

10.30 μ^{10}) were absent. Infrared analysis showed that the product consisted of $64 \pm 2\%$ bicyclo[2.2.2]octan-2-ol and $36 \pm 2\%$ axial-bicyclo[3.2.1]octan-2-ol.

The *p*-nitrobenzoate of the deamination product melted at $101.5\text{--}102.5^\circ$ after single recrystallizations from aqueous ethanol and petroleum ether. When this derivative was mixed with bicyclo[2.2.2]octan-2-yl *p*-nitrobenzoate (m.p. $107.6\text{--}108.0^\circ$) the mixture melted at $104.0\text{--}106.5^\circ$.

Bicyclo[2.2.2]octan-2-yl acetate (III, X = OAc) was submitted to the conditions of the deamination (methylamine hydrochloride, sodium nitrite, acetic acid). After saponification pure bicyclo[2.2.2]octan-2-ol, m.p. $220.6\text{--}221.8^\circ$, was isolated in 76% yield. The infrared spectrum was identical with that of an authentic sample.

Hydrolysis of Bicyclo[2.2.2]octan-2-yl *p*-Toluenesulfonate (III, X = OTs).—A solution of 3.00 g. (0.0107 mole) of III (X = OTs), m.p. $54.2\text{--}55.0^\circ$, in 55 ml. of 80% aqueous acetone containing 0.95 ml. (0.0117 mole) of pyridine was heated at 50° for 40 hr. This corresponds to over 99% reaction.¹¹ The solution was cooled and the acetone was allowed to evaporate under an air jet until crystallization of the product began. Water was added, and the mixture was extracted several times with ether. The ether extract was washed with 5% hydrochloric acid, then with water, and dried (magnesium sulfate). Removal of the ether left 1.113 g. (82%) of alcohol. After sublimation (90° , aspirator vacuum) the melting point was $204.4\text{--}205.6^\circ$.

Gas chromatography of the hydrolysis product (ethyl acetate solution) using a 6-ft. column of 20% diglycerol-on-Celite (115°, helium flow rate 16 ml./min.) produced two broad, partially overlapping peaks. The retention times of these corresponded to bicyclo[2.2.2]octan-2-ol (III, X = OH) and axial-bicyclo[3.2.1]octan-2-ol (IVa, X = OH).

The infrared spectrum was similar to that of the product resulting from deamination of 2-aminobicyclo[2.2.2]octane, *i.e.*, a composite of the spectra of III and IVa (X = OH). Bands characteristic of equatorial-bicyclo[3.2.1]octan-2-ol (IVb, X = OH) were not present. Infrared analysis showed that the mixture consisted of $55 \pm 2\%$ III (X = OH) and $45 \pm 2\%$ IVa (X = OH).

Acetolysis of equatorial-Bicyclo[3.2.1]octan-2-yl *p*-Toluenesulfonate (IVb, X = OTs).—A solution of 500 mg. (0.00178 mole) of IVb (X = OTs), m.p. $80.1\text{--}80.8^\circ$, and 155 mg. (0.00189 mole) of sodium acetate in 9 ml. of anhydrous acetic acid was heated at 60° for 9 days (over 99% reaction).¹¹ After cooling, the solution was poured into water and the resulting mixture was extracted with pentane for 24 hr. The pentane was removed by slow distillation and replaced with 25 ml. of 1 *M* methanolic potassium hydroxide.

After the resulting solution had refluxed for 1 hr., it was diluted with water and extracted with pentane for 24 hr. Removal of the pentane followed by sublimation (90° , aspirator vacuum) gave 217 mg. (96%) of equatorial-bicyclo[3.2.1]octan-2-ol (IVb, X = OH), m.p. $176.0\text{--}178.7^\circ$. The infrared spectrum was identical with that of authentic IVb (X = OH).¹⁰

Addition of Acetic Acid to Bicyclo[2.2.2]octene (V).—A solution of 512 mg. (0.00473 mole) of V in 10 ml. of 0.092 *M* *p*-toluenesulfonic acid in acetic acid was refluxed for 6 hr. Then solid sodium acetate was added to the cooled solution and the resulting solution was diluted with water and extracted with pentane for 14 hr. The pentane was removed by slow distillation and replaced with 25 ml. of 1 *M* methanolic potassium hydroxide. After the resulting solution had refluxed for 1 hr., it was diluted with water and extracted with pentane for 24 hr. The pentane extract was washed with two 5-ml. portions of 20% aqueous silver nitrate, then with water, and dried (magnesium sulfate). Removal of the solvent followed by sublimation (90° , aspirator vacuum) of the residual solid gave 360 mg. (59%) of alcoholic material, m.p. $191.5\text{--}193.8^\circ$. After one recrystallization from petroleum ether the melting point was $199.4\text{--}201.5^\circ$.

The infrared spectrum of the product was a composite of those of bicyclo[2.2.2]octan-2-ol (III, X = OH) and axial- and equatorial-bicyclo[3.2.1]octan-2-ol (IVa and IVb, X = OH). The relative intensities of the bands at 11.80μ (III), 10.10μ (IVb) and 10.40μ (IVa) indicated that approximately equal amounts of the three components were present.

Bicyclo[2.2.2]octan-2-yl acetate (III, X = OAc) was submitted to the conditions of the addition reaction. The yield of product, after one sublimation, was 68%, m.p. $194.5\text{--}196.8^\circ$. The infrared spectrum was indistinguishable from that of the alcohol resulting from saponification of the adduct obtained from the addition of acetic acid to V.

Infrared Analysis.—The compositions of the binary mixtures of III and IVa (X = OH) were determined by a previously described method.²⁸ The transmittance of samples was arbitrarily set at 100% at 2.4μ for the calculations. The spectra of 10% carbon disulfide solutions of the samples were determined with a Baird model B double beam infrared spectrophotometer equipped with a sodium chloride prism. The same set of cells was used for all of the determinations. The method was checked with three synthetic mixtures of III and IVa (X = OH). The average difference between the experimental and actual values of the compositions of these three samples was 1.7%.

(28) H. E. Zimmerman, *J. Am. Chem. Soc.*, **78**, 1168 (1956).

[CONTRIBUTION FROM THE RESEARCH AND DEVELOPMENT DEPARTMENT, AMERICAN OIL CO., WHITING, IND.]

Organic Ions in the Gas Phase. VIII. Bicycloheptadiene

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Evidence has been reported that the three C_7H_8 isomers, toluene, cycloheptatriene-1,3,5 and spiro[2.4]heptadiene-1,3, dissociate under electron impact to a common $C_7H_7^+$ species, the tropylium ion. Furthermore, energetics data on toluene and cycloheptatriene have been interpreted as reflecting decomposition to this common product from a common excited state, $C_7H_8^{+*}$, of the molecular ion. Both suggestions have now been extended, on the basis of mass-spectral and energetics evidence, to include a fourth isomer, bicyclo[2.2.1]heptadiene-2,5. This compound exhibits also a major competing dissociation path, which resembles a reverse Diels-Alder reaction and leads to $C_5H_6^+$ and C_2H_2 .

Evidence has been reported that the $C_7H_7^+$ ion formed from toluene under electron impact is the completely symmetrical tropylium ion, and that it results from dissociation of an excited ionized molecule, $C_7H_8^{+*}$, in which the eight hydrogen atoms have almost completely lost identity.^{1,2} Pronounced similarity of the mass spectra of two isomeric compounds cycloheptatriene-1,3,5 and spiro-

[2.4]heptadiene-1,3 to that of toluene has suggested^{2,3} that all three compounds dissociate to give a common $C_7H_7^+$ species—the tropylium ion. For toluene and cycloheptatriene, the energies of the $C_7H_8^{+*}$ intermediates were found equal within experimental error; a single intermediate thus seems common to the two systems.²

If the similar behavior of these isomers arises from identical reaction intermediates, the same behavior might be expected from other C_7H_8 iso-

(1) P. N. Rylander, S. Meyerson and H. M. Grubb, *J. Am. Chem. Soc.*, **79**, 842 (1957).

(2) S. Meyerson and P. N. Rylander, *J. Chem. Phys.*, **27**, 901 (1957).

(3) V. Hanuš, *Nature*, **184**, 1796 (1959).

mers that could give the same intermediates. The isomer bicyclo[2.2.1]heptadiene-2,5 is known to be easily converted thermally to toluene and cycloheptatriene.^{4,5} We therefore examined the mass spectrum of this compound⁶ and determined the energy of formation of the $C_7H_7^+$ ion. The energetics required measuring the heat of combustion of bicycloheptadiene and the appearance potential of the $C_7H_7^+$ ion. The appearance potentials of this ion formed from toluene and cycloheptatriene were measured to establish consistency with previously reported values.^{2,7} Incidentally, the ionization potentials of the three compounds were measured; for bicycloheptadiene, this appears to be the first report of such a measurement.

Experimental

Bicycloheptadiene, purchased from Shell Chemical Corp., was purified by gas chromatography. Each chromatographically separated batch was examined by infrared, ultraviolet and mass spectrometry, and only those containing no detectable impurities were used. Cycloheptatriene² also was purified by gas chromatography. Toluene was an A.P.I. standard hydrocarbon.

Mass-spectrometric measurements were made on a Consolidated model 21-102 instrument. Mass spectra were measured at an electron energy of 70 volts; appearance and ionization potentials, at a repeller voltage of 1.5 volts and an ionizing current of 9 microamperes. Argon (ionization potential: 15.76 e.v.) was used to calibrate the energy scale in some runs; furan (ionization potential: 9.05 e.v.) in others. Results of potential measurements are listed in Table I, with available literature values for comparison.

TABLE I
APPEARANCE AND IONIZATION POTENTIALS

| | $A(C_7H_7^+)$, e.v. | | | $I(C_7H_8)$, e.v. | | | | |
|-------------------|----------------------|----------------|------|--------------------|-----------------|------|------------------|----|
| | This work | Lit. | Ref. | This work | Lit. | Ref. | | |
| Toluene | 11.89 | 11.8 ± 0.1 | 7 | 9.14 | 9.23 ± 0.04 | a | | |
| | 11.87 | | | 9.03 | | | $9.20 \pm .05$ | 11 |
| | 11.71 | | | 9.03 | | | $8.821 \pm .01$ | b |
| | 11.71 | | | 8.91 | | | $8.820 \pm .005$ | c |
| Cycloheptatriene | 10.61 | 10.4 ± 0.1 | 2 | 8.52 | $8.55 \pm .1$ | d | | |
| | 10.38 | | | 8.52 | | | | |
| | 10.38 | | | 8.51 | | | | |
| Bicycloheptadiene | <9.64 | <9.56 | | 8.48 | 8.76 | | | |
| | | | | 8.58 | | | | |
| | | | | 8.58 | | | | |

^a J. D. Morrison and A. J. C. Nicholson, *J. Chem. Phys.*, **20**, 1021 (1952). ^b K. Watanabe, *ibid.*, **22**, 1564 (1954). ^c V. J. Hammond, W. C. Price, J. P. Teegan and A. D. Walsh, *Disc. Faraday Soc.*, **9**, 53 (1950). ^d A. G. Harrison, L. R. Honnen, H. J. Dauben, Jr., and F. P. Lossing, *J. Am. Chem. Soc.*, **82**, 5593 (1960). We are indebted to the authors for access to this paper before publication.

Appearance and ionization potentials were measured by Honig's critical-slope method,⁸ in which the electron energy is selected that corresponds to the point on the semi-log plot of the ionization-efficiency curve at which the slope attains a "critical" value: $(1/2.303)(2/3kT)$. Although this method is quite as arbitrary as other commonly used methods of estimating ionization potentials by electron

(4) W. M. Halper, G. W. Gaertner, E. W. Swift and G. E. Pollard, *Ind. Eng. Chem.*, **50**, 1131 (1958).

(5) W. G. Woods, *J. Org. Chem.*, **23**, 110 (1958).

(6) Drs. V. Hanuš and Z. Dolejšek, of the Institute of Physical Chemistry, Czechoslovak Academy of Sciences, Prague, have informed us that they have also examined the mass spectrum of bicycloheptadiene, as well as that of a fifth isomer, 1-ethinylcyclopentene, and a sixth, 3-ethinylcyclopentene. Their observations on bicycloheptadiene agree with ours reported here. They find that the spectra of 1- and 3-ethinylcyclopentene also resemble closely those of other C_7H_8 isomers.

(7) D. O. Schissler and D. P. Stevenson, *J. Chem. Phys.*, **22**, 151 (1954).

(8) R. E. Honig, *ibid.*, **16**, 105 (1948).

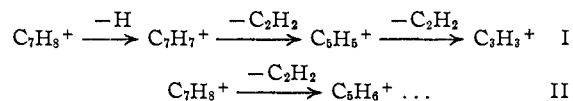
impact,⁹ it appears to give results that are more reproducible and in better accord with spectroscopic values.^{10,11} It seems not to have been used previously to measure appearance potentials of fragment ions,¹² except for one measurement² made in this Laboratory and repeated in the present work.

Contrary to experience with many fragment ions, the $C_7H_7^+$ ions from toluene and cycloheptatriene gave semi-log curves with maximum slopes great enough that the points corresponding to the critical slope were clearly defined. For the $C_7H_7^+$ ion from bicycloheptadiene, the maximum slope was slightly less than the critical slope; thus, we defined only an upper limit close to the appearance potential. Despite the difficulty, we preferred the critical-slope to the vanishing-current method because the tails of all three $C_7H_7^+$ curves were too long to permit confident evaluation of the point of vanishing current.

We are indebted to D. O. Harper and Herschel Hunt of Purdue University for measuring the heat of combustion of bicycloheptadiene. The equipment and procedure have been described elsewhere.¹³ Results of five individual measurements on liquid bicycloheptadiene at 298.16° in kcal. per mole are: -988.96, -990.83, -988.69, -989.37, and -989.24. We used the average value, -989.4, in our computations. A single measurement on toluene, made to check the experimental procedure, gave -934.01 kcal. per mole, in close agreement with the reported value of -934.5.¹⁴

Discussion

The mass spectra of bicycloheptadiene and cycloheptatriene are shown in Fig. 1. In light of the earlier work, the resemblance between them is not surprising, although present knowledge of the reactions involved is too meager to permit predicting it with confidence. The one feature that sharply differentiates the spectrum of bicycloheptadiene is the intense peak at mass 66—second in intensity only to the $C_7H_7^+$ peak at 91. Comparison of the spectra in Fig. 1 suggests that bicycloheptadiene dissociates largely by two competing paths



The first, which appears to be common to all the C_7H_8 isomers studied thus far, presumably involves rearrangement of the parent ion to a seven-membered ring. The second is responsible for the peak at mass 66 but contributes no other very prominent peaks.

Path I.—Path I is defined by three metastable peaks¹⁵



in the spectra of the three C_7H_8 isomers studied in this Laboratory.¹⁶ The ions produced— $C_7H_7^+$,

(9) A. J. C. Nicholson, *ibid.*, **29**, 1312 (1958).

(10) J. D. Morrison, *ibid.*, **19**, 1305 (1951).

(11) I. Omura, K. Higasi and H. Baba, *Bull. Chem. Soc. Japan*, **29**, 501 (1956).

(12) F. H. Field and J. L. Franklin, "Electron Impact Phenomena," Academic Press, Inc., New York, N. Y., 1957, p. 34.

(13) T. Tsuzuki and H. Hunt, *J. Phys. Chem.*, **61**, 1668 (1957).

(14) E. J. Prosen, R. Gilmont and F. D. Rossini, *J. Research Natl. Bur. Standards*, **34**, 65 (1945).

(15) H. M. Rosenstock, A. L. Wahrhaftig and H. Eyring, "The Mass Spectra of Large Molecules. II. The Application of Absolute Rate Theory," University of Utah, Salt Lake City, 1952, pp. 95 ff.

(16) Drs. Hanuš and Dolejšek have observed these metastable peaks in the spectra of all the C_7H_8 isomers included in their studies.

$C_5H_5^+$ and $C_3H_3^+$ —dominate the spectra, accounting for 61%, 63%, and 51% of the total fragmentation intensities of toluene, cycloheptatriene and bicycloheptadiene, respectively. The lower value for bicycloheptadiene reflects competition by other modes of dissociation.

For comparison with the energy of $C_7H_8^{+*}$, the lowest-energy state of the toluene and cycloheptatriene ions capable of dissociating to $C_7H_7^+$ and H, we have estimated the energy of the corresponding species from bicycloheptadiene. This energy was obtained from the thermochemical relationship

$$\begin{aligned}\Delta H_f(C_7H_8^{+*})(g) &= \Delta H_f(C_7H_7^+)(g) + \Delta H_f(H)(g) \\ &= A(C_7H_7^+) + \Delta H_f(BCH)(g)\end{aligned}$$

The heat of formation, $\Delta H_f(BCH)(g)$, of gaseous bicycloheptadiene was found from

$$\begin{aligned}\Delta H_f(BCH)(g) &= -\Delta H_c(BCH)(l) + \\ &\Delta H_f(4H_2O)(l) + \Delta H_f(7CO_2)(g) + \Delta H_{vap}(BCH)\end{aligned}$$

The heat of vaporization, $\Delta H_{vap}(BCH)$, was estimated to be 9 kcal. per mole from the known values 9.08¹⁷ for toluene and 9.25¹⁸ for cycloheptatriene. The value found for $\Delta H_c(BCH)(l)$, -989.4 kcal. per mole, combined with $\Delta H_f(H_2O)(l)$ ¹⁹ and $\Delta H_f(CO_2)(g)$ ¹⁹ gives 66.8 kcal. per mole or 2.90 e.v. per molecule for the heat of formation of bicycloheptadiene. The upper limit found for the appearance potential of $C_7H_7^+$ is 9.6 e.v. Thus, the energy of $C_7H_8^{+*}$ from bicycloheptadiene must be slightly less than 12.5 e.v.—in good agreement with the 12.3 e.v. arrived at by the same computation for both toluene and cycloheptatriene.²

Path II.—The high intensity at mass 66 indicates that path II contributes significantly to the decomposition of bicycloheptadiene ion. Empirically, this ionic reaction resembles the reverse Diels–Alder reaction of bicycloheptadiene from which cyclopentadiene and acetylene are obtained.^{4,5} A similar reverse Diels–Alder reaction can account for major features of the mass spectra of bicyclo[2.2.1]heptene-2²⁰ and dicyclopentadiene.²¹ $C_5H_6^+$ is the most abundant ion in both spectra, which strongly resemble each other and that of cyclopentadiene.^{21,22} By analogy with the thermal decomposition product, the $C_5H_6^+$ ion may indeed have a cyclopentadiene structure; however, without further evidence, other stable ionic structures—ethenylcyclopropene or even conjugated acyclic structures—are possible.

Whatever its structure, further dissociation of $C_5H_6^+$ probably accounts for the greater intensity of the $C_3H_3^+$ ion in the spectrum of bicycloheptadiene than in those of toluene or cycloheptatriene;

(17) F. D. Rossini, *et al.*, "Selected Values of Physical and Thermodynamic Properties of Hydrocarbons," Carnegie Press, Pittsburgh, Pa., 1953, p. 443.

(18) H. L. Finke, D. W. Scott, M. E. Gross, J. F. Messerly and G. Waddington, *J. Am. Chem. Soc.*, **78**, 5469 (1956).

(19) D. D. Wagman, J. E. Kilpatrick, W. J. Taylor, K. S. Pitzer and F. D. Rossini, *J. Research Natl. Bur. Standards*, **34**, 143 (1945).

(20) Unpublished spectrum of a sample furnished by C. J. Norton (see S. Winstein, M. Shatavsky, C. Norton and R. B. Woodward, *J. Am. Chem. Soc.*, **77**, 4183 (1955)).

(21) American Petroleum Institute Research Project 44, "Catalog of Mass Spectral Data," Carnegie Inst. of Technology, Pittsburgh, Pa., 1947–1959.

(22) R. H. Roberts and S. E. Johnsen, *Anal. Chem.*, **20**, 690 (1948).

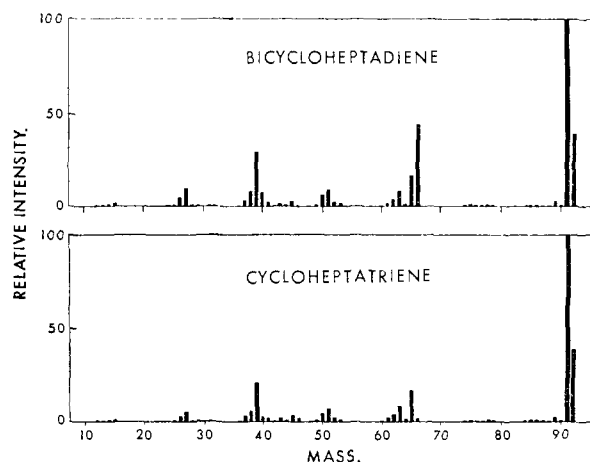


Fig. 1.—Mass spectra of C_7H_8 isomers.

the intensity of $C_3H_3^+$ is exceeded only by that of $C_5H_6^+$ in the spectra of bicycloheptene and dicyclopentadiene, and by those of $C_5H_6^+$ and $C_5H_5^+$ in the spectrum of cyclopentadiene.

Conclusion

From the virtual identity of the energies of $C_7H_8^{+*}$ formed from the three isomeric compounds the earlier suggestion² that toluene and cycloheptatriene ions dissociate to $C_7H_7^+$ *via* a common state can now be extended to include bicycloheptadiene. The same state probably is involved in the dissociation of spiroheptadiene and any other C_7H_8 isomers that may be found to dissociate by path I. If so, the appearance potential of $C_7H_7^+$ for any such isomer then can be used to estimate the heat of formation of that isomer.

A parallel may be drawn between reactions of bicycloheptadiene induced by electron impact and by heat. Easy thermal isomerization to a mixture of toluene and cycloheptatriene^{4,5} implies the existence of non-ionic states common to at least pairs of isomers—and perhaps to all three.²³

All the C_7H_8 isomers examined thus far show $C_5H_6^+$ ion, although in markedly different yields. This ion accounts for 15% of the total fragment-ion intensity in the spectrum of bicycloheptadiene, as contrasted with 0.4% and 0.8% in those of toluene and cycloheptatriene. Possibly the formation of $C_5H_6^+$ ion from all of these compounds proceeds through a common excited $C_7H_8^{+*}$ ion, just as tropylium ion forms from them. The structure of the parent isomer then would determine only the distribution of decomposition between the available common paths and not uniquely different paths. If decomposition by path II is related mechanistically to reversion of a Diels–Alder adduct, then the parent ion from bicycloheptadiene, which initially must have the adduct configuration, might lead to a large yield from this path relative to product yields from competing decomposition paths. Parent $C_7H_8^+$ ions from other isomers, which would have to rearrange prior to formation of $C_5H_6^+$, would give lower relative yields of $C_5H_6^+$.

(23) The referee has advised us that studies just completed in his laboratory show that the thermal isomerization of bicycloheptadiene proceeds first to cycloheptatriene and then to toluene, and that the two products are not formed from a common non-ionic intermediate.