Tetrahedron Vol. 35, pp. 1317 to 1319
Pergamon Press Ltd., 1979. Printed in Great Britain

PROPELLANES—XLVIII

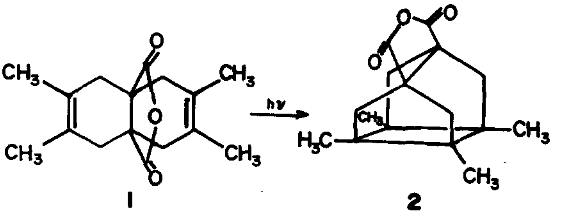
INTRAMOLECULAR [2+2] PHOTOCYCLOADDITIONS OF VARIOUS [4.4.3]PROPELLA-3,8-DIENES†

P. Ashkenazi and D. Ginsburg*
Department of Chemistry, Israel Institute of Technology, Haifa, Israel

(*Received in the UK* 14 *November* 1978)

Abstract—Irradiation of a series of [4.4.3]propella-3,8-dienes which differ in the structure of the 5-membered hetero-ring gives in most cases competing intramolecular [2+2] photocycloaddition yielding cage products along with the intermolecular addition products whose configurations were not determined.

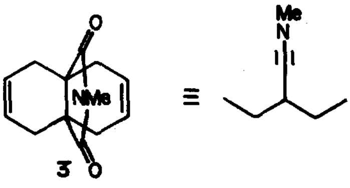
Nine years ago it was reported that the dienic anhydride 1 gave upon irradiation the cage compound 2 in 44% yield but to our knowledge a full paper did not appear after the preliminary report.[1] Since we had available a series of similar 3,8-dienes, albeit unsubstituted by four Me groups, we studied the effect of irradiation upon its members. We had earlier reported the effect of irradiation upon certain isomeric 2,4-dienes[2] and certain 2,4,7,9-tetraenes[3] so that a study of the 3,8-dienes appeared to be in order so that we might adduce additional conformational correlations within the propellane series.[4]



1

2

We have calculated the preferred conformations of some 3,8-dienes using Eu(DPM)$_3$ as a shift reagent instudying their NMR spectra.[4] Although this work indicates specific preferences, e.g. for 3 and 4 as shown in their Newman projections, i.e. *exo–exo* boats and *endo–endo* boats, respectively, for each of the pertinent cyclohexene rings, we realize that there are but small differences in energy between an *exo* and an *endo* boat conformation in the dynamic equilibrium between them. Thus one would not necessarily expect that 4 should undergo more [2+2] *intra*molecular cycloaddition than 3 because of such conformational reasons. In the event, the result was clear-cut since 4 which, on this basis, would be more prone to give a cage product gave neither *intra* nor *inter*molecular product whilst 3 gave both. The latter merely points up the trivial energy barrier to be overcome between 3a and 3b, the latter being the conformation which affords a cage product 5 in 47% yield as compared to 27% *inter*molecular dimer (or dimers).



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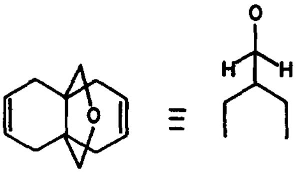

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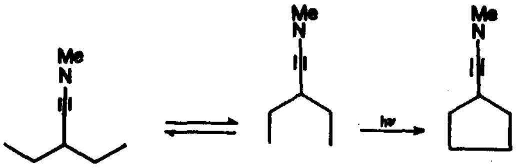

3a 3b 5

The dimers are presumed to contain configurational isomers of both the *syn*- and *anti*-type but these could not be separated into the individual components.

Table 1 summarizes the results of irradiation of a series of [4.4.3] propella-3,8-dienes.

EXPERIMENTAL

IR spectra were measured using a Perkin–Elmer 257 or 237 spectrometer, NMR spectra on a varian T-60 instrument and mass spectra on a MAT-711 (100 eV) and an Atlas CH$_4$ (70 eV) instrument. M.ps are uncorrected.

Experiments were conducted in order to determine the optimal time of irradiation, solvent and concentration. Table 1 includes these optimal conditions. In these conditions of dilution all of the substrates were sufficiently soluble in benzene. Use of MeOH lowers the yield, t-BuOH being a much better solvent. Acetone interacts with the substrate. Use of cyclohexane which contained no benzene afforded no cage product. N$_2$ purging did not influence the yield. O$_2$ purging afforded less cage and more dimer than described in Table 1 and also caused the formation of small amounts of phenol and biphenyl. Under such conditions oxidation of the propellane substrate also occurs as shown below.

Irradiation of dienic methylimide 3. Irradiation was conducted with 6 separate solns of substrate (110 mg) in thiophene-free benzene (150 ml) in quartz tubes using 254 nm lamps in a Rayonette reactor during 24 hr. The product mixture was chromato-

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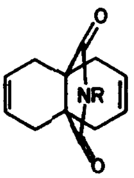
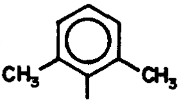
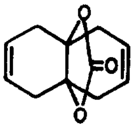
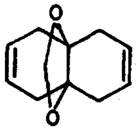
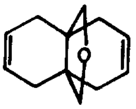
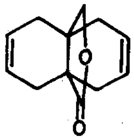
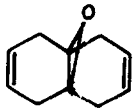
†Part XLVII. I. Landheer and D. Ginsburg, *Rec. Trav. Chim.* in press.

Table 1. Irradiation of 150 mg substrate/200 ml benzene/24 hr at 254 nm/N_2



Composition of product (%)

R	Substrate	Cage product	Dimer	Total
CH_3	14	47	27	88
C_6H_5	20	18	15	53
	16	16	34	66
H	28	8	33	69
	59	14	30	103
	20	16		36
	90	—	—	90
	82	—	—	82
	92	—	—	92

†The balance to make up 100% is intractable polymer.

graphed on preparative silica plates (20 × 20 cm. Kieselgel 60, PF 254, Merck), chloroform as eluant affording (per batch) starting material (90 mg; 14%), cage product (310 mg; 47%) and dimer (175 mg; 27%).

For purposes of comparison, similar irradiation (24 hr) of substrate (307 mg) in thiophene-free benzene (400 ml) with N_2 purging for 1 hr before irradiation gave starting material (14 mg; 5%), cage product (124 mg; 41%) and dimer (105 mg; 35%).

With similar purging with O_2, substrate (154 mg) in benzene (200 ml) gave starting material (40 mg; 26%), cage (30 mg; 20%, dimer + propellanol (70 mg; 46%).

Finally, use of a low pressure Hanovia lamp (450 w) with N_2 bubbling for 24 hr in a quartz tube with 266 mg substrate in 450 ml benzene gave 51 mg starting material (19%), 91 mg cage product (34%) and 100 mg dimer (38%).

The cage product 5 had m.p. 113–114° (benzene–hexane). (Found: C, 71.87; H, 6.91; N, 6.45; M.W. 217.1104. $C_{13}H_{15}NO_2$ requires: C, 71.86; H, 6.99; N, 6.45%; M.W. 217.1102). IR ($CHCl_3$): 1810, 1770, 1690, 1020 cm^{-1}. NMR ($CDCl_3$): τ 6.90 (s, 3 H, NCH_3); 7.05 (br, 4 cyclobutyl H); 8.40 (AB, 8 allylic H). M.S.: M^+, 217 (67); 163 (100); 162 (60); 132 (12).

The corresponding dimer mixture was an oil, soluble in chloroform. (Found: N, 6.95; M.W. 434.2236. $C_{26}H_{30}N_2O_4$ requires: N, 6.45%; M.W. 434.2205). IR ($CHCl_3$): 1805, 1770, 1680, 910 cm^{-1}. NMR ($CDCl_3$): τ 4.15 (m, 4 vinylic H); 6.90 (m, 4 cyclobutyl H); 7.05, 7.10 (s, s, 6 H, NCH_3); 7.20–8.30 (m, 16 allylic H). M.S.: M^+, 434 (1.8); 217 (32); 215 (21); 162 (100); 131 (71).

In a run which was carried out in presence of O_2, the dimeric fraction was extracted with CCl_4. Evaporation of solvent and addition of hexane afforded a hexane-insoluble product which appeared to be the impure allylic oxidation product of the starting material, i.e. the 3,8-dien-2-ol, possibly a mixture of the two possible epimers. (Found: M.W. 233.1048. $C_{13}H_{15}NO_3$ requires:

233.1051). IR ($CHCl_3$): 3480, 1770, 1690 cm^{-1}. NMR ($CDCl_3$): τ 4.10 (m, 4 vinylic H); 6.30 (br, $O\underline{H}$); 7.05 (s, 3 H, $NC\underline{H}_3$); 7.70 + 8.20 − 8.80 (AB superimposed on m, allylic H). M.S.: M^+, 233 (4); 231 (3); 217 (54); 215 (7); 179 (3); 170 (100); 146 (16); 132 (50); 131 (56).

Irradiation of the dienic phenylimide. Irradiation as above of 521 mg substrate in 750 ml thiophene-free benzene, divided into 5 runs gave after separation 102 mg starting material (20%), 93 mg cage compound (18%) and 78 mg dimer (15%).

The cage product had m.p. 226–227° (benzene). (Found: C, 77.29; H, 6.21; N, 5.08; M.W. 279.1328. $C_{18}H_{17}NO_2$ requires: C, 77.39; H, 6.13; N, 5.01%; M.W. 279.1259). IR ($CHCl_3$): 1790, 1720, 1360, 1120 cm^{-1}. NMR ($CDCl_3$): τ 2.50 (s, 5 arom H); 7.05 (br, 4 cyclobutyl H); 8.25 (AB, 8 allylic H). M.S.: M^+, 279 (55); 225 (100); 224 (89).

The dimer was an oil. (Found: M.W. 558.2521. $C_{36}H_{34}N_2O_4$ requires: 558.2518). IR ($CHCl_3$): 1780, 1710, 1390 cm^{-1}. NMR ($CDCl_3$): τ 2.60 (m, 10 arom H); 4.00 (m, 4 vinylic H); 6.80 (m, 4 cyclobutyl H); 7.05–8.50 (m, 16 allylic H). M.S.: M^+, 558 (33); 279 (23); 226 (57); 225 (82); 224 (100).

The product yield could be raised by irradiation of 101 mg of the dienic phenylimide in benzene (100 ml) + t-BuOH (50 ml). Isolation gave aprox equal fractions of cage product and dimer (*ca* 30% each).

Irradiation of the dienic 2,6-*dimethylphenylimide.* Irradiation as above of 509 mg substrate in 750 ml thiophene-free benzene, divided into 5 runs gave after separation 80 mg starting material (16%), 80 mg cage product (16%) and 170 mg dimer (34%).

The cage product had m.p. 216–217° (benzene). (Found: C, 77.69; H, 6.75; N, 4.54; M.W. 307.1544. $C_{20}H_{21}NO_2$ requires: C, 78.14; H, 6.89; N, 4.56%; M.W. 307.1571). IR ($CHCl_3$): 1770, 1720, 1700, 1390, 1170 cm^{-1}. NMR ($CDCl_3$): τ 2.75 (m, 3 arom H); 7.00 (4 cyclobutyl H); 7.80 (s, 6 H, $C\underline{H}_3$); 8.20 (AB, 8 Allylic H). M.S.: M^+, 307 (100); 253 (80); 131 (18).

The dimer was an oil. (Found: $M^+/2$ 307. $C_{40}H_{42}N_2O_4$ requires: M.W. 614). IR ($CHCl_3$): 1740, 1700, 1360, 1150 cm^{-1}. NMR ($CDCl_3$): τ 2.90 (m, 3 arom H); 4.20 (m, 4 vinylic H); 7.00 (m, 4 cyclobutyl H); 7.30–8.70 (m, 16 allylic H). M.S.: $M^+/2$, 307 (100); 252 (15); 131 (32).

Irradiation of the dienic unsubstituted imide. Irradiation as above of 393 mg imide in 600 ml thiophene-free benzene, divided into 4 runs gave after separation 110 mg recovered imide (28%) 30 mg cage product (8%) and 130 mg dimer (33%).

The cage compound was an oil, soluble in benzene–hexane. (Found: M.W. 203.0947. $C_{12}H_{13}NO_2$ requires: 203.0947). IR ($CDCl_3$): 3400, 1770, 1720 cm^{-1}. NMR ($CDCl_3$): τ 7.10 (br, 4 cyclobutyl H); 7.30 (AB, 8 allylic H). M.S.: M^+, 203 (100); 131 (87).

The dimer was an oil. (Found: $M^+/2$, 203. $C_{24}H_{13}N_2O_4$ requires: M.W. 406). IR ($CHCl_3$): 3380, 1770, 1710 cm^{-1}. NMR ($CDCl_3$): τ 4.05 (m, 4 vinylic H); 6.80–8.70 (m, 4 cyclobutyl + 16 allylic H).

Irradiation of the dienic carbonate. Irradiation as above of 393 mg carbonate in 600 ml thiophene-free benzene, divided into 4 runs gave after separation 232 mg recovered starting material (59%), 54 mg cage compound (14%) and 118 mg dimer (30%).

The cage product had m.p. 198–200° (benzene). (Found: C, 68.65; H, 6.09; M.W. 192.0791. $C_{11}H_{12}O_3$ requires: C, 68.73; H, 6.29%; M.W. 192.0787). IR ($CHCl_3$): 1860, 1790, 1160, 1110 cm^{-1}. NMR ($CDCl_3$): τ 7.15 (m, 4 cyclobutyl H); 8.20 (AB, 8 allylic H). M.S.: M^+, 192 (17); 138 (100).

The dimer was an oil. (Found: C, 68.53; H, 6.11; $M^+/2$, 192. $C_{22}H_{24}O_6$ requires: C, 68.73; H, 6.29%; M.W. 394). IR ($CHCl_3$): 1800, 1340, 1060 cm^{-1}. NMR ($CDCl_3$): τ 4.00 (m, 4 vinylic H); 6.70 (m, 4 cyclobutyl H); 7.00–8.40 (m, 16 allylic H). M.S.: $M^+/2$, 192 (9); 170 (68); 138 (32); 133 (100).

Irradiation of the dienic methylenedioxy compound. Irradiation as above of 140 mg substrate in 200 ml thiophene-free benzene afforded after separation 47 mg starting material (34%) and 23 mg (17%) cage compound.

The cage product was an oil. (Found: M.W. 178.0900. $C_{11}H_{14}O_2$ requires: 178.0993). IR ($CHCl_3$): 1310, 970 cm^{-1}. NMR ($CDCl_3$): τ 4.95 (s, 4 H, $C\underline{H}_2O$); 7.30 (m, 4 cyclobutyl H); 8.45 (AB, 8 allylic H). M.S.: M^+, 178 (19); 123 (100).

The dienic ether, the dienic lactone and the dienic epoxide from isotetralin were in the main recovered unchanged upon irradiation as shown in Table 1, also in acetone as solvent.

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