9-Azabicyclo[4.2.1]nona-2,4,7-triene and Derivatives[1]

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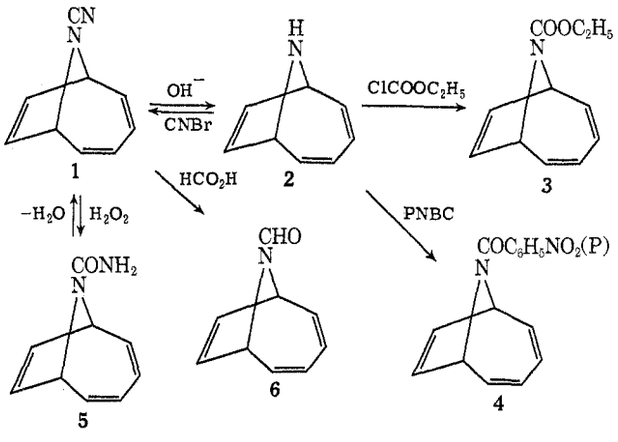
The preparation of parent 9-azabicyclo[4.2.1]nona-2,4,7-triene and certain N-substituted derivatives is described. Selective saturation of the general [4.2.1]-triene system through catalytic hydrogenation and epoxidation is also detailed.

In recent years we recorded our active interest in C_8H_8X heterobicyclics in terms of their response to heat and light[2,3] as well as their unique potential as heteronin progenitors.[4] Our participation in this area dates to a report describing the reaction of cyanonitrene with cyclooctatetraene to yield two isomeric C_8H_8NCN bicyclic substances, one of which was shown to possess the novel skeleton shown in **1**.[2] We now wish to record additional chemical information relating to this general system. Specifically, we report on a number of select chemical transformations of **1**, including its conversion to the parent amine **2**. For the most part our interest in the compounds described herein derives from their obvious potential as appropriate models for studying the stereoelectronic factors controlling possible reorganization and cheletropic[5] processes.

Functionalization on Nitrogen.—The chief emphasis in our earlier description of **1** was mechanistic rather than synthetic, so that no effort was exerted at optimizing the yield. In the present report we describe a modified work-up procedure whereby as many as 4 g of **1** become routinely available from single runs (see Experimental Section).[6]

Conversion of **1** to the parent substance **2** was accomplished in good yield (*ca.* 71%) on heating the nitrile with 10% sodium hydroxide in aqueous acetone (Scheme I).[7] The bicyclic amine is a thermally stable, air-sensitive, colorless liquid displaying the following spectral characteristics: mass spectrum *m/e* (rel intensity) 119 (P^+, 60), 91 (100); ν_{neat}^{NH} 3250 cm^{-1}; $\lambda_{max}^{C_6H_{12}}$ 245 nm (ϵ 2300); nmr (60 MHz, $CDCl_3$) τ 3.50–4.20 (4 H, m), 4.69 (2 H, s), 5.70 (2 H, d, J = 5 Hz), 8.45 (1 H, s, exchanges with D_2O). Secure chemical evidence for structure **2** derives from its ready reversal to **1** (nmr, ir, melting point) on treatment with cyanogen bromide and its conversion to the N-substituted derivatives shown in **3** and **4** on exposure to ethyl chloroformate and *p*-nitrobenzoyl chloride, respectively.

SCHEME I



While **2** undoubtedly represents the ideal progenitor to a variety of N-substituted derivatives, introduction of an N substituent may in some cases be forced directly on **1**. This is properly exemplified by the ready conversion of this cyanamide to urea **5** on treatment with H_2O_2 in acetone and to formamide **6** on exposure to hot formic acid in the presence of BF_3.[10] It is interesting to note that the two bridgehead hydrogens of **6** are magnetically distinct, each appearing as a doublet, τ 4.85 (J = 5.5 Hz) and 5.22 (J = 5.5 Hz), in the nmr spectrum. This induced asymmetry in the neighborhood of the bridgehead positions is no doubt introduced by the *N*-formyl substituent and is best reasoned in terms of restricted rotation about the amide linkage. Of course the operation of such a process would necessarily constrain the formyl group within the plane defined by the C–N–C bridge so that its hydrogen would be exposed to the same chemical environment. This notion is fully substantiated by the appearance of the aldehydic resonance (τ 2.02) in singlet form. It is also perhaps interesting to note that within the present line of reasoning the carboethoxyl and carbamoyl analogs of **6** must possess N substituents that are freely rotating at ambient temperature, since the bridgehead protons of either **3** or **5**

(1) Work submitted (July 1970) by R. P. C. in partial fulfillment of the requirements for the Ph.D. degree in Chemistry.

(2) (a) A. G. Anastassiou, *J. Amer. Chem. Soc.*, **87**, 5512 (1965); (b) A. G. Anastassiou, *ibid.*, **90**, 1527 (1968).

(3) A. G. Anastassiou and R. P. Cellura, *Chem. Commun.*, 762 (1967).

(4) A. G. Anastassiou, S. W. Eachus, R. P. Cellura, and J. H. Gebrian, *ibid.*, 1133 (1970), and references cited therein.

(5) R. B. Woodward and R. Hoffmann, "The Conservation of Orbital Symmetry," Academic Press, New York, N. Y., 1970.

(6) We thank Dr. R. M. Lazarus for his contribution at optimizing the yield of **1**.

(7) The various substances depicted in Scheme I are obviously of interest as potential models for studying the effect that substituent electronegativity may have on the course of the thermal and photochemical bond-relocation processes available to this general system. Further, parent amine **2** is clearly well suited structurally for a study of the general stereoelectronic factors controlling heteroatom extrusion, which ought to be readily triggered on generation of the corresponding diazene, *i.e.*, in the manner described earlier for a dimeric counterpart of **2**.[8] In fact, **2** may well prove to be an ideal model for assessing the relative merits of linear *vs.* nonlinear cheletropy *within the same molecule*, since the two isolated π segments of the molecule are expected to oppose one another in this connection.[9] Specifically, while the influence of the ethylene portion of the molecule ought to manifest itself in such a way as to induce a *linear* extrusion of N_2, analogous participation by the butadiene segment should promote the process in a nonlinear fashion.[9]

(8) A. G. Anastassiou and R. M. Lazarus, *Chem. Commun.*, 373 (1970).

(9) This conclusion was arrived at on employing the method of analysis described earlier by D. M. Lemal and S. D. McGregor, *J. Amer. Chem. Soc.*, **88**, 1335 (1966).

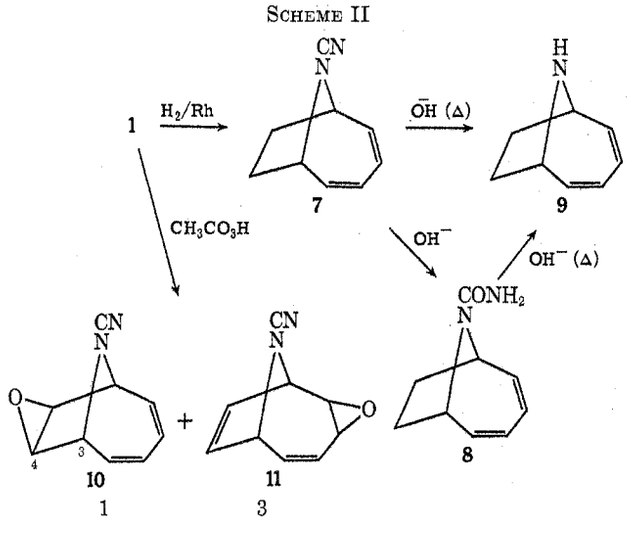
(10) Mechanistically, the overall conversion of **1** to **6** is best viewed as a reduction–hydrolysis process whereby initial hydride transfer from formic acid to **1** produces the corresponding imino (–CH=NH) derivative, which is in turn converted to **6** on hydrolysis. For related instances see H. Kauffman and P. Rannwitz, *Ber.*, **45**, 766 (1912); A. Kovache, *Ann. Chim. (Paris)*, **10**, 184 (1918).

are magnetically equivalent, the pair in each case appearing as a clean 2 H doublet ($J \cong 4.5$–5.0 Hz).

Selective Double-Bond Saturation.—Attention in this project was next directed at modifying the general π system of **1** through selective saturation of one of its olefinic centers in the hope of obtaining additional models for studying the constraints imposed on this rigid system by orbital symmetry. In particular, the various dienes that are formally accessible in this manner might prove useful in assessing the degree to which linear or nonlinear cheletropy might be "forbidden" in the triene counterpart **2**.

Careful partial hydrogenation of **1** over 5% rhodium on charcoal produced a single dihydro derivative displaying the following spectral characteristics: mass spectrum m/e (rel intensity) 146 (P^+, 10); ν_{KBr}^{CN} 2245 cm^{-1}; $\nu_{max}^{CH_3CN}$ 257 nm (ϵ 4630); nmr (60 MHz, $CDCl_3$) τ 3.98 (4 H, narrow m), 5.71 (2 H), and 7.75 (4 H). The nmr spectrum demands that the substance be symmetrical and that it possess four olefinic, two allylic, and four paraffinic protons, while the uv characteristics establish the presence of the same diene chromophore as in **1**. This information effectively singles out structure **7** for the product of partial hydrogenation. Mild hydrolysis (10% aqueous NaOH) of **7** led to the corresponding carbamoyl derivative **8** (Scheme II), which was characterized

SCHEME II



on the basis of entirely consistent spectral and microanalytical data. Under more vigorous hydrolytic conditions (*ca.* 40% methanolic KOH) **7** produced, in good yield, the corresponding amine **9**, which was isolated as an air-sensitive, colorless liquid and formulated on the basis of its spectral and microanalytical characteristics. Further, in order to establish that the various transformations described for the dihydro system occur without skeletal rearrangement, we effected the conversion of **9** to **7** on treatment with cyanogen bromide and that of **8** to **9** on hydrolysis with methanolic KOH.

Epoxidation provided yet another means of selectively saturating **1**. Thus, treatment of this substance with peracetic acid produced a mixture of two monoepoxides in a ratio of *ca.* 3:1. The two were separated pure by column chromatography and are characterized by the following spectral data: **minor isomer**, mass spectrum m/e (rel intensity) 160 (P^+, 5); ν_{KBr}^{CN} 2250 cm^{-1}; $\lambda_{max}^{CH_3CN}$ 247 nm (ϵ 4250); nmr (60 MHz, $CDCl_3$) τ 3.91 (4 H, broad s), 5.56 (2 H, d, $J = 3.5$ Hz), 6.31 (2 H, s); **major isomer**, mass spectrum m/e (rel intensity) 160 (P^+, 48); ν_{KBr}^{CN} 2250 cm^{-1}; $\lambda_{max}^{CH_3OH}$ 212 nm (ϵ ~3700); nmr (60 MHz, $CDCl_3$) τ 3.8–4.0 (4 H, m), 5.1 (1 H, m), 5.30 (1 H, d, $J = 5.0$ Hz), 6.40 (1 H, dd, $J = 4.0$, 2.5 Hz), 6.78 (1 H, t, $J = 4.0$ Hz). This information clearly requires that the minor component be symmetrical (nmr) and that it possess a conjugated diene chromophore (uv) and that the major isomer be, by contrast, devoid of both molecular symmetry (nmr) and diene chromophore (uv). Hence, one's choice is effectively limited to structures **10** and **11** for the minor and major isomeric epoxides, respectively. Further, the nmr spectrum of **10** provides some useful clues regarding stereochemistry. Thus, the appearance of the epoxide protons as a sharp singlet in this case is no doubt suggestive of an exo disposition for the epoxide function, as examination of Dreiding molecular models reveals the H_3–H_4 dihedral angle to be *ca.* 80° for the exo arrangement and *ca.* 20° for the endo disposition.

Finally, brief comparison of the nmr chemical shifts of the butadiene moieties of **1** and **2** to those of their dihydro analogs **7** and **9** reveals a shift, 18 and 12 Hz, respectively, to higher field in the case of the latter. It is tempting to interpret this difference to the occurrence of an intramolecular Diels–Alder ($_\pi4_s + _\pi2_s$) interaction between the two olefinic entities in **1** and **2** with the $_\pi4_s$ segment behaving in its normal *donor* capacity, *i.e.*, to a situation where there occurs net transfer of electron density from butadiene to ethylene.

Presently, we are actively examining the various substances described herein in terms of molecular reorganization, cheletropy, and response to certain choice reagents.

Experimental Section[11]

Preparation of *N*-Cyano-9-azabicyclo[4.2.1]nona-2,4,7-triene (1).[6]—To a rapidly stirring solution of cyclooctatetraene (50 ml) in ethyl acetate (3800 ml) maintained at the reflux temperature (*ca.* 80°) was added a fresh solution of cyanogen azide[12] (*ca.* 25 g) in ethyl acetate (220 ml) over a period of 4 hr. After stirring for an additional 30 min (total nitrogen evolution *ca.* 75% theory) the reaction mixture was cooled and suction filtered through a bed of Merck anhydrous neutral alumina (*ca.* 900 g). Evaporation of the filtrates at the water aspirator at *ca.* 45° gave an orange oil, from which cyclooctatetraene was removed at 30° and *ca.* 0.5 mm. The residue was dissolved in methylene chloride (*ca.* 50 ml) and the resulting solution was applied onto a column of Woelm activity IV *acidic* alumina (200 g). Elution with benzene (*ca.* 500 ml) gave a yellow solution which was concentrated to *ca.* 30 ml and added dropwise to rapidly stirring petroleum ether (bp 30–60°, *ca.* 500 ml) to yield **1** (2.5–4.0 g) as a white, crystalline solid, mp 101–103°.[2]

Preparation of 9-Azabicyclo[4.2.1]nona-2,4,7-triene (2).—A solution of *N*-cyano-9-azabicyclo[4.2.1]nona-2,4,7-triene (**1**) (1.2 g, 0.0083 mol) in 10% (w/v) aqueous sodium hydroxide

(11) All melting points were obtained with a Thomas-Hoover capillary melting point apparatus and are uncorrected. Infrared spectra were recorded on a Perkin-Elmer 137 infrared spectrophotometer. Ultraviolet spectra were determined with either a Perkin-Elmer, Model 202, or a Cary 14 spectrophotometer. Proton nuclear magnetic resonance spectra were obtained with a Varian Model A-60 spectrometer; tetramethylsilane was employed as the internal standard throughout. Mass spectra were recorded with a Hitachi Model RMU-6E single focusing spectrometer. Microanalyses were performed at Galbraith Laboratories, Knoxville, Tenn.

(12) See ref 2b.

solution (40 ml) and acetone (5 ml) was maintained at reflux (*ca.* 100°), under nitrogen and with constant stirring, for a period of 16 hr. After cooling to room temperature the acetone was drawn off at the water aspirator and to the remaining solution were added sodium hydroxide pellets (*ca.* 6 g). The mixture was stirred until all the sodium hydroxide dissolved and then extracted with chloroform (6 × 20 ml). The combined extracts were washed with water (2 × 20 ml), dried over calcium sulfate, and concentrated, first at water aspirator pressure and then at *ca.* 0.5 mm, to a yellow oil (0.8 g). Short-path distillation under reduced pressure gave 9-azabicyclo[4.2.1]nona-2,4,7-triene (**2**) (0.69 g, 71%) as a colorless liquid: bp 58–59° (0.25 mm); ir (neat) 3250 (NH), 1395, 1110, 955, 880, and 765 cm^{-1}; uv (C_6H_{12}) 245 nm (ϵ 2300); nmr (100 mg/0.3 ml $CDCl_3$) τ 3.50–4.20 (4 H, m), 4.69 (2 H, s), 5.70 (2 H, d, J = 5 Hz), 8.45 (1 H, s, exchanges with D_2O); mass spectrum (20 eV), parent ion at m/e 119, base peak at m/e 91.

Reaction of 9-Azabicyclo[4.2.1]nona-2,4,7-triene (2) with Cyanogen Bromide. Formation of 1.—To a solution of 9-azabicyclo[4.2.1]nona-2,4,7-triene (**2**) (80 mg, 0.68 mmol) and triethylamine (0.2 ml) in methylene chloride (3 ml) was added at *ca.* 0°, under nitrogen and with constant stirring, a solution of cyanogen bromide (78 mg, 0.74 mmol) in methylene chloride (5 ml). After the addition was completed (1 hr), the mixture was allowed to warm to room temperature and stirred at this temperature for an additional 23 hr. The resulting suspension was then filtered and the filtrate was concentrated at water aspirator pressure to a white solid (120 mg). Elution of this material with benzene on a column packed with silica gel and benzene gave *N*-cyano-9-azabicyclo[4.2.1]nona-2,4,7-triene (**1**) (97 mg, 98%) identical in all respects (melting point, ir, nmr) with authentic material.

Reaction of *N*-Cyano-9-azabicyclo[4.2.1]nona-2,4,7-triene (1) with 88% Formic Acid. Formation of 6.—A mixture of *N*-cyano-9-azabicyclo[4.2.1]nona-2,4,7-triene (**1**) (144 mg, 1 mmol), 88% formic acid (0.085 ml, ~1 mmol), and one drop of boron trifluoride etherate was maintained at the reflux temperature for a period of 1 hr. The solution was then diluted with 2 ml of water and extracted with methylene chloride (3 × 5 ml). The combined organic extracts were then washed successively with 10% (w/v) sodium carbonate solution (2 × 5 ml) and water (2 × 5 ml). The solution was dried over calcium sulfate, filtered, and concentrated, first at water aspirator pressure and then at *ca.* 0.5 mm. The crude orange oil obtained (120 mg) was purified by distillation under reduced pressure into a micro cup. The distillate solidified on standing to give *N*-formyl-9-azabicyclo-[4.2.1]nona-2,4,7-triene (**6**) (100 mg, 64%) as white crystals: mp 45–46°; ir (KBr) 1690 (C=O), 1450, 1410, 1005, 930, and 760 cm^{-1}; uv (CH_3CN) max 252 nm (ϵ 2700); nmr ($CDCl_3$) τ 2.02 (1 H, br s), 3.50–4.15 (4 H, m), 4.55 (2 H, s), 4.85 (1 H, d, J = 5.50 Hz), 5.22 (1 H, d, J = 5.50 Hz); mass spectrum (20 eV), parent ion at m/e 147, base peak at m/e 118.

Anal. Calcd for C_9H_9NO: C, 73.45; H, 6.16; N, 9.52. Found: C, 73.45; H, 6.06; N, 9.54.

Preparation of *N*-Carboethoxy-9-azabicyclo[4.2.1]nona-2,4,7-triene (3).—To a solution of 9-azabicyclo[4.2.1]nona-2,4,7-triene (**2**) (457 mg, 3.8 mmol) and triethylamine (0.53 ml, 385 mg, 3.8 mmol) in ethyl ether (15 ml) was added, at 0°, under nitrogen and with constant stirring, a solution of ethyl chloroformate (415 mg, 3.8 mmol) in ethyl ether (5 ml). After the addition was completed (1 hr) the solution was allowed to warm to room temperature and then stirred for an additional 8 hr. The mixture was filtered free of precipitate and the filtrate was washed first with 10% sodium carbonate solution (2 × 10 ml) and then water (5 × 10 ml). The solution was dried over calcium sulfate, filtered, and concentrated, first at water aspirator pressure and then at *ca.* 0.5 mm, to a crude yellow oil (700 mg). Distillation under reduced pressure (bath temp *ca.* 90°, 0.25 mm) into a micro cup gave *N*-carboethoxy-9-azabicyclo[4.2.1]nona-2,4,7-triene (**3**) (600 mg, 81%) as a colorless liquid: ir (neat) 1750 (C=O), 1450, 1410, 1360, 1310, 1280, 1125, 905, 870, and 775 cm^{-1}; uv (C_6H_{12}) max 252 nm (ϵ 2200); nmr (CCl_4) τ 3.60–4.33 (4 H, m), 4.69 (2 H, d, J ~ 1 Hz), 5.24 (2 H, d, J = 4.5 Hz), 6.05 (2 H, q), 8.88 (3 H, t); mass spectrum, parent ion at m/e 191, base peak at m/e 162.

Preparation of *N*-Carbamoyl-9-azabicyclo[4.2.1]nona-2,4,7-triene (5).—To a solution of *N*-cyano-9-azabicyclo[4.2.1]nona-2,4,7-triene (**1**) (392 mg, 3.0 mmol) and 30% hydrogen peroxide (7 ml) in acetone (8 ml) was added, under nitrogen and with constant stirring, an aqueous solution of sodium carbonate (2 g/15 ml) over a temperature range of 5–10°. Upon completion of the addition (3 hr) the suspension was allowed to warm slowly to room temperature and was stirred for an additional 18 hr. The mixture was then filtered to remove the precipitate which formed during the reaction and the filtrate was extracted with methylene chloride (5 × 20 ml). The combined extracts were in turn washed with water (2 × 10 ml), dried over calcium sulfate, filtered, and concentrated at water aspirator pressure to a cream-colored solid (300 mg). Recrystallization from ethyl acetate gave pure *N*-carbamoyl-9-azabicyclo[4.2.1]nona-2,4,7-triene[13] (250 mg, 52%) as white crystals: mp 182–183°; ir (KBr) 3380 and 3180 (NH), 1650 and 1620 (C=O), 1445, 1140, 1090, 895, 855, 763, and 740 cm^{-1}; uv (CH_3OH) max 255 nm (ϵ 1980); nmr (33 mg/0.3 ml DMSO-d_6) τ 3.55–4.50 (6 H, m, 2 H exchangeable with CD_3COOD), 4.55 (2 H, s), 5.18 (2 H, d, J = 5.0 Hz); mass spectrum, parent ion at m/e 162, base peak at m/e 118.

Anal. Calcd for $C_9H_{10}N_2O$: C, 66.65; H, 6.21; N, 17.27. Found: C, 66.34; H, 6.23; N, 17.17.

Dehydration of *N*-Carbamoyl-9-azabicyclo[4.2.1]nona-2,4,7-triene (5). Formation of 1.—A mixture of *N*-carbamoyl-9-azabicyclo[4.2.1]nona-2,4,7-triene (**5**) (40 mg, 0.24 mmol) and *p*-toluenesulfonyl chloride (138 mg, 0.72 mmol) in pyridine (5 ml) was heated with constant stirring over a steam bath for 1.5 hr. The solution was poured onto ice water (100 ml) and then extracted with methylene chloride (3 × 20 ml). The combined organic extracts were dried over calcium sulfate, filtered, and concentrated at water aspirator pressure to a white solid (35 mg, 100%) identified as *N*-cyanoazabicyclo[4.2.1]nona-2,4,7-triene (**1**) (melting point, ir, nmr).

Reaction of *N*-Cyano-9-azabicyclo[4.2.1]nona-2,4,7-triene (1) with Commercial Peracetic Acid. Formation of 10 and 11.—To a solution of *N*-cyano-9-azabicyclo[4.2.1]nona-2,4,7-triene (**1**) (1 g, 7 mmol) in methylene chloride (20 ml) was added, with constant stirring at *ca.* 20°, a solution of commercial peracetic acid (1.5 ml, 0.85 g, 11 mmol) in methylene chloride (5 ml). After the addition was completed (30 min) the solution was maintained at *ca.* 30° for 44 hr and then concentrated to a red liquid at water aspirator pressure. The liquid was dissolved in benzene (50 ml) and the resulting solution was washed with 10% sodium hydroxide solution (5 × 10 ml) and water (2 × 10 ml), dried over calcium sulfate, filtered, and concentrated to an oil which solidified on standing. The nmr spectrum ($CDCl_3$) of this substance displays, besides a signal characteristic of **1**, new absorptions at τ 3.58–4.00, 5.12, 5.21, 5.56, 6.31, 6.42, and 6.70.

The mixture was dissolved in benzene and placed on a column (350 × 20 mm) packed with silica gel–benzene. Elution with benzene afforded a white, crystalline compound (0.375 g) characterized as **1** (melting point, ir, nmr). Elution with benzene was continued until all of **1** was removed (200 ml). Continued elution with petroleum ether–ethyl ether (1.5:1.0, v/v) afforded two distinct fractions. The first (40 ml) contained pure 7,8-epoxy-*N*-cyano-9-azabicyclo[4.2.1]nona-2,4-diene (**10**) (0.125 g, 11%) as white crystals: mp 98–99°; ir (KBr) 2250 (C≡N), 1235 and 1215 (▷O), 1180, 928, 855, 792, 730, and 704 cm^{-1}; uv (CH_3CN) max 247 nm (ϵ 4250); nmr ($CDCl_3$) τ 3.91 (4 H, br s), 5.56 (2 H, d, J = 3.5 Hz), 6.31 (2 H, s); mass spectrum, parent ion at m/e 160, base peak at m/e 131.

Anal. Calcd for $C_9H_8N_2O$: C, 67.49; H, 5.03; N, 17.49. Found: C, 67.27; H, 4.94; N, 17.36.

The second fraction (150 ml) contained pure 2,3-epoxy-*N*-cyano-9-azabicyclo[4.2.1]nona-4,7-diene (**11**) (0.370 g, 31%) as white crystals: mp 101–102°; ir (KBr) 2250 (C≡N), 1230 (▷O), 975, 920, 895, 885, 795, 775, and 715 cm^{-1}; uv (MeOH) max 212 nm (ϵ 3650); nmr ($CDCl_3$) τ 3.8–4.0 (4 H,m), 5.1 (1 H, m), 5.30 (1 H, d, J = 5.0 Hz), 6.40 (1 H, dd, J = 4.0, 2.5 Hz), 6.78 (1 H, t, J = 4.0 Hz); mass spectrum, parent ion at m/e 160, base peak at m/e 68.

Anal. Calcd for $C_9H_8N_2O$: C, 67.49; H, 5.03; N, 17.49. Found: C, 67.06; H, 5.04; N, 17.49.

Similar results were obtained when the peracid employed was either *m*-chloroperbenzoic acid or perphthalic acid.

Preparation of *N*-Cyano-9-azabicyclo[4.2.1]nona-2,4-diene (7).—A solution of *N*-cyano-9-azabicyclo[4.2.1]nona-2,4,7-triene (**1**) (0.75 g, 0.0052 mol) in tetrahydrofuran (25 ml) and 5% rhodium on charcoal catalyst (0.75 g) was treated with hydrogen

(13) This compound was also isolated in good yield from the low-temperature (~70°) alkaline hydrolysis of **1**. However, the exact experimental details for this process have not been worked out.

at room temperature and atmospheric pressure. Uptake was stopped after a total of 235 ml (60% theory) of hydrogen had been absorbed.[14] The mixture was filtered free of catalyst and the filtrate was concentrated under water aspirator pressure to a white solid (0.75 g). The nmr spectrum ($CDCl_3$) of this material displayed signals at τ 3.98, 5.75, and 7.85 and no absorptions characteristic of **1**. The solid was dissolved in benzene and placed on a column (350 × 20 mm) packed with silica gel–benzene. Elution with (7:3 v/v) petroleum ether–ethyl ether (20 ml) afforded pure *N*-cyano-9-azabicyclo[4.2.1]nona-2,4-diene (0.62 g, 82%) as white crystals: mp 70–71.5°; ir (KBr) 2245 (C≡N), 1350, 1220, 1105, 920, 895, 870, and 715 cm^{-1}; uv (CH_3CN) max 257 nm (ϵ 4630); nmr ($CDCl_3$) τ 3.98 (4 H, m), 5.71 (2 H, m), 7.5–7.9 (4 H, m); mass spectrum, parent ion at *m/e* 146, base peak at *m/e* 58.

Anal. Calcd for $C_9H_{10}N_2$: C, 73.94; H, 6.89; N, 19.16. Found: C, 74.06; H, 6.94; N, 19.20.

Preparation of *N*-Carbamoyl-9-azabicyclo[4.2.1]nona-2,4-diene (8).—A solution of *N*-cyano-9-azabicyclo[4.2.1]nona-2,4-diene (**7**) (146 mg, 1 mmol) in 10% (w/v) aqueous sodium hydroxide solution (10 ml) and acetone (2 ml) was maintained at reflux (*ca.* 100°) under nitrogen and with constant stirring for 8 hr. Upon cooling to room temperature the acetone was removed under aspirator pressure and to the remaining solution was added solid sodium hydroxide (1.5 g). The mixture was stirred until all the sodium hydroxide had dissolved and was then extracted with chloroform (4 × 20 ml), and the organic layer was dried over calcium sulfate. Concentration at water aspirator pressure gave a white solid, which on recrystallization from ethyl acetate produced pure *N*-carbamoyl-9-azabicyclo[4.2.1]nona-2,4-diene (**8**) as white crystals: mp 169–170°; ir (KBr) 3350 and 3180 (NH), 1650 and 1620 (C=O), 1440, 1160, 1085, 925, 895, 855, 763, and 685 cm^{-1}; uv (CH_3CN) max 255 nm (ϵ 1600); nmr (DMSO-d_6, 53 mg/0.3 ml) τ 3.7–4.6 (6 H, m, 2 H exchangeable with D_2O/CDCOOD), 5.5–5.7 (2 H, m), 7.7–8.2 (4 H, m); mass spectrum, parent ion at *m/e* 164, base peak at *m/e* 73.

Anal. Calcd for $C_9H_{12}N_2O$: C, 65.83; H, 7.37; N, 17.06. Found: C, 65.93; H, 7.25; N, 16.80.

Preparation of 9-Azabicyclo[4.2.1]nona-2,4-diene (9) from *N*-Cyano-9-azabicyclo[4.2.1]nona-2,4-diene (7).—A solution of *N*-cyano-9-azabicyclo[4.2.1]nona-2,4-diene (**7**) (1.0 g, 0.0068 mol) and potassium hydroxide (25 g) in methanol (60 ml) was maintained at reflux (*ca.* 100°) under nitrogen and with constant stirring for 8 hr. The solution was then concentrated at water aspirator pressure to a semisolid, which in turn was suspended in petroleum ether (150 ml). The suspension was boiled under nitrogen with constant stirring for 2 hr. The petroleum ether layer was separated, extracted with water (2 × 25 ml), and dried over calcium sulfate. Concentration of the solution at water aspirator pressure gave a crude yellow oil (0.68 g). Short-path distillation under reduced pressure gave pure 9-azabicyclo[4.2.1]-nona-2,4-diene (**9**) (0.55 g, 66%) as an air-sensitive, colorless oil: bp 118–119° (0.1 mm); ir (neat) 3250 (NH), 3000, 1440, 1420, 1100, 1040, 948, 875, 847, 755, and 708 cm^{-1}; uv (CH_3CN) max 248 nm (ϵ 2200); nmr ($CDCl_3$, 100 mg/0.3 ml) τ 3.6–4.5 (4 H, m), 6.0–6.5 (2 H, m), 7.8–8.0 (4 H, m), 8.07 (1 H, s, exchangeable with D_2O/CD_3COOD); mass spectrum, parent ion at *m/e* 121, base peak at *m/e* 91.

(14) Before filtration, a 1-ml sample aliquot was worked up separately and analyzed by nmr. If any **1** was present the solution was further hydrogenated until none of this substance remained.

Preparation of 9-Azabicyclo[4.2.1]nona-2,4-diene (9) from *N*-Carbamoyl-9-azabicyclo[4.2.1]nona-2,4-diene (8).—A solution of *N*-carbamoyl-9-azabicyclo[4.2.1]nona-2,4-diene (**8**) (164 mg, 1 mmol) and potassium hydroxide (2.5 g) in methanol (6 ml) was maintained at reflux (*ca.* 80°) under nitrogen and with constant stirring for 8 hr. The solution was then concentrated at water aspirator pressure to a semisolid, which was in turn suspended in petroleum ether (150 ml) and the suspension was maintained at reflux under nitrogen with constant stirring for 2 hr. The organic layer was separated, extracted with water (2 × 25 ml), and dried over calcium sulfate. Concentration of the solution at water aspirator pressure gave a crude yellow oil (90 mg, 73%) with spectral properties (ir, nmr) identical with those of authentic 9-azabicyclo[4.2.1]nona-2,4-diene (**9**) prepared from the hydrolysis of *N*-cyano-9-azabicyclo[4.2.1]nona-2,4-diene.

Reaction of 9-Azabicyclo[4.2.1]nona-2,4-diene (9) with Cyanogen Bromide. Formation of 7.—To a solution of 9-azabicyclo[4.2.1]nona-2,4-diene (**9**) (121 mg, 1 mmol) and triethylamine (101 mg, 1 mmol) in methylene chloride (10 ml), maintained at *ca.* 0°, was added, under nitrogen and with constant stirring, a solution of cyanogen bromide (105 mg, 1 mmol) in methylene chloride (5 ml). After the addition had been completed (1 hr) the solution was allowed to warm to room temperature and stirred at this temperature for an additional 23 hr. The solution was then filtered and the filtrate was concentrated at water aspirator pressure to a white solid (130 mg). Recrystallization from carbon tetrachloride gave a crystalline white compound (120 mg, 82%) with melting point and spectral characteristics (ir, nmr) identical with those of authentic *N*-cyano-9-azabicyclo[4.2.1]nona-2,4-diene (**7**).

Preparation of *N*-(*p*-Nitro)benzoyl-9-azabicyclo[4.2.1]nona-2,-4,7-triene (4).—To a solution of 9-azabicyclo[4.2.1]nona-2,4,7-triene (**2**) (119 mg, 1 mmol) and triethylamine (101 mg, 1 mmol) in dry benzene (5 ml), maintained at a gentle reflux temperature, was added under nitrogen and with constant stirring a solution of *p*-nitrobenzoyl chloride (185 mg, 1 mmol) in dry benzene (10 ml). After the addition was completed (30 min) the solution was filtered to remove precipitated solid. Concentration of the filtrate at the water aspirator gave a crude yellow solid, which on recrystallization from boiling carbon tetrachloride gave pure *N*-(*p*-nitro)benzoyl-9-azabicyclo[4.2.1]nona-2,4,7-triene (**4**) (250 mg, 82%) as yellow crystals: mp 112–114°; ir 1650 (C=O), 1525, 1430, 1345, 870, 845, and 720 cm^{-1}; nmr ($CDCl_3$) τ 1.6–1.8 (2 H, m), 2.4–2.5 (2 H, m), 3.6–4.0 (4 H, m), 4.50 (2 H, s), 5.3–5.4 (2 H, m); mass spectrum (20 eV) parent (base) ion at *m/e* 268.

Anal. Calcd for $C_{15}H_{12}N_2O_3$: C, 67.16; H, 4.51; N, 10.44. Found: C, 67.05; H, 3.96; N, 10.55.

Registry No.—**2,** 6789-38-4; **3,** 35105-34-1; **4,** 35105-35-2; **5,** 35105-36-3; **6,** 35105-37-4; **7,** 35105-38-5; **8,** 35105-39-6; **9,** 7129-31-9; **10,** 35105-41-0; **11,** 35105-42-1.

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