materials were isolated by preparative gas chromatography. As expected, both the di- and trichloroperfluorocyclopentenes produced the same mixture of red and magenta dyes when treated with sodium cyanide in acetonitrile.

Experimental Section

3-Fluoro-1,1,4,5,5-pentacyano-2-azapentadienide Carbanion.—A mixture of 25.0 g of 1,2-dichlorohexafluorocyclopentene, 25.0 g of 100-mesh sodium cyanide, and 200 ml of ordinary acetonitrile was stirred 4 hr at room temperature. The reaction mixture became somewhat warm for about 30 min but then cooled. The mixture was then filtered through a bed of Celite with the aid of several washings with small quantities of acetonitrile. The filtrate was concentrated to dryness under vacuum with gentle warming. The greenish black, amorphous residue (13.5 g) was dissolved in 200 ml of 10% sodium chloride solution containing 10 ml of concentrated sulfuric acid. This solution was extracted with 200 ml of ether. The ether phase was then washed with another 200-ml portion of 10% sodium chloride solution before being neutralized with 10% tetramethylammonium hydroxide solution, taking care not to exceed a pH of 7. The mixture was left in the refrigerator for about 1 hr to crystallize before being filtered. The filter cake was then washed with small portions of water before being dried in the desiccator. The crude product, mp 170–190°, weighed 7.15 g. This consisted mainly of red dye with some magenta dye impurity. Several fractional recrystallizations from hot water were required to separate the components. The pure red dye melts at 216–218° without decomposition.

Anal. Calcd for $C_{13}H_{12}FN_7$: C, 54.73; H, 4.24; N, 34.37. Found: C, 55.37; H, 4.66; N, 34.46.

The molecular weight was determined ebullioscopically in acetone with tetramethylammonium pentacyanopropenide as the reference material. *Anal.* Calcd: mol wt, 285. Found: mol wt, 291.

The pure magenta dye melts at 261–263° without decomposition. *Anal.* Calcd for $C_{15}H_{12}FN_7$: C, 58.24; H, 3.91; N, 31.70. Calcd for $C_{16}H_{12}N_7F$: C, 59.81; H, 3.77; N, 30.52. Found: C, 58.30; H, 4.20; N, 31.16.

The molecular weight was determined ebullioscopically in acetone with tetramethylammonium pentacyanopropenide as the reference material. *Anal.* Calcd: mol wt, 309 or 321. Found: mol wt, 344.

The red dye may also be prepared free of magenta dye contamination by carrying out the reaction with tetrahydrofuran instead of acetonitrile. In this solvent the reaction mixture was stirred for 1 week. The work-up is otherwise identical with the above.

The tetraphenylphosphonium salts of 1 and 2 were prepared in water by exchange between the sodium or tetramethylammonium salts of 1 and 2 and tetraphenylphosphonium iodide. The precipitated tetraphenylphosphonium salts were recrystallized from a 1:1 acetone–water solution. The tetraphenylphosphonium salt of 1 melted at 169–171° without decomposition. *Anal.* Calcd for $C_{33}H_{20}FN_6P$: C, 72.59; H, 3.58; N, 14.94; P, 5.51. Found: C, 72.37; H, 3.85; N, 14.47; P, 5.40.

The pure tetraphenylphosphonium salt of 2 melted at 212–214°. *Anal.* Calcd for $C_{35}H_{20}FN_6P$: C, 73.16; H, 3.51; F, 3.31; N, 14.63; P, 5.39. Calcd for $C_{36}H_{20}FN_6P$: C, 73.72; H, 3.44; F, 3.24; N, 14.33; P, 5.28. Found: C, 74.02; H, 3.85; F (by difference), 2.89; N, 13.99; P, 5.25.

The tetraphenylarsonium salts of 1 and 2 were also prepared by metathesis in H_2O. The precipitated salts were removed by filtration, dried, and recrystallized from benzene. The pure tetraphenylarsonium salt of 1 is obtained in large, ruby needles, mp 161–163°. *Anal.* Calcd for $C_{33}H_{20}AsFN_6$: C, 66.67; H, 3.39; As, 12.60; F, 3.20; N, 14.14. Found: C, 66.84; H, 3.51; As, 13.76; F, 3.04; N, 14.28.

The tetraphenylarsonium salt of 2 prepared in the same way occurs in large needles with a metallic blue sheen, mp 208°. *Anal.* Calcd for $C_{35}H_{20}AsFN_6$: C, 67.97; H, 3.26; As, 12.11; F, 3.07; N, 13.59. Calcd for $C_{36}H_{20}AsFN_6$: C, 68.58; H, 3.20; As, 11.88; F, 3.01; N, 13.33. Found: C, 68.70; H, 3.50; As, 11.83; F, 2.87; N, 13.46.

Cesium 3-Fluoro-1,1,4,5,5-pentacyano-2-azapentadienide Dioxanate.—Eight grams of crude sodium salt of 1 was refluxed with 100 ml of dioxane for 0.5 hr and then the mixture was filtered. The filter cake when dried weighed 8.7 g and melted with evolution of dioxane at 140–150°. A solution of 7.32 g of the dioxanate in 22 ml of H_2O was added to a solution of 15.2 g of cesium fluoride in 10 ml of H_2O. A viscous syrup separated which slowly turned into crystals, which were filtered and dried, mp 163–165° (4.40 g). This was dissolved in a hot solution of 4 ml of acetonitrile and 10 ml of dioxane. On cooling, shiny, gray crystals formed which were filtered and dried under vacuum over P_2O_5, mp 175–176°. *Anal.* Calcd for $C_{13}H_8CsN_6FO_2$: C, 36.14; H, 1.87; F, 4.40; N, 19.45. Found: C, 36.79; H, 2.01; F, 4.27; N, 19.07.

Heating the salt at 130° (0.5 mm) for 22 hr removed nearly all of the dioxane.

Registry No.—1,2-Dichlorohexafluorocyclopentene, 706-79-6; tetramethylammonium salt of **1**, 7731-11-5; tetraphenylphosphonium salt of **1**, 7771-13-3; tetraphenylarsonium salt of **1**, 7731-12-6; cesium 3-fluoro-1,1,4,5,5-pentacyano-2-azapentadienide dioxanate, 7731-13-7.

The Reaction of 9,9-Dibromobicyclo[6.1.0]non-2-ene with Methyllithium[1]

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The reaction of *gem*-dibromocyclopropanes with methyllithium, magnesium, or sodium on alumina to give allenes has been shown to be quite general.[3] The reaction takes other courses in certain cases where the rate of allene formation is diminished owing to its strain energy.[4] We wish to describe here the reaction of 9,9-dibromobicyclo[6.1.0]non-2-ene (I) which is of the latter type.[5]

Treatment of I with a large excess of methyllithium afforded a hydrocarbon fraction which was at first thought to be homogeneous.[5] However, very careful vapor–liquid chromatography showed it to consist of two compounds in the ratio 2:1. A small amount of each has now been obtained by repeated preparative vapor–liquid chromatography and the data which follow show the components of this mixture to be tricyclo-

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(1) Sponsored by the Robert A. Welch Foundation. Work was done at the University of Texas.

(2) Department of Chemistry, University of Utah.

(3) W. von E. Doering and P. M. LaFlamme, *Tetrahedron*, **2**, 75 (1958); L. Skattebøl, *Tetrahedron Letters*, No. 3, 167 (1961); L. Skattebøl, *Chem. Ind.* (London), 2146 (1962); L. Skattebøl, *Acta Chem. Scand.*, **17**, 1683 (1963); P. D. Gardner and M. Narayana, *J. Org. Chem.*, **26**, 3518 (1961).

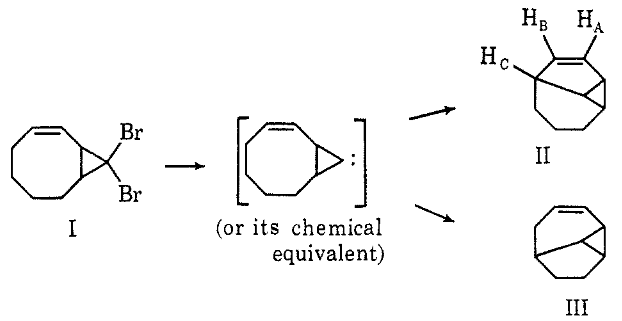
(4) W. R. Moore and H. R. Ward, *ibid.*, **25**, 2073 (1960); W. J. Ball and S. R. Landor, *Proc. Chem. Soc.*, 143 (1961); W. R. Moore, H. R. Ward, and R. F. Merritt, *J. Am. Chem. Soc.*, **83**, 2019 (1961); E. T. Marquis and P. D. Gardner, *Tetrahedron Letters*, No 25, 2793 (1966).

(5) Mention of the product of this reaction was made earlier[6] and on the basis of ozonolysis and hydrogenation I was stated to be 1,3,6-cyclononatriene. The work of Watthey and Winstein[7] has adequately shown this is not so. A repetition in our laboratories of each experiment on which the assignment was based has failed to give the results previously reported[6] and these data should therefore be disregarded.

(6) D. Devaprabhakara, C. G. Cardenas, and P. D. Gardner, *J. Am. Chem. Soc.*, **85**, 1553 (1963); D. Devaprabhakara, Ph.D. Dissertation, University of Texas, 1962, p 32.

(7) J. W. H. Watthey and S. Winstein, *J. Am. Chem. Soc.*, **85**, 3715 (1963); D. S. Glass, J. W. H. Watthey, and S. Winstein, *Tetrahedron Letters*, 377 (1965).

SCHEME I



[6.1.0.0^{5,9}]non-6-ene (II) and tricyclo[6.1.0.0^{5,9}]non-2-ene (III), respectively. (See Scheme I.) Because only a small portion of the mixture could be separated, many of the data reported here were obtained from the mixture. The nmr spectra of II and III are shown in Figures 1 and 2, respectively. Principal features in the spectrum of II are a one-proton olefinic doublet centered at τ 4.38 (H_A, J = 6.0 cps) further split into triplets ($J \sim 2$ cps),[8] a one-proton olefinic doublet centered at 4.70 (J = 6.0 cps, H_B) further split into doublets ($J \sim 2$ cps), and a one-proton multiplet (H_C) centered at 6.88. This last resonance is in a position characteristic of a bridgehead proton allylic to both a double bond and a cyclopropane ring.[9] Double-resonance experiments showed that irradiation of the τ 6.88 signal simplified the 4.70 signal. It should be noted that the coupling constant for the olefinic signals of II is consistent with others observed for olefinic protons on five-membered rings.[11] The spectrum of III exhibits two olefinic doublets centered at τ 4.12 and 4.28 (J = 10.5 cps). Similarly, the coupling constant for the olefinic signals of III is as expected for a six-membered ring.[11]

Diimide reduction of a mixture of II and III afforded a *single* product thus establishing that the two substances have the same skeletal structure and are double-bond isomers. This product, presumed to be tricyclo[6.1.0.0^{5,9}]nonane (IV), gave a complex nmr spectrum but, significantly, its highest field signal is a multiplet centered at τ 9.2. This is suggestive of a cyclopropane ring but rules out the possibility of a methylene group in the cyclopropane ring, since this type system would give rise to signals in the τ 10 region.[12]

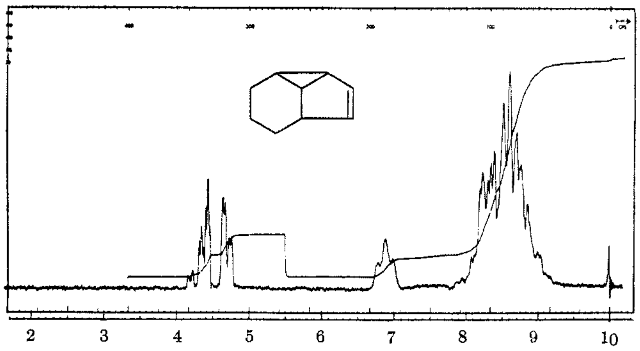


Figure 1.—Nmr spectrum of tricyclo[6.1.0.0^{5,9}]non-6-ene (II).

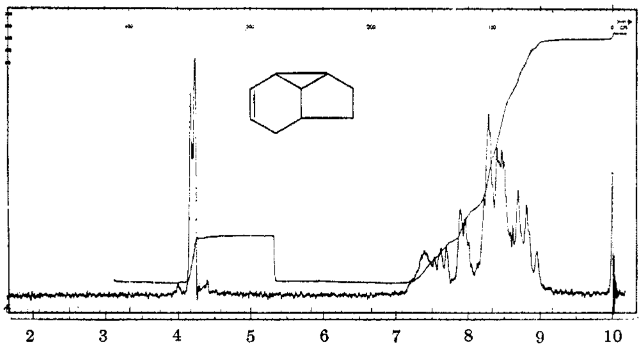


Figure 2.—Nmr spectrum of tricyclo[6.1.0.0^{5,9}]non-2-ene (III).

The 6,5-ring fusion in II and III was established by a two-step sequence involving thermal 1,5-hydrogen transfer[14] and reduction. A *single* product which has been shown to be *cis*-bicyclo[4.3.0]nona-2,8-diene (V, 73%) was obtained by heating the mixture of II and III in an ampoule at 170°. The nmr spectrum of V displays olefinic signals over the range τ 3.9–4.8 (four protons), a multiplet centered at 6.92 (one proton, bisallylic), and a multiplet extending from 7.25 to 9.00. Catalytic hydrogenation (1.95 mole equiv) of V afforded a mixture of *cis-* and *trans*-bicyclo[4.3.0]nonane (VI) in the ratio 78:22. These compounds were identified by comparing their chromatographic retention times and nmr spectra of the mixture with those of authentic samples.[15] Confirmatory evidence for the structure of V is provided by the fact that base-catalyzed isomerization gave bicyclo[4.3.0]nona-1(6),3-diene (VII) and an isomeric conjugated diene (27:73). The identity of VII was established by spectral and chromatographic retention time comparisons with an authentic sample.[16] Base-catalyzed isomerization of VII gave the same product mixture. (See Scheme II.)

The absence of a CH$_2$ group in the cyclopropane ring in IV and the establishment of the structure of V leaves no doubt that the ring system of II and III is correctly represented. Moreover, the mechanism of the 1,5-hydrogen transfer reaction is sufficiently well understood[14] that it may be concluded that, of the double-bond isomers possible in this ring system, only II and III could give rise to V thermally.

A point of some interest in the I → II + III transformation is the apparent absence of any product re-

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(8) This does not necessarily indicate two coupling constants of 2 cps, but rather two coupling constants which *sum* to 4 cps. For excellent discussions of "virtual coupling," see J. I. Musher and E. J. Corey, *Tetrahedron*, **18**, 791 (1962), and P. Laszlo and P. von R. Schleyer, *J. Am. Chem. Soc.*, **86**, 1171 (1964). The weak signal at τ 4.2 in the spectrum of II is due to contamination by a trace of III.

(9) This signal is very close in chemical shift to that reported for the analogous hydrogen atom in tricyclo[5.1.0.0^{4,8}]oct-2-ene.[10]

(10) O. L. Chapman, G. W. Borden, R. W. King, and B. Winkler, *ibid.*, **86**, 2660 (1964).

(11) O. L. Chapman, *ibid.*, **85**, 2014 (1963). To our knowledge no violations of these empirical rules have been observed for five- and six-membered cycloalkenes.

(12) K. B. Wiberg and B. J. Nist, *ibid.*, **83**, 1226 (1961); D. J. Patel, M. E. H. Howden, and J. D. Roberts, *ibid.*, **85**, 3218 (1963); J. A. Pople, W. G. Schneider, and H. J. Bernstein, "High Resolution Nuclear Magnetic Resonance," McGraw-Hill Book Co., Inc., New York, N. Y., 1959, pp 236, 285, and 289. An excellent model for comparison is tricyclo[5.1.0.0^{4,8}]octane which gives signals at no higher field than τ 8.9.[13] By contrast, the spectrum of bicyclo[4.1.0]heptane has cyclopropane CH$_2$ signals at τ 9.9–10.2 (one proton) and 9.4–9.7 (one proton). The remaining two cyclopropane protons (bridgehead) give a multiplet at τ 9.0–9.4.

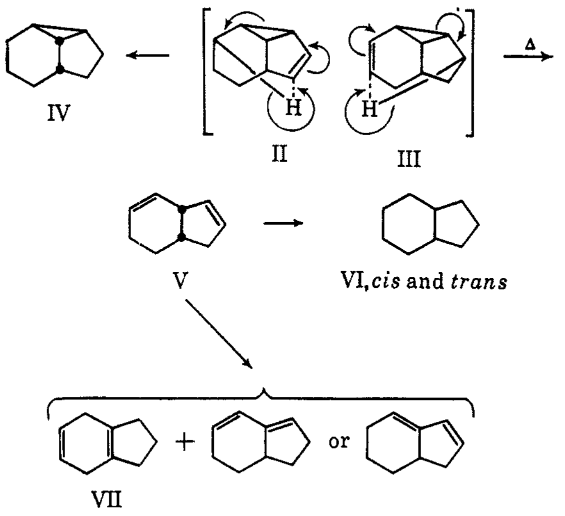
(13) J. Zirner and S. Winstein, *Proc. Chem. Soc.*, 235 (1964).

(14) *Cf.* W. R. Roth and B. Peltzer, *Angew. Chem., Intern. Ed. Engl.*, 440 (1964); R. J. Ellis and H. M. Frey, *Proc. Chem. Soc.*, 221 (1964).

(15) The commercially available mixture was separated by preparative vapor–liquid chromatography and the components were identified by their physical properties: N. L. Allinger and J. C. Coke, *J. Am. Chem. Soc.*, **82**, 2553 (1960).

(16) K. G. Untch, *ibid.*, **85**, 345 (1963).

SCHEME II



sulting from insertion of the carbenoid intermediate on ether (solvent). The yield of intramolecular insertion products appears to be higher in this case than in any other studied to this time.[4,17]

Experimental Section

Reaction of 9.9-Dibromobicyclo[6.1.0]non-2-ene with Methyllithium.—A solution of 64 g (0.22 mole) of 9,9-dibromobicyclo-[6.1.0]non-2-ene (1)[18] in 200 ml of anhydrous ether was placed in a large, three-necked flask which was outfitted with a dropping funnel, stirrer, and a nitrogen-purge system. Ethereal methyllithium, prepared from 42.0 g (6.0 g-atoms) of lithium, 469 g (3.3 moles) of methyl iodide, and 1.1 l. of anhydrous ether, was filtered directly into the dropping funnel. The system was purged with nitrogen and cooled to −35 to −40°. The methyllithium solution was added dropwise with stirring while the temperature of the reaction mixture was maintained at −35°. When addition was complete the mixture was allowed to warm to room temperature. Water was added *very* cautiously from the dropping funnel to destroy excess methyllithium and the reaction mixture was then processed in the usual manner. Solvent was removed from the dried ethereal solution by fractional distillation and the residue was flash distilled under reduced pressure to give 13.5 g (51%) of a mixture of II and III. Varpor–liquid chromatography revealed that only trace contaminants were present. A preparative unit[19] was used to separate small samples of pure II and III for nmr studies (Figures 1 and 2).

Anal. Calcd for C_9H_{12}: C, 89.94; H, 10.06. Found: C, 89.80; H, 10.12.

Diimide Reduction of II and III.—A mixture of 6.2 g (0.051 mole) of a mixture of II and III (2:1), 20.0 g (0.10 mole) of dipotassium azodicarboxylate, and 175 ml of methanol was placed in a 1-l., three-necked flask outfitted with a dropping funnel. The system was purged with nitrogen and stirred magnetically while acetic acid (175 ml) was added at a rate of 4 drops/min. Stirring was continued for 2 days and the mixture was then poured into cold water and processed by pentane extraction. Solvent was removed using a fractionating column. The residue was examined by vapor–liquid chromatography and found to consist of a new compound and unreacted III (80:20). The mixture was recycled twice through the reduction procedure to produce only a minor improvement (85:15). This material (4.07 g, 65%) was finally separated by vapor–liquid chromatography to give pure tricyclo[6.1.0.0^{5,9}]nonane (IV) which, after sublimation at 30° (0.1 mm), melted at 43–45°.

Anal. Calcd for C_9H_{14}: C, 88.45; H, 11.55. Found: C, 88.61; H, 11.20.

Thermal Isomerization of II and III.—The 2:1 mixture of II and III (2.6 g) was sealed with a crystal of hydroquinone under nitrogen in a Pyrex ampoule. The tube was immersed in an oil bath and heated to 170° for 65 hr. Bulb-to-bulb distillation of this material afforded 1.9 g (73%) of *cis*-bicyclo[4.3.0]nona-2,8-diene (V) which appeared to be pure by vapor–liquid chromatography, $n^{24}{}_{\mathrm{D}}$ 1.5205.

Anal. Calcd for C_9H_{12}: C, 89.94; H, 10.06. Found: C, 89.72; H, 10.29.

Catalytic Hydrogenation of *cis*-Bicyclo[4.3.0]nona-2,8-diene (V).—To a presaturated mixture of 20 mg of 5% palladium-carbon and 5.0 ml of methanol contained in a microhydrogenator was added 91.1 mg of IV. The mixture was then stirred magnetically under 1 atm of hydrogen. One mole equivalent was absorbed rapidly and a second was absorbed much more slowly (1.95 total). Analysis by vapor–liquid chromatography, using several columns and authentic samples for comparison, showed the product to consist of 78% *cis*-bicyclo[4.3.0]nonane, 22% *trans*-bicyclo[4.3.0]nonane (VI), and smaller amounts of indan and an unidentified component.

Base-Catalyzed Isomerization of *cis*-Bicyclo[4.3.0]nona-2,8-diene (V).—Dry potassium *t*-butoxide, prepared from 0.33 g of potassium, was dissolved in 25 ml of dry dimethyl sulfoxide which had been purged with dry nitrogen. To the solution was added 0.88 g of V. The solution was stirred at 30° for 30 min and then quenched by pouring into cold water. The product was isolated in the usual way by ether extraction and evaporation of solvent through a fractionating column. Bulb-to-bulb distillation gave 0.50 g (57%) of a mixture which was shown by vapor–liquid chromatography to be bicyclo[4.3.0]nona-1(6),3-diene (VII) and a conjugated isomer in the ratio 27:73. The spectral properties of VII were identical with those of an authentic sample.[16] The same mixture was obtained by treatment of pure VII with base under the conditions described for the isomerization of V.

Registry No.—9,9-Dibromobicyclo[6.1.0]non-2-ene, 2570-08-3; methyllithium, 917-54-4; II, 7603-32-9; III, 7603-33-0; IV, 3103-88-6; V, 7603-35-2; *cis*-bicyclo-[4.3.0]nonane, 4551-51-3; VI, 3296-50-2; VII, 7603-37-4.

Synthesis of Simple Tricyclo[4.4.4.0^{1,6}] Compounds[1]

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Our interest in tricyclic systems of the $[n.n.n.0^{1,n+2}]$ type[2] and possession of some of the required compounds in connection with another synthesis has led us to examine, as simply constructed models of such systems, some 2,2-disubstituted cyclohexanones whose side chains are capable of forming additional rings by condensation at the ketone function.

As precursors, compounds of the general type of II and V are readily available because of the curious fact that unsymmetrical ketones usually undergo the Michael reaction at the more highly substituted α position;[3] consequently, two successive Michael condensations on cyclohexanone will tend to produce

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(17) E. T. Marquis and P. D. Gardner, *Chem. Commun.*, 726 (1966).

(18) C. L. Osborn, T. C. Shields, B. A. Shoulders, J. F. Krause, H. V. Cortez, and P. D. Gardner, *J. Am. Chem. Soc.*, **87**, 3158 (1965).

(19) This separation could be effected only by use of a 12 ft × 1/8 in. column containing 35% of a saturated solution of silver nitrate in tetraethylene glycol on Chromosorb P. Resolution was not complete and recycling was necessary.

(1) Support for this work from the donors of The Petroleum Research Fund of The American Chemical Society and from the Rutgers Research Council is gratefully acknowledged.

(2) (a) S. M. McElvain and G. R. McKay, Jr., *J. Am. Chem. Soc.*, **77**, 5601 (1955); (b) G. Snatzke and G. Zanati, *Ann.*, **684**, 62 (1965).

(3) H. O. House, "Modern Synthetic Reactions," W. A. Benjamin, Inc., New York, N. Y., 1965, p 209, and references there cited.