

2.06% chlorine, signifying the presence of $6 \pm 2\%$ of 1-chloro-1,2-diphenylethylene (unknown stereochemistry).

Rambert-Bäcklund Rearrangement of IXa.—A mixture of 3.1 g. (0.01 mole) of IXa, 25 ml. of dioxane, and 15 ml. of 2 *N* sodium hydroxide solution was refluxed with stirring for 16 hr. Upon cooling the solution, there was added 60 ml. of water. The aqueous solution was extracted with three 30-ml. portions of methylene chloride, acidified with concentrated hydrochloric acid, and treated with 1.5 g. (0.015 mole) of *p*-toluidine. The mixture was warmed with scratching until the resulting oil had crystallized. After cooling, this solid was filtered and dried to afford 1.7 g. (47.3%) of the *p*-toluidine salt of phenanthrene-9-sulfonic acid (XV), m.p. 210–216°. Recrystallization of this salt from water yielded pale yellow needles of XV, m.p. 231–232° [reported m.p. 229° (235° cor.),¹² m.p. 230–232°¹³]. The infrared spectrum of this material (in Nujol) was identical with that of an authentic specimen.⁷

The combined organic layers were dried, filtered and evaporated to give 1.0 g. (47.6%) of 9-chlorophenanthrene, m.p. 49–50°. Recrystallization of this sample from aqueous ethanol

afforded white needles, m.p. 52.5–53° (reported¹⁴ m.p. 53–53.5°). The infrared spectrum of this material was likewise superimposable on that of an authentic specimen.⁷

Attempted Ramberg-Bäcklund Rearrangement of IXb.—A mixture of 1.0 g. (2.93 mmoles) of IXb, 5 ml. of dioxane, and 8 ml. of 2 *N* sodium hydroxide solution was refluxed with stirring for 16 hr. The cooled solution was treated with 25 ml. of water and extracted with three 20-ml. portions of chloroform. The combined organic layers were dried, filtered, and evaporated to give 900 mg. (90% recovery) of IXb, m.p. 165–175°.

Treatment of the acidified aqueous layer with *p*-toluidine gave no detectable quantities of a salt. Longer reaction times gave analogous results.

Acknowledgment.—The author gratefully acknowledges support of this work in part by Petroleum Research Fund Grant 169G, administered by the American Chemical Society, and in part by a grant awarded through the office of the Vice President for Research, The Ohio State University.

(12) L. F. Fieser, *J. Am. Chem. Soc.*, **51**, 2460 (1929).

(13) Sr. M. G. Solomon and D. J. Hennessy, *J. Org. Chem.*, **22**, 1649 (1957).

(14) P. B. D. de la Mare, N. V. Klassen, and R. Koenigsberger, *J. Chem. Soc.*, 5285 (1961).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UPJOHN CO., KALAMAZOO, MICH.]

Unsaturated Heterocyclic Systems. VIII. 2,3-Dihydro-1H-azepines¹⁻³

BY LEO A. PAQUETTE⁴

RECEIVED APRIL 15, 1964

The lithium aluminum hydride reduction of 1,3-dihydro-2H-azepin-2-ones has been found to afford seven-membered cyclic dienamines. Although the secondary cyclic dienamine **3a** is quite unstable, tertiary analogs are remarkably stable when the proper precautions are observed. Treatment of the 2,3-dihydro-1H-azepines with perchloric acid afforded crystalline perchlorates resulting from protonation at the δ -carbon atom. The cyclic dienamines have been found to enter very vigorously into Diels-Alder reactions and to photoisomerize as normal conjugated cycloheptadienes.

Among the many intriguing areas of organic chemistry currently under investigation, study of the properties and reactivities of enamines has contributed most significantly to the progress of synthetic methods. Evidence to this effect is given by the wide variety of problems in which enamines have found application.⁵ The reactions of enamines have been so varied and numerous that studies in this area have only in rare circumstances progressed beyond the use of simple enamines and cyclic enamines. We wish now to report, in some detail, the preparation and selected reactions of a class of novel seven-membered cyclic dienamines, the 2,3-dihydro-1H-azepines.⁶

(1) Unsaturated Heterocyclic Systems. VII: L. A. Paquette, *J. Am. Chem. Soc.*, **85**, 4053 (1963).

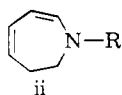
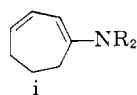
(2) For a preliminary account of a portion of this work, see L. A. Paquette, *Tetrahedron Letters*, 2027 (1963).

(3) Presented in part at the Gordon Research Conference on Heterocyclic Chemistry, New Hampton, N. H., Aug. 24–28, 1964.

(4) Correspondence should be addressed to the Department of Chemistry, The Ohio State University, Columbus 10, Ohio.

(5) For a recent review of enamine chemistry, see J. Szmuszkovicz, "Advances in Organic Chemistry, Methods and Results," Vol. IV, R. A. Raphael, E. C. Taylor, and H. Wynberg, Ed., Interscience Publishers, Inc., New York, N. Y., 1963; see also G. Stork, A. Brizzolara, H. Landesman, J. Szmuszkovicz, and R. Terrell, *J. Am. Chem. Soc.*, **85**, 207 (1963).

(6) In keeping with the nomenclature of enamines,⁵ we propose that i be termed a "dienamine," and ii be referred to as a "cyclic dienamine."



(7) For examples of dienamines such as i, see A. A. Bothner-By, R. S. Schutz, R. R. Dawson, and M. L. Solt, *J. Am. Chem. Soc.*, **84**, 52 (1962); E. Leete, *ibid.*, **84**, 55 (1962).

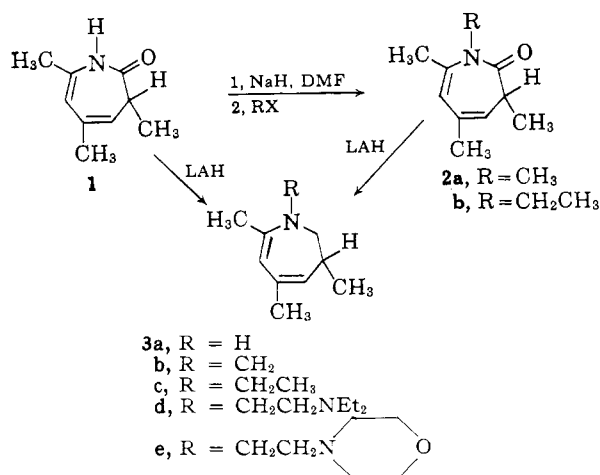
Preparation.—Recently, the interesting ring expansion of the sodium salts of 2,6-dialkyl- and 2,4,6-trialkylphenols with ethereal chloramine at 120–150° was reported from this laboratory.⁸ The unique 1,3-dihydro-2H-azepin-2-ones which result from this reaction appeared to represent, because of the degree of unsaturation present in this heterocyclic system, excellent substrates for the preparation of cyclic dienamines.

Lithium aluminum hydride reduction of 1,3-dihydro-3,5,7-trimethyl-2H-azepin-2-one (**1**) in ethereal solution under an atmosphere of nitrogen afforded, after appropriate alkaline work-up, a white solid (**3a**, see below) which rapidly decomposed exothermically on exposure to the atmosphere with the liberation of white fumes. Although a very small amount of unreduced dihydroazepinone **1** could be isolated from the dark residue, the remainder of the decomposition product was a dark intractable resin. This result, despite the fact that product isolation was not achieved, suggested that cyclic dienamine formation was occurring and prompted further study.

In earlier papers of this series,^{8,9} it was shown that treatment of **1** with sodium hydride in dimethylformamide produced an anion which when alkylated gave rise to N-substituted derivatives such as **2a** and **2b**. When 1,3-dihydro-1,3,5,7-tetramethyl-2H-azepin-2-one (**2a**) was prepared by this method and subjected to lithium aluminum hydride reduction, there was obtained in 91.8% yield a colorless liquid which yellowed

(8) L. A. Paquette, *ibid.*, **84**, 4987 (1962); **85**, 3288 (1963).

(9) L. A. Paquette and J. K. Reed, *J. Med. Chem.*, **6**, 771 (1963).

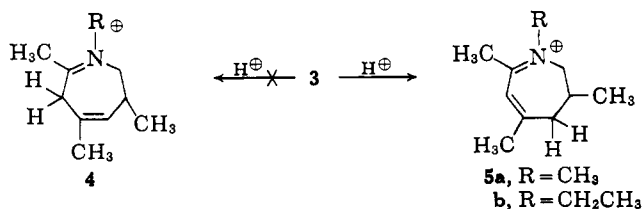


rapidly on exposure to air. The infrared spectrum of this material (**3b**) displayed characteristic enamine absorption at 1635 cm^{-1} ¹⁰ and a broad C=C stretching band at 1595 cm^{-1} . In the ultraviolet, the observed absorption maximum in ether solution at $301\text{ m}\mu$ (7050) was consistent with, and confirmatory for, the 2,3-dihydro-1,3,5,7-tetramethyl-1H-azepine formulation **3b**. The n.m.r. spectrum of **3b** (see Experimental) was very similar to that of the dihydroazepinone **2a** in the region of olefinic protons and methyl substituents and served to remove from consideration any structures which may have resulted from over-reduction during the lithium aluminum hydride treatment.

Similarly, reduction of 1,3-dihydro-1-ethyl-3,5,7-trimethyl-2H-azepin-2-one (**2b**) with lithium aluminum hydride afforded in 79% yield a colorless liquid which yellowed on exposure to air. From intense infrared bands at 1635 and 1585 cm^{-1} , and ultraviolet absorption at $305\text{ m}\mu$ (7500), could be inferred the cyclic diene structure **3c**. The n.m.r. spectrum of this material was in complete accordance with the 2,3-dihydro-1H-azepine formulation.

We have found the cyclic dienamines **3b** and **3c** to be stable for prolonged periods when stored under an atmosphere of nitrogen at -5 to -10° .

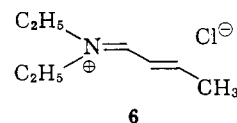
Salt Formation.—Examination of the 2,3-dihydro-1H-azepines synthesized above showed that they possess a new combination of features familiar to enamine chemistry. Firstly, whereas it is well known that enamines are protonated on the β -carbon when treated with acid to give immonium salts, the cyclic dienamines **3** offer two possible sites (in addition to the nitrogen atom) where proton attachment may occur (see **4** and **5**).



The site of protonation of acyclic conjugated dienamines has recently been studied by Opitz and Merz¹¹; these workers showed that protonation by a strong acid gives first the kinetic product, *i.e.*, protonation on nitro-

gen, and that this product then equilibrates to the thermodynamically more stable "en-immonium salt."

In this work, mild treatment of an ethereal solution of **3b** with ethanolic perchloric acid gave rise to a highly crystalline perchlorate salt. The structure of the salt was established as **5a** on the basis of its infrared absorption bands at 1680 (C=N⁺) and 1605 cm^{-1} (C=C) and because of its ultraviolet absorption in ethanol at $272\text{ m}\mu$ (4950). Given the spectral data of **5a**, a comparison with the ultraviolet absorption of, for example, 1-diethylamino-1,3-butadiene hydrochloride (**5**)¹¹ seems appropriate. The reported absorption of **6** [$\lambda_{\text{max}}^{\text{CH}_3\text{CN}}$ $250\text{ m}\mu$ ($10,700$)] demonstrates a decrease in λ_{max} and



an increase in ϵ_{max} relative to the values for **5a**. These data merely reflect another example of the effect of extended conjugation in an acyclic system when related to an isocyclic analog; this effect is best ascribed to the transoid nature of the acyclic counterpart (see **6**) in solution. The isocyclic system of necessity must remain cisoid.

Similarly, 2,3-dihydro-1-ethyl-3,5,7-trimethyl-1H-azepine (**3c**) was readily converted to the crystalline perchlorate **5b** which displayed infrared maxima (Nujol) at 1675 and 1610 cm^{-1} and ultraviolet absorption (ethanol) at $273\text{ m}\mu$ (8000).

The perchlorate salts were obtained as white crystalline solids which slowly yellowed on standing at room temperature and finally, after several months, were transformed to light brown semisolids. The perchlorates of structure **5** are readily acceptable as equilibration products in view of their mode of preparation and recrystallization.

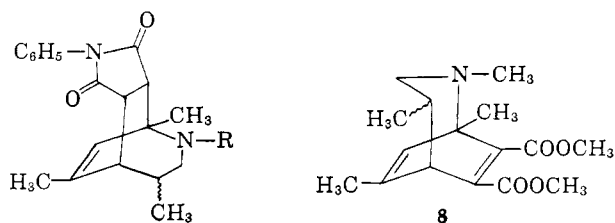
Diels-Alder Studies.—A second obvious feature of the cyclic dienamine molecule is its cisoid conjugated diene system. A consequence of this structural unit should be reflected in its capability to function as a diene in the Diels-Alder reaction; furthermore, the increase in electron density in the conjugated dienoid unit produced by the proximity of the basic nitrogen atom would be expected to enhance greatly the rate of the diene synthesis.

Initially, the possibility that adducts of 2,3-dihydro-3,5,7-trimethyl-1H-azepine (**3a**) might be obtained, provided that purification of **3a** was not attempted, appeared most attractive. Lithium aluminum hydride reduction of the dihydroazepinone **1** as described above produced the white solid cyclic dienamine **3a** which was immediately dissolved in benzene and treated with an equimolar solution of N-phenylmaleimide in benzene. An exothermic reaction was observed with the formation of a deep red color which rapidly faded to pale yellow. From the reaction mixture was obtained the crystalline adduct **7a**. In confirmation of this structural assignment was the elemental analysis, infrared maxima at 3320 (N-H), 1768 and 1709 cm^{-1} (imide carbonyls), and a lack of ultraviolet absorption other than that ascribed to the phenyl ring. In addition, the n.m.r. spectrum of **7a** was in full agreement with the proposed structure. Some measure of further support came from the ready acetylation of **7a** to produce the N-

(10) N. J. Leonard and V. W. Gash, *J. Am. Chem. Soc.*, **76**, 2781 (1954).

(11) G. Opitz and W. Merz, *Ann.*, **652**, 139 (1962).

acetyl derivative **7b** in quantitative yield. The stereoformula **7** has been assigned to the compounds of this series solely on the basis of the maximum overlap of unsaturated centers considered likely in the transition state leading to product formation.



Application of this reaction to the cyclic dienamines **3b-e** afforded the adducts **7b-c** in very good yields (see Table I). Again in these examples, a transient deep red color formed immediately on admixture of the diene and the dienophile; within 1 min. the color of the solution had completely faded and gave rise to a pale yellow hue. A strong exotherm was also invariably observed.

Reaction of the cyclic dienamine **3b** with dimethylacetylene dicarboxylate in benzene solution was vigorously exothermic. In addition to some tarry by-products,¹² there was obtained in fair yield the crystalline 1:1 adduct **8**. The assignment of structure was made on the basis of infrared, ultraviolet, and n.m.r. spectral data (see Experimental). Evidently, the consequence of extending the conjugation of an enamine to a cyclic dienamine is sufficient to divert at least a portion of the numerous possible reactions down the path to a Diels-Alder type adduct.¹²

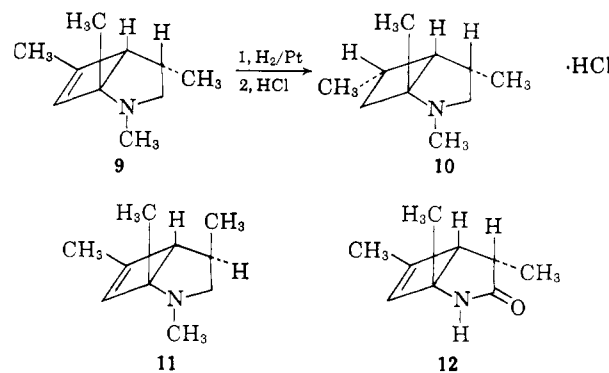
The effect of the basic nitrogen atom (and the accompanying high electron density) on the reactivity of these heterocycloheptadienes toward dienophiles is very striking. Alder and Molls¹³ have observed that cycloheptadiene reacts very sluggishly in the diene synthesis, and Paquette¹⁴ has demonstrated the reluctance of the closely related dihydroazepinones to condense with dienophiles.

Photochemistry.²—The well-established phenomenon of valence-bond tautomerism of conjugated cycloheptadienes to bicyclo[3.2.0]heptenes under conditions of photoactivation has only recently been extended to heterocyclic counterparts.¹⁵ The 2,3-dihydro-1H-azepines appeared to us to represent another example of the type of heterocyclic system which, upon irradiation, might be expected to photoisomerize in the above sense. For this study, we selected what appeared to be

one of the more stable of the cyclic dienamines, namely the N-methyl derivative **3b**.

Irradiation of a dry, purified tetrahydrofuran solution of **3b** in an atmosphere of nitrogen with an unfiltered 200 watt Hanovia lamp for 3 days afforded an 81% yield of a stable colorless liquid. That a light-induced reaction had been observed was demonstrated by the lack of ultraviolet absorption of this material above 236 mμ. The photoproduct actually consisted (gas chromatographic analysis) of a mixture of isomers in a ratio of approximately 6:1.

The major component was identified as **9** on the basis of the following evidence. The photoisomer, which analyzed properly for C₁₀H₁₇N, showed, in addition to



its lack of ultraviolet absorption, infrared maxima at 3015 and 1627 cm.⁻¹ (N-CH₃ stretching). Catalytic reduction of **9** proceeded with the uptake of 1 mole of hydrogen and gave a dihydro derivative, characterized as the hydrochloride, **10**.¹⁶ Structural assignment **9** was also in accord with the nuclear magnetic resonance spectrum which displayed resonance peaks very similar to those assigned to **12**. Most conclusively, a direct comparison of **9** with the product of methylation and lithium aluminum hydride reduction of **12** (of known stereochemistry)^{15b} showed them to be identical. In addition, the picrates of the two samples were alike in melting points and infrared absorptions, and a mixture melting point showed no depression.

The minor isomer was not obtained in sufficient quantity for characterization, but the nuclear magnetic resonance absorptions of this sample were similar to that of the major component. On this basis, structure **11** has been assigned to the minor isomer.

Thus, the photochemical behavior of the cyclic dienamine **3b** parallels the photoisomerization of normal conjugated cycloheptadienes and gives rise to the 2-azabicyclo[3.2.0]hept-6-ene system.

Experimental¹⁷

2,3-Dihydro-1,3,5,7-tetramethyl-1H-azepine (3b).—To a stirred slurry of 7.6 g. (0.20 mole) of lithium aluminum hydride in 150 ml. of anhydrous ether under an atmosphere of nitrogen was slowly added a solution of 33.0 g. (0.20 mole) of 1,3-dihydro-1,3,5,7-tetramethyl-2H-azepin-2-one (**2a**)⁸ in 50 ml. of anhydrous ether. The mixture was refluxed with stirring for 3 hr., cooled in ice, and treated cautiously with 7.5 ml. of water, 7.5 ml. of 25% sodium hydroxide solution, and 22 ml. of water in that order. The precipitated inorganic salts were separated by filtration and washed well with ether. The combined filtrates were evaporated

(16) The stereochemistry of the 6-methyl in **10** has been assigned solely on the basis of steric factors which were likely operative when **9** approached the catalyst surface.

(17) Melting points are corrected, while boiling points are uncorrected. The ultraviolet data reported herein were obtained solely on freshly prepared solutions.

(12) The uncharacterizable by-products could have resulted from cycloaddition reactions of the cyclic dienamine with the proposed dienophile, followed by more extensive reactions of this intermediate adduct. For examples of this cycloaddition phenomenon with simple enamines, see G. A. Berchtold and G. F. Uhlig, *J. Org. Chem.*, **28**, 1459 (1963); K. C. Brannock, R. D. Burpitt, V. W. Goodlett, and J. G. Thweatt, *ibid.*, **28**, 1464 (1963); C. F. Huebner and E. Donoghue, *ibid.*, **28**, 1732 (1963).

(13) K. Alder and H. H. Molls, *Ber.*, **89**, 1960 (1956).

(14) L. A. Paquette, *J. Org. Chem.*, **29**, 2851 (1964).

(15) The known examples are muconic anhydride: (a) G. J. Fonken, *Chem. Ind. (London)*, 1575 (1961); and the 1,3-dihydro-2H-azepin-2-ones: (b) L. A. Paquette, *J. Am. Chem. Soc.*, **86**, 500 (1964); (c) O. L. Chapman and E. D. Hoganson, *ibid.*, **86**, 498 (1964).

TABLE I
 ADDUCTS OF 2,3-DIHYDRO-1H-AZEPINES WITH N-PHENYLMALEIMIDE

Compd.	M.p., °C.	Yield, %	Formula	Carbon, %		Hydrogen, %		Nitrogen, %	
				Calcd.	Found	Calcd.	Found	Calcd.	Found
7c	98–98.5 ^a	63.6	C ₂₀ H ₂₄ N ₂ O ₂	74.04	74.39	7.46	7.53	8.64	8.42
7d	149–150 ^b	76.1	C ₂₁ H ₂₆ N ₂ O ₂	74.52	74.76	7.74	8.02	8.28	8.17
7e	183 ^c	79.2	C ₂₅ H ₃₇ Cl ₂ N ₃ O ₂	62.23	62.60	7.73	8.03	8.71	8.51
7f	185–186 ^c	79.5	C ₂₅ H ₃₅ Cl ₂ N ₃ O ₃	60.48	60.10	7.11	7.35	8.46	8.30

^a From ether–hexane. ^b From ethyl acetate. ^c From aqueous acetone.

and the residual pale yellow oil was distilled *in vacuo* to give 27.7 g. (91.8%) of colorless cyclic dieneamine **3b**, b.p. 50–54° (1.0 mm.). This material was not characterized *per se* because of its instability, but identified by conversion to its perchlorate salt.

The n.m.r. spectrum of **3b** showed the resonance peaks at (c.p.s.): 1-methyl, 173, singlet; 3-methyl, 63, doublet ($J = 7$ c.p.s.); 5-methyl, 109, triplet ($J = 1.5$ c.p.s.); 7-methyl, 117, singlet; 2-hydrogens, 190 and 168, doublet of quartets (AB with small additional splits) ($J = 14, 3$ c.p.s.); 3-hydrogen, 147 (resolution inadequate for unambiguous assignment); 4-hydrogen, 313, broad singlet; 6-hydrogen, 275, singlet.

2,3-Dihydro-1,3,5,7-tetramethyl-1H-azepinium perchlorate (5a) was prepared in the usual manner and crystallized on scratching. One recrystallization of this material from acetone containing a small amount of ether gave pure **5a** as white prisms, m.p. 106–106.5°.

Anal. Calcd. for C₁₀H₁₈ClNO₄: C, 47.71; H, 7.21; N, 5.56. Found: C, 47.46; H, 7.25; N, 5.35.

2,3-Dihydro-1-ethyl-3,5,7-trimethyl-1H-azepine (3c).—Reduction of 7.7 g. (0.043 mole) of 1,3-dihydro-1-ethyl-3,5,7-trimethyl-2H-azepin-2-one (**2b**) with 1.6 g. (0.043 mole) of lithium aluminum hydride in ether was performed as described above. Distillation of the resulting oil *in vacuo* gave 5.6 g. (79.0%) of colorless cyclic dieneamine **3c**, b.p. 61–64° (1 mm.), $n_D^{25} 1.5176$. The n.m.r. spectrum of this sample was very similar to that of **3b**, with the expected additional resonance lines attributable to the N-ethyl group.

3,4-Dihydro-1-ethyl-3,4,6-trimethyl-2H-azepinium perchlorate (5b) was obtained as a white solid, m.p. 99–101° (from acetone–ether).

Anal. Calcd. for C₁₁H₂₀ClNO₄: C, 49.71; H, 7.59; N, 5.27. Found: C, 50.33; H, 7.63; N, 5.66.

General Procedure for Diene Synthesis with N-Phenylmaleimide. 1,4,9-Trimethyl-N-phenyl-2-azabicyclo[3.2.2]non-8-ene-6,7-dicarboximide (**7a**).—To a slurry of 2.84 g. (0.075 mole) of lithium aluminum hydride in 150 ml. of anhydrous ether was added 15.1 g. (0.10 mole) of 1,3-dihydro-3,5,7-trimethyl-2H-azepin-2-one (**1**)⁸ in several portions. The mixture was refluxed with stirring under nitrogen for 3 hr. The reaction mixture was cooled in ice and treated with 3 ml. of water, 3 ml. of 25% sodium hydroxide solution, and 8 ml. of water in that order. The precipitated inorganic salts were separated by filtration and the filtrate was evaporated to give a very fluffy, highly unstable, white solid. This material was dissolved in 50 ml. of dry benzene and this solution was added in one portion to a solution of 17.3 g. (0.10 mole) of N-phenylmaleimide in 75 ml. of dry benzene. An exothermic reaction occurred with the formation of a red color which rapidly faded to yellow. After standing overnight at room temperature, the solution was evaporated under reduced pressure and the residue was chromatographed on Florisil.¹⁸ Elution with hexane afforded 4.1 g. of recovered N-phenylmaleimide. Elution, with hexane–ether (9:1) afforded 3.0 g. of recovered dihydroazepinone **1**. Elution with ether provided 3.9 g. (15.9% based on recovered **1**) of the adduct **7a**, m.p. 121–122.5°. Two recrystallizations of this material from ether–hexane gave pure white stars, m.p. 123.5–124.5°; ν_{Nujol} 3320 (N–H), 1768 and 1709 cm.⁻¹ (imide carbonyls).

Anal. Calcd. for C₁₉H₂₂N₂O₂: C, 73.52; H, 7.14; N, 9.03. Found: C, 73.49; H, 7.00; N, 8.89.

2-Acetyl-1,4,9-trimethyl-N-phenyl-2-azabicyclo[3.2.2]non-8-ene-6,7-dicarboximide (7b).—A mixture of 0.96 g. (3.0 mmoles) of **7a** and 5 ml. of acetic anhydride was heated on a steam bath for 2 hr. with protection from atmospheric moisture. During this period solution was effected. The solution was allowed to stand overnight at room temperature and crystals separated.

(18) Florisil is a magnesia–silica gel adsorbent manufactured by the Floridin Co., Tallahassee, Fla.

The crystals were filtered, washed with hexane, and dried to give 1.0 g. (100%) of **7b**, m.p. 226.5–228°. Recrystallization of this material from aqueous acetic acid gave the analytical sample as white prisms, m.p. 229–230.5°; ν_{Nujol} 1768, 1710, and 1656 cm.⁻¹ (amide and imide carbonyls).

Anal. Calcd. for C₂₁H₂₄N₂O₃: C, 71.57; H, 6.86; N, 7.95. Found: C, 71.91; H, 7.03; N, 7.79.

1,2,4,9-Tetramethyl-2-azabicyclo[3.2.2]nona-6,8-diene-6,7-dicarboxylic Acid Dimethyl Ester (8).—Reduction of 8.3 g. (0.05 mole) of **2a** with 1.9 g. (0.05 mole) of lithium aluminum hydride in ether was performed as described above. A solution of 7.1 g. (0.05 mole) of dimethyl acetylenedicarboxylate in 35 ml. of benzene was added in one portion to a solution of the resulting cyclic dieneamine (**3b**) in 35 ml. of benzene. A vigorous exothermic reaction was observed. After standing at room temperature for 2 hr., the solution was evaporated under reduced pressure. Chromatography of the dark oil on Florisil¹⁸ and elution with ether–hexane (1:1) afforded an orange oil which crystallized on scratching. There was obtained 6.9 g. (36.3%) of product, m.p. 67–79°. Pure **8** was obtained as white prisms from hexane; m.p. 89.5–91°, ν_{Nujol} 1740 and 1715 cm.⁻¹ (ester carbonyls), λ_{max}^{EtOH} 220.5 sh (3900) and 292 sh μ (650).

Anal. Calcd. for C₁₆H₂₃NO₄: C, 65.06; H, 8.53; N, 4.74. Found: C, 65.37; H, 8.20; N, 4.87.

1,2,4,6-Tetramethyl-2-azabicyclo[3.2.0]hept-6-ene (9 and 11).—A solution of 20 g. (0.132 mole) of the cyclic dieneamine **3b** in 400 ml. of dry, purified tetrahydrofuran was irradiated in a nitrogen atmosphere with a 200-watt Hanovia lamp at room temperature for 3 days. The solvent was carefully evaporated and the residual liquid was distilled to give 16.1 g. (80.6%) of colorless liquid, b.p. 28° (1 mm.), $n_D^{25} 1.4568$ (reported for pure **9**,^{15b} b.p. 61° (11 mm.), $n_D^{25} 1.4560$). Gas chromatography of a sample of this material on a 6-ft. column containing 10% polyester (LAC-446) on Diatoport S at 115° indicated two components in a ratio of approximately 6:1.

Anal. Calcd. for C₁₀H₁₇N: C, 79.40; H, 11.34; N, 9.26. Found: C, 80.00; H, 11.10; N, 8.87.

1,2,4,6-Tetramethyl-2-azabicyclo[3.2.0]hept-6-ene picrate was prepared treating either the 6:1 mixture of bases or a pure sample of **9** (obtained by preparative gas chromatography) with ethanolic picric acid, m.p. 212–214° (from ethanol). Infrared spectra of pure **9** and its picrate were superimposable on those of authentic samples.^{15b} A mixture melting point of the picrates was undepressed.

Anal. Calcd. for C₁₆H₂₀N₄O₇: C, 50.52; H, 5.30; N, 14.73. Found: C, 50.48; H, 4.93; N, 14.63.

1,2,4,6-Tetramethyl-2-azabicyclo[3.2.0]heptane Hydrochloride (10).—A solution of 2.0 g. (0.0132 mole) of **9** in 50 ml. of ethanol containing 200 mg. of platinum oxide was hydrogenated at atmospheric temperature and pressure. The uptake of hydrogen ceased after the consumption of 1 mole. The catalyst was separated by filtration and the filtrate was treated with a slight excess of ethereal hydrogen chloride and evaporated under reduced pressure. Trituration of the residue with ether induced crystallization. The solid was separated by filtration and dried to give 1.7 g. (68.0%) of white solid from ethanol–ether; m.p. 213.5–215°. This sample was identical by the usual criteria with an authentic sample, m.p. 213.5–215.^{15b}

Anal. Calcd. for C₁₀H₂₀ClN: C, 63.30; H, 10.63; N, 7.38. Found: C, 63.61; H, 10.87; N, 7.15.

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