plotted against time (sec.). The following tabulation presents crude data from a typical run:

ETHYL BENZOYLACETATE 2,4-DINITROPHENYLHYDRAZONE (STABLE)

λ_{max} 550 mμ, A_o 2.25

Time, sec.	20	40	60	80	100	120	140
A_t	1.92	1.57	1.28	1.06	0.90	0.75	0.65

2,4-Dinitrophenylhydrazone of ethyl benzoylacetate (stable). To a solution at room temperature of 6.5 g. (33.8 mmoles) of ethyl benzoylacetate in 25 ml. of 95% ethanol was added sufficient reagent (prepared according to Shriner and Fuson[3]) to furnish an equimolar amount of 2,4-dinitrophenylhydrazine. Precipitation occurred within a minute. The precipitate was filtered after 2 hr. at room temperature, washed with ethanol, and recrystallized from ethanol-ethyl acetate. Yield of orange crystals 10.7 g. (85%), m.p. 161.5–163.5°. An analytical sample was recrystallized from glacial acetic acid and air dried, m.p. 163–164°.

Anal. Calcd. for $C_{17}H_{16}O_6N_4 \cdot C_2H_4O_2$: C, 53.0; H, 4.64; N, 13.0. Found: C, 53.3, 53.2; H, 4.82, 4.61; N, 13.2, 13.3.

It was recrystallized from ethanol-ethyl acetate and dried overnight at 78° (1 mm.), m.p. 164–166°. $\lambda_{max}^{CHCl_3}$ 378 mμ (ϵ = 27,500), 241 mμ (ϵ = 16,350); $\lambda_{max}^{CHCl_3}$ 3.05 μ (NH), 5.77 μ (ester C = O). Peaks at 6.93 μ and 9.05 μ are present in the stable, but not present or very weak in the unstable form.

Anal. Calcd. for $C_{17}H_{16}O_6N_4$: C, 54.8; H, 4.33; N, 15.0. Found: C, 54.8; H, 4.50; N, 15.0.

2,4-Dinitrophenyl hydrazone of ethyl benzoylacetate (unstable form). Saturated solutions of the stable form of the 2,4-dinitrophenylhydrazone of ethyl benzoylacetate in benzene were exposed in borosilicate glass flasks to sunlight over a period of 2 weeks. The solvent was removed *in vacuo*, and the residue was extracted with two 5-ml. portions of 95% ethanol. The ethanolic solution was evaporated *in vacuo*, and the residue was recrystallized four times from benzene–petroleum ether (b.p. 65–110°). The best yield was 5% of orange crystals, m.p. 121–122.5°. $\lambda_{max}^{CHCl_3}$ 364 mμ (ϵ = 24,760); 257 mμ (ϵ = 13,380); $\lambda_{max}^{CHCl_3}$ 3.05 μ (NH), 5.77 μ (C = O). A peak at 9.28 μ is present in the unstable form, but absent in the stable.

Anal. Calcd. for $C_{17}H_{16}O_6N_4$: N, 15.0. Found: N, 15.2.

Conversion of unstable to stable isomer. A solution of 2 mg. of the 2,4-dinitrophenylhydrazone of ethyl benzoylacetate in 2 ml. of 95% ethanol containing a droplet (approx. 20 mg.) of concd. hydrochloric acid was boiled for 1 min. Removal of the solvent *in vacuo* left a residue which melted at 160–163° and gave an ultraviolet spectrum identical with that of the stable form. Thermal isomerization was relatively slow; thus a melt held at 140° took about 15 min. to resolidify so that remelting occurred at about 155–161°.

1-(2,4-Dinitrophenyl)-3-phenyl-5-pyrazolone. To a solution of 0.100 g. (0.260 mmole) of the 2,4-dinitrophenylhydrazone of ethyl benzoylacetate in a mixture of 3 ml. benzene and 1 ml. of absolute ethanol at room temperature was added 0.5 ml. of a solution of 2.55 g. of sodium in 100 ml. of absolute ethanol. After 15 min. at room temperature, the solution was acidified with glacial acetic acid, and petroleum ether (b.p. 30–65°) was added until precipitation was complete. The precipitate was recrystallized twice from benzene–petroleum ether. Yield of light yellow crystals was 0.062 g. (71%), m.p. 203–204°. $\lambda_{max}^{CHCl_3}$ 350 mμ (ϵ = 10,800), 300 mμ (ϵ = 16,000); $\lambda_{max}^{CHCl_3}$ 5.86 μ (C = O), no peak at 3 μ.

Anal. Calcd. for $C_{15}H_{10}O_5N_4$: N, 17.2. Found: N, 17.5.

Acknowledgment. The combustion and ultraviolet and infrared data were obtained in the Analytical Section of Standard Research Institute. The authors are indebted to Mr. L. F. Johnson of Varian Associates for the NMR spectra. This work was supported by the Division Research Committee of Stanford Research Institute.

MENLO PARK, CALIF.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, DUKE UNIVERSITY]

The Synthesis of 2-Aza-1,2-dihydrodicyclopentadienes[1,2]

CHICITA F. CULBERSON AND PELHAM WILDER, JR.

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The synthesis of the isomeric *endo*- and *exo*-2-aza-1,2-dihydrodicyclopentadienes and several *N*-alkyl derivatives is described.

The facile rearrangement of *endo*-dicyclopentadiene and its 1,2-dihydro derivative (I) to 9-substituted *exo* compounds by addition of halogen acids, sulfuric acid, acetic acid, or formic acid has been fully demonstrated.[3-5] Recently a study of 2-oxa-1,2-dihydro-*endo*-dicyclopentadiene (II) has indicated that under similar conditions, addition of acids to the norbornylene double bond leads to little or no structural rearrangement.[6] An investigation of the effects of a nitrogen atom in the 2-position of 1,2-dihydro-*endo*-dicyclopentadiene upon reactions with acidic reagents[7] has lead to the synthesis of several 2-aza derivatives. Only three *N*-alkylated derivatives of 2-aza-1,2-dihydro-*endo*-

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[1] Presented in part before the Division of Organic Chemistry, 135th National Meeting of the American Chemical Society, Boston, Mass., April 5-10, 1959.

[2] Taken in part from a dissertation submitted by Chicita F. Culberson to the Graduate School of Duke University in partial fulfillment of the requirements for the Ph.D. degree (1959).

[3] P. D. Bartlett and A. Schneider, *J. Am. Chem. Soc.*, **68**, 6 (1946).

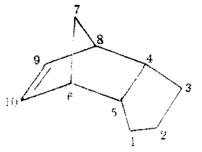
[4] H. A. Bruson and T. W. Riener, *J. Am. Chem. Soc.*, **67**, 723, 1178 (1945); *J. Am. Chem. Soc.*, **68**, 8 (1946).

[5] P. Wilder, Jr., Chicita F. Culberson, and G. T. Youngblood, *J. Am. Chem. Soc.*, **81**, 655 (1959).

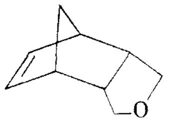
[6] Chicita F. Culberson, J. H. Seward, and P. Wilder, Jr., *J. Am. Chem. Soc.*, **82**, 2541 (1960).

[7] P. Wilder, Jr. and Chicita F. Culberson, *J. Am. Chem. Soc.*, **81**, 2027 (1959).

dicyclopentadiene (III) have been previously reported and the isomeric 2-aza-1,2-dihydro-*exo*-dicyclopentadiene (IV) represents the first member of a new heterocyclic ring system. The results of the synthetic portion of the study of the 2-aza system are presented here. The reactions of 2-aza-1,2-dihydrodicyclopentadiene will be discussed in a subsequent paper.



I



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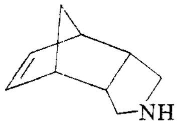
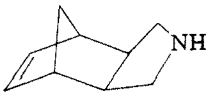


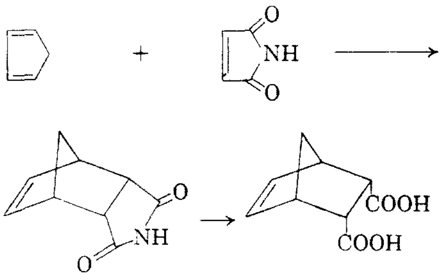
III



IV

In 1954 Rice, Ried, and Grogan,[8] studying a number of cyclic amines for testing as hypotensive agents, found that *N*-alkyl derivatives of *endo*-bicyclo[2.2.1] - 5 - heptene - 2,3 - dicarboxylic acid imide (V) were readily reduced with lithium aluminum hydride to the corresponding *N*-substituted amines. Nine imides, butyl through dodecyl, were synthesized by treating the anhydride IX with the appropriate amine and then heating the reaction mixture for two hours at 160–170°. Arnold and Searle[9] had previously prepared a large number of *N*-substituted imides by refluxing the anhydride and the amine in an inert solvent while removing the water formed during the reaction. The boiling points of the imides prepared by Rice and also reported by Arnold are not in agreement, and it seemed possible that thermal rearrangement to the *exo* form might have occurred during the two-hour heating at 160–170°. It is shown in the present study, however, that the *N*-hexylamine reported by Rice does not have the *exo* configuration expected if the imide had rearranged during its synthesis.

Although the unsubstituted amine, 2-aza-1,2-dihydro-*endo*-dicyclopentadiene (III) has not been previously reported, the imide (V) from which it is prepared is known. Harvey[10] synthesized the imide by a Diels-Alder addition of maleimide and cyclopentadiene in ether at room temperature. The product, obtained in 93% yield, was hydrolyzed with base to the known *endo-cis*-bicyclo[2.2.1]-5-heptene-2,3-dicarboxylic acid (VI). The Diels-Alder addition was also effected by Blomquist and Winslow[11] who showed the identity of this product to that obtained by refluxing the diammonium salt of the *endo-cis* acid VI in acetic anhydride. The same imide was prepared by Morgan *et al.*[12] by heating a mixture of the *endo* anhydride IX and ammonium carbonate to a temperature of 200°. The yield by this method was only 45%, doubtless because some of the product was lost by a reversal of the Diels-Alder addition of maleimide and cyclopentadiene. The reverse Diels-Alder reaction occurs[10] upon heating the imide V above its melting point (187°). The imide was also synthesized by Morgan in 84% yield by directing a stream of ammonia gas over the molten anhydride at 170° and a modification of this method has been used in the present study, maleimide required for the direct Diels-Alder reaction not being readily available.



V VI

Lithium aluminum hydride reduction of the unsubstituted imide V, essentially according to the method of Rice *et al.*,[8] yields the secondary amine, 2-aza-1,2-dihydro-*endo*-dicyclopentadiene (III). This amine, purified by repeated vacuum sublimation, is obtained as a soft colorless solid which absorbs carbon dioxide from the atmosphere with extreme rapidity. Because of this instability, a melting point of the pure amine is not a useful identification and an elemental analysis in close agreement with the calculated is difficult to obtain. The compound is more readily identified through its benzenesulfonamide and its picrate, which give good melting points and elemental analyses. The unsaturated secondary amine III is rapidly reduced, over Adams' catalyst at one atmosphere of hydrogen, to 2-azatetrahydro-*endo*-dicyclopentadiene, a compound also easily carbonated and best identified by its benzenesulfonamide or its picrate.

Two *N*-substituted derivatives of 2-aza-1,2-dihydro-*endo*-dicyclopentadiene were synthesized by lithium aluminum hydride reduction of the appropriate imides according to the method of Rice. The *N*-alkylated imides were prepared directly from the unsubstituted imide V by a modification of a method previously used to alkylate

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(8) L. M. Rice, E. E. Ried, and C. H. Grogan, *J. Org. Chem.*, **19**, 884 (1954).

(9) H. W. Arnold and N. E. Searle, U. S. Patent **2,462,835** (1949).

(10) S. C. Harvey, *J. Am. Chem. Soc.*, **71**, 1121 (1949).

(11) A. T. Blomquist and E. C. Winslow, *J. Org. Chem.*, **10**, 149 (1945).

(12) M. S. Morgan, R. S. Tipson, A. Lowy, and W. E. Baldwin, *J. Am. Chem. Soc.*, **66**, 404 (1944).

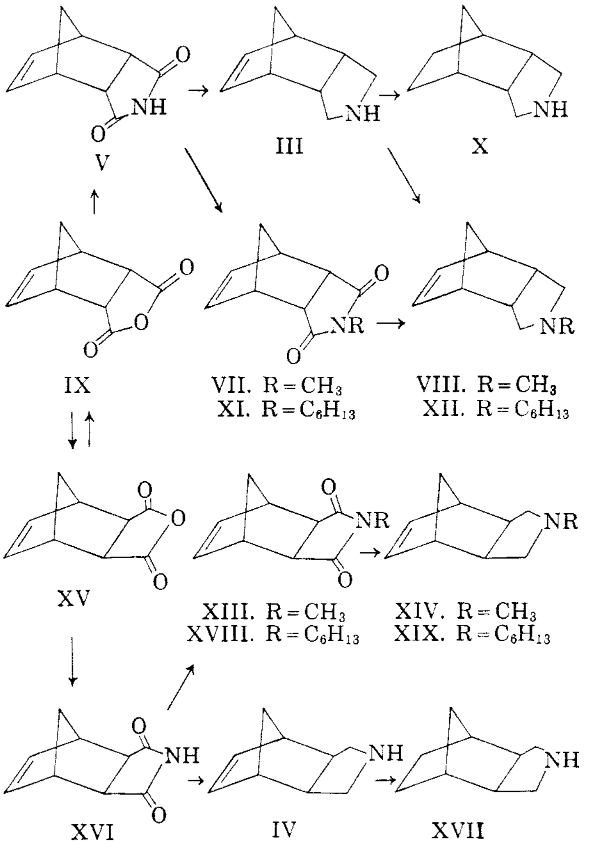
the potassium salts of phthalimide[13] and 2,4-thiazolidinedione.[14] A mixture of potassium carbonate, alkyl halide and unsubstituted imide in dimethylformamide, stirred for ten hours at room temperature, yielded the substituted imide. A separate synthesis and isolation of the potassium salt of the imide V was unnecessary. Under these mild conditions thermal rearrangement cannot occur and excellent yields of substituted imides are obtained. The *N*-methyl imide VII which gave a melting point in agreement with that reported by Arnold[9] was smoothly reduced to the corresponding *N*-methyl-2-aza-1,2-dihydro-*endo*-dicyclopentadiene (VIII). This liquid tertiary amine readily forms a methiodide and a picrate and is much more stable toward carbonation than the previously described secondary amines.

The *N*-hexyl imide XI prepared at room temperature as described above was reduced with lithium aluminum hydride to the *N*-hexyl amine XII. The physical constants of this amine and the melting point of its methiodide are close to those reported by Rice, and quite different from those of the *exo* isomer described below. Both the *N*-hexyl and the *N*-methyl amines are also obtained in small yield by alkylation of the unsaturated secondary amine III with the appropriate alkyl halides.

To provide further evidence of the *endo* configuration of the amines discussed above the corresponding *exo* isomers were prepared. The *endo* anhydride IX was thermally equilibrated with its *exo* isomer by the method of Craig[15] and the *exo* anhydride was isolated by fractional recrystallization from benzene. Treating the *exo* anhydride with heat and ammonia gas yielded the *exo* imide XVI apparently contaminated with some of the *endo* isomer either because the starting anhydride was not pure or because thermal rearrangement occurred during the reaction. The *exo* imide XVI was purified by fractional recrystallization from water. Reduction with lithium aluminum hydride yielded 2-aza-1,2-dihydro-*exo*-dicyclopentadiene (IV), a liquid which carbonated immediately upon exposure to the atmosphere. The benzenesulfonamide and the picrate of this amine were shown by melting point and mixed melting point to be different from the derivatives obtained from the *endo* amine III. Catalytic reduction of the *exo* amine IV yielded the low-melting solid 2-azatetrahydro-*exo*-dicyclopentadiene (XVII).

The *N*-methyl and *N*-hexyl derivatives of 2-aza-1,2-dihydro-*exo*-dicyclopentadiene (IV) were prepared by lithium aluminum hydride reduction of the *N*-methyl and *N*-hexyl *exo* imides formed from the unsubstituted imide by the same method used to obtain the *endo* isomers.

The purity of the saturated and unsaturated secondary amines (III, X, IV, and XVII) and the *N*-methyl amines (VIII and XIV) was verified by gas chromatography. The secondary amines were passed through a two-meter column of firebrick and polypropylene glycol at 191°. The *N*-methyl amines were tested with a similar column at 150°. Under the conditions used the retention times of the unsaturated secondary amines III and IV were very close and small amounts of one mixed with the other would not have been detectable. But saturating the *endo* isomer decreased the retention time by about one minute while the retention time of the saturated *exo* isomer was increased about one minute. Thus the retention times of the saturated *endo* and *exo* isomers differed by two minutes and since these derivatives were prepared in high yield, their purity helps to establish the purity of the unsaturated amines.



EXPERIMENTAL[16]

endo-Bicyclo[2.2.1]-5-heptene-2,3-dicarboxylic acid imide (V). The imide was prepared by the method of Morgan *et al.*[12] except that a lower reaction temperature was used. A stream of ammonia gas was passed through 300 g. (1.8 moles) of solid *endo* anhydride IX at 120°. The solid melted and the temperature increased to 150° with a vigorous expulsion of water vapor and ammonia. When the melt resolidified, the

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[13] J. C. Sheehan and W. A. Bolhofer, *J. Am. Chem. Soc.*, **72**, 2786 (1950).

[14] Chien-Pen Lo and E. Y. Shropshire, *J. Org. Chem.*, **22**, 999 (1957).

[15] D. Craig, *J. Am. Chem. Soc.*, **73**, 4889 (1951).

[16] Melting points and boiling points are uncorrected. Analyses are by Galbraith Microanalytical Laboratories, Knoxville, Tenn., and Drs. Weiler and Strauss, 164 Banbury Road, Oxford, England.

reaction was allowed to cool and recrystallization of the product from water yielded 262 g. (88%) of the imide; 250 g. in the first crop, m.p. 185–186.5° and 12 g. in the second crop, m.p. 184–186.5°. A small amount of the imide was recrystallized again from water, m.p. 186–187° (reported[12] m.p. 186.5–187°).

exo-Bicyclo[2.2.1]-5-heptene-2,3-dicarboxylic acid imide (XVI). Ammonia gas was passed through 16.4 g. (0.10 mole) of solid *exo* anhydride XV[15] and the temperature was raised. At about 120° the solid melted and the temperature increased to 130° with a release of ammonia and water after which the melt resolidified. Several recrystallizations from water yielded 9.5 g. (71%) of the *exo* imide, m.p. 163.5–164°; mixed melting point with the *endo* isomer, 135–149°.

Anal. Calcd. for $C_9H_9NO_2$: C, 66.24; H, 5.56. Found: C, 66.06; H, 5.46.

Alkylation of the endo and exo imides V and XVI. (*1*) *With methyl iodide.* A mixture of 8.2 g. (0.050 mole) of the unsubstituted imide, 7.2 g. (0.052 mole) of potassium carbonate, 9.0 g. (0.063 mole) of methyl iodide, and 40 ml. of dimethyl formamide was stirred vigorously overnight, diluted to about 400 ml. with water, and extracted with chloroform. The extract was washed with water, 10% sodium hydroxide, and again with water and was then dried over magnesium sulfate. Chloroform was removed under diminished pressure and the product, which solidified on standing, was recrystallized from water.

The *endo* imide V yielded 7.4 g. (85%) of the *N*-methyl derivative VII, m.p. 105–106° (reported[9] m.p. 105–107°).

The *exo* imide XVI yielded 5.9 g. (67%) of the *N*-methyl derivative XIII, m.p. 103–104°; mixed melting point with the *endo* isomer, 75–85°.

Anal. Calcd. for $C_{10}H_{11}NO_2$: C, 67.78; H, 6.26. Found: C, 67.52; H, 6.06.

(*2*) *With hexyl bromide.* The imides were alkylated with hexyl bromide by the same method used to form the *N*-methyl derivatives except that 8.2 g. (0.052 mole) of the bromide was used.

The *endo* imide yielded 11.6 g. (94%) of the *N*-hexyl derivative XI, b.p. 137–138°, 0.25 mm., n_D^{24} 1.5023 (reported[8] b.p. 125–130°, 0.3 mm., n_D^{25} 1.4996).

From 4.1 g. (0.025 mole) of the *exo* imide XVI and half quantities of the other reagents indicated above, 5.8 g. (94%) of the *N*-hexyl derivative XVIII was obtained, b.p. 138–139°, 0.20 mm., n_D^{23} 1.5049.

Anal. Calcd. for $C_{15}H_{25}N$: C, 82.13; H, 11.49. Found: C, 81.96; H, 11.29.

The infrared spectra of the *exo* and *endo N*-hexyl imides are almost identical in the region 2.0–7.5 μ but are quite different at longer wave lengths, as would be expected.

2-Aza-1,2-dihydro-endo-dicyclopentadiene (III). A solution of 20.0 g. (0.53 mole) of lithium aluminum hydride in 600 ml. of dry ether was stirred rapidly while 32.6 g. (0.20 mole) of solid *endo* imide was added in small portions through a Gooch addition tube. The reaction was refluxed and stirred overnight and then it was immersed in an ice bath and neutralized by cautious addition of water. As soon as the white precipitate began to coagulate, the mixture was filtered rapidly with suction. The ether filtrate was dried over magnesium sulfate and the ether removed yielding 22 g. (82%) of crude *endo* amine III. The product could not be distilled due to solidification and sublimation. A sample was purified by repeated sublimation, m.p. 117–119° with sublimation at about 55°.

Anal. Calcd. for $C_9H_{13}N$: C, 79.95; H, 9.69. Found: C, 79.84; H, 9.81.

A benzenesulfonamide was prepared and recrystallized from 95% ethanol, m.p. 107–108°.

Anal. Calcd. for $C_{15}H_{17}NO_2S$: C, 65.42; H, 6.22. Found: C, 65.26; H, 6.24.

A picrate was prepared, m.p. 196.5–198°.

Anal. Calcd. for $C_{15}H_{16}N_4O_7$: C, 49.45; H, 4.43. Found: C, 49.57; H, 4.19.

2-Azatetrahydro-endo-dicyclopentadiene (X). The *endo* amine III (2.03 g., 0.015 mole) in 50 ml. of absolute ethanol was reduced at room temperature over Adams' catalyst with hydrogen at atmospheric pressure. In less than 25 min. uptake of hydrogen was complete. Solvent was removed under diminished pressure and the residue was taken up in ether and transferred to a sublimation tube. The ether was removed and the product sublimed under reduced pressure yielding 1.84 g. (90%) of the saturated amine X, m.p. 123–124° with sublimation beginning at about 75° and softening at about 105°.

Anal. Calcd. for $C_9H_{15}N$: C, 78.77; H, 11.02. Found: C, 78.91; H, 11.01.

A benzenesulfonamide was prepared and recrystallized from absolute ethanol, m.p. 168–168.5°.

Anal. Calcd. for $C_{15}H_{19}NO_2S$: C, 64.95; H, 6.90. Found: C, 64.80; H, 6.76.

A picrate was prepared and recrystallized from 95% ethanol, m.p. 215–217° dec.

Anal. Calcd. for $C_{15}H_{18}N_4O_7$: C, 49.18; H, 4.95. Found: C, 49.22; H, 5.03.

Alkylation of the endo amine III *with hexyl bromide. N-Hexyl-2-aza-1,2-dihydro-endo-dicyclopentadiene* (XII). A mixture of 6.75 g. (0.05 mole) of the *endo* amine III, 8.25 g. (0.05 mole) of hexyl bromide, and 2.65 g. (0.025 mole) of sodium carbonate in 25 ml. of absolute ethanol was stirred under reflux for 48 hr. Some ethanol was removed under diminished pressure and the residue was taken up in ether and water. The aqueous layer was acidified with 10% hydrochloric acid and extracted with ether to remove unchanged hexyl bromide. The aqueous solution was then made basic and extracted with ether. This extract was washed with water and dried over magnesium sulfate. Removal of the ether and distillation of the residue yielded 4.1 g. (37%) of the *N*-hexyl amine XII, b.p. 96–97°/0.6 mm., n_D^{30} 1.4872 (reported[8] b.p. 83–85°/0.3 mm., n_D^{25} 1.4873).

A methiodide was prepared and purified by dissolving in absolute ethanol and precipitating with anhydrous ether, m.p. 171–172° (reported[8] m.p. 175°).

N-Hexyl-2-aza-1,2-dihydro-endo-dicyclopentadiene (XII). Ten grams (0.040 mole) of the *N*-hexyl imide XI, reduced with lithium aluminum hydride according to the method of Rice *et al.*,[8] yielded 6.95 g. (78%) of the *N*-hexyl amine XII, b.p. 90–91.5°/0.15 mm.

A methiodide was prepared, m.p. 169.5–170.5°; a mixed melting point with the methiodide of the *N*-hexyl amine obtained by alkylation of the *endo* amine III was not depressed.

Methylation of the endo amine III. *N-Methyl-2-aza-1,2-dihydro-endo-dicyclopentadiene* (VIII). A solution of 6.75 g. (0.05 mole) of the *endo* amine III in 50 ml. of benzene was treated dropwise with stirring with 7.0 g. (0.05 mole) of methyl iodide. After 20 min. the benzene was extracted with water and the aqueous solution made basic with 10% sodium hydroxide and extracted with ether. The ether extract was washed with water and dried over magnesium sulfate. Removal of the ether and distillation of the residue yielded 1.47 g. (20%) of the *N*-methyl amine VIII, b.p. 84–85°/15 mm.

A methiodide was prepared, m.p. 254–256°; a mixed melting point with the derivative of the *N*-methyl amine obtained by reduction of the *N*-methyl imide VII was not depressed.

N-Methyl-2-aza-1,2-dihydro-endo-dicyclopentadiene (VIII). Twenty-seven grams (0.15 mole) of the solid *N*-methyl imide VII was added in small portions to a solution of 13 g. (0.35 mole) of lithium aluminum hydride in 800 ml. of dry ether. After stirring under reflux for 15 hr., the reaction was worked up in the usual way. Distillation of the crude product yielded 20.0 g. (89%) of the *N*-methyl amine, b.p. 80–81°/15 mm., n_D^{23} 1.5050.

Anal. Calcd. for $C_{10}H_{15}N$: C, 80.48; H, 10.13. Found: C, 80.61; H, 10.13.

From the amine a methiodide was prepared and purified by precipitation from absolute ethanol with anhydrous ether, m.p. 256.5–257.5°.

Anal. Calcd. for $C_{11}H_{18}IN$: C, 45.37; H, 6.23. Found: C, 45.28; H, 6.42.

A picrate was prepared and recrystallized from 95% ethanol, m.p. 222–223° dec.

Anal. Calcd. for $C_{16}H_{18}N_4O_7$: C, 50.13; H, 4.73. Found: C, 50.11; H, 4.75.

2-Aza-1,2-dihydro-exo-dicyclopentadiene (IV). The *exo* amine IV was prepared from the *exo* imide XVI by exactly the same method used to prepare the *endo* isomer. From 20 g. (0.12 mole) of the imide was obtained 11.1 g. (68%) of the *exo* amine IV after one distillation, b.p. 89–90°/16 mm. A sample was further purified by distillation, b.p. 73–74°/7.5 mm.

Anal. Calcd. for $C_9H_{13}N$: C, 79.95; H, 9.69. Found: C, 79.58; H, 9.89.

A benzenesulfonamide was prepared, m.p. 113–113.5°; mixed melting point with the benzenesulfonamide of the *endo* amine III, 86–92°.

Anal. Calcd. for $C_{15}H_{17}NO_2S$: C, 65.42; H, 6.22. Found: C, 65.26; H, 6.26.

A picrate was prepared, m.p. 196.5–198° dec.; mixed melting point with the picrate of the *endo* isomer, 185–193° dec.

Anal. Calcd. for $C_{15}H_{16}N_4O_7$: C, 49.45; H, 4.43. Found: C, 49.60; H, 4.47.

2-Azatetrahydro-exo-dicyclopentadiene (XVII). From 2.03 g. (0.015 mole) of the *exo* amine IV dissolved in 25 ml. of absolute ethanol and reduced at one atmosphere of hydrogen over Adams' catalyst, 1.81 g. (89%) of the saturated amine was obtained after two sublimations. A sample was prepared by resublimation, m.p. 44–45°.

Anal. Calcd. for $C_9H_{15}N$: C, 78.77; H, 11.02. Found: C, 78.78; H, 11.27.

A benzenesulfonamide was prepared, m.p. 100–101°; mixed melting point with the benzenesulfonamide of the saturated *endo* amine X, 98–124°.

Anal. Calcd. for $C_{15}H_{19}NO_2S$: C, 64.95; H, 6.90. Found: C, 64.64; H, 6.78.

N-Hexyl-2-aza-1,2-dihydro-exo-dicyclopentadiene (XIX). A solution of 4.5 g. (0.018 mole) of the *N*-hexyl imide in anhydrous ether was added slowly to 1.7 g. (0.046 mole) of lithium aluminum hydride in anhydrous ether. The reaction was worked up in the usual way and after one distillation 3.8 g. (95%) of the *N*-hexyl amine, b.p. 94–95°/0.2 mm., was obtained.

Anal. Calcd. for $C_{15}H_{25}N$: C, 82.13; H, 11.49. Found: C, 81.96; H, 11.29.

A methiodide was prepared by dissolving the amine in absolute ethanol and adding excess methyl iodide. After a short time anhydrous ether was added to precipitate the derivative which was purified by redissolving in absolute ethanol and precipitating with anhydrous ether, m.p. 204–206°, mixed melting point with the methiodide of the *endo* isomer XII, 111–163°.

Anal. Calcd. for $C_{16}H_{28}IN$: C, 53.18; H, 7.81. Found: C, 53.06; H, 8.05.

N-Methyl-2-aza-1,2-dihydro-exo-dicyclopentadiene (XIV). From 5.0 g. (0.028 mole) of the *N*-methyl imide XIII reduced with 2.5 g. (0.066 mole) of lithium aluminum hydride in 150 ml. of anhydrous ether was obtained 4.1 g. (98%) of the *N*-methyl amine after one distillation, b.p. 74–77°/14 mm. A sample was further purified by redistillation, b.p. 77–78°/14 mm., n_{D}^{23} 1.4995.

Anal. Calcd. for $C_{10}H_{15}N$: C, 80.48; H, 10.13. Found: C, 80.72; H, 10.13.

A methiodide was prepared, m.p. 273.5–274.5°; mixed melting point with the methiodide of the *endo* *N*-methyl amine VIII, 224–253°.

Anal. Calcd. for $C_{11}H_{18}IN$: C, 45.37; H, 6.23. Found: C, 45.59; H, 6.20.

A picrate was prepared, m.p. 225–228° dec.; mixed melting point with the picrate of the *endo* isomer, 222.5–225° dec.

Anal. Calcd. for $C_{16}H_{18}N_4O_7$: C, 50.13; H, 4.73. Found: C, 49.89; H, 4.82.

Gas chromatography: Of the secondary amines. A modified Perkin-Elmer Model 154B vapor fractometer was used. The 6 mm. × 2 m. column was packed with one part Union Carbide polypropylene glycol-1025 on four parts firebrick (Fischer Columpak, 30–60 mesh, acid washed) by weight.[17] The retention times at 191° and 35 ml./min. helium flow are given below:

Amine	Retention Time, Min.
III	7.6
X	6.8
IV	7.3
XVII	8.3

Except for amines III and IV the retention times were sufficiently different to prove the absence of each of the other amines. Since the retention times of the saturated amines are quite different, the analysis of these derivatives helps to establish the purity of the unsaturated amines with respect to each other.

Of the N-methyl amines. A Model 154C Perkin-Elmer vapor fractometer was used. The 6 mm. × 2 m. column contained 1:4 by weight Union Carbide polypropylene glycol-1025 on Johns-Manville Chromosorb W (30/60). At 150° and about 65 ml./min. helium flow the retention times were 8.8 min. for the *endo* isomer VIII and 7.6 min. for the *exo* isomer XIV.

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DURHAM, N. C.

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[17] This column had been used for some time and the exact proportion of liquid to solid phase was no longer precisely known.