

amidst the BA states. It is probable that the reason the singlet does not follow the triplet is that there is a 1A_1 , CT state, lying slightly lower in energy than the 1L_a state.

It is thus clear that a quantitative account of the effect of twisting perturbations on the spectra of dimethylanilines requires an approach such as Mataga's¹⁷ which includes BA-CT interaction. Further, we conclude that the sterically hindered

(17) N. Mataga and S. Mataga, *Bull. Chem. Soc. of Japan*, **32**, 600 (1959). See also T. E. Peacock, *Molec. Phys.*, **3**, 453 (1960).

anisole system provides a better test of twisting theories formulated for BA states.

Summary

The *o* and *o,o'*-alkyl substituted anisoles yield the "normal" steric effect on substituted benzene spectra, whereas the much quoted "classical" case of *o,o'*-alkyl substituted N,N-dimethylanilines is actually anomalous, due to interaction of the 2500 Å., CT state with the BA states. The dimethylaniline 2500 Å., CT state is assigned as 1A_1 from the anomalous behavior of the ${}^1L_a \leftarrow {}^1A$ band.

[CONTRIBUTION FROM THE SPECTROSCOPY LABORATORY AND DEPARTMENT OF CHEMISTRY, MASSACHUSETTS INSTITUTE OF TECHNOLOGY, CAMBRIDGE, MASSACHUSETTS]

Synthesis and Vibrational Spectrum of Bicyclo[3.2.0]hepta-2,6-diene¹

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Bicyclo[3.2.0]hepta-2,6-diene was prepared by pyrolysis of the S-methyl xanthate of *exo*-bicyclo[3.2.0]hept-2-en-6-ol, while pyrolysis of the corresponding *endo*-xanthate gave predominantly tropilidene. The xanthates were prepared from the corresponding alcohols which were prepared by lithium aluminum hydride reduction of bicyclo[3.2.0]hept-2-en-6-one. Infrared and Raman spectra of the bicyclic diene and related compounds are reported. The spectra support the bicyclic structure, as does the fact that the diene is readily isomerized thermally to tropilidene.

In order to decide whether bicyclo[3.2.0]hepta-2,6-diene (VII) was a possible structural basis for the interpretation of the vibrational spectrum of tropilidene,^{3,4} the synthesis of the bicyclic hydrocarbon was undertaken. Since Dryden⁵ had reported that tropilidene is the product of the solvolysis of the methane sulfonate of bicyclo[3.2.0]hept-2-en-6-ol (V), presumably because of rearrangement of the cyclobutyl carbonium ion, a preparative method which does not involve a carbonium ion intermediate was sought.

An attempt was made to prepare the diene by pyrolysis of the quaternary ammonium hydroxide IV (Fig. 1). Little or no hydrocarbon could be produced by this route, presumably because of the difficulty of forming the quaternary ammonium hydroxide. E. Vogel⁶ reported the preparation of a bicyclo[3.2.0]heptadiene, n^{20}_D 1.4751., in low yield by this route. Vogel also reported that an attempt to prepare the N,N-dimethylamine by the Eschweiler-Clark procedure gave almost entirely the monomethylamine, which supports the above presumption that the difficulty in this route lies in incomplete methylation due to steric hindrance about the nitrogen atom.

Accordingly, it was decided to prepare the diene by pyrolysis of the corresponding ester. Bailey, Cunov and Nickolas⁷ showed that the high temperature required for the pyrolysis of acetates

(about 450°) causes thermal cleavage of the cyclobutane ring, and Roberts and Sauer⁸ found that the pyrolysis of the S-methyl xanthate of cyclobutanol gives only butadiene. However, olefins which contain a cyclobutane ring have been prepared by pyrolysis of the methyl xanthate,⁹ and it has been proposed by Vogel¹⁰ that 3,4-dialkylcyclobutenes are more stable to thermal cleavage than other cyclobutenes. It was therefore decided to try the xanthate pyrolysis.

Bicyclo[3.2.0]hept-2-ene-6-one (I) was reduced with lithium aluminum hydride and upon careful distillation, the reduction product was separated into the pair of epimers Va and Vb. The configuration of these alcohols was assigned as shown in Fig. 1 because Va is lower boiling than Vb, forms the phenylurethane more slowly than Vb, and the infrared spectrum (Fig. 4) shows less intermolecular hydrogen bonding than that of Vb. The S-methyl xanthates were prepared and pyrolyzed by heating to reflux in a distillation flask.

The *endo*-xanthate VIa gave an 85:15 mixture of tropilidene and a second hydrocarbon, and the *exo*-xanthate VIb gave a 15:85 mixture of tropilidene and the same second hydrocarbon. Pyrolysis of the *exo*-isomer occurred at 230-235°, and the total yield of hydrocarbon product was 68%, while the *endo* isomer required a temperature of 300°, and the yield of hydrocarbon product was 44%.

The second hydrocarbon absorbed two molar equivalents of hydrogen to form bicyclo[3.2.0]heptane. It showed only end absorption in the ultraviolet and had infrared and Raman frequencies at 1605 and 1560 cm.⁻¹. Thus the hydrocarbon must be either VII or VIII, and the spectroscopic data indicate that VII is the preferred structure.

(1) This work is a portion of the Ph.D. thesis of M. V. Evans, Massachusetts Institute of Technology, January, 1958.

(2) Department of Chemistry, University of Wisconsin, Madison 6, Wisconsin.

(3) M. V. Evans and R. C. Lord, "Abstracts of Papers," 130th Meeting, American Chemical Society, Atlantic City, N. J., September 16, 1956, p. 41-R.

(4) M. V. Evans and R. C. Lord, *J. Am. Chem. Soc.*, **82**, 1876 (1960).

(5) H. L. Dryden, *ibid.*, **76**, 2841 (1954).

(6) E. Vogel, private communication to Professor A. C. Cope.

(7) W. J. Bailey, C. H. Cunov and L. Nickolas, *J. Am. Chem. Soc.*, **77**, 2787 (1955).

(8) J. D. Roberts and C. W. Sauer, *ibid.*, **71**, 3925 (1949).

(9) B. A. Kasansky, *Ber.*, **69B**, 950 (1936).

(10) E. Vogel, *Angew. Chem.*, **66**, 640 (1954).

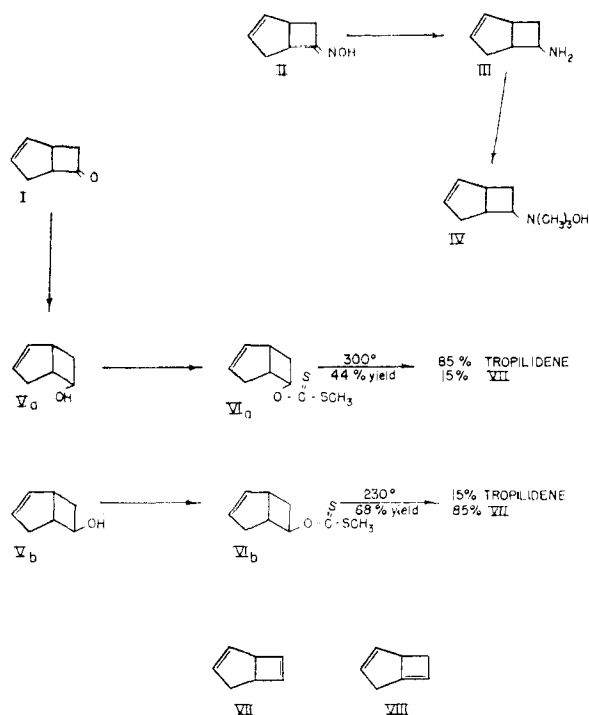


Fig. 1.—Synthetic route to bicyclo[3.2.0]hepta-2,6-diene.

The hydrocarbon rearranged exclusively to tropilidene upon pyrolysis, and since it is predicted that VIII would cleave to give 2-vinylcyclopentadiene, VII was assigned as the correct structure.

TABLE I
RAMAN SPECTRUM OF BICYCLO[4.2.0]OCT-7-ENE

Frequency, cm. ⁻¹	Estimd. intensity	Frequency, cm. ⁻¹	Estimd. intensity
230	4	1019	4
327	3	1024	2
381	6	1058	10
438	2	1097	1
487	1	1115	2
524	1	1141	6
619	1	1172	0
707	3	1185	0
723	6	1288	1
749	3	1309	2
761	3	1336	1
773	3	1441	5
790	8	1556	9
831	6	1561	9
845	1	1565	4
862	1	2849	6
878	7	2864	7
915	2	2916	10
935	3	3037	8
985	6		

Discussion of Spectra. Infrared spectra of bicyclo[4.2.0]oct-7-ene, bicyclo[3.2.0]hept-2-ene and bicyclo[3.2.0]hepta-2,6-diene are shown in Fig. 2, and the Raman spectra of these compounds and bicyclo[3.3.0]oct-2-ene are shown in Tables I to IV. Infrared spectra of bicyclo[3.2.0]hept-2-ene-6-one and *exo*- and *endo*-bicyclo[3.2.0]hept-2-ene-6-ol are shown in Figs. 3 and 4.

TABLE II
RAMAN SPECTRUM OF BICYCLO[3.2.0]HEPT-2-ENE

Frequency, cm. ⁻¹	Estimd. inten.	Polariz.	Frequency, cm. ⁻¹	Estimd. inten.	Polariz.
256	6	dp?	1106	9	p
358	4	p	1159	2	p
448	5	p	1172	3	p
630	4	p	1223	3	dp?
699	4	p	1236	2	p
724	3	p	1279	3	dp?
765	3	dp	1298	1	p
839	5	p	1351	0	p
866	0	p	1432	5	dp
890	4	p	1443	5	p
927	6	p	1606	8	p
938	8	p	2841	2	p
957	7	dp	2851	1	p
999	1	p	2910	9	p
1040	7	p	2935	10	p
1051	2	dp	2959	8	dp?
1088	3	p	3051	4	p

TABLE III
RAMAN SPECTRUM OF BICYCLO[3.2.0]HEPTA-2,6-DIENE

Frequency, cm. ⁻¹	Approx. inten.	Polariz.	Frequency, cm. ⁻¹	Approx. inten.	Polariz.
185	15	dp	1107	55	dp?
256	45	dp	1141	30	p
401	15	dp	1159	30	p
471	20	dp	1190	2	dp
663	10	dp	1250	10	dp?
697	3	p	1260	10	dp
728	15	p	1281	15	p
782	15	p	1299	2	dp?
820	25	p	1345	5	dp
832	10	dp	1439	30	dp?
882	5	p	1557	50	p (0.1)
911	2	dp?	1607	65	p (0.1)
934	35	p	2940	25	
946	35	dp?	2911	80	
1002	25	dp?	2939	60	
1008	25	dp?	3043	100	
1023	30	dp?	3050	100	
1077	45	p	3116	25	

The most striking feature of the spectra of bicyclo[4.2.0]oct-7-ene, bicyclo[3.2.0]hept-2-ene and bicyclo[3.2.0]hepta-2,6-diene is the almost complete coincidence between the infrared and Raman spectra of each compound, as is to be expected for molecules of little or no symmetry. The intensities of many bands are, however, quite different in the infrared and Raman spectra, particularly the double-bond stretching vibrations, which are among the strongest lines in the Raman spectrum of each compound but weak in the infrared spectrum. In fact the infrared bands are often so weak that overtones in the 1500-1700 cm.⁻¹ region are of comparable intensity. Hence the Raman spectra are of greater value in locating the fundamental frequencies of the double-bond vibrations.

The double-bond frequencies in these compounds are of particular interest. In all the compounds studied which contain the bicyclo[3.2.0]hept-2-ene skeleton, the double-bond frequency appeared at 1605 ± 3 cm.⁻¹ and in bicyclo[3.3.0]oct-2-ene at 1617 cm.⁻¹. These values are very

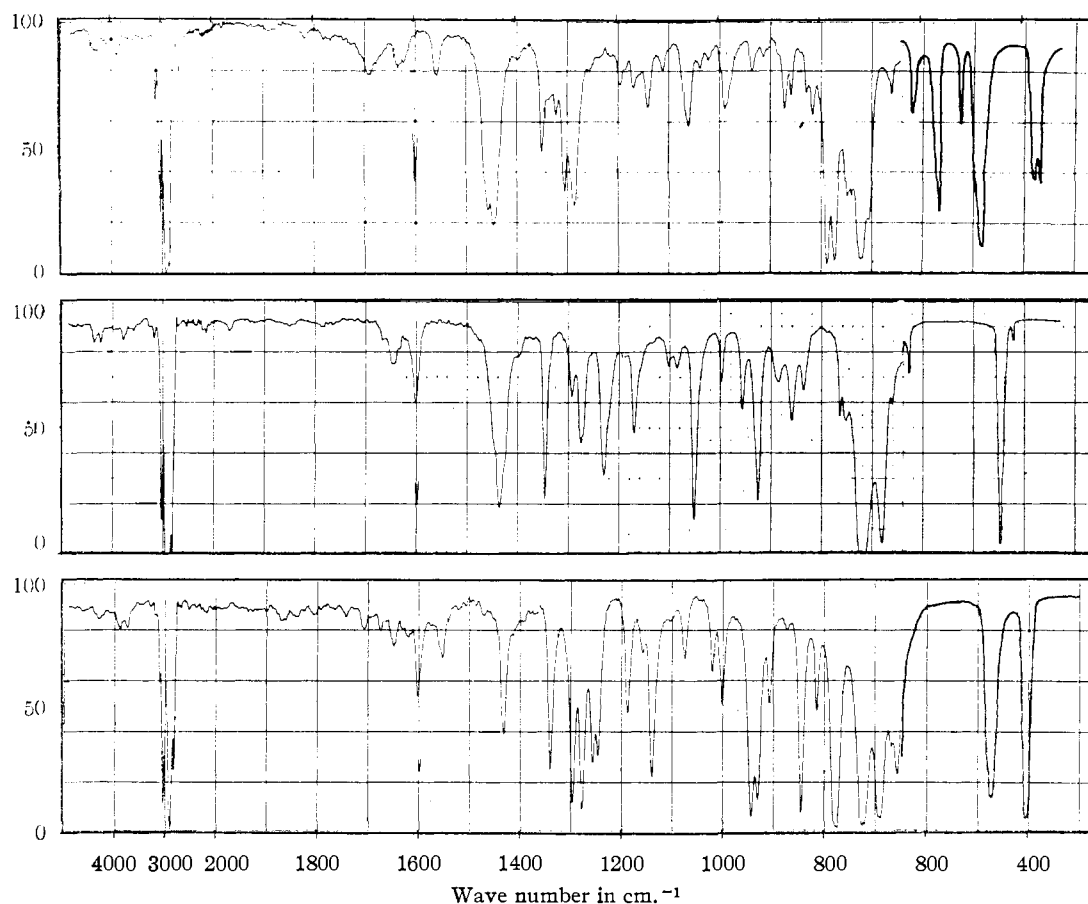


Fig. 2.—Infrared spectra of bicyclo[4.2.0]oct-7-ene (top); bicyclo[3.2.0]hept-2-ene (center); bicyclo[3.2.0]hepta-2,6-diene (bottom). Sample thickness was 0.25 mm., 300–640 cm^{-1} ; 0.025 mm., 640–5000 cm^{-1} in all three spectra.

close to the double bond frequency of 1611 cm^{-1} observed for cyclopentene. A similar constancy of the four membered-ring double-bond frequency

is observed in the case of bicyclo[4.2.0]oct-6-ene (triplet, average 1560 cm^{-1}), bicyclo[3.2.0]hepta-2,6-diene (1557 cm^{-1}) and cyclobutene (1566 cm^{-1}). The observation that the double bond frequencies in bicyclo[3.2.0]hepta-2,6-diene are essentially the same as those in similar compounds containing only cyclopentene or cyclobutene double bonds indicates both that the mechanical interaction of the two modes of vibration must be very slight even though the frequencies are nearly the same and the double bonds are separated by only one carbon atom and that the effects of additional strain in the bicyclo compounds are small.

A detailed comparison of the spectra of bicyclo[3.2.0]hepta-2,6-diene and bicyclo[4.2.0]oct-7-ene with that of cyclobutene shows that virtually all the frequencies other than that of the double bond and those of the CH stretching and deformation vibrations are sufficiently shifted to prevent a definite assignment of the bands.

Experimental¹¹

Bicyclo[3.2.0]hept-2-en-6-one Ketoxime.—To 19.6 g. (0.173 mole) of bicyclo[3.2.0]hept-2-en-6-one which was prepared as described by Blomquist and Kwiatak,¹² in 150 ml. of ethanol-water (1:1) was added first 11.2 g. (0.087 mole) of potassium carbonate and then 15.2 g. (0.218 mole)

(11) Elemental analyses by S. M. Nagy and associates. All melting points and boiling points are uncorrected.

(12) A. T. Blomquist and J. Kwiatak, *J. Am. Chem. Soc.*, **73**, 2098 (1951).

TABLE IV

RAMAN SPECTRUM OF BICYCLO[3.3.0]OCT-2-ENE			
Frequency, cm^{-1}	Estimd. intensity	Frequency, cm^{-1}	Estimd. intensity
205	7	1003	3
287	3	1028	6
357	1	1047	6
386	2	1106	8
443	4	1150	0
539	2	1168	1
554	2	1182	3
574	2	1227	2
674	1	1260	2
704	5	1275	2
732	4	1295	4
760	1	1310	2
777	2	1323	1
793	6	1354	2
808	6	1445	8
830	1	1467	1
859	1	1617	7
877	0	2846	3
904	6	2862	5
935	6	2905	9
959	3	2948	10
970	2	3049	5
988	4		

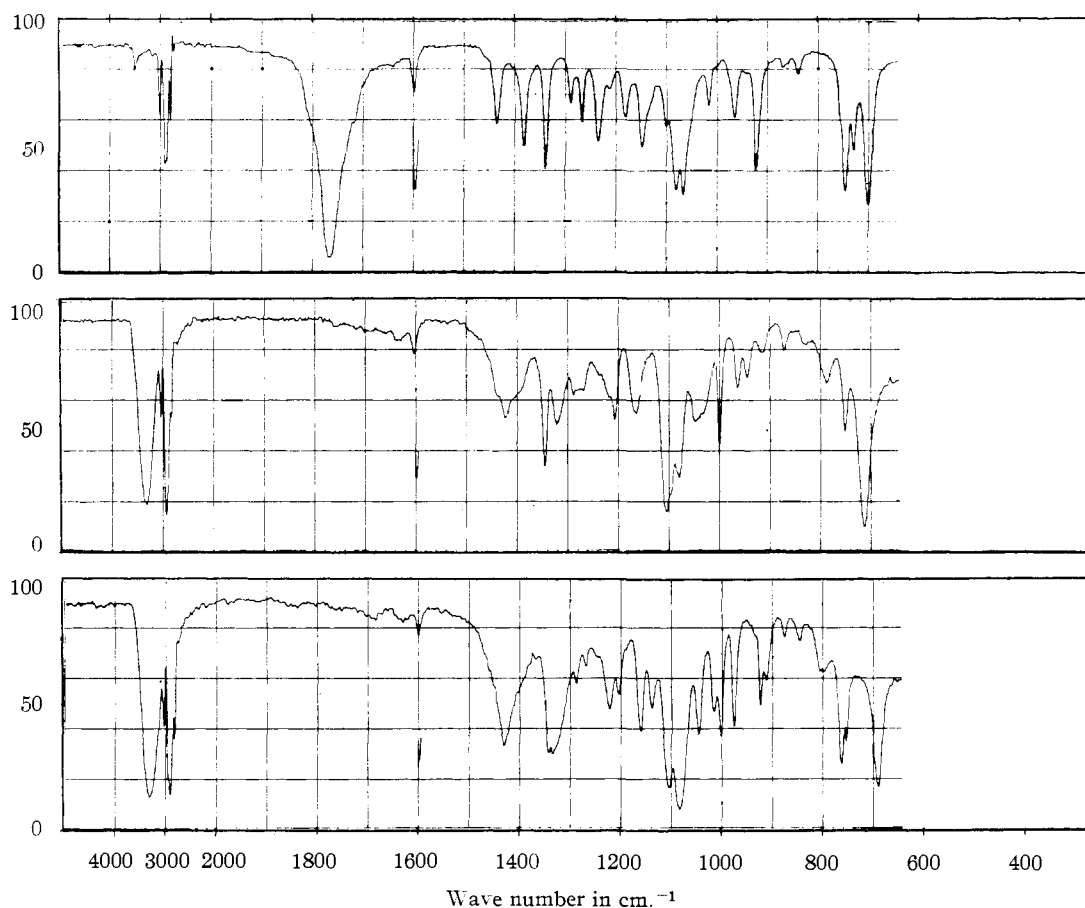


Fig. 3.—Infrared spectra of bicyclo[3.2.0]hept-2-ene-6-one (top); *endo*-bicyclo[3.2.0]hept-2-ene-6-ol (center); *exo*-bicyclo[3.2.0]hept-2-ene-6-ol (bottom); capillary liquid films in all three cases.

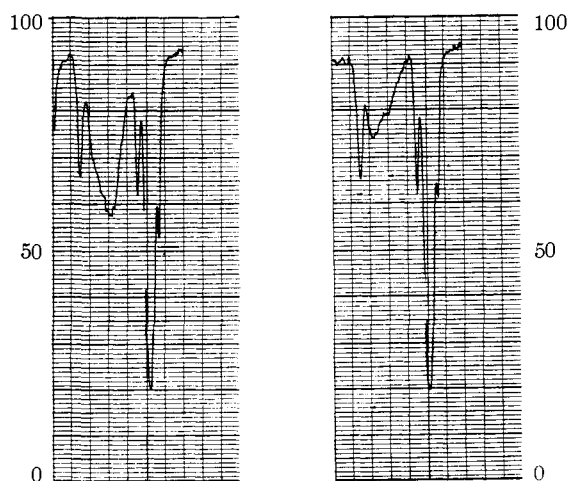


Fig. 4.—Infrared spectra (4000–2600 cm^{-1}) of 1.5% solutions of bicyclo[3.2.0]hept-2-ene-6-ols in CCl_4 ; sample thickness, 0.5 mm. left, *exo* compound; right, *endo* compound.

of hydroxylamine hydrochloride in small portions. The solution was heated on a steam-bath for 1.5 hr., saturated with salt and extracted with three 50-ml. portions of ether. The ether extracts were combined and dried over MgSO_4 . The ether and ethanol were removed by distillation through a 15-cm. Vigreux column, and the remainder was distilled through a Holzman column; b.p. 112° (10 mm.); yield 16.2 g. (76%). Calcd. for $\text{C}_7\text{H}_9\text{ON}$: C, 68.27; H, 7.36;

N, 11.37. Obsd: C, 66.93, 66.92; H, 7.42, 7.44; N, 11.35.

Bicyclo[3.2.0]hept-2-en-yl-6-amine.—To 8.0 g. of lithium aluminum hydride in 150 ml. of anhydrous ether in a 500-ml. three-necked flask with dropping funnel and reflux condenser was added with ice-cooling and stirring a solution of 15.85 g. of the oxime in 50 ml. of ether. The addition was completed in 1 hr., and the mixture was stirred at room temperature overnight. Then 6.75 ml. of water was added dropwise followed by 6.75 ml. of 15% potassium hydroxide solution and finally by 20 ml. of water. The reaction mixture was filtered by suction and the precipitate washed three times with ether and discarded. The aqueous portion of the reaction mixture was extracted with ether, then made basic with an excess of sodium hydroxide and extracted three times with ether. The ether layers were combined, dried over potassium hydroxide and the ether removed by distillation through a 15 cm. Vigreux column. The product was distilled through a Holzman column; b.p. 95° (102 mm.) n_D^{25} 1.4950; weight of product, 10.42 g. (75%).

Attempted Conversion of the Above Amine to Bicyclo[3.2.0]hept-2-ene-6-diene.—10.42 g. (0.105 mole) of the amine (was dissolved in 100 ml. of methanol, 11.2 g. 0.105 mole) of sodium carbonate and 100 g. (0.7 mole) of iodomethane added, and the mixture stirred at reflux for ten days, after which the low boiling materials were removed under reduced pressure and the product dried at 0.1 mm. for 4 hr. The product was placed in a Soxhlet apparatus and extracted for four days with chloroform. The chloroform was removed under reduced pressure and the resulting brown solid was crystallized from 95% ethanol and dried overnight at 0.05 mm. over CaSO_4 ; m.p. $174\text{--}185^\circ$. Calcd. for $\text{C}_{10}\text{H}_{16}\text{NI}$: C, 43.03; H, 6.49. Obsd.: C, 41.48; H, 6.39; weight of product 12.2 g. All of this material was stirred with 10.2 g. (0.044 mole) of Ag_2O and 10 ml. of water overnight, protected from atmospheric CO_2 by an Ascarite tube.

The mixture was then filtered and washed with water. The filtrate and washings were frozen and lyophilized at 0.1 mm. for 6 hr. The resulting brown sirup was pyrolyzed as described by Bumgardner¹³ at 120° and 20–10 mm. nitrogen pressure. The contents of the Dry Ice traps were combined and shaken with 10% sulfuric acid. No hydrocarbon layer remained. The solution was extracted with pentane, the extracts dried over magnesium sulfate and the pentane removed by distillation through a 15 cm. Vigreux column. No fraction boiling over 55° at 750 mm. was obtained.

Bicyclo[3.2.0]hept-2-en-6-ol.—A solution of 49.6 g. (0.46 mole) of bicyclo[3.2.0]hept-2-en-6-ol in 300 ml. of anhydrous ether was added dropwise to a slurry of 17.5 g. (0.46 mole) of lithium aluminum hydride in 250 ml. of ether. The flask was cooled with ice and the ketone was added over a 0.5 hr. period. The reaction mixture was stirred with cooling for an additional 20 minutes, after which 20% ethyl acetate in USP ether was added until evolution of heat ceased, and finally 50 ml. of 4:1 ethanol–water. The reaction mixture was poured into a 1 liter continuous extractor and sufficient water was added to make 750 ml. of aqueous phase. This material was extracted with ether for three days. The ether was then removed under reduced pressure and the product dried over K₂CO₃ and distilled through a 10 mm. X 45 cm. spinning band column. The combined fractions boiling from 96.5 to 97.2° at 48 mm. (*n*_D²⁵ 1.5003 to 1.4998) were found by vapor phase chromatographic analysis on a polyethylene glycol on firebrick column to be a 90:10 mixture of two components, and similarly the combined fractions with boiling point 104°, *n*_D²⁵ 1.4931 were found to be a 9:91 mixture of the same components. The infrared spectra of these fractions show that they are both similar alcohols and that the lower boiling alcohol is less heavily hydrogen bonded than the higher boiling one, as would be expected for a pair of epimers (Fig. 4). The total ratio of *endo* to *exo* alcohols is 0.7 to 1, and the total yield is 31.3 g. (64%). Phenylurethans were formed and crystallized twice from ethanol–water. Calcd. for C₁₄H₁₈O₂N: C, 73.34; H, 6.59. Obsd.: *exo* C, 73.38; H, 6.73; *endo* C, 73.17; H, 6.81. Melting points: *exo* 134–134.5°, *endo* 111–112.5°. The *exo* alcohol formed the phenylurethan immediately upon warming to 100° with phenyl isocyanate, while the *endo* required several hours at 100° before sufficient phenylurethan was obtained for purification.

A 10-mg. sample of each alcohol was hydrogenated with platinum dioxide in ethanol.¹⁴ Observed hydrogen uptake was: *exo* 0.994 equivalent per mole, *endo* 0.980 equivalent per mole.

S-Methyl Xanthate of *endo*-B-bicyclo[3.2.0]hept-2-ene-6-ol.—To 5.15 g. (0.047 mole) of the *endo* alcohol in an ice-cooled 60 ml. of nickel crucible was added 2.62 g. (0.047 mole) of potassium hydroxide. The mixture was pounded with an 8 in. X 1/4 in. stainless steel rod until the KOH pellets were thoroughly crushed, and then 4.5 ml. (0.047 mole) of carbon disulfide was added in small portions with stirring. The reaction mixture resembled dry peanut butter at the end of the addition. The solid was dissolved in a minimum of warm acetone (about 50°) and decanted into about 7 ml. of pentane to precipitate the potassium xanthate. A red oil remained in the crucible. The xanthate precipitate was filtered and dried overnight at 0.1 mm.; m.p. 208–210°, yield 5.9 g. (63%).

All of this material was dissolved in 100 ml. of acetone and cooled to 0°. Four ml. of iodomethane was added in after which it was heated to reflux overnight. The acetone was then removed under reduced pressure and the methyl xanthate was dissolved in diethyl ether. The inorganic salts were removed by filtration, the filtrate was dried over MgSO₄, and the ether was removed under reduced pressure. The product was distilled in a 5 cm. Holzman column; b.p. 87° at 0.4 mm., *n*_D²⁵ 1.5807, yield 3.4 g. (37%).

Pyrolysis of the Methyl Xanthate of *endo*-Bicyclo[3.2.0]hept-2-en-6-ol.—15.05 g. of the methyl xanthate was placed in a 30-ml. distilling flask equipped with two thermocouple wells: one immersed in the liquid, and the other just below the sidearm. The sidearm was connected to a Dry Ice trap, the outlet of which was protected from atmospheric water by a Drierite tube. The flask was heated on a sand-

bath and the heating rate was adjusted so that the liquid boiled slowly but the takeoff temperature was below 125°. The liquid began to decompose at 220°, and shortly afterwards the liquid temperature rose to 300° and remained at this value until only a small residue remained in the flask. Five ml. of cold pentane was added to the contents of the Dry Ice trap, and the trap was warmed cautiously to room temperature to distil off the methyl mercaptan and carbonyl sulfide, and then the contents of the trap were distilled through a 15 cm. Vigreux column. The material boiling between 107 and 114° at 745 mm., yield 3.06 g. (44%), was found by vapor phase chromatography on a di-(2-ethyl hexyl) sebacate on firebrick column to be an 85:15 mixture of tropilidene and a second hydrocarbon.

Methyl Xanthate of *exo*-Bicyclo[3.2.0]hept-2-en-6-ol.—In the same manner 2.8 g. of the *exo* alcohol was converted to the potassium xanthate in 54% yield, m.p. above 230° dec. This was then converted to the methyl xanthate, b.p. 92–96° at 1.3 mm., *n*_D²⁵ 1.5771 in 72% yield.

Pyrolysis of the Methyl Xanthate of *exo*-Bicyclo[3.2.0]hept-2-en-6-ol.—The above procedure was repeated with 8.93 g. of the *exo*-methyl xanthate. The pyrolysis began at 218°, the bulk of the liquid decomposed at 230–235°, and the temperature at the end of the pyrolysis was 270°. The hydrocarbon fraction boiling between 93 and 99° at 745 mm. was found to be a 15:85 mixture of tropilidene and the second hydrocarbon. The weight of this fraction was 2.8 g. (68%).

Properties of the Second Hydrocarbon.—All the hydrocarbon product from the xanthate pyrolyses was separated by vapor phase chromatography on a 1/2 in. X 8 ft. silicone oil on firebrick column into samples of tropilidene and of the second hydrocarbon. The second hydrocarbon absorbed 103% of two molar equivalents of hydrogen,¹⁴ showed only end absorption in the ultraviolet and had infrared bands at 1605 and 1560 cm.⁻¹ which indicate that one double bond is in a five-membered ring and that the other is in a four-membered ring; *n*_D²⁵ 1.4705, calcd. for C₇H₈: C, 91.25; H, 8.75. Obsd.: C, 90.97; H, 8.96. The hydrogenation was repeated in ether at 0° over platinum dioxide and the reduction product was isolated by vapor phase chromatography. The infrared spectrum of this product was identical with that of an authentic sample of bicyclo[3.2.0]heptane.

The hydrocarbon was pyrolyzed by injecting 0.01-ml. samples of a 10% ether solution into a silicone oil on firebrick chromatographic column operated at 70°. The temperature of the preheater was raised and the composition of the effluent mixture was studied as a function of the preheater temperature. The indicated temperature is probably quite different from the actual decomposition temperature of the sample because of the cooling effect of the vaporization of the ether solvent. No change in the composition of the sample was observed until 340°, when a peak appeared at the retention time observed for tropilidene. At 400° the ratio of tropilidene to starting material was 65:35, and at 415° only tropilidene was observed. The pyrolysis was repeated several times and the tropilidene peak was collected until sufficient sample was obtained for an infrared spectrum. The infrared spectrum of the pyrolysis product was identical with that of an authentic sample of tropilidene. A sample of bicyclo[2.2.1]hepta-2,5-diene was injected at 405° and only about 1% conversion to tropilidene was observed. Two other products of lower molecular weight also were observed.

Bicyclo[3.2.0]hept-2-ene.—This sample was prepared as described by Blomquist and Kwiatek¹² and had *n*_D²⁵ 1.4623 after purification by gas phase chromatography.

Bicyclo[3.3.0]oct-2-ene.—This sample was obtained from Dr. P. E. Peterson.

Bicyclo[4.2.0]oct-7-ene.—This sample was obtained from Dr. R. Gleason and had *n*_D²⁵ 1.4726.

Acknowledgments.—The authors here wish to thank Dr. P. E. Peterson and Professor W. R. Moore for their many suggestions, particularly concerning the use of gas-phase chromatography for the thermal rearrangement studies. We wish also to thank Dr. E. Vogel for a detailed description of his work on the preparation of bicyclo[3.2.0]heptadiene by Hoffman degradation. The study was supported in part by National Science Foundation grant G-1892.

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(14) N. Clauson-Klaus and F. Limbourg, *Acta Chim. Scand.*, **1**, 884 (1947).