SMALL RING COMPOUNDS-II.¹ A STUDY ON [4.3.2]PROPELLAN-7-ONE AND [5.3.2]PROPELLAN-2-ONE

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Abstract – [4.3.2]Propellan-7-one and [5.3.2]propellan-2-one have been synthesized and their particular behavior in the mass spectral fragmentation is discussed.

INTRODUCTION

Many propellanes² containing small rings are of considerable theoretical and synthetic interest.^{3a-f} Further to our investigations, we report the synthesis of [4.3.2]propellan-7-one 1 and [5.3.2]propellan-2-one 2, which are 3-dimensionally fused tri-cyclic ketones having a cyclobutane ring, and, particularly, discuss their fragmentation behavior.



RESULTS AND DISCUSSION

The compound 1, synthesized by photocycloaddition of ethylene with bicyclo[4.3.0]non-1(6)en-7-one 3, has an IR absorption at 1730 cm⁻¹ arising from a saturated 5-membered ring ketone and no NMR absorption in the olefinic region. Moreover, mass spectral and elemental analyses confirm the structure of 1.

In a similar manner, compound 2 was synthesized from [5.3.0]dec-1(7)-en-2-one 4 and ethylene and the structure assigned on the basis of its IR, NMR and mass spectra in addition to a correct elemental analysis.

The mass spectrum of 1 at 14 eV shows a single



intense peak at m/e 136 corresponding to loss of 28 mass unit besides a parent peak at m/e 164, while the spectrum at 70 eV shows complex peaks below m/e 136, whose pattern is nearly the same as that of 3 at 70 eV. These results suggest that at 14 eV molecular ion 5 fragments by cleavage of cyclobutane ring to generate only a metastable fragment ion ascribable to an enone cation 6, while at 70 eV the enone cation 6 undergoes further fragmentation to give various smaller fragments (m/e 108, 94 and 79) (Scheme 1).

The spectrum of 2 at 15 eV shows a single intense peak at m/e 150 besides a parent peak at m/e178. In the spectrum at 70 eV the fragmentation pattern below m/e 150 is similar to that of 4 (m/e121, 108, 93 and 79). Accordingly, the cyclobutane ring is cleaved to an enone cation 7 (Scheme 2).

In order to characterize the fragmentation of 1 as a typical propellanone, we examined the mass spectra of cyclic ketones, such as cyclopentanone 8, *cis*-bicyclo[4.3.0]nonan-7-one 9 and *cis*-bicyclo-[3.2.0]heptan-2-one 10 which constitute the skeleton of 1.

Mono- and bi-cyclic ketones, such as 8^4 and





SCHEME 2



trans-1-decalone,⁵ fragment by α cleavage with or without hydrogen rearrangement, as shown below.



For 9, the α bond cleavage mainly occurs to give cations 11 (m/e 109) and 12 (m/e 81) produced by the process a and a cation 13 (m/e 55) produced by the process b (Scheme 3).

*Unlike the case of 1, no remarkable fragment peak is observed in the mass spectrum at 15 eV.

In the case of 10, as well as 1, it is predicted that the predominant process is probably the cleavage of the cyclobutane ring, which leads to the formation of an enone cation. The mass spectrum of 10 at 70 eV*, however, shows the peaks of m/e 81 and m/e 55 assigned to the α cleavage ions formed by the process a and b respectively. On the other hand, the presence of the peaks of m/e 82, 54, 53 and 39 indicates that the alternative process c takes place by cleavage of the cyclobutane ring to generate a cyclopentenone cation 14⁶ (Scheme 4).

As described, mono- and bi-cyclic ketones fragment by cleavage of α bond whether they have a cyclobutane ring or not. The propellanones 1 and 2, however, fragment exclusively by cleavage of cyclobutane ring to lose an ethylene molecule. In view of these facts, the particular fragmentation behavior of propellanones 1 and 2 is probably due to the presence of a 3-dimensionally fused rings system. In 1 and 2, the cyclobutane ring, having large strain energy, may receive considerable steric repulsion by other two proximate rings. Con-









sequently, the cleavage of cyclobutane ring in primary step occurs predominantly to generate stable enone cations 6 and 7. Further study is in progress and will be reported shortly.

EXPERIMENTAL

All mass spectra were recorded on a Hitachi RMU-6E mass spectrometer and all samples used were purified by a Varian Aerograph 90-P gaschromatograph before measurements.

Bicyclo [4.3,0] non-1(6)-en-7-one 3. The enone 3 was prepared according to the procedure of Dev.^{7.8} Mass m/e (%) 70 eV, 136(92, M⁺), 108(29), 94(86) and 79(100).

[4.3.2] Propellan-7-one 1. A soln of 4.0 g of 3 in 200 ml benzene was saturated with ethylene and irradiated through Pyrex filter using a 500-W high pressure mercury lamp for 20 hr. After removal of the solvent, distillation gave 2.0 g of crude 1, b.p. 54-56.5°/3 mm, which was purified by preparative GLPC for analysis; m.p. 48-50°; IR cm⁻¹, 2950 and 2850 (CH₂), 1730 (CO) and 1445 (CH₂); NMR(CCl₄) τ , 7.40–7.78 (m, 2H), 7.88–8.38 (m, 6H) and 8.38–9.10 (m, 8H); mass m/e (%) 70 eV, 164 (14, M⁺), 136(100, $-C_2H_4$), 108(19), 94(77) and 79(45); 14 eV, 164(62) and 136(100). 2,4-Dinitrophenylhydrazone, m.p. 125.5–126.5° (Found: C, 59.22; H, 6.06; N, 16.29. C_{1.7}H₂₀N₄O₄ requires: C, 59.29; H, 5.85; N, 16.27). The yield of 1 based on 3 used was determined by GLPC analysis to be 50%.

Bicyclo[5.3.0] non-1(7)-en-2-one 4. The enone 4 was prepared according to the procedure of Dev⁹ and Cope.¹⁰ Mass m/e (%) 70 eV, 150(91, M⁺), 121(81), 108(100), 93(54), and 79(63).

[5.3.2] Propellan-2-one 2. A soln of 4 (2.0g) in 100 ml benzene was saturated with ethylene and irradiated through Pyrex filter using 500-W high pressure mercury lamp for 37 hr. After removal of the solvent, distillation gave 0.8g of crude 2, b.p. 77-82%5 mm, which was purified by preparative GLPC for analysis; m.p. 44-46°; IR cm⁻¹, 2950 and 2850 (CH₂), 1690 (CO) and 1450 (CH₂); NMR(CCl₄) τ , 7.25-7.75 (m, 2H), 7.8-8.15 (m, 4H) and 8.2-8.8 (m, 12H); mass m/e (%) 70 eV, 178(36. M⁺), 150(100, -C₂H₄), 121(54), 108(66), 93(49) and 79(56); 15 eV, 178(83) and 150(100) (Found: C, 80.63; H, 10.42. C₁₂H₁₈O requires: C, 80.85; H, 10.18%). The yield of 2 based on 4 used was determined by GLPC analysis to be 30%.

cis-*Bicyclo*[4.3.0]*nonan*-7-one 9. The compound 9 was prepared by Diels-Alder reaction of cyclopent-2-en-1-one with butadiene followed by catalytic hydrogenation.¹¹⁻¹³ Mass m/e (%) 70 eV, 138(66, M⁺), 109(39, $-C_2H_5$), 81(79, -CO) and 55(28, $C_3H_3O^+$).

cis-Bicyclo[3.2.0]heptan-2-one 10. Irradiation of cyclopent-2-en-1-one with excess of 1,2-dichloroethylene provided a stereoisomeric mixture of the adducts.^{14,15} Ketalization and dechlorination of the adducts followed by catalytic hydrogenation gave the ethylene ketal of 10, which was hydrolized to 10 in a usual manner. Analytically pure sample was obtained by preparative GLPC; $n_D^{10-0} 1.4726$; IR cm⁻¹, 2900 and 2850 (CH₂), 1720 (CO) and 1450 (CH₂); NMR (CCl₄) τ , 6-75–7-25 (m, H) and 6-75–8-50 (m, 9H); mass m/e (%) 70 eV, 110(61, M⁺), 82(42), 81(22), 55(100), 54(62), 53(22) and 39(36); 15 eV, 110(100) (Found: C, 76-09; H, 9-28. C₇H₁₀O requires: C, 76-32; H, 9-15).

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