

The crude adduct mixtures from these addition reactions were in each case fractionated in order to remove most of the conventional, liquid, Markovnikov-type adducts. In the case of the hydrogen bromide adduct mixtures, the distillation was discontinued after the fraction boiling at 54–56° and 89–90 mm. was collected, and in the case of the hydrogen chloride adduct mixtures, after the fraction boiling at 69–70° was collected. The remaining liquid distillation residue was in each case further separated by preparative g.l.c. if the pure isomers were the desired products. The dibromo compounds could be also obtained as a crystalline mixture consisting of approximately 5–10% of the *cis* and 90–95% of the *trans* isomer by crystallization of the above distillation residue in cold pentane.

Preparative G.l.c. The separation of the isomeric 1,3-dihalo-1,3-dimethylcyclobutanes was carried out on an Aerograph Autoprep Model A-700. A 20 ft. \times $\frac{3}{8}$ in. i.d. column packed with 20% silicone on Chromosorb was used. Operating conditions for the separation of the isomeric 1,3-dichloro-1,3-dimethyl-

cyclobutanes were as follows: detector cell temperature, 150°; detector cell current, 200 ma.; injector part temperature, 148°; collector temperature, 123°; column temperature, 113°; helium flow, 80 cc./min. For the separation of the isomeric 1,3-dibromo-1,3-dimethylcyclobutanes, the conditions were the following: detector cell temperature, 160°; detector cell current, 200 ma.; injector part temperature, 150°; collector temperature, 130°; column temperature, 130°; helium flow, 140 cc./min. The corresponding isomers were in each case collected as colorless, crystalline materials.

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Dehydrohalogenation of Halo- and Dihalocyclopropanes

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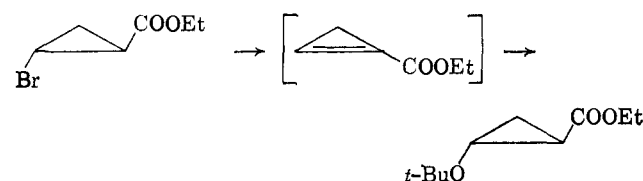
Contribution from the Department of Chemistry, University of Texas,
Austin, Texas. Received March 19, 1965

The dehydrohalogenation of halocyclopropanes to cyclopropenes has been shown to be a very facile reaction when induced by strong base systems such as potassium *t*-butoxide in dimethyl sulfoxide. The fate of the cyclopropene is dictated by its gross molecular structure as well as by the base employed in its formation. In the absence of a nucleophile and when the base itself is a poor nucleophile, the product is in general that resulting from double-bond migration to a position of greater stability outside of the three-membered ring. This is followed in some cases by skeletal rearrangement.

The methods most commonly used for the synthesis of cyclopropenes and alkylencyclopropanes are (a) Hofmann elimination,^{1,2} (b) alkylene transfer systems,³ and (c) condensation reactions involving substituted cyclopropenones.³ The light-induced decomposition of alkylidenepyrazolines⁴ and the Favorskii reaction⁵ have also been used with success.

Wiberg, Barnes, and Albin in 1957 described the conversion of ethyl *trans*-2-bromocyclopropanecarboxylate to ethyl *trans*-2-*t*-butoxycyclopropanecar-

boxylate by reaction with potassium *t*-butoxide (KO-*t*-Bu) in *t*-butyl alcohol and presented good evidence for the intermediacy of a cyclopropene.⁶ This appears to be the only example of this rather direct route to cyclopropenes. The ready availability of dihalocyclopropanes⁷ and halocyclopropanes⁸ makes



the approach appear quite attractive. On the other hand, Parham and co-workers⁹ have shown that treatment of *gem*-dichlorocyclopropanes with boiling quinoline or pyridine leads largely to ring opening concurrent

(1) N. J. Demjanow and M. Dojarenko, *Ber.*, **56**, 2200, (1923); M. J. Schlatter, *J. Am. Chem. Soc.*, **63**, 1733 (1941).

(2) K. B. Wiberg and W. J. Bartley, *ibid.*, **82**, 6375 (1960).

(3) R. F. Bleiholder and H. Shechter, *ibid.*, **86**, 5032 (1964), and references cited therein; E. F. Ullman and W. J. Fanshawe, *ibid.*, **83**, 2379 (1961); A. S. Kende and P. T. Izzo, *ibid.*, **86**, 3587 (1964); P. S. Skell and L. D. Wescott, *ibid.*, **85**, 1023 (1963).

(4) A. C. Dey and M. C. Whiting, *Proc. Chem. Soc.*, 368 (1964).

(5) R. Breslow, J. Posner, and A. Krebs, *J. Am. Chem. Soc.*, **85**, 234 (1963).

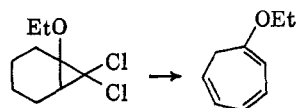
(6) K. B. Wiberg, R. K. Barnes, and J. Albin, *ibid.*, **79**, 4994 (1957). An attempt to generalize this approach to more elaborately substituted cyclopropenes led only to ring-opened products: S. M. McElvain and P. L. Weyna, *ibid.*, **81**, 2579 (1959).

(7) (a) W. von E. Doering and A. K. Hoffmann, *ibid.*, **76**, 6162 (1954); (b) W. E. Parham, R. W. Soeder, and R. M. Dodson, *ibid.*, **84**, 1755 (1962); (c) P. S. Skell and A. Y. Garner, *ibid.*, **78**, 3409, 5430 (1956).

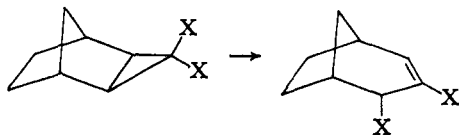
(8) (a) D. Seyferth, H. Yamazaki, and D. L. Alleston, *J. Org. Chem.*, **28**, 703 (1963); (b) K. Hofmann, S. F. Orochena, S. M. Sax, and J. A. Jeffrey, *J. Am. Chem. Soc.*, **81**, 992 (1959); (c) G. L. Closs and L. E. Closs, *ibid.*, **82**, 5723 (1960).

(9) W. E. Parham, R. W. Soeder, J. R. Throckmorton, K. Kuncl, and R. M. Dodson, *ibid.*, **87**, 321 (1965), and references to earlier work cited therein.

with dehydrochlorination, *e.g.*, as shown below. It is known, however, that many dihalocyclopropanes are

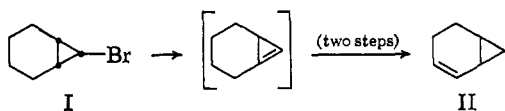


thermally unstable, giving rise to isomeric products.¹⁰ Such a rearrangement preceding dehydrochlorination



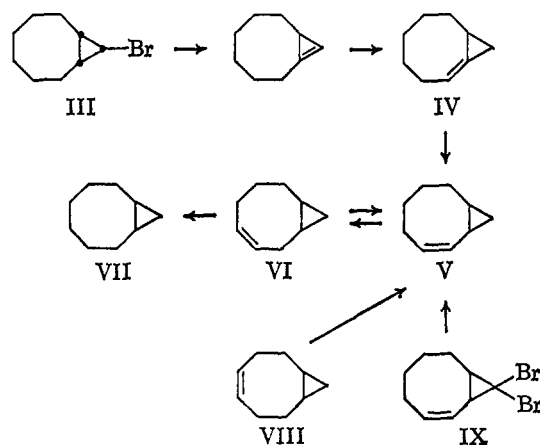
could easily account for most of the products isolated.⁹ We wish now to report results obtained in a study using KO-*t*-Bu in dimethyl sulfoxide (DMSO), a base system sufficiently strong to permit dehydrohalogenation of halocyclopropanes at room temperature.

The reaction of *cis*-7-bromobicyclo[4.1.0]heptane (I) with excess KO-*t*-Bu in DMSO at room temperature afforded bicyclo[4.1.0]hept-2-ene (II) in 24% yield. The identity of II was suspected by comparison of its



n.m.r. and infrared spectra with data reported¹¹ and later established with certainty by comparison with spectral data of authentic material prepared by an alternate route. Although the formation of a cyclopropene intermediate in this reaction was largely surmised, its presence has subsequently been established by trapping experiments.¹² It is thus clear that the strain energy of the intermediate is sufficiently great that a rapid base-catalyzed migration of the double bond occurs.

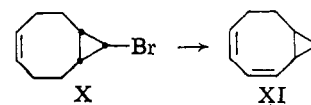
A more efficient dehydrobromination was observed in the case of *cis*-9-bromobicyclo[6.1.0]nonane (III). Its reaction with KO-*t*-Bu in DMSO, allowed to proceed until monitoring established that no starting material remained, gave a mixture of two olefins (95:5) in 80% yield. Separation of the two was effected by preparative vapor-liquid chromatography. The major component was found to be bicyclo[6.1.0]non-1-ene (IV) from n.m.r. and hydrogenation data. Its n.m.r. spectrum possessed a one-proton multiplet at τ 4.2 as well as the expected broad multiplet at higher field. Catalytic hydrogenation required 1 mole equiv. of hydrogen and afforded bicyclo[6.1.0]nonane, identical in all respects with a sample prepared either by a Simmons-Smith reaction with cyclooctene or by the sodium-methanol reduction of *trans*-9-bromobicyclo[6.1.0]nonane. The minor product accompanying the formation of IV was shown to be bi-



cyclo[6.1.0]non-2-ene (V)¹³ by comparison of its properties with those of an authentic sample prepared by the sodium-ammonia reduction of 9,9-dibromobicyclo[6.1.0]non-2-ene (IX). Further treatment of either IV or V with the basic medium employed in their formation established that the former is completely transformed to the latter which in turn gives rise to bicyclo[6.1.0]non-3-ene (VI). The n.m.r. spectrum of VI exhibits a multiplet (two protons) centered at τ 4.4 (vinyl protons), a broader multiplet between 7.3 and 9.5 (11 protons), and another at 10.1 (0.9 proton). Hydrogenation required 1.3 mole equiv. of hydrogen and gave bicyclo[6.1.0]nonane (VII) and methylcyclooctane (2:1 ratio), both identified by comparisons with authentic materials. It is interesting to note that, under the conditions used, VII does not undergo hydrogenolysis, thus suggesting that the formation of methylcyclooctane probably involves ring rupture prior to reduction of the double bond.

The equilibrium composition in the V \rightarrow VI interconversion was found to be 80:20 at 30°. Moreover, the same composition could be obtained by the base-catalyzed isomerization of bicyclo[6.1.0]non-4-ene (VIII). It is thus clear that all of the isomeric bicyclo[6.1.0]nonenes have been encountered in this study and that at 30° V is, by a substantial margin, the most thermodynamically stable.

Dehydrobromination of *cis*-9-bromobicyclo[6.1.0]non-4-ene (X) with either KO-*t*-Bu or NaO-*t*-Bu in DMSO afforded pure (vapor-liquid chromatography) bicyclo[6.1.0]nona-2,4-diene (XI) in 57-70% yields. Infrared, ultraviolet, and n.m.r. spectra of this substance were identical with data reported by Roth.¹⁴



Reduction required 2 mole equiv. of hydrogen and gave VII, identical with an authentic sample. Although intended here as a further example of the formation and *in situ* isomerization of cyclopropenes, this sequence giving rise to XI is felt to be somewhat more convenient than that reported.

(10) J. Sonnenberg and S. Winstein, *J. Org. Chem.*, 27, 748 (1962); W. R. Moore, W. R. Moser, and J. E. LaPrade, *ibid.*, 28, 2200 (1963); R. C. De Selms and C. M. Combs, *ibid.*, 28, 2206 (1963); E. Bergman, *ibid.*, 28, 2210 (1963); T. C. Shields and P. D. Gardner, unpublished.

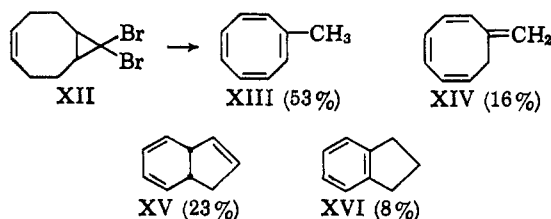
(11) W. R. Moore, H. R. Ward, and R. F. Merritt, *J. Am. Chem. Soc.*, 83, 2019 (1961).

(12) T. C. Shields, B. A. Shoulders, and P. D. Gardner, unpublished.

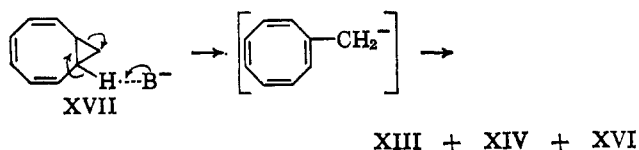
(13) W. von E. Doering and W. R. Roth, *Angew. Chem.*, 75, 27 (1963), prepared this substance in a different way but did not describe its characterization. Its thermal isomerization to 1,4-cyclonadiene is also described and was used in this study as further confirmation of structure V.

(14) W. R. Roth, *Ann.*, 671, 10 (1964).

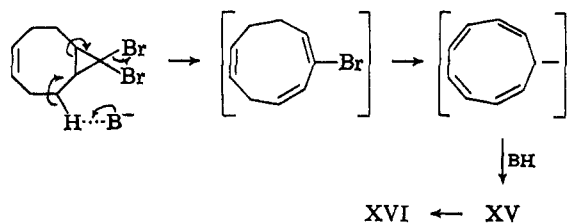
Finally, the behavior of 9,9-dibromobicyclo[6.1.0]-non-4-ene (XII) in strongly basic medium was examined. It was found that four hydrocarbons were formed in ratios which varied as experimental parameters were changed. At 40–45° during a 3.5-hr. reaction time, a 63% yield of the mixture was obtained. Retention times were quite close and preparative vapor-liquid chromatography did not allow a complete separation. A sufficient enrichment of each was obtained, however, to permit its identification. N.m.r. data and comparisons of retention times of the four components with authentic samples of two of them established their identity as methylcyclooctatetraene (XIII, 53%), 7-methylenecycloocta-1,3,5-triene (XIV, 16%), bicyclo[4.3.0]nona-2,4,7-triene (XV, 23%), and indan (XVI, 8%). The bases for these identifications are described in the Experimental section. By analogy with other cases encountered in this study, it was felt that the origin of XIII and XIV probably involved a series of dehydrobrominations and double bond migrations culminating in bicyclo[6.1.0]nona-2,4,6-triene (XVII). Good analogy for the XVII → XIII + XIV conversion is found in the base-catalyzed rearrangement of cyclooctatetraene oxide to cyclooctatrienone reported by



Cope and Tiffany.¹⁵ Support for this hypothesis was obtained by preparing a sample of XVII¹⁶ and submitting it to conditions employed in the dehydrobromination of XII. The principal products formed (85% yield) were XIII (55%), XIV (27%), and XVI (8%), but no XV could be detected in the reaction mixture.



The formation of members of the bicyclo[4.3.0] family (XV and XVI) from the dehydrobromination of XII indicates that a competitive mechanism similar to that suggested by Parham, *et al.*,⁹ is operative. Katz and Garratt have shown that cyclononatetraenide ion is



relatively stable but that its conjugate acid undergoes a rapid Cope rearrangement to XV.¹⁷ This fact, coupled

(15) A. C. Cope and B. D. Tiffany, *J. Am. Chem. Soc.*, **73**, 4158 (1951).

(16) E. Vogel, O. Ross, and K. H. Disch, *Ann.*, **653**, 55 (1962); E. Vogel, W. Wiedemann, H. Keifer, and W. F. Harrison, *Tetrahedron Letters*, **11**, 673 (1963).

(17) T. J. Katz and P. J. Garratt, *J. Am. Chem. Soc.*, **85**, 2852 (1963).

with the observation that XV undergoes an essentially instantaneous isomerization to indan (XVI) when submitted to the conditions used in its formation in this study, leaves little doubt that the XV isolated exists in solution as cyclononatetraenide ion. The formation of XV isolated thus occurs at the moment of quench. The fact that indan is one of the products indicates that the low concentration of *t*-butyl alcohol formed in the reaction and/or DMSO itself serves as a proton donor (BH) providing a slow bleed-off through XV. It is noteworthy, however, that some XV is still formed upon quench following reactions of 100-hr. duration. The addition of very small amounts of *t*-butyl alcohol, a considerably stronger acid than DMSO, was observed to increase the ratio XVI:XV.

The formation of even a low yield of indan in the base-catalyzed isomerization of XVII is surprising and very interesting. More data is required before a mechanism for this transformation can be singled out.

Experimental

cis-7-Bromobicyclo[4.1.0]heptane (I). This substance was prepared by the method developed by Hofmann, *et al.*,^{8b} for other *cis*-bromocyclopropanes. Its n.m.r. spectrum is in excellent agreement with reported data.^{8a}

Bicyclo[4.1.0]hept-2-ene (II). Potassium *t*-butoxide was prepared by the reaction of 6.0 g. of potassium with 350 ml. of *t*-butyl alcohol (freshly distilled from calcium hydride directly into the reaction flask) under a nitrogen atmosphere. After distillation of excess alcohol the base was heated at 90° for 30 hr. at 0.5 mm. Dry (100 ml. distilled from calcium hydride) dimethyl sulfoxide (DMSO) was introduced into the flask and the mixture was stirred under nitrogen for 0.5 hr. While cooling with an ice bath, a solution of 7.0 g. of I in 20 ml. of dry DMSO was added. The cooling bath was removed when it became apparent that the initial exothermic reaction period was over, and the mixture was then stirred at room temperature for 2.5 hr. It was quenched with cold water and extracted with four small portions of pentane. Processing of the extracts in the usual manner and fractionation to remove pentane left a residue which was then flash distilled into a cold trap. This distillate (0.90 g.) was found to be a single substance by vapor-liquid chromatography on several columns. Its n.m.r. spectrum exhibited olefin signals (two protons) centered at τ 4.0 and 4.7, in agreement with data reported¹¹ and superimposable on a spectrum of material prepared by an alternate route.

Bicyclo[6.1.0]non-1-ene (IV). 9,9-Dibromobicyclo[6.1.0]nonane¹⁸ (8.5 g.) was dissolved in 60 ml. of glacial acetic acid and heated to 60°. While stirring vigorously, 22.5 g. of zinc dust was added in several portions during 2 hr. and then stirring was continued (60°) for 30 hr. The mixture was poured into ice and water and extracted with pentane. Processing the extract in the usual manner and removal of solvent, followed by distillation of the residue, afforded 5.2 g. of colorless liquid, b.p. 71° (1.7 mm.). Vapor-liquid chromatography showed it to be a mixture of two substances (90:10) which could be preparatively separated.

(18) P. D. Gardner and M. Narayana, *J. Org. Chem.*, **26**, 3518 (1961).

The major product, *cis*-9-bromobicyclo[6.1.0]nonane (III),^{8a} was identified by examination of its n.m.r. spectrum which exhibited a one-proton triplet centered at τ 6.83 ($J = 7.7$ c.p.s.). The *trans* isomer was identical in all respects with a sample prepared by an alternate route.¹²

Potassium *t*-butoxide, prepared as described above from 5.0 g. of potassium, was dissolved in 200 ml. of dry DMSO in a nitrogen atmosphere. To this solution was added 5.0 g. of *cis*-9-bromobicyclo[6.1.0]nonane (III) and stirring under nitrogen was continued for 6 hr. or until a monitor sample indicated the disappearance of all starting material. The mixture was quenched in ice-water and processed by pentane extraction in the usual manner. Flash distillation (0.1 mm.) afforded 2.4 g. of hydrocarbon which was found to consist of 95% bicyclo[6.1.0]non-1-ene (IV) and 5% bicyclo[6.1.0]non-2-ene (V).¹³ Pure samples of each were obtained by vapor-liquid chromatography.

Anal. Calcd. for C₉H₁₄ (IV): C, 88.45; H, 11.55. Found: C, 88.44; H, 11.39.

Anal. Calcd. for C₉H₁₄ (V): C, 88.45; H, 11.55. Found: C, 88.39; H, 11.25.

The n.m.r. spectrum of IV possessed a multiplet at τ 4.2 (one proton) and a complex multiplet extending from 7.5 to 9.7 (13 protons). Its infrared spectrum exhibited a band at 1025 cm.⁻¹ which may be attributed to the cyclopropane ring.¹⁹

Catalytic reduction of IV required 1 mole equiv. of hydrogen and afforded only bicyclo[6.1.0]nonane (VII), identical with an authentic sample.

The identity of V was established by a comparison of its properties with those of a sample prepared as follows.

9,9-Dibromobicyclo[6.1.0]non-2-ene (IX). Following the general procedure of Doering and Hoffmann,^{7a} the reaction between 270 g. of 1,3-cyclooctadiene,²⁰ 20 g. of potassium, 600 ml. of dry *t*-butyl alcohol, and 139 g. of bromoform, produced 100 g. of IX, b.p. 74–75° (0.15 mm.), n^{25}_D 1.5678.

Anal. Calcd. for C₉H₁₂Br₂: C, 38.60; H, 4.32; Br, 57.07. Found: C, 38.42; H, 4.20; Br, 57.30.

Bicyclo[6.1.0]non-2-ene (V). Into a dry, three-necked, round-bottom flask equipped with mechanical stirrer (glass paddle), Dry Ice-acetone condenser (attached to a mercury trap), and dropping funnel was distilled 1200 ml. of anhydrous ammonia. Sodium (32.5 g.) was added in several pieces and allowed to react completely. The mixture was stirred for 30 min. during the addition of a solution of 50.0 g. of 9,9-dibromobicyclo[6.1.0]non-2-ene (IX) in 100 ml. of anhydrous ether and then for an additional 10 hr. Solid ammonium chloride was added to destroy unreacted sodium and, after rinsing down the walls of the flask with a little methanol, the flask was allowed to stand open in a hood to permit evaporation of ammonia. Water (1000 ml.) and ether were added to the residue for a normal work-up by ether extraction. Concentration of the dried ether extracts by evaporation of solvent through a long Vigreux column and distillation of the residue afforded 13.5 g. of V, b.p. 50–52° (0.1 mm.). This substance was identical with that

obtained from III. Its n.m.r. spectrum exhibited a complex multiplet at τ 4.2–4.8 (two protons), a very complex multiplet at 7.3–9.5 (11 protons), and a multiplet at 10.1–10.3 (one proton).

Base-Catalyzed Isomerization of Bicyclo[6.1.0]non-2-ene (V). *t*-Butyl alcohol (150 ml.) was distilled from calcium hydride into an oven-dried, three-necked reaction flask outfitted with a serum cap, magnetic stirring bar, and stopcock. Potassium (4.0 g.) was added and allowed to react in a dry nitrogen atmosphere. Solvent was removed at aspirator pressure and the residue was dried at 70° (0.05 mm.) for 32 hr. While purging with dry nitrogen, 125 ml. of freshly distilled (calcium hydride) DMSO was added and the mixture was stirred until homogeneous. Bicyclo[6.1.0]non-2-ene (3.1 g.) was added through the serum cap. The mixture was stirred at 30° and monitored at regular intervals by hypodermic syringe withdrawal of aliquots. Reaction was allowed to proceed for 186 hr. although the product ratio became static after 18 hr. Analysis by vapor-liquid chromatography on four columns of different retention characteristics showed the product mixture to consist of starting material (V) and a new substance (VI) in the ratio 80:20, respectively. The minor product was shown from the following data, and by exclusion, to be bicyclo[6.1.0]non-3-ene (VI). Its n.m.r. spectrum exhibited a multiplet centered at τ 4.4 (two protons), one at 7.3–9.5 (11 protons), and one at 10.1 (0.9 proton). Catalytic reduction (Pd-C) required 1.3 mole equiv. of hydrogen and afforded a 2:1 mixture of bicyclo[6.1.0]nonane (VII) and methylcyclooctane, respectively, identified by comparison with authentic samples. Compound VI was easily distinguished from the remaining isomer in the series, bicyclo[6.1.0]non-4-ene (VIII).²¹

Anal. Calcd. for C₉H₁₄: C, 88.45; H, 11.55. Found: C, 88.01; H, 11.39.

Base-Catalyzed Isomerization of Bicyclo[6.1.0]non-4-ene (VIII).²² Potassium *t*-butoxide was prepared from 1.6 g. of potassium as described for the isomerization of V and dissolved (nitrogen) in 100 ml. of dry DMSO. Bicyclo[6.1.0]non-4-ene (0.80 g.) was injected through a serum cap and reaction was allowed to proceed, as evidenced by monitoring, until the product mixture became constant (279 hr.). Its composition was determined by vapor-liquid chromatography using four columns of different retention characteristics to be a mixture of only V and VI in the ratio 80:20 (30°), respectively. An n.m.r. spectrum of this mixture was identical with that of the mixture obtained from the equilibration of V.

Bicyclo[6.1.0]nona-2,4-diene (XI). Glacial acetic acid (200 ml.) and 33.1 g. of 9,9-dibromobicyclo[6.1.0]non-4-ene (XII)²³ were placed in a three-necked flask equipped with a condenser, mechanical stirrer, and solid-addition flask. While stirring, 75 g. of zinc dust was added slowly during 1 hr. The reaction mixture was then stirred at 50° for 24 hr. Following the addition of 300 ml. of cold water, the mixture was suction filtered and the filtrate was extracted with three por-

(21) A. C. Cope, S. Moon, and C. H. Park, *J. Am. Chem. Soc.*, **84**, 4843 (1962).

(22) This substance was prepared by the method of Cope, Moon, and Park²¹ as well as by the sodium-ammonia reduction of 9,9-dibromobicyclo[6.1.0]non-4-ene²³ using the procedure described for V.

(23) L. Skattebøl, *Tetrahedron Letters*, **5**, 167 (1961).

(19) K. Nakanishi, "Infrared Absorption Spectroscopy," Holden-Day, Inc., San Francisco, Calif., 1962, p. 20.

(20) Columbian Carbon Co.

tions of pentane. Processing the extracts in the usual manner and distillation of the residue remaining after evaporation of solvent afforded 10.7 g. of *cis*-9-bromobicyclo[6.1.0]non-4-ene (X), b.p. 55–56° (0.2 mm.). Its n.m.r. spectrum exhibited a multiplet at τ 4.45 (two protons, vinyl), a triplet centered at 6.76 (one proton, $J = 7.6$ c.p.s.), a multiplet extending from 7.2 to 8.4 (eight protons), and a multiplet centered at 8.96 (two protons). The coupling constant for the τ 6.76 triplet, due to the C-9 proton, was in the range expected for the *cis* isomer.^{8a} Analytical vapor-liquid chromatography indicated the *trans* isomer to be present to the extent of only 2%.

Anal. Calcd. for C₉H₁₃Br: C, 53.75; H, 6.15; Br, 39.7. Found: C, 53.75; H, 6.53; Br, 39.9.

To a solution of potassium *t*-butoxide (prepared from 5.0 g. of potassium as described in the synthesis of II) dissolved in 200 ml. of dry DMSO was added 5.0 g. of X. The mixture was stirred under nitrogen (30°) for 2 hr., quenched in ice-water, and processed by pentane extraction. Removal of solvent and flash distillation of the residue at 0.5 mm. afforded 1.7 g. of bicyclo[6.1.0]nona-2,4-diene (XI) which was pure by vapor-liquid chromatography on several columns having different retention characteristics; $\lambda_{\text{max}}^{\text{E.O.H}}$ 234 m μ (log ϵ 3.75) (lit.¹⁴ λ_{max} 234 m μ (log ϵ 3.81)). Its n.m.r. spectrum consisted of a series of complex multiplets centered at τ 4.5 (four protons), 7.6 (two protons), 8.2 (one proton), 8.6 (two protons), 9.2 (two protons), and 10.2 (one proton). Catalytic hydrogenation required 92% of the theoretical volume for two double bonds and gave VII, identical in all respects with authentic material.

Dehydrobromination of 9,9-Dibromobicyclo[6.1.0]non-4-ene (XII). A solution of potassium *t*-butoxide (35.8 g.) in 625 ml. of dry DMSO was prepared as described for the preparation of II. A solution of 21.0 g. of XII in 25 ml. of DMSO was added dropwise and with stirring (40–45°) during 3 hr. The reaction was quenched after an additional 30 min. by pouring into 3 l. of cold water. Isolation of the product by extraction with pentane and the usual processing of the extracts gave a dark red liquid. Flash distillation (40–52° at 3 mm.) afforded 5.6 g. of light yellow liquid which was found by vapor-liquid chromatography to be a mixture of XIII (53%), XIV (16%), XV (23%), and XVI (8%). Preparative chromatography allowed only a partial separation of the four but permitted identification of each as follows. The first of three fractions (90% XIII; 10% XV) gave a very simple n.m.r. spectrum possessing a rather sharp singlet at τ 4.31 (seven protons) and a very sharp singlet at 8.26 (three protons). The former is due to ring protons and the latter to a methyl group. The infrared spectrum of this fraction is superimposable with one of authentic methylcyclooctatetraene.²⁴ The identity of the minor component as XV was suggested by a comparison of its chromatographic retention times on several columns with those of an authentic sample.²⁵ This identification was confirmed by examination of the second fraction which was found to contain XIII (51%), XV (40%), and XIV (8%). The n.m.r. spectrum of this frac-

(24) A. C. Cope and H. C. Campbell, *J. Am. Chem. Soc.*, **74**, 179 (1952). We are indebted to Professor Cope for making available to us a spectrum of XIII.

(25) K. Alder and H. A. Dortmann, *Ber.*, **87**, 1905 (1954).

tion exhibits the two sharp singlets characteristic of XIII which, due to their simplicity, permitted the identification of XV without difficulty. The ultraviolet spectrum²⁶ exhibits maxima at 252 m μ (log ϵ 3.60), 262 (3.68), 271 (3.64), and 282 (3.41). A spectrum of authentic material²⁵ exhibits maxima at 252 m μ (log ϵ 3.46), 262 (3.55), 271 (3.50), and 282 (3.21).

Fraction C was found to contain 73% of XIV, 24% of XVI, and a trace of XIII. Although pure XIV could not be isolated from this mixture, it was obtained in another way²⁷ and used for its identification here; n.m.r. spectra of the two established, with certainty, that the major component was XIV. Moreover, a mixture prepared from pure XIV and indan gave an n.m.r. spectrum identical with that of fraction B.

Base-Catalyzed Isomerization of Bicyclo[6.1.0]nona-2,4,6-triene (XVII). A sample of XVII was prepared from cyclooctatetraene by the Simmons-Smith method²⁸ in 5.4% yield and was found to be identical with an authentic sample.¹⁶ This synthetic route appears to be inferior to that reported previously.^{16,29}

Bicyclo[6.1.0]nona-2,4,6-triene (XVII, 1.43 g.) was added (nitrogen) to a solution of 9.0 g. of potassium *t*-butoxide in 170 ml. of dry DMSO. The mixture was stirred for 20 min. and quenched in ice-water. The usual work-up by pentane extraction and fractional distillation of the residue remaining after evaporation of solvent gave three fractions: A (0.493 g.), b.p. 51–52° (11 mm.); B (0.085 g.), b.p. 58–59° (11 mm.); and C (0.232 g.), b.p. 54–55° (4 mm.). Vapor-liquid chromatography indicated each of these to be a mixture of XIII, XIV, and XVI in the ratios A, 76:16:5; B, 41:42:15; and C, 15:45:22. The ratios of XIII, XIV, and XVI in the composite were 55:27:11. Identification of each component was made as described in the preceding experiment.

Base-Catalyzed Isomerization of Bicyclo[4.3.0]nona-2,4-diene (XV). A solution of 2.1 g. of dry potassium *t*-butoxide in 37 ml. of dry DMSO (nitrogen) was prepared in a flask outfitted with a serum cap and placed in a bath maintained at 40°. While the solution was being stirred, 0.45 g. of XV²⁵ was added from a syringe. The first monitor sample was withdrawn after 15 sec. Vapor-liquid chromatography indicated that no starting material remained and that the only substance present was indan (XVI). Comparison of the properties of an isolated product with those of an authentic sample confirmed the identification.

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(26) A small correction in extinction coefficients for methylcyclooctatetraene absorption was necessary.

(27) H. V. Cortez and P. D. Gardner, unpublished. This substance (XIV) exhibits very strong infrared absorption at 11.3, 12.1, and 13.95 μ . Its n.m.r. spectrum exhibits a complex multiplet centered at τ 3.99 (six protons), two singlets at 5.02 and 5.27 (two protons, exocyclic methylene), and a multiplet centered at 6.88 (two protons, bisallylic). It absorbs in the ultraviolet at λ_{max} 271 m μ (log ϵ 3.54), λ_{sh} 228 m μ (log ϵ 3.99), and λ_{sh} 223 m μ (log ϵ 4.08). Hydrogenation required 4 moles equiv. of gas and gave only methylcyclooctane, identified by comparisons with an authentic sample.

(28) H. E. Simmons, E. P. Blachard, and R. D. Smith, *J. Am. Chem. Soc.*, **86**, 1347 (1964). R. S. Shank and H. Schechter, *J. Org. Chem.*, **24**, 1825 (1959).

(29) We are indebted to Professor E. Vogel for providing an infrared spectrum of XVII.