# PROPELLANES-XX

## THE THERMAL BEHAVIOR OF 11,13-DIOXO-12-METHYL-12-AZA[4.4.3]PROPELLA-2,4,7,9-TETRAENE<sup>a</sup>

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Abstract -- The products formed by heating the title compound were isolated and their mode of formation is discussed.

The wealth of isomers on the energy surface of the  $(CH)_{10}$  system, whether they arise thermally or photochemically, whether they are formed in a concerted manner in obedience to the Woodward-Hoffmann rules, or through the intermediacy of radicals in stepwise fashion, or in apparent violation of the rules, has been reviewed recently.<sup>1</sup> We have been studying the behavior of more stable derivatives of the  $(CH)_{10}$  parent compounds. Certain tetraenic propellanes fall within this definition as well as some of their reaction products.<sup>2</sup>

Heating of the title compound 1 slightly above its m.p. caused rapid (intermolecular) dimerization in high yield. A small amount of N-methylphthalimide was also formed.<sup>2c</sup> We still hoped that we could isolate or prove the intermediacy of a [10] annulene derivative. We therefore turned to experiments



employing certain organometallic catalysts<sup>20</sup> and to *intra*molecular thermal conditions. We report herein our results of the latter experiments. We decided to use a static system after preliminary experiments in a flow system indicated that we needed a longer reaction time in order to isolate products. We are fully aware that concurrent with this decision we afford conditions for the occurrence of secondary processes and permit the establishment of equilibria so that there is more of an opportunity to isolate the thermodynamically, rather than the kinetically-controlled products. In our case many of the primary products exit the system due to a process which is irreversible under our reaction conditions, i.e. aromatization.

Our "static" system comprised a sealed tube containing 1 in dibutyl ether (9): acetone (1), maintained at  $300^{\circ}$  for 2.5 hr. Under these conditions the products recorded in scheme 1 were isolated.

We recognize compound 4 as an old friend, having been formed, however, by a sequence which encompasses a photochemical step before the thermal steps in which it is formed:  $1 \xrightarrow{h\nu} 9$  $\xrightarrow{\Delta} 10 \xrightarrow{\Delta} 4.^{2a,e}$ 

Apparently, 4 has been formed in a forbidden reaction if it is indeed formed via the above sequence which includes the intermediate 9. This is reminiscent of the forbiddeness of the formation of cis-9,10-dihydronaphthalene from prebull-valene via a reverse[4+4]cycloaddition.<sup>3</sup>

Another interesting product is 8. We have observed its azulene analog 11 isolated in very low yield in low temperature irradiation of 1 alongside the major product  $9.^{2a}$ 

The product 3 has already been obtained as a minor product accompanying the dimer of  $1.2^{c}$ 

We have studied the thermal behavior of the ether analog of 4 and found it to give, also in a sequence which is at least partly forbidden thermally, the *cis*-9,10-dihydronaphthalene derivative 12 as well as 13, the aromatic analog of  $7.^{2b}$ 

Of course, problems posed by conservation of orbital symmetry may be less worrisome if one were certain that the problematical steps occur through the intermediacy of radicals. The review on the  $(CH)_n$  rearrangements and interconversions<sup>1</sup> emphasizes the problems that still exist because of the experimental difficulties involved. These have tended to lead to less mechanistic proof and to more published speculation. We appreciate that our discussion will sin in the same direction.

It is possible to write different mechanisms for the formation of each product in a thermally allowed

<sup>&</sup>quot;Part XIX, M. Korat, D. Tatarsky and D. Ginsburg, Tetrahedron 28, 2315 (1972)







SCHEME 1







process. The formation of 3 from 1 (or from 10) is possible in a retro-Diels-Alder reaction.<sup>4</sup> The formation of 2 thermally is consistent with a series of two forward Diels-Alder reactions.<sup>2c</sup> The formation of 5 may be explained as a combination of a forward and retro-Diels-Alder reaction as shown

in scheme 2. This proposal apes that already suggested for a very similar case. 3a

The formation of the compounds 6 and 7 at different states of oxidation may be explained either by the allowed often-invoked ring opening of 14 to a [10]annulene derivative  $15^5$  followed by



reclosure of the annulene to afford an isomeric structure as shown in scheme 3. Also shown in this scheme is the analogy employing a thermal Cope rearrangement.<sup>6</sup>

The formation of 4 and 8 may be interpreted in terms of thermal sigmatropic rearrangements or through biradical intermediates. A [1,3] carbon shift occurs more readily upon irradiation because it is of the [1s,3s] type. The thermal reaction is [1s,3a] and for this reason biradical formation may competitively intervene. Nevertheless a number of cases have been proved to be thermal [1s,3a]-C shifts.<sup>7</sup> Scheme 4 shows the analogous formation of 4 and 8.<sup>8</sup>

We are aware of the greater esthetic appeal of



one chart which interconnects all of the products in concerted thermally-allowed processes throughout. Such a presentation would undoubtedly be preferable to the above separate schemes but it is not possible to write such a unified scheme. There is no problem in writing a more esthetic single scheme interrelating our products in a hybrid of concerted processes and stepwise processes involving radicals; such a scheme would include propellanes, prebullvalenes, and bullvalenes as well as derivatives including the parent tetracyclic system in 9. At this stage, however, we do not think it is justified to use additional space in order to present this exercise.

#### **EXPERIMENTAL**

Heating 1 in a flow system (a) Sublimation or injection of 1 into a pyrex tube filled with glass beads at 600° and  $10^{-3}$  mm did not yield results. (b) When the pyrex tube (22 cm long, 24 mm dia) filled with glass beads (3 mm dia) was placed in an oven at 458° and dry  $N_2$  was used as a carrier gas (flow rate 40 ml/min) and 0.5 ml portions of a soln of 1 (1.0 g in 25 ml dry acetone) were injected at time intervals ( $\sim 10$  sec) into the tube, eventually (10-15 min) products were collected (640 mg) in a trap cooled in liquid air. The glass beads were extracted with chloroform, affording mainly dimer 2, m.p. 309-10°2c and unidentified polymer. The product mixture found in the trap was dissolved in CH<sub>2</sub>Cl, and chromatographed on florisil (60-100; 130 g). Elution was carried out with CH<sub>2</sub>Cl<sub>2</sub>-light petroleum (60-70°) starting with pure light petroleum and increasing volume of CH<sub>2</sub>Cl<sub>2</sub> by 2.5 ml/100 ml solvent mixture.

In a typical run the products in order of their elution were 1 (80 mg; 8%); 3 (100 mg; 10%); 5 (78 mg; 8%); 7 (149 mg; 15%); 8 (80 mg; 8%); 6 (63 mg; 6%); a green mixture (67 mg; 7%). The dimer was obtained in 20-30%yield.

Purification of the various fractions that requires this, included crystallization, TLC on neutral alumina and sublimation. Details will be described below.

Below 450° the conversion of 1 into products was appreciably lower.

Heating 1 in a static system. Preliminary experiments



#### **SCHEME** 4

showed that increased dilution, not surprisingly, reduced the extent of dimerization. The optimal temp was found to be within the range  $280-300^{\circ}$ . The experiments were carried out in sealed tubes during 2.5 hr. Raising the time to 24 hr did not significantly alter the composition of the product mixture (NMR of crude).

A solution of 1 (900 mg) was dissolved in a mixture of peroxide-free di-n-butyl ether and acetone (400 ml; 9:1). Aliquots (20 ml) were introduced into evacuated pyrex pressure tubes (45 cm long, int diam 10 mm) and the tubes were sealed and heated for 2.5 hr at  $300^{\circ} \pm 3^{\circ}$ . The color of the soln (previously colorless) turned light green.

After opening of the tubes the solvent was removed at reduced pressure by heating in a bath whose temp was 50°. The green residue (926 mg, contains some butyl ether) was treated with acetone (5 ml). The colorless crystalline 7 (28 mg) precipitated and was removed by filtration.

The residue in CH<sub>2</sub>Cl<sub>2</sub> was chromatographed on florisil (60-100; 130 g) and eluted by CH<sub>2</sub>Cl<sub>2</sub>-light petroleum (60-70°) starting with pure light petroleum and adding 1 ml of CH<sub>2</sub>Cl<sub>2</sub> per 125 ml solvent mixture and removing the final product with pure CH<sub>2</sub>Cl<sub>2</sub>. The products were eluted in the following order: 1 (37.5 mg; 5%), 5 (20 mg; 2%), m.p. 165-166° (chloroform-hexane). Lit.<sup>9</sup> m.p. 166-167°. Its IR spectrum is similar to that recorded.<sup>9</sup> It gave M<sup>+</sup>, m/e 211. We prepared the corresponding anhydride,<sup>10</sup> as in our hands the N-methylimide could not be prepared analogously.<sup>10</sup> Rather the "*bis*-adduct"\* was obtained. A very low yield (25 mg from 10.5 g styrene and



<sup>\*</sup>Mode of formation:

30 g maleic anhydride) of the desired product was obtained, m.p.  $167-167\cdot5^{\circ}$  (EtOH). Lit.<sup>10</sup> m.p.  $168-169^{\circ}$ . IR (KBr): 1838, 1770 cm<sup>-1</sup> (anhydride CO).

Attempted synthesis of 5. A mixture of distilled styrene (0.62 g), freshly crystallized N-methylmaleimide (0.74 g), hydroquinone (10 mg) and dry toluene (10 ml) was heated in a sealed tube (25 cm long, 8 mm diam) at 170-180° for 5.5 hr. The tube contained a clear soln which deposited a yellowish solid after cooling. The supernatant liquid was removed and the yellow solid was triturated with ether. The colorless residue (260 mg) was crystallized from MeOH, affording a product, m.p. 188-190° (13.5%). This was the bis-adduct.\* (Found: C, 66.44; H, 5.50; N, 8.64. C<sub>18</sub>H<sub>18</sub>N<sub>2</sub>O<sub>4</sub> requires: C, 66.24; H, 5.56; N, 8.58%); IR(KBr): 1775, 1700 cm<sup>-1</sup> (imide CO); NMR (acetone-d<sub>6</sub>):  $\tau$  2·10 (t, 1 ArH); 2·72 (m, 3 ArH); 5.72 (d, 1 benzylic H); 6.60 (m, 3 H); 7.07, 7.10 (2s, 6 NCH<sub>3</sub>); 7.70-7.00 (m, 4 H); M.S., M<sup>+</sup>, 326; 268, 254, 214. The NMR spectrum of the anhydride exhibited bands in CDCl<sub>3</sub> (T-60 Varian): τ 1·10 (m, 1 H); 1·58-2·21 (m, 5H). For 5: 1.10 (m, 1 H); 1.65-2.40 (m, 5 H); 6.80 (s, NCH<sub>3</sub>).

This was followed by 3 (120 mg; 13%), m.p. 133° identical by admixture with an authentic specimen and by IR and NMR spectra. Compound 4 (20 mg; 2%), m.p. 205° was similarly identical to an authentic specimen.<sup>2a</sup>

Next to be eluted was 7 (75 mg; 8.5%; total yield 103 mg; 11%), m.p. 239-240°. It was identical to the authentic specimen prepared for comparison.<sup>11</sup> Compound 6 (10 mg; 1%), m.p. 180-181° (EtOH) was assigned its structure on the basis of M<sup>+</sup>, m/e 213; IR(KBr): 1765, 1695, 1660, 1600 cm<sup>-1</sup>; and NMR spectrum (CDCl<sub>3</sub>):  $\tau$  2.24 (d), 2.65 (s), total 5 H; 6.99 (s, NCH<sub>3</sub>); 6.55-7.21 (m, 2 benzylic, 1 allylic H). Compound 8 (20 mg; 2%), m.p. 205° was identical to the authentic specimen prepared

\*See previous page.

for comparison.<sup>12</sup> Finally, the dimer 2 (140 mg; 15%) was identical to an authentic specimen.<sup>2c</sup>

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