 4-chloro-5-dichloromethylbenzonornadiene as the progenitor of the chloroaldehyde.[14] This sequence, then nucleophilic attack on aromatic chlorine,[15] with a different final hydrolysis step could therefore also account for alkyl benzoate formation from tetrahalonorcarenes in KOR/DMSO-KOR/THF media.

One of us (A.S.M.) thanks the S.E.R.C. for the award of a postgraduate studentship.

References and Notes

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5. N.m.r. ($CDC\ell_3,\delta$) ^1H: 6.74, 6.61 (m,each 2H) 3.28 (m 4H) 2.7-3.5 (complex m 8H) 1.92 (m 4H) ^{13}C: exo isomer 4-140.81 (C-10,11) 141.83 (C-2,8) 70.14 (C-4,6) 68.92 (C-5) 53,19 (C-1,9) 51.89 (C-12) 34.65 (C-3,7); endo isomer 3 - corresponding signals at 142.56, 142.36, 71.64, 68.78, 53.49, 52.08, 34.41. Satisfactory C,H composition and m/e 294 (M^+) 259 $(M-Cl)^{+\cdot}$ 223 $(M-HCl_2)^{+\cdot}$ with correct $^{35}Cl/^{37}Cl$ abundances.
6. N.m.r. ($CDC\ell_3,\delta$) ^1H: 6.87 (m 2H H-10,11) 3.34 (m 2H H-1,9) 2.7-3.5 (complex m 4H H 3,7) 1.98 (m 2H H-12,12) ^{13}C [with $Cr(acac)_3$]: 142.60 (C-10,11) 142.41 (C-2,8) 71.64 (C-4,6) 68.78 (C-5) 53.54 (C-1,9) 52.13 (C-12) 34.41 (C-3,7) all signals of the correct relative intensity. Found: m/e 295.9527 $C_{12}H_{10}{}^{35}C\ell_3{}^{37}C\ell$ requires 295.9530.
7. N.m.r. ($CDC\ell_3,\delta$) ^1H: 3.84 (m, 1H H-10) 2.6-3.4 (complex m 6H H-3,7 and H-1,9) 1.90 (m, 2H H-12,12) 1.88 and 1.60 (each d and 1H, ^2J 11.5 Hz H-11,11) ^{13}C: 140.03 and 133.18 (quat., C-2,8) 58.00 and 53.78 ($\geqslant$CH, C-1,9) 44.7 ($>CH_2$, C-11) 44.31 ($\geqslant$CH, C-10) 39.61 ($>CH_2$, C-12) 32.37 and 32.03 ($>CH_2$, C-3,7) all with appropriate $^1H/^{13}C$ coupling, quat. C-4,5,6 v. weak. Satisfactory C,H composition and m/e 330 ($M^{+\cdot}$) 295 $(M-Cl)^{+\cdot}$ 269 $(M-C_2H_2C\ell)^{+\cdot}$ with the correct isotopic abundances.
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10. 9: satisfactory C,H composition; m/e 240 $M^{+\cdot}$ 212 $(M-CO)^{+\cdot}$ 184 $(M-CO-C_2H_4)^{+\cdot}$ Nmr ($CDC\ell_3,\delta$) ^1H: 7.17, 7.14 (each s, H-3,7) 3.28 (m, H-1,9) 1.84, 1.60 (each dm ^2J 9.7 Hz, H-12,12) 1.9-2.1 and 1.3-1.5 (each complex m, $-CH_2CH_2-$) all signals with correct relative intensity. In $^2H_2SO_4$-H-3,7 shifted downfield to 8.35, 8.46 with H-1,9 at 3.75.[16a] ^{13}C: 177.87 (CO) 157.38, 153.49 (quat. C-5,6) 143.85 (quat. C-2,8) 129.23, 125.47 (C-3,7) 47.32, 47.20 (C-1,9) 43.19 (C-12) 26.69, 26.51 (C-10,11) with appropriate $^1H/^{13}C$ coupling. ν 1600 vs $cm.^{-1}$ (CO) λ, ($\varepsilon \times 10^{-3}$) (hexane): 234 (12.8) 249 (10) 245 (9.0) 260 (10) 316 (4.5) 326 (4.4) 344 (2.9) 357 (1.6) 365 (0.5).[16b] Similar $^1H/^{13}C$ nmr, i.r. and u.v. for compounds 7 and 8 both having m/e 274 ($M^{+\cdot}$) 184 $(M-CO-C_2H_3C\ell)^{+\cdot}$ with $M^{+\cdot}$ 273.9723 ($C_{12}H_9{}^{35}C\ell_3O$ requires 273.9717).
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(Received in UK 23 August 1983)