Tetrahedron Letters No. 25, pp. 2361-2364, 1971. Pergamon Press. Printed in Great Britain.

ELECTROPHILIC REACTIONS OF 2,3-DICARBOMETHOXY-7-ISOPROPYLIDINEQUADRICYCLANE

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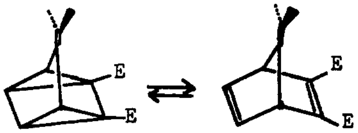
(Received in USA 18 May 1971; received in UK for publication 24 May 1971)

The very strained title compound[1] 1 only decomposes thermally by 2,6:3,5 bond cleavage to give the norbornadiene form 2,[2] in contrast to 1,4-diphenyl-1 and the 7-oxa analogue 3.[3] We have investigated electrophilic reactions of 1 in an effort to obtain cleavage of other bonds in the molecule. Acidic catalysis gave addition of nucleophiles to the 3,5 bond, and predominate formation of the endo ester addition product. Thus treatment of 1 with sulfuric acid or silver salts in methanol gave good yields of the methanol adduct endo ester 4, m. 93-95°, spectral data consistent, and room temperature treatment with hydroiodic acid gave an 82:18 mixture of endo and exo HI adducts; endo (5a) m. 115–116°, exo (5b) m. 90-92°. The proton assignment of the nmr spectra (Table 1) was verified by observing the expected changes when H_3 was replaced by D. The major (115-116°) isomer was assigned as the endo ester 5a on the basis of silver-assisted solvolysis, for it gave immediate precipitation of silver iodide upon treatment with silver perchlorate in methanol, and a 71% conversion to the lactone 6, m. 107-108°, ir 5.56 (lactone), 5.78 (ester). In contrast, the 90-92° ester



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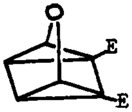

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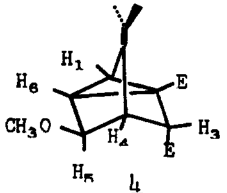

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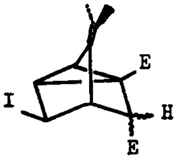
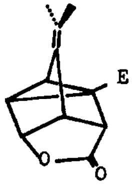


5a: ester endo
5b: ester exo



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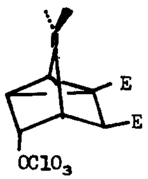

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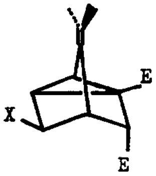
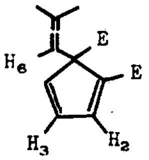


15a: X= $OClO_3$
15b: X= F

gave much slower silver iodide precipitation when reacted under identical conditions, and formed no lactone, indicating an exo configuration for the ester group. Silica gel tlc gave a product which we believe to be a cyclopropylcarbinyl perchlorate (presumably 7) from its nmr spectrum[4] (Table 1).

Electrophilic reagents clearly cause cleavage of the 3,5 bond of 1. It might be hoped that by employing non-nucleophilic anion and solvent, a rearrangement of the incipient C_5 carbonium ion derived from 1 could be observed, instead of just its trapping products. A rearrangement does occur upon treatment of 2 derivatives with electrophilic reagents, although in this case the 1,2 bond cleaves initially, leading to hydroxyfulvene derivatives.[3] Rearrangement was obtained by treating 1 with silver fluoroborate in methylene chloride for two days at room temperature. A 30-60% yield of a new isomer of 1 in addition to 10-20% of the norbornadiene isomer 2 was formed (analysis by nmr), and isolated by crystallization from pentane in about 20% yield. We assign structure 8 to this new compound, m. 42-45°, nmr (Table 2), mass spec P 248; ir 5.74, 5.81, 5.1 (very weak, possibly 5% of the CH intensity); uv (ethanol) 283 ($3.84x10^3$), 252 ($2.76x10^3$), on the basis of the following experiments.



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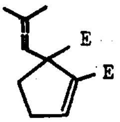

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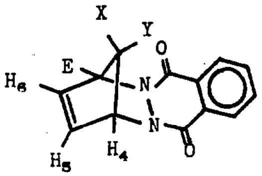


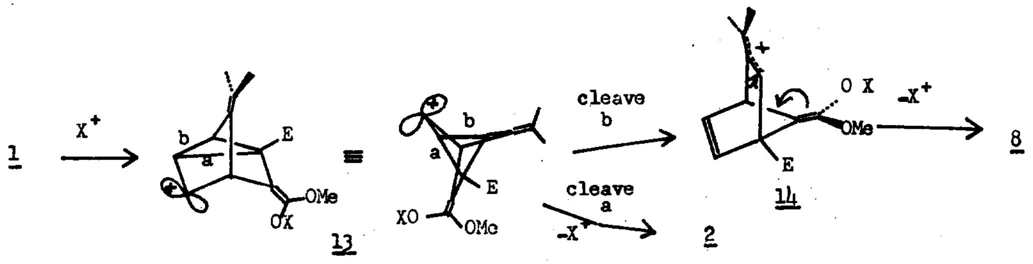
11: X,Y= E,C_3HMe_2

12: X,Y= H,H

Reduction of 8 with diimide in pyridine gave the dihydro compound 9 (mass spec P 250); the nmr (Table 2) demonstrates that a disubstituted double bond adjacent to a vinyl proton had been reduced. The presence of the suspected 1-carbomethoxycyclopentadiene structure in 8 receives conformation upon comparison of the chemical shifts of the ring protons with those of 1-carbomethoxycyclopentadiene (10), as did comparison of the nmr spectra of the respective 2,3-diazaquinone adducts[5] 11 and 12; 11 (partial nmr, major isomer of two obtained as an inseparable mixture), 7.14 (dd, 5,1.6,H_6), 7.00 (dd,5.2,2.5,H_5), 5.52(dd, 2.5,1.6,H_4), 5.58(hept.,3,H_8), 1.75(2d,3,2Me); 12 (partial nmr) 6.98(dd,5.5,1.5

H_6), 6.70 (dd,5.5,2.5H_5), 5.90(m,H_4) Establishment of the 5,5-disubstituted 1-carbomethoxycyclopentadiene fragment leaves only a carbomethoxy group and a C_3HMe_2 fragment to be assigned. The only way consistent with the spectral data is that shown in 8, which uniquely explains the coupling pattern, J=2.9Hz to each of the two non-equivalent methyl groups (for dimethylallene, J=3.03[6]).

Formation of 8 in preference to 2 from the presumed intermediate 13 requires that bond b cleave more easily than a. These bonds are in virtually equivalent positions with respect to the carbonium ion p orbital axis, but cyclopropylcarbonyl delocalization of bond a should be inhibited by the presence of the ester group, while that of bond b is enhanced by the isoprepylidine group. Formation of 8 could then be stepwise, proceeding through 14, which can collapse to the observed product by loss of "X^+".



The initially formed carbonium ion 13 is trapped even by very poor nucleophiles; silver perchlorate gives 15a in addition to 8. The cyclopropylcarbinyl structure 15a was assigned[4] on the basis of the nmr (Table 1), and mass spectrum: P 348, 350 (2.9:1 ratio), i.e. 1+$HClO_4$. Finally, some samples of commercial silver fluoroborate gave the HF adduct 15b, m. 75-76.5°, as a serious contaminant.

A study of the chemistry of 8 is in progress.

Acknowledgement

We thank the National Science Foundation for financial support of this work, including a major equipment grant.

Table 1. NMR Spectra of some Isopropylidine Tricyclane Derivatives

Compound[a]	H_1(dd)	H_3(d)	H_4("quint")	H_5(t)	H_6(dt)
5a	2.63(5,1.2)	2.83(1.6)	3.02(1.4)	4.38(1.5)	2.84(5,1.4)
5b	2.84(5.3,1.4)	2.98(1.6)	3.09(1.6)	4.08(1.5)	2.59(5.3,1.4)
6	2.92(m)		3.25(m)	4.78[b]	2.57(5.4,2)[c]
7	2.95(5,2)	3.39(2)	3.23(2)	4.99(2)	2.43(5,2)
15a	2.75(5,1.5)	2.95(2)	3.24(2)	5.05(2)	2.41(5.2,1.5)
15b	2.79(5.7,1.5)[d]	2.98(m)	3.49(m)	4.77(59,2)[d]	2.27(5.7,1.6)[e]

a. Multiplicities appear in heading J values (Hz) after chemical shifts (from TMS); methyl and carbomethoxy absorptions are not listed.

b. multiplicity ddd, 2.9, 2.2, 0.7; c. multiplicity dd; d. multiplicity dt.; e. multiplicity d of multiplets (ca. quartets).

Table 2. NMR Spectra of Compounds Related to 8

Compound	H_2(t)	H_3,H_4	H_6	=CMe_2(2 d)
8	7.27(2)	6.51[a]	5.59(2.9)[b]	1.62 (2.9)
9	7.02 (2)	2.42(4H)	5.68(3)[b]	1.68 (3)
10	7.28(2)	6.58(m)	----	----

a. 2 overlapping dd, j 5,2. b. multiplicity, heptet.

References

1. The strain energy of quadricyclane itself has been calculated to be 101.1 kcal/mole, P. v. R. Schleyer, J. E. Williams, and R. R. Blanchard, J. Amer. Chem. Soc., 92, 2377 (1970).
2. For a review, see H. Prinzbach, Pure and Applied Chem., 16, 17 (1968).
3. a. H. Prinzbach and P. Vogel, Helv. Chim. Acta., 52, 396 (1969).

   b. A. W. McCulloch, B. Stanovnik, D. G. Smith, and A. G. Innes, Can. J. Chem., 49, 241 (1971).
4. Once the structures were realized, we stopped work on the cyclopropylcarbinyl perchlorates; they should be hazardously explosive.
5. T. J. Kealy, J. Amer. Chem. Soc., 84, 986 (1962).
6. S. Sternhell, Quart. Rev., 23, 236 (1969).