

## Reactions of Helium Tritiide Ions with Gaseous Bicyclo[*n*,1,0]alkanes. Evidence for Gaseous Bicycloalkylium Ions

By Fulvio Cacace,\* Angelo Guarino, and Maurizio Speranza, Laboratorio di Chimica Nucleare del C.N.R., Istituto di Chimica Farmaceutica, University of Rome

The reactivity of the HeT<sup>+</sup> ion from the β-decay of molecular tritium towards bicyclo[2,1,0]pentane, bicyclo[3,1,0]hexane, and bicyclo[4,1,0]heptane has been investigated in the gas phase. The radio gas chromatographic analysis of the labelled reaction products revealed in all the systems studied the formation of a tritiated hydrocarbon retaining the bicyclic structure of the starting substrate. This observation can be rationalized by postulating the intermediacy of the corresponding gaseous bicycloalkylium ion, formed *via* the exothermic triton transfer from the HeT<sup>+</sup> to the organic substrate, and suggests the occurrence of protonated bicycloalkanes in the gas phase. Owing to the considerable exothermicity of the electrophilic attack, a large fraction of the bicycloalkylium ions cannot be stabilized by collision in the pressure range investigated, 100—300 Torr, and undergoes various fragmentation and isomerization processes involving the cleavage of one or more C—C bonds. The mechanistic implications of these processes are discussed, and the gas-phase reactivity of the bicyclo[*n*,1,0]alkanes towards the strong Brønsted acid HeT<sup>+</sup> is compared with their behaviour under the attack of milder electrophiles in solution.

MUCH attention has been given to the correlation of stability and reactivity with structure of bicyclic and polycyclic cations, particularly those involving the cyclopropane ring. Since the ionic chemistry of the bicycloalkanes has been mostly studied in solution, we investigated a typical gas-phase reaction, the triton trans-

fer from a strong, gaseous Brønsted acid, the helium tritiide ion from the β-decay of molecular tritium, to simple bicyclo[*n*,1,0]alkanes, in order to establish the occurrence of gaseous bicycloalkylium ions and to gather information on their stability and reactivity.

Applications of HeT<sup>+</sup> to the study of gas-phase

electrophilic processes have been reviewed,<sup>1</sup> and its reactions with gaseous alkanes,<sup>2</sup> cycloalkanes,<sup>3-5</sup> and arenes<sup>6-8</sup> have been described.

The technique based on the use of HeT<sup>+</sup> appears singularly well suited to the study of strained bicycloalkanes, since it can provide structural information on the products from the rearrangement and isomerization of cyclic systems not normally available from other methods such as mass spectrometry.

#### EXPERIMENTAL

**Materials.**—Bicyclo[2,1,0]pentane was kindly provided by Professor P. G. Gassmann, and its purity was checked by g.l.c. on a 7.5 m  $\beta\beta'$ -oxydipropionitrile column operated at 45 °C and a 3 m Silicone oil column operated at 45 °C. No purification of the sample was required.

Bicyclo[3,1,0]hexane, prepared by the Simmons–Smith reaction,<sup>9</sup> was purified by preparative g.l.c. on a 10 m diisodecyl phthalate column at 147 °C. The sample was analysed on a 3 m diisodecyl phthalate column at 52 °C and a 7.5 m  $\beta\beta'$ -oxydipropionitrile column at 80 °C. Bicyclo[4,1,0]heptane, prepared by the Simmons–Smith reaction, was purified by preparative g.l.c. with a 2 m diisodecyl phthalate column programmed from 50 to 150 °C, and its purity was checked with the following columns: diisodecyl phthalate, 3 m at 90 °C;  $\beta\beta'$ -oxydipropionitrile, 7.5 m at 90 °C; Apiezon L grease, 1.8 m at 92 °C; and Silicone oil, 3 m at 87 °C.

Tritium gas was purchased from CEA (France) and its HT content was determined by gas–solid chromatography<sup>10</sup> on a 5 m Al<sub>2</sub>O<sub>3</sub>–Fe<sub>2</sub>O<sub>3</sub> column at –196 °C. Oxygen and hydrocarbons used for identification in the radio–g.l.c. analysis of the products were commercial samples whose purity was checked by g.l.c.

**Procedure.**—The bicycloalkanes were stored in sealed Pyrex bulbs at 90 °C in the presence of a tracer activity of tritium and of a small mole fraction of oxygen, used as a scavenger of thermal radicals.

The storage conditions were as follows. Bicyclo[2,1,0]pentane, 300 Torr; oxygen, 10 Torr (all pressures measured at 90 °C); T<sub>2</sub>, 2 mCi; volume of the vessels, 250 ml; storage period, 208–261 days. Bicyclo[3,1,0]hexane, 120 Torr; oxygen, 20 Torr; T<sub>2</sub>, 2 mCi; volume of the bulbs, 500 ml; storage period, 223–259 days. Bicyclo[4,1,0]heptane, 100 (and 140) Torr; oxygen, 10 Torr; T<sub>2</sub>, 2 mCi; volume of the vessels, 500 ml; storage period 250–263 days.

The labelled products were analysed as follows. The contents of the reaction vessels were expanded into evacuated Pyrex bulbs of sufficient volume to prevent the condensation of the parent bicycloalkane at room temperature. Aliquot portions of the gaseous mixture were then subjected to radio–g.l.c. with a flow ionization chamber<sup>11</sup> and/or a flow proportional counter<sup>12</sup> for the detection of tritium. The yield of each labelled product was deduced from the

ratio of its activity to the *total* activity of the HeT<sup>+</sup> ions formed within the system during the storage period, as calculated from the initial activity of T<sub>2</sub> and its known decay rate. The tritiated products were analysed on the following columns: T<sub>2</sub> and C<sub>1</sub>–C<sub>3</sub> alkanes, 5 A molecular sieves, 2 m at 90 °C, and 550 DC Silicone oil, 0.5 m, in series

#### Yields of tritiated products from the reaction of HeT<sup>+</sup> ions with bicycloalkanes

Product	Yield (%) <sup>a</sup>
Bicyclopentane	
Bicyclo[2,1,0]pentane	3.8
Methane	16.1
Ethene	0.5
Propene	12.2
2-Methylbut-2-ene	1.4
Cyclopentene	5.7
Unknown A (C <sub>4</sub> ?)	2.3
Unknown B (C <sub>4</sub> ?)	1.2
Unknown C (C <sub>5</sub> ?)	1.8
Total	45.0
Bicyclohexane	
Bicyclo[3,1,0]hexane	1.7
Methane	12.4
Propene	4.0
<i>trans</i> -Pent-2-ene	2.9
1-Methylcyclopentene	0.4
Unknown D (C <sub>4</sub> ?)	5.2
Total	26.6
Bicycloheptane	
Bicyclo[4,1,0]heptane	<i>ca.</i> 6.2
Methane	15.2
Ethene	1.9
Propene	14.2
<i>cis</i> -But-2-ene	2.3
2-Methylbut-2-ene + <i>trans</i> -pent-2-ene	8.1
Total	<i>ca.</i> 47.9

<sup>a</sup> See text.

with AgNO<sub>3</sub>–ethylene glycol, 3 m at 20 °C; C<sub>4</sub>–C<sub>7</sub> hydrocarbons, squalane, 8–13 m, 74–100 °C, and acetylacetone, 12 m at 20 °C; C<sub>5</sub>–C<sub>7</sub> alkenes, cycloalkenes, and bicycloalkanes, 550 DC silicone oil, 0.5–2.5 m, in series with AgNO<sub>3</sub>–ethylene glycol, 1.5–3.5 m, 20–35 °C; bicycloheptane, diisodecyl phthalate, 4 m at 100 °C, and tricresyl phosphate, 4 m at 88 °C.

#### RESULTS

The yields of the tritiated products from the triton transfer to the bicyclic substrates are given in the Table. The *absolute* values listed are affected by relatively large errors, estimated as *ca.* 20%, caused by the uncertainty in the absolute measurement of the T<sub>2</sub> activity introduced into the system. The standard deviation of the yields, calculated from the results of duplicate runs, is considerably lower, (5–10%), except for the yield of bicyclo[4,1,0]heptane

<sup>1</sup> F. Cacace and G. Perez, *J. Chem. Soc. (B)*, 1971, 2089.

<sup>2</sup> F. Cacace, R. Cipollini, and G. Ciranni, *J. Chem. Soc. (B)*, 1972, 84.

<sup>3</sup> H. E. Simmons and R. D. Smith, *J. Amer. Chem. Soc.*, 1959, **81**, 4256.

<sup>4</sup> M. A. Smith and E. H. Carter, 'Tritium in the Physical and Biological Sciences,' International Atomic Energy Agency, Vienna, 1962, vol. 2, p. 121.

<sup>5</sup> F. Cacace, *Nucleonics*, 1961, **19**, 45.

<sup>6</sup> G. Stöcklin, F. Cacace, and A. P. Wolf, *Z. analyt. Chem.*, 1963, **194**, 406.

<sup>1</sup> F. Cacace, *Adv. Phys. Org. Chem.*, 1970, **8**, 79.

<sup>2</sup> F. Cacace, R. Cipollini, and G. Ciranni, *J. Amer. Chem. Soc.*, 1968, **90**, 1122.

<sup>3</sup> F. Cacace, M. Caroselli, R. Cipollini, and G. Ciranni, *J. Amer. Chem. Soc.*, 1968, **90**, 2222.

<sup>4</sup> F. Cacace, A. Guarino, and M. Speranza, *J. Amer. Chem. Soc.*, 1971, **93**, 1088.

<sup>5</sup> F. Cacace, A. Guarino, and E. Possagno, *J. Amer. Chem. Soc.*, 1969, **91**, 3131.

<sup>6</sup> F. Cacace and S. Caronna, *J. Amer. Chem. Soc.*, 1967, **89**, 6848.

whose relatively low volatility prevented a direct determination by radio-g.l.c. and made it necessary to resort to the static counting of the labelled bicycloalkane, isolated and purified by preparative g.l.c., in a Nuclear Chicago Mark I liquid scintillation spectrometer.

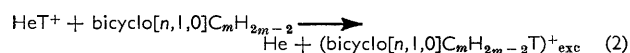
All the tritiated products listed, except four, were identified by comparison of their g.l.c. retention volumes with those of authentic samples on several columns. Though a positive assignment was not made, it appears from their chromatographic behaviour that products, A, B, and D correspond to tritiated C<sub>4</sub> hydrocarbons, and C to a tritiated C<sub>5</sub> hydrocarbon.

#### DISCUSSION

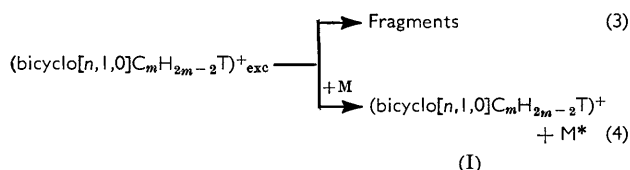
By analogy with conclusions from previous studies, it is suggested that the labelled bicycloalkanes are formed *via* a mechanism whose first step is the exothermic triton transfer (2) from the HeT<sup>+</sup> Brønsted acid from the β-



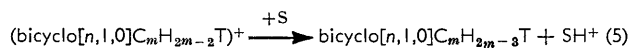
decay (1) of T<sub>2</sub> to the gaseous substrate, yielding an excited bicycloalkylium ion followed by the partial



stabilization [reactions (3) and (4)] of the intermediate in the organic gas and by the quenching of the stabilized



bicycloalkylium ion by the fast, thermoneutral transfer of a proton to another molecule of substrate,<sup>13</sup> which leads to the formation (5) of the tritiated bicycloalkane.



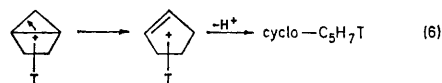
We assume that the tritonated species (I) retains a bicyclic structure, and therefore we regard the isolation of labelled bicycloalkanes as strong evidence for the occurrence of bicycloalkylium ions as discrete intermediates in the gas phase.

This interpretation is supported by recent result on the reaction of the HeT<sup>+</sup> ion with gaseous *cis*- and *trans*-1,2-dimethylcyclopropane, showing that the cyclic products are necessarily formed *via* a mechanism not involving the cleavage of the ring.<sup>4</sup>

Formation of the (M + 1)<sup>+</sup> ions in the protonation of gaseous cyclo- and bicyclo-alkanes with CH<sub>5</sub><sup>+</sup> and C<sub>2</sub>H<sub>5</sub><sup>+</sup> ions in methane at 1 Torr was observed by Field and Munson in their 'chemical ionization' mass-spectro-

metric work.<sup>14</sup> However, while obviously unable to determine the structure of the protonated species, these authors postulated the cleavage of a ring bond as a necessary consequence of the electrophilic attack, thus excluding a cyclic or, respectively, bicyclic structure for the observed (M + 1)<sup>+</sup> ions. Their suggestion was largely based on energetic considerations, and on the behaviour of alkanes larger than ethane towards the attack of gaseous Brønsted acids.

When account is taken of the differences in the energetics of the reaction,<sup>15</sup> the efficiency of collisional stabilization in different gases at considerably different pressures, the much longer time required for the detection of the ions in the mass spectrometer, and the different reaction temperature, it appears that the suggestion of Field and Munson need not conflict with our results, nor with those obtained in the study of the HeT<sup>+</sup> attack on gaseous cycloalkanes.<sup>3</sup> Indeed, several features of the 'chemical ionization' mass spectra showing the effect of structural factors similar to those found in the gas-phase tritiation of cycloalkanes<sup>3</sup> suggest, together with the present results, that at least a fraction of the (M + 1)<sup>+</sup> ions observed by Field and Munson could well retain the original cyclic or bicyclic structure of the substrate. If the yields of the final products reflect the ability of the corresponding tritonated intermediates to survive isomerization and fragmentation, our results clearly indicate that the introduction of a cyclopropane ring in the molecules of cyclopentane and cyclohexane considerably enhances the probability of C-C bond cleavage during the lifetime of the free, gaseous bicycloalkylium ion. Such a finding could be expected, on the grounds of the higher strain undoubtedly present in the bicyclic species than in the corresponding monocyclic ions, and is clearly demonstrated by a comparison of the yields of cyclo-C<sub>5</sub>H<sub>9</sub>T (11.1%) and cyclo-C<sub>6</sub>H<sub>11</sub>T (9.7%)<sup>3</sup> with those of bicyclo[2,1,0]C<sub>5</sub>H<sub>7</sub>T (3.8%) and bicyclo[3,1,0]-C<sub>6</sub>H<sub>9</sub>T (1.7%). The fragmentation of the bicycloalkylium ions appears also highly sensitive to specific structural factors. Thus, the major C<sub>5</sub> product from the gas-phase tritiation of bicyclo[2,1,0]pentane is represented by labelled cyclopentane, whose formation involves the internal cleavage (6) of the cyclopropane ring according to a mechanism that finds a close analogy in the internal cleavage of bicyclo[2,1,0]pentane promoted by acid attack in solutions.<sup>16</sup> On the other hand, no labelled cyclohexene was isolated among the products



from the attack of the HeT<sup>+</sup> on bicyclo[3,1,0]hexane, and the external cleavage of the cyclopropane ring leading to

<sup>13</sup> Similar reactions were frequently observed both in the gas phase and in solution. In addition to refs. 1—6, see (a) V. Aquilanti and G. G. Volpi, *J. Chem. Phys.*, 1966, **44**, 2307; (b) M. Inoue and S. Wexler, *J. Amer. Chem. Soc.*, 1969, **91**, 5730; (c) R. H. Lawrence and R. F. Firestone, *ibid.*, 1965, **87**, 2288; (d) G. A. Olah and R. H. Schlosberg, *ibid.*, 1968, **90**, 2726.

<sup>14</sup> F. H. Field and M. S. B. Munson, *J. Amer. Chem. Soc.*, 1967, **89**, 4272.

<sup>15</sup>  $\Delta H^0$  Value of CH<sub>5</sub><sup>+</sup> is 229 (ref. 14) and that of HeT<sup>+</sup> is ca. 320 kcal mol<sup>-1</sup>; W. A. Chupka and M. E. Russel, *J. Chem. Phys.*, 1968, **49**, 5426.

<sup>16</sup> R. T. La Ronde and Le Roy S. Forney, *J. Amer. Chem. Soc.*, 1963, **85**, 3767; see also R. S. Boikess and M. Mackay, *J. Org. Chem.*, 1971, **36**, 901 for the non-ionic gas-phase reaction of HCl with bicyclo[2,1,0]pentane and bicyclo[4,1,0]heptane.

methylcyclopentene, a major reaction pathway in solution, does not represent a significant reaction channel in the gas phase, as shown by the low yield of tritiated 1-methylcyclopentene from the labelled bicyclohexylium ion.

We regard our results as a direct evidence of the

occurrence of stable bicyclo[ $n,1,0$ ]alkylium ions in the gas phase.

We thank Professor P. G. Gassman (Ohio State University) for bicyclo[2,1,0]pentane.

[2/1380 Received, 15th June, 1972]

---