Anal. Calcd for $C_{24}H_{17}ClOS_2$: C, 68.45; H, 4.07; Cl, 8.42; S, 15.23. Found: C, 68.55; H, 4.18; Cl, 8.42; S, 14.93.

The proton nmr showed absorption at δ 5.58 (relative area 1, methine proton) and 7.85 (relative area 1, heterocyclic proton), with complex phenyl proton absorption in the range 6.6–7.1 (relative area 15). The starting material (V) shows methylene absorption at δ 3.65 (relative area 2), heterocyclic proton absorption at δ 3.65 (relative area 2), heterocyclic proton absorption at 7.77 (relative area 1), and complex phenyl proton absorption at 6.7–7.2 (relative area 15).

5-Phenyl-1,2-dithiole-$\Delta^{3,\alpha}$-malonitrile (X).—A solution of 40.0 g (0.206 mole) of 5-phenyl-1,2-dithiol-3-one (VIII[7]) and 20 g (0.30 mole) of malononitrile in 100 ml of phosphorus oxychloride was heated on a steam bath for 5.5 hr, cooled, and carefully decomposed with ice. The product was filtered, washed, and dried. It was digested with carbon disulfide at room temperature and filtered; the operation was repeated with dioxane, yielding 45 g (90%), mp 208–214° dec. Dioxane (20 ml/g) gave golden brown crystals, mp 229° dec, in a recovery of 70–75%.

Anal. Calcd for $C_{12}H_6N_2S_2$: C, 59.51; H, 2.50; N, 11.57; S, 26.43. Found: C, 59.56; H, 2.60; N, 11.39; S, 26.60.

Under similar conditions 4,5-benzodithiol-3-one (IX[8]) gave 4,5-benzo-1,2-dithiole-$\Delta^{3,\alpha}$-malonitrile (XI), mp 250–254° dec (AcOH).

Anal. Calcd for $C_{10}H_4N_2S_2$: C, 55.53; H, 1.86; N, 12.96; S, 29.65. Found: C, 55.21; H, 1.95; N, 12.92; S, 29.85.

α-Cyano-5-phenyl-1,2-dithiole-$\Delta^{3,\alpha}$-acetamide (XII).—A mixture of 10.0 g (0.041 mole) of 5-phenyl-1,2-dithiole-$\Delta^{3,\alpha}$-malononitrile (X) and 10 g of sodium hydroxide in 750 ml of water was stirred and refluxed for 5.5 hr, cooled, and filtered. Acidification of the filtrate gave 8.8 g (82%) of product, mp 246–258°. Acetic acid gave golden brown needles, mp 254–257°.

Anal. Calcd for $C_{12}H_8N_2OS_2$: C, 55.39; H, 3.10; N, 10.77; S, 24.60. Found: C, 55.33; H, 3.11; N, 10.62; S, 24.74.

This compound was recovered unchanged after being dissolved in dilute aqueous sodium hydroxide and refluxed for 48 hr. It is also resistant to dilute sulfuric acid.

α-Cyano-5-phenyl-1,2-dithiole-$\Delta^{3,\alpha}$-thioacetamide (XIII).—One gram (3.8 mmoles) of XII and 0.85 g (3.8 mmoles) of phosphorus pentasulfide were stirred and refluxed for 25 min in 50 ml of pyridine. Careful dilution followed by filtration gave 0.72 g (68%) of brown product, which decomposed at approximately 245–250°. Crystallization from acetic acid raised the decomposition point to about 255°. It can also be crystallized from butyl acetate or nitromethane.

Anal. Calcd for $C_{12}H_8N_2S_3$: C, 52.18; H, 2.92; N, 10.14; S, 34.76. Found: C, 51.60; H, 2.90; N, 10.00; S, 34.71.

One-half gram of this compound was refluxed for 5 hr in 200 ml of water containing 2.0 g of sodium hydroxide. Acidification of the solution gave 0.40 g of unchanged starting material.

Both XII and XIII show nitrile stretching frequencies at about 2190 cm^{-1}, NH_2 stretching frequencies near 3400 and 3500 cm^{-1}, and NH_2 deformation at about 1620 cm^{-1} (Nujol). A carbonyl stretching frequency at about 1660 cm^{-1} is present in XII but absent in XIII.

Acknowledgment.—The author is greatly indebted to Miss Vera Jordan and Miss Jessie L. Gove for spectral data, and to John J. Kobliska and his staff for microanalyses.

---

[8] E. W. McClelland, L. A. Warren, and J. H. Jackson, *J. Chem. Soc.*, 1582 (1929).

The 2,3-Diazabicyclo[2.2.1]heptyl Ring System. I. Synthesis and Characterization of Some 5-Substituted Derivatives[1]

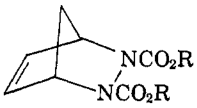
Evan L. Allred, Clyde L. Anderson, and Richard L. Smith

Department of Chemistry, University of Utah, Salt Lake City, Utah 84112

Received March 22, 1966

A survey of the feasibility of the synthesis of 5-substituted 2,3-diazabicyclo[2.2.1]heptyl derivatives by addition to the carbon–carbon double bond of 2,3-dicarboalkoxy-2,3-diazabicyclo[2.2.1]hept-5-enes is reported. Attempted additions of water (H^+) and formic acid were unsuccessful. Hydroboration–oxidation of Ia was successful giving 2,3-dicarbomethoxy-*exo*-2,3-diazabicyclo[2.2.1]heptan-5-ol along with two partially fragmented products. The latter were identified as 4-(N,N′-dicarbomethoxyhydrazino)cyclopentene and 3-(N,N′-dicarbomethoxyhydrazino)cyclopentanol. The synthesis and characterization of 2,3-dicarbomethoxy-2,3-diazabicyclo[2.2.1]heptan-5-one and 2,3-dicarbomethoxy-*endo*-2,3-diazabicyclo[2.2.1]heptan-5-ol also are described. Epoxidation of Ia afforded 2,3-dicarbomethoxy-*exo*-2,3-diazabicyclo[2.2.1]-5,6-epoxyheptane.

Although the 2,3-diazabicyclo[2.2.1]heptyl ring system has been known for 41 years,[2] it appears that C-substituted derivatives are almost entirely unknown. This system with appropriate substituents is of considerable theoretical interest, and also offers a potential synthetic route to some very interesting substituted bicyclo[2.1.0]pentanes.[3] From the original work of Diels and co-workers[2] and from subsequent work,[4] the 2,3-dicarboalkoxy-2,3-diazabicyclo[2.2.1]hept-5-enes Ia and Ib appeared to be attractive starting materials for the synthesis of 5- and 5,6-substituted 2,3-diazabicyclo[2.2.1]heptyl derivatives. These materials are obtained in essentially quantitative yield *via* the facile Diels–Alder reaction between dialkyl azodicarboxylates and cyclopentadiene.[2,4] According to published reports, bromination of the carbon–carbon double bond of Ib proceeds in a normal manner to give the 5,6-dibromide in high yield.[2,4] In this paper we report an investigation of some other additions to the carbon–carbon double bond of I. We also describe the preparation and characterization of four substituted 2,3-diazabicyclo[2.2.1]heptyl derivatives.



Ia, R = CH_3
b, R = CH_2CH_3

Attempted Addition of Water (H^+) and Formic Acid.—Recently Stille and Anyos[5] reported on the treatment of Ib with 10% hydrochloric acid under conditions of continuous reflux. The isolated products, diethyl hydrazodicarboxylate, carbon dioxide, nitrogen, and cyclopentadiene, were accounted for on the basis

---

[1] For a preliminary communication of a part of these results, see E. L. Allred, C. L. Anderson, and R. L. Smith, *Tetrahedron Letters*, **No. 9**, 951 (1966).

[2] O. J. Diels, J. H. Blum, and W. Koll, *Ann.*, **443**, 242 (1925).

[3] R. Criegee and A. Rimmelin, *Ber.*, **90**, 414 (1957).

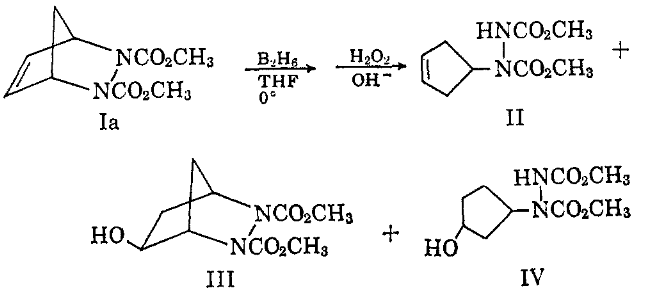
[4] (a) J. C. J. MacKenzie, A. Rodgman, and G. F. Wright, *J. Org. Chem.*, **17**, 1666 (1952); (b) A. Rodgman and G. F. Wright, *ibid.*, **18**, 465 (1953).

[5] J. K. Stille and T. Anyos, *ibid.*, **27**, 3352 (1962).

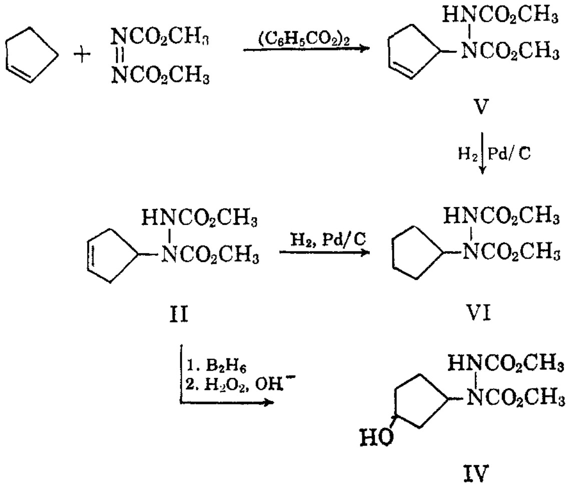
of an initial reverse Diels–Alder reaction, followed by partial hydrolysis, decarboxylation, and diimide reduction. We have reexamined this reaction at a considerably lower temperature hoping to avert fragmentation of the molecule and effect hydration of the double bond. However, treatment of Ib with aqueous 20% *p*-toluenesulfonic acid at 50° for an extended time still resulted in fragmentation. A substantial yield (*ca.* 50%) of diethyl hydrazodicarboxylate was isolated and identified.

Formic acid has been reported to undergo facile addition to carbon–carbon double bonds.[6] A brief examination was made of the reaction of I with formic acid. A mixture of Ia and 97–100% formic acid containing a catalytic trace of boron trifluoride was heated at 100° for 13.5 hr. The only reaction product isolated and identified was dimethyl hydrazodicarboxylate in 63% yield.

Hydroboration.—We next turned our attention to hydroboration–oxidation of Ia. The *in situ* hydroboration[7] of Ia in tetrahydrofuran at 0°, followed by oxidation, produced three products, II, III, and IV. The compounds are numbered in the order of elution from a Florisil chromatography column.



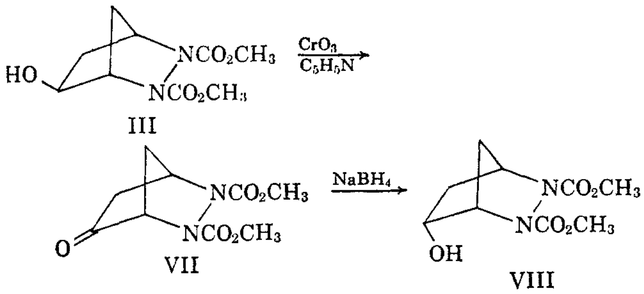
The structure of II was established as 4-(N,N′-dicarbomethoxyhydrazino)cyclopentene with the aid of elemental analyses and spectral data. Characteristic infrared absorptions indicated NH, $C{=}O$, and CONH structural features. The nmr spectrum was definitive with a two-vinyl-proton singlet, a one-proton quintet ($J \sim 7$ cps), and a four-proton methylene doublet ($J \sim 7$ cps). The only structure compatible with this is the 4-substituted cyclopentene derivative II. For additional confirmation, isomeric 3-(N,N′-dicarbomethoxyhydrazino)cyclopentene (V) was synthesized by allylic addition of dimethyl azodicarboxylate to cyclopentene according to the method of Huisgen and Jacob.[8] The nmr spectra and the infrared spectra in the fingerprint region were very different for II and V. Hydrogenation of II and V with 10% palladium on charcoal gave the same cyclopentane derivative VI.



The structure of IV was assigned readily on the basis of infrared absorptions and the fact that hydroboration–oxidation of II gave IV in high yield.

The third product, III, proved to be the desired 2,3-dicarbomethoxy-2,3-diazabicyclo[2.2.1]heptan-5-ol. Assignment of the structure was based on analyses and spectral data. The infrared spectrum showed only strong absorptions for OH and $C{=}O$ functions. The nmr spectrum was entirely consistent with the assigned structure and clearly showed the correct numbers and kinds of tertiary, methylene, and methoxyl hydrogens.

The question of the configuration at C-5 for III was settled by the synthesis of its epimer VIII. Oxidation of III with chromium trioxide in pyridine[9] afforded 2,3-dicarbomethoxy-2,3-diazabicyclo[2.2.1]heptan-5-one (VII). Analyses and spectral data of VII were in complete agreement with the assigned structure. The infrared spectrum showed no absorption in the 2.7–3.2-μ region and the nmr spectrum displayed the correct number of tertiary, methylene, and methoxyl protons. Reduction of ketone VII with sodium borohydride in methanol produced alcohol VIII which proved to be isomeric with III. The two alcohols had the same analyses but different melting points and spectral properties. The infrared spectra showed somewhat different hydroxyl absorptions and were distinctly different in the fingerprint region. Nmr spectra of III and VIII showed the same number of protons but displayed some chemical shift differences. The six methoxyl protons of VIII appeared as two very sharp-three proton singlets in contrast to the sharp six-proton singlet of III. A chemical shift difference of *ca.* 21–24 cps was observed for the protons at C-5 (*vide infra*).



Assignment of configuration at C-5 for epimers III and VIII was based on several lines of evidence.

Reduction of rigid bicyclic ketones like bicyclo[2.2.1]heptan-2-one with complex metal hydrides has been found to proceed by hydride transfer to the less hindered *exo* side of the carbonyl group to give the *endo* alcohol as the chief product.[10,11] Inspection of molecular models indicates that the steric situation is similar for ketone VII. By analogy, alcohol VIII obtained from

---

[6] H. B. Knight, R. E. Koos, and D. Swern, *J. Am. Chem. Soc.*, **75**, 6212 (1953).

[7] H. C. Brown, "Hydroboration," W. A. Benjamin, Inc., New York, N. Y., 1962, p 88.

[8] R. Huisgen and F. Jacob, *Ann.*, **590**, 37 (1954).

[9] G. I. Poos, G. E. Arth, R. E. Beyler, and L. H. Sarett, *J. Am. Chem. Soc.*, **75**, 423 (1953).

[10] S. Beckmann and R. Mezzar, *Ber.*, **89**, 2738 (1956).

[11] H. C. Brown and H. R. Deck, *J. Am. Chem. Soc.*, **87**, 5620 (1965).

the sodium borohydride reduction of VII has the *endo* configuration. Thus, the hydroboration product alcohol III has the *exo* configuration.[12] The exact degree of stereoselectivity of the hydroboration reaction is not known. However, the *exo*/*endo* ratio is large. It was found that *ca.* 5% of VIII could be detected in III by infrared analysis. We found no indication of VIII in any of the fractions from the chromatographic purification of III.[13]

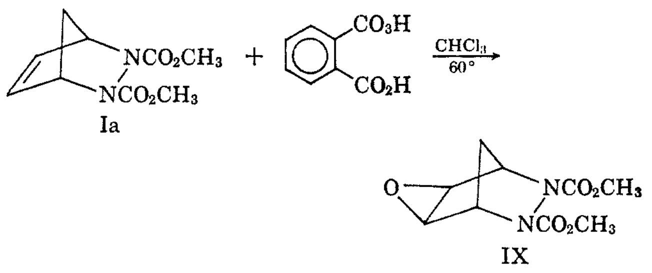
Infrared data obtained for III and VIII in the first overtone region of the O–H stretching absorption (1.4–1.5 μ) are in complete agreement with these configuration assignments. In dilute carbon tetrachloride solution *exo* isomer III showed only a single band at 1.414 μ. This is entirely analogous to the free O–H absorption found at 1.414 μ for *exo*-bicyclo[2.2.1]heptan-2-ol.[14] In contrast, *endo* alcohol VIII exhibited the free O–H band at 1.410 and another band at 1.456 μ. The latter band undoubtedly is a consequence of the *endo* structure and represents an intramolecularly bonded O–H stretching absorption. No studies of similar hydrazino structures appear to be available for comparison of the infrared frequency shift ($\Delta\nu$) between free O–H and intramolecular bonded OH···N. There are a few reports of intramolecular OH···N bonding with other systems;[15] the $\Delta\nu$ for VIII is well within the range of frequency differences found for these systems.

The nmr spectra of III and VIII are also consistent with the assigned configurations. Musher[16] has noted that for bicyclo[2.2.1]heptan-2-ols *endo* protons are upfield from *exo* protons by 21 to 32 cps. We have observed a similar chemical shift situation with the related structures III and VIII. A one-proton resonance (doublet, $J \sim 7$ cps) at τ 5.90 for III is shifted to low field for VIII and appears superimposed on another proton at *ca.* τ 5.5. Since this is the only large proton shift found in the spectra of the two isomers, it is reasonable to assign these signals to the C-5 protons. The magnitude of this chemical shift difference (between 21 and 24 cps) is in accord with a C-5 proton orientation of *endo* and *exo* for III and VIII, respectively.

Initially, much difficulty was encountered in obtaining reproducible conversions of Ia to the desired alcohol III *via* hydroboration–oxidation. Yields of III varied from 20 to 90% of theory. After considerable experimentation several factors were found to be important.[17] Hydroboration by the *in situ* method led to product which contained as much as 20–40% of IV. This was circumvented by using a diborane solution which was free of any salts. The temperature of oxidation and the order of addition of sodium hydroxide and hydrogen peroxide were found to greatly affect the II/III product ratio. Oxidation of the organoborane reaction mixture by addition of an aqueous solution of sodium hydroxide and hydrogen peroxide at 0° almost entirely eliminated the formation of II. With these considerations yields of 85–90% III were isolated consistently.

Epoxidation.—Another potential approach to 5- or 5,6-substituted 2,3-diazabicyclo[2.2.1]heptyl derivatives is *via* a 5,6-epoxide structure. In this regard we have examined the addition of peracid to the carbon–carbon double bond of I.

Reaction of monoperphthalic acid with Ia at 30° in ether for 12 days resulted in less than 10% conversion to epoxide. In this case a quantitative yield of phthalic acid was recovered. On the chance that a satisfactory addition might occur at higher temperature, a reaction using a large excess of peracid was carried out in chloroform at 60°. With these conditions a 50% yield of product IX was attained. One disadvantage of the higher temperature was an accompanying side reaction which resulted in cleavage of the 2,3-diazabicyclo[2.2.1]heptyl ring structure.



The structure of IX was established as 2,3-dicarbomethoxy-2,3-diazabicyclo[2.2.1]-5,6-epoxyheptane by analyses and spectral data. An infrared spectral analysis showed no absorption in the 2.7–3.2- or 6.1–6.8-μ regions. A strong absorption was found near 11.9 μ which is characteristic of epoxides.[18] Vinyl protons were absent in the nmr spectrum. Comparison of the nmr spectrum of IX with that of hydrogenated Ia showed one C-7 proton of IX to be shifted downfield by *ca.* 9 cps and the other proton shifted upfield by *ca.* 26 cps from the C-7 protons of hydrogenated Ia. Based on a recent nmr study of the epoxides of bridged ring systems[19] this indicates an *exo* configuration for the epoxide ring of IX. The known stereochemistry of the epoxidation of bicyclo[2.2.1]hept-2-ene is consistent with this.[18]

In summary, the above results serve to point out the appreciable tendency of system I toward ring cleavage as a consequence of addition or attempted addition to the carbon–carbon double bond. The severe conditions required for epoxidation also indicate a significant retardation toward electrophilic addition.

Experimental Section

Melting points were taken by the capillary tube method and are uncorrected. The infrared spectra were determined as Nujol mulls with a Beckman IR-5A spectrophotometer. The near-infrared spectra (1.4–1.5 μ) were determined in carbon tetrachloride at *ca.* 0.005 *M* concentration with a Cary 14 recording spectrophotometer. Nmr spectra were obtained with a Varian Model A-60 spectrometer in deuteriochloroform using tetramethylsilane as an internal standard.

---

[12] This result is consistent with the hydroboration of bicyclo[2.2.1]hept-2-ene which occurs from the *exo* side: ref 7, pp 15 and 126.

[13] The two alcohols were eluted in different solvents as indicated in the Experimental Section.

[14] R. Piccolini and S. Winstein, *Tetrahedron Letters*, **No. 13**, 4 (1959); R. Piccolini, Ph.D. Dissertation, University of California at Los Angeles, Los Angeles, Calif., 1959.

[15] H. H. Freedman, *J. Am. Chem. Soc.*, **83**, 2900 (1961), and references cited therein.

[16] J. A. Musher, *Mol. Phys.*, **6**, 93 (1963).

[17] A detailed study of the mechanism of the formation of II and IV is reported in the following paper: E. L. Allred and R. L. Smith, *J. Org. Chem.*, **31**, 3498 (1966).

[18] S. B. Soloway and S. J. Cristol, *ibid.*, **25**, 327 (1960), and other references cited therein.

[19] K. Tori, K. Kitahonoki, Y. Takano, H. Tanida, and T. Tsuji, *Tetrahedron Letters*, **No. 11**, 559 (1964).

2,3-Dicarboalkoxy-2,3-diazabicyclo[2.2.1]hept-5-enes Ia and Ib.—These compounds were prepared from cyclopentadiene and the corresponding dialkyl azodicarboxylate according to the procedure of Rodgman and Wright.[4]

Reaction of Ib with 20% *p*-Toluenesulfonic Acid.—A solution of 3.6 g (0.015 mole) of Ib and 9.5 g (0.055 mole) of *p*-toluenesulfonic acid in 37 ml of water was stirred at 50–52° for 3 weeks. After this time the reaction mixture (black) was neutralized to pH 7 with sodium bicarbonate. The neutralized water solution was extracted continuously with ether for 23 hr in a liquid–liquid extractor. The ether extract was dried with magnesium sulfate and the solvent was removed under reduced pressure leaving 1.3 g of crude concentrate. On the basis of the infrared spectrum, this material appeared to be mostly diethyl hydrazodicarboxylate. Three recrystallizations from ether yielded 0.6 g of pure diethyl hydrazodicarboxylate, mp 133–134°, mmp 133–135° with authentic sample (lit.[20] mp 134–135°). The infrared spectrum of the purified product was identical with the spectrum of authentic material.

Reaction of Ia with Formic Acid.—A mixture of 2.12 g (0.01 mole) of Ia, 0.09 g of boron trifluoride etherate, and 4.4 ml of 97–100% formic acid (Matheson) was heated and stirred at 98–100° for 13.5 hr. The black reaction mixture was poured into 50 ml of water and extracted with three 25-ml portions of ether. The combined ether extract was dried over magnesium sulfate and evaporated under reduced pressure to give 2.0 g of black, tar-like residue. This was chromatographed on Floridin Co. 100–200 mesh Florisil using dichloromethane, ether, and ether–methanol as eluent solvents. A total of 0.92 g (63.5%) of dimethyl hydrazodicarboxylate was recovered, mp 127–131°. This product had an infrared spectrum identical with the one of authentic dimethyl hydrazodicarboxylate.[20]

Hydroboration–Oxidation of Ia.—Two different general procedures were used. Representative examples of each method are described.

A. **Modified *in situ* Method.**—Diborane was generated under an atmosphere of nitrogen by addition of 9.4 g (0.067 mole) of boron trifluoride etherate to a stirred mixture of 2.04 g (0.054 mole) of sodium borohydride in 250 ml of tetrahydrofuran at 0°. To this cold mixture was added 21.20 g (0.1 mole) of Ia in 50 ml of tetrahydrofuran. The reaction mixture was allowed to warm slowly to room temperature. After standing overnight under nitrogen a mixture of 10 ml of 30% hydrogen peroxide and 20 ml of 3 *N* sodium hydroxide was added dropwise. Most of the solvent was removed under reduced pressure and the residue was taken up in ether. The ether solution was dried with anhydrous magnesium sulfate and the solvent was removed under vacuum to give 20 g of crude concentrate. This material was chromatographed on 500 g of 100–200 mesh Florisil. The order of solvents employed for elution were pentane, dichloromethane, ether, and ether–methanol mixtures. Compounds recovered in the order of elution were starting material Ia (2.1 g, 10% recovery), II (4.9 g, 26% of theory), III (8.6 g, 42% of theory), and IV (4.3 g, 21% of theory). Component III was eluted mostly in ether.

An analytical sample of II, 4-(N,N′-dicarbomethoxyhydrazino)cyclopentene, was prepared by repeated recrystallization from ether–pentane solvent, mp 117.5–118°. The infrared spectrum showed characteristic absorptions at 3.08 (NH), 5.81 (C=O), and 6.56 μ (CONH); nmr spectrum, τ 7.50 (4 H, doublet, $J \sim 7$ cps, >CH$_2$), 6.28 (6 H, singlet CO$_2$CH$_3$), 5.06 (1 H, quintet, $J \sim 7$ cps, ⋗CH), 4.35 (2 H, singlet, HC=CH), and 2.62 (1 H, broad singlet, NH).

Anal. Calcd for $C_9H_{14}N_2O_4$: C, 50.46; H, 6.59; N, 13.08. Found: C, 50.61; H, 6.43; N, 13.20.

Initially, considerable difficulty was experienced in getting III, 2,3-dicarbomethoxy-*exo*-2,3-diazabicyclo[2.2.1]heptan-5-ol, to crystallize; a sample finally solidified after long standing. Recrystallization from ether gave an analytical sample, mp 113–114°. Characteristic infrared absorptions were at 2.90 (OH) and a doublet at 5.71 and 5.88 μ (C=O); nmr spectrum, τ 8.4 (2 H, complex, >CH$_2$), 7.9 (2 H, complex, >CH$_2$), 6.35 (1 H, broad singlet, concentration dependent, OH), 6.23 (6 H, singlet, CO$_2$CH$_3$), 5.90 (1 H, doublet, $J \sim 7$ cps, ⋗CH), 5.64 (1 H, singlet ⋗CH), and 5.45 (1 H, singlet, ⋗CH).

Anal. Calcd for $C_9H_{14}N_2O_5$: C, 46.95; H, 6.13; N, 12.17. Found. C, 46.83; H, 6.29; N, 12.01.

Several recrystallizations of IV, 3-(N,N′-dicarbomethoxyhydrazino)cyclopentanol, from ether–pentane solvent produced an analytical sample, mp 146–147.5°. Characteristic infrared absorptions were at 2.90 (OH), 3.08 (NH), and a doublet at 5.82 and 5.92 (C=O), and 6.55 μ (CONH).

Anal. Calcd for $C_9H_{16}N_2O_5$: C, 46.54; H, 6.94; N, 12.06. Found: C, 46.45; H, 6.94; N, 12.06.

B. **Preparative Procedure for III.**—Diborane free of sodium borohydride and boron trifluoride was prepared according to the procedure of Brown and co-workers.[21] The diborane was generated by the addition of 96.28 g (1.42 moles) of boron trifluoride in 250 ml of diglyme[22] to 42.4 g (1.17 moles) of sodium borohydride in 400 ml of diglyme. The diborane was passed through a solution of 1 g of sodium borohydride in 10 ml of diglyme into 1000 ml of tetrahydrofuran. Active hydride for this stock solution was determined by injecting a known amount of the solution into an ethylene glycol–diglyme mixture and measuring the hydrogen evolution with a gas buret. The solution was 1.0 *M* in borane (BH$_3$).

A solution of 50 g (0.236 mole) of Ia in 420 ml of tetrahydrofuran was added in 20 min to 241 ml of 1.0 *M* borane in tetrahydrofuran at 0°. After the reaction mixture had stirred at 0° for an additional 2.5 hr, water was added cautiously to hydrolyze the excess borane. The mixture was oxidized by the addition of a cold solution made from 32 ml of 30% hydrogen peroxide and 43 ml of 6 *N* sodium hydroxide. The oxidant was added at such a rate and with sufficient cooling that the temperature was kept at 0°. Following addition of oxidant, the reaction mixture was stirred 2 hr at 0°. The tetrahydrofuran solution was removed and the residue was extracted with tetrahydrofuran. The combined tetrahydrofuran solution was dried over magnesium sulfate. Evaporation of the solvent under reduced pressure yielded 56.3 g of crude concentrate. Chromatography on Florisil with dichloromethane–ether eluent resulted in the isolation of 46 g (86%) of III.

3-(N,N′-Dicarbomethoxyhydrazino)cyclopentene (V).—A mixture of 6.5 g (0.095 mole) of cyclopentene, 6.4 g (0.044 mole) of dimethylazodicarboxylate, and 0.22 g of benzoyl peroxide were stirred at reflux temperature for 6 hr. Upon standing overnight at room temperature a white solid separated. Filtration gave 5 g (53%) of V, mp 125–127°. Recrystallization from ether–pentane produced an analytical sample, mp 127–128°. The nmr spectrum showed signals at τ 7.9 (4 H, complex multiplet, >CH$_2$), 6.27 (3 H, singlet, CO$_2$CH$_3$), 6.23 (3 H, singlet, CO$_2$CH$_3$), 4.66 (1 H, singlet, ⋗CH), 4.35 (1 H, singlet, C=CH), 3.98 (1 H, singlet, C=CH), and 3.28 (1 H, broad singlet, NH).

Anal. Calcd for $C_9H_{14}N_2O_5$: C, 50.46; H, 6.59; N, 13.08. Found: C, 50.24; H, 6.54; N, 12.88.

N,N′-Dicarbomethoxyhydrazinocyclopentane (VI). A. From II.—When 0.2142 g (0.001 mole) of II in 20 ml of ethanol was subjected to hydrogenation over 0.040 g of 10% palladium-on-charcoal catalyst at 1 atm of pressure, 0.001 mole of hydrogen was rapidly absorbed. Removal of catalyst and solvent afforded 0.216 g (100%) of VI, mp 96–97°.

B. **From V.**—When 0.2142 g (0.001 mole) of V was hydrogenated under identical conditions, 0.001 mole of hydrogen was absorbed and 0.2143 g (99%) of VI was recovered, mp 96–97°. A mixture melting point of the two samples was 96–97°. The infrared spectra of the two samples were identical.

An analytical sample was prepared by recrystallization from ether–pentane solvent, mp 98–98.5°.

Anal. Calcd for $C_9H_{16}N_2O_4$: C, 49.99; H, 7.46; N, 12.96. Found: C, 49.95; H, 7.42; N, 12.66.

3-(N,N′-Dicarbomethoxyhydrazino)cyclopentanol (IV).—A diborane solution was prepared by the addition of 0.86 ml (0.007 mole) of boron trifluoride etherate to a stirred mixture of 0.19 g (0.005 mole) of sodium borohydride in 15 ml of tetrahydrofuran at 0°. To this cold mixture was added 2.14 g (0.01 mole) of II in 15 ml of tetrahydrofuran. The reaction mixture was allowed to warm to room temperature and stand overnight. The mixture was oxidized by addition of 4 ml of a 50:50 mixture of 30% hydrogen peroxide and 6 *N* sodium hydroxide. The oxidized sample was dried over magnesium sulfate and the tetrahydrofuran was removed under reduced pressure to give 2.03 g (87%) of crude IV, mp 133–138°. Recrystallization from ether–pentane gave pure IV, mp 146–147.5°. The infrared spectrum of this product

---

(20) J. C. Kauer, "Organic Syntheses," Coll. Vol. IV, John Wiley and Sons, Inc., New York, N. Y., 1963, p 411.

(21) G. Zweifel, K. Nagase, and H. C. Brown, *J. Am. Chem. Soc.*, **84**, 188 (1962).

(22) H. C. Brown and G. Zweifel, *ibid.*, **83**, 1241 (1961).

was identical with the one for the analytical sample of IV (*vide supra*).

2,3-Dicarbomethoxy-2,3-diazabicyclo[2.2.1]heptan-5-one (VII).—To a stirred suspension of chromium trioxide–pyridine complex prepared from 28 g of chromium trioxide and 216 ml of pyridine was added 11.5 g (0.05 mole) of III in 35 ml of pyridine. The mixture was stirred overnight at room temperature. Most of the pyridine was removed under reduced pressure leaving a brown residue. This was extracted with six 200-ml portions of ether. Evaporation of the combined ether extract gave 11.0 g of crude product. This material was chromatographed on 180 g of Florisil. Elution with dichloromethane yielded 6.2 g (54%) of VII and elution with ether resulted in recovery of 3.0 g of starting material III. An analytical sample of VII was prepared by recrystallization from dichloromethane–pentane solvent, mp 87–88°. A characteristic infrared absorption doublet was found at 5.62 and 5.81 μ (C=O); nmr spectrum, τ 8.00 (2 H, singlet, >CH$_2$), 7.67 (2 H, singlet, >CH$_2$), 6.22 (3 H, singlet, CO_2CH_3), 6.18 (3 H, singlet, CO_2CH_3), 5.66 (1 H, singlet, ⩾CH), and 5.05 (1 H, singlet, ⩾CH).

Anal. Calcd for $C_9H_{12}N_2O_5$: C, 47.37; H, 5.30; N, 12.28. Found: C, 47.34; H, 5.24; N, 12.25.

2,3-Dicarbomethoxy-*endo*-2,3-diazabicyclo[2.2.1]heptan-5-ol (VIII).—To 1.81 g (0.008 mole) of VII in 50 ml of methanol at −10° was added 0.60 g (0.016 mole) of sodium borohydride in 50 ml of 80% aqueous methanol. The mixture was stirred at *ca.* 0° for 30 min and then at room temperature for 3 hr. To the reaction mixture was added 500 ml of tetrahydrofuran and 100 g of anhydrous magnesium sulfate. Following filtration, the solvent was removed under reduced pressure to give 1.7 g of concentrate. This was chromatographed on 30 g of Florisil. The desired *endo* alcohol VIII (0.5 g, 27%) was eluted in dichloromethane. This solidified upon standing. The remainder of the reaction product was eluted with 10% methanol-ether. This material was an oil and could not be induced to crystallize. On the basis of an nmr spectrum, it appeared to be an *endo* alcohol with one of the carbomethoxy groups removed. An analytical sample of VIII was prepared by recrystallization from dichloromethane–pentane solvent, mp 135–136°. Characteristic infrared absorptions were at 2.88 (OH) and a doublet at 5.76 and 5.88 μ (C=O); nmr spectrum, τ 8.25 (4 H, complex, >CH$_2$), 7.11 (1 H, broad singlet, concentration dependent, OH), 6.23 (3 H, singlet, CO_2CH_3), 6.21 (3 H, singlet, CO_2CH_3), 5.55 (2 H, singlet, ⩾CH), and 5.35 (1 H, singlet, ⩾CH).

Anal. Calcd for $C_9H_{14}N_2O_5$: C, 46.95; H, 6.12; N, 12.17. Found: C, 46.90; H, 6.16; N, 12.01.

Epoxidation of I.—Two different sets of reaction conditions were used.

A. **Ether Solvent at 30°.**—A solution of 9.10 g (0.05 mole) of monoperphthalic acid in 90 ml of ether[23] was added to a stirred solution of 10.0 g (0.042 mole) of Ib in 90 ml of ether. The disappearance of peracid was followed by titration with thiosulfate. After 12 days at *ca.* 30° 98% of the peracid had disappeared. The phthalic acid was removed by filtration (6.5 g, 99%) and the filtrate was extracted with enough ice-cold 5% sodium bicarbonate to remove the excess monoperphthalic acid. The ether solution was dried with anhydrous magnesium sulfate and the ether was removed under vacuum to give 8.5 g of concentrate. This material had an infrared spectrum almost identical with that of starting Ib.

The above procedure was repeated with Ia except that the ratio of monoperphthalic acid to Ia was increased to 3:1. An nmr spectrum of the crude reaction product indicated the possible formation of a small amount of epoxide structure. Crystallization from dichloromethane–pentane solvent afforded 8% of a solid material, mp 125–130°; five recrystallizations gave mp 141–143°. This was identified as 2,3-dicarbomethoxy-*exo*-2,3-diazabicyclo[2.2.1]-5,6-epoxyheptane (IX) by spectral data: characteristic infrared absorptions, 5.74 and 5.88 (doublet) and 11.65 μ;[18] nmr spectrum, τ 8.24 (1 H, doublet, $J \sim 11$ cps, C-7), 8.16 (1 H, doublet, $J \sim 11$ cps, C-7), 6.47 (2 H, singlet, ⩾CH), 6.19 (6 H, singlet, CO_2CH_3), and 5.23 (2 H, singlet, ⩾CH). [For comparison, the nmr spectrum of hydrogenated Ia was τ 8.32 (2 H, singlet, C-7), 8.23 (4 H, singlet, >CH$_2$), 6.18 (6 H, singlet, CO_2CH_3), and 5.40 (2 H, singlet, ⩾CH).] An analytical sample was prepared by vacuum sublimation, mp 147–147.5°.

Anal. Calcd for $C_9H_{12}N_2O_5$: C, 47.37; H, 5.30; N, 12.28. Found: C, 47.09; H, 5.36; N, 12.17.

B. **Chloroform Solvent at 60°.**—A solution of 31 g (0.17 mole) of monoperphthalic acid in 450 ml of ether[23] was added to 10.6 g (0.05 mole) of Ia in 250 ml of ether. No apparent reaction had occurred after refluxing overnight. The ether was removed and replaced with 500 ml of chloroform. After refluxing (60°) for 20 hr the precipitated phthalic acid was removed and the chloroform solution was washed with aqueous sodium bicarbonate. The chloroform layer was dried with magnesium sulfate and the solvent was removed under vacuum to give 8.8 g of crude product. The infrared spectrum of this material showed significant NH (3.1 μ) and CONH (6.5 μ) absorptions. Crystallization from dichloromethane–pentane solvent afforded 6.0 g of IX. The product had an infrared spectrum comparable to the above analytical sample, mp 132–135°.

Acknowledgment.—This study was supported by the National Science Foundation, Grant No. GP-3534. C. L. A. was the recipient of a National Science Foundation Science-Faculty Fellowship (1963–1964). We wish to thank Mr. Ken Sierecki for assistance with some of the synthetic work.

---

[23] Prepared according to the method of E. E. Royals and L. H. Harrell, *J. Am. Chem. Soc.*, **77**, 3405 (1955).