μ; uv, $\lambda_{\max}^{\text{EtOH}}$ 264 mμ (ε 21,415); nmr ($CDCl_3$), δ 2.20 (4 H, m, CCH_2CH_2C), 3.52 (4 H, m, $CH_2N^+CH_2$), 4.39 (2 H, m, $N{=}CCH_2$), 6.52 (1 H, m, CHAr), 7.68 (8 H, m, $C_{12}H_8Cl_2$).

Anal. Calcd for $C_{19}H_{19}Cl_3N_2$: C, 59.8; H, 5.0; Cl, 27.9; N, 7.3. Found: C, 59.6; H, 5.2; Cl, 26.9; N, 7.1.

A solution of **8** in ethanol treated with excess 70% perchloric acid gave an immediate precipitate of **8** perchlorate, mp 249.5–250°.

Anal. Calcd for $C_{19}H_{19}Cl_3N_2O_4$: C, 51.2; H, 4.3; Cl, 23.9; O, 14.4. Found: C, 51.3; H, 4.4; Cl, 23.8; O, 14.3.

Sodium Hydroxide Conversion of 8 into 9.—A mixture of 1.0 g of **8** and 50 ml of 2 *N* sodium hydroxide was stirred for 3 hr at room temperature. The oil that separated during this time was extracted with chloroform, dried (Na_2SO_4), filtered, and concentrated *in vacuo* to give 0.900 g of an oil that solidified on standing. Crystallization from ethanol–water gave 0.539 g of yellow **9**: mp 96–96.5°; ir (KBr), 6.72, 9.21, and 9.93 μ; uv, $\lambda_{\max}^{\text{EtOH}}$ 280 mμ (ε 25,000), 373 (7500); nmr ($CDCl_3$), δ 1.86 (4 H, m, CCH_2CH_2C), 3.29 (4 H, m, CH_2NCH_2), 6.90 (2 H, AB, J = 17 cps, $\overset{|}{\text{H}\text{C}}{=}\underset{|}{\text{C}}\text{H}$), 7.38 (8 H, m, $C_{12}H_8Cl_2$).

Anal. Calcd for $C_{19}H_{18}Cl_2N_2$: C, 66.1; H, 5.3; Cl, 20.5. Found: C, 66.3; H, 5.3; Cl, 20.5.

Lithium Aluminum Hydride Reduction of 8 to 10.—To a stirred slurry of 0.99 g (0.026 mol) of lithium aluminum hydride in 45 ml of anhydrous tetrahydrofuran maintained under a nitrogen atmosphere there was added in one portion 5.0 g (0.013 mol) of **8**. The mixture was refluxed for 18 hr, cooled in an ice bath, and treated successively with 5.0 ml of ethyl acetate, 2.0 ml of 2 *N* sodium hydroxide, 3.0 ml of water, and 5 g of anhydrous sodium sulfate. The salts were filtered off and the filtrate was concentrated *in vacuo* to give an oil that crystallized from ligroin. Recrystallization from methanol gave 0.64 g (24%) of **10**: mp 90–91.5°; ir ($CHCl_3$), 6.33, 6.48 and 6.76 μ; uv, $\lambda_{\max}^{\text{EtOH}}$ 230 mμ (ε 8100), 314 (22,000); nmr ($CDCl_3$), δ 1.91 (4 H, m, CCH_2CH_2C), 3.31 (4 H, m, CH_2NCH_2), 7.05 (1 H, s, $ArCH{=}$), 7.35 (4 H, A_2B_2, C_6H_4).

Anal. Calcd for $C_{11}H_{13}ClN_2$: C, 63.3; H, 6.2; Cl, 17.0; N, 13.4. Found: C, 63.6; H, 6.5; Cl, 17.1; N, 13.4.

A solution of 0.605 g (0.0043 mol) of *p*-chlorobenzaldehyde and 0.371 g (0.0043 mol) of N-aminopyrrolidine in 1.0 ml of ethanol was warmed on a water bath for about 5 min and then cooled in an ice bath. The resultant solid was filtered off and crystallized from ethanol to give 0.714 g of **10**, mp 91–92°. Comparison of the infrared spectrum and the mixture melting of **10** prepared from **8** showed them to be identical.

Registry No.—**4a,** 17288-70-9; **4a**·HCl, 17288-66-3; **4b,** 17288-71-0; **5a,** 17288-72-1; **6a,** 17288-73-2; **6a** perchlorate, 17288-74-3; **7a,** 17288-75-4; **7a** methiodide, 17326-50-0; **8,** 17288-76-5; **8** perchlorate, 17288-77-6; **9,** 17288-79-8; **10,** 17288-78-7.

Acknowledgment.—The authors thank Mr. Paul Schirm for assistance in the synthetic work and Mr. Urs Stoeckli for analytical and instrumental analyses.

Bromination of 1,2-Cyclononadiene. Preparation of *cis*- and *trans*-2,3-Dibromocyclononene[1]

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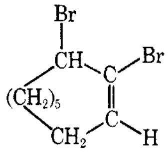
Halogen additions to only a relatively few allenes have been reported.[2] In no case where geometrical isomerism of the carbon–carbon double bond of the monoaddition product was possible has the stereochemistry been determined.[3]

The reaction of 1 mol of bromine with 1,2-cyclononadiene in carbon tetrachloride has been investigated and shown to yield a mixture of *cis*- and *trans*-2,3-dibromocyclononene (**1** and **2**, respectively). The twice-distilled material (about 30% yield) was shown by gas chromatography (Carbowax 20M liquid phase) to consist of 85% of **1** and **2**. Treatment of this material with either aqueous or ethanolic silver nitrate immediately gave a precipitate, indicating the presence of an allylic bromine atom. The presence of a carbon–carbon double bond was indicated by a medium intensity ir absorption at 1635 cm^{-1}. When the twice distilled material was debrominated with either zinc or magnesium, 1,2-cyclononadiene was the sole product detected by gas chromatography, and both of the major peaks of the starting material had completely disappeared.



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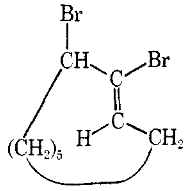

2

A sample of **1** and **2** purified by gas chromatography (the sample consisted of the two major components which had retention times of 28.0 and 30.5 min on a Carbowax 20M column at 152°) gives the following nmr spectrum: two overlapping triplets centered at τ 3.89 (J = 8.8 cps) and 4.11 (J = 8.8 cps) with a total relative area of 1.0 correspond to a vinyl proton split by adjacent methylene protons in each of the two isomers (**1** and **2**); a quartet at 4.86 (J = 5.3 cps) and a quintet at 5.84 (J = 5.8 cps) with a total relative area of 1.0 correspond to the methine protons of the two isomers;[4,5] a complex absorption between 7.05 and 8.90 with a total relative area of 12.0 corresponds to the 12 methylene protons.

An attempt was made to isolate **1** and **2** by preparative gas chromatography using a Carbowax 20M column. Because the 30.5-min peak tailed into the 28.0-min peak, it was not possible to collect a sample significantly enriched in the 28.0-min retention time component. The separation of the component with the 30.5-min retention time was accomplished, however. Its nmr spectrum revealed a triplet (J = 8.8 cps) at τ 4.11 (relative area = 1.0), a quintet (J = 5.8 cps) at 5.84 (relative area = 1.0), and a complex multiplet between 7.05 and 8.90 (relative area = 12.0). The peaks at τ 3.89 and 4.86 as well as part of the com-

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[1] From the Ph.D. Thesis of M. J. Millam, University of the Pacific, 1966.

[2] S. Patai, "The Chemistry of Alkenes," John Wiley and Sons, Inc., New York, N. Y., 1964, p 1074 ff.

[3] The stereochemistry of the double bond of the monobromination product of 2,3-pentadiene has recently been reported, however: W. L. Waters and M. J. Caserio, Abstracts, the 155th National Meeting of the American Chemical Society, San Francisco, Calif., March 1968, No. P43.

[4] A simple first-order analysis predicts that the two nonequivalent methylene protons[5] adjacent to the asymmetric carbon will split the methine proton into a quartet. The quartet observed at τ 4.86 accounts for the methine proton of one isomer. The methine proton at τ 5.84 has a more complex splitting than that simply predicted.

[5] L. M. Jackman, "Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry," Pergamon Press, New York, N. Y., 1959; G. M. Whitesides, D. Holtz, and J. D. Roberts, *J. Amer. Chem. Soc.*, **86**, 2628 (1964), and references therein.

plex multiplet between 7.05 and 8.90 in the nmr spectrum of the mixture, therefore, belong to the isomer with the shorter (28.0 min) retention time.

The difference in the chemical shifts of the vinyl protons of the two isomers allows, in principle, a stereochemical assignment of the double bonds. Bhacca, Johnson, and Shoolery[6] have reported that for 2,3-dibromopropene the vinyl proton *trans* to the vinyl bromine atom resonates at τ 4.38 and the vinyl proton *cis* to the vinyl bromine atom resonates at 3.98. Thus, the proton *cis* to the vinyl bromine atom, according to this assignment, is deshielded relative to the *trans* proton by 0.40 ppm. The same relative assignments were made for 2,3-dichloropropene, also, with a chemical shift difference of 0.17 ppm. Based upon the relative chemical shift values and coupling constants observed for the isomeric 1,2,3-trichloropropenes, Mortimer[7] has made assignments for the vinyl protons of 2,3-dichloropropene that are in agreement with the foregoing. In contrast, Whipple, Goldstein, and McClure[8] have reported the reverse assignments for the vinyl protons of 2,3-dibromopropene and 2,3-dichloropropene without specifying how they were arrived at.

Due to uncertainties inherent in assigning chemical shifts to isomeric protons within the same molecule, it is more profitable to examine relative vinyl proton chemical shifts in isomeric pairs. De Wolf and Baldeschwieler[9] have carried out a complete analysis of the nuclear magnetic resonance spectra of the isomeric 1-fluoro-, 1-chloro-, and 1-bromopropenes. The vinyl proton on the 2-carbon atom in each case had a lower field chemical shift value for the *trans* isomer (vinyl hydrogen and halogen atoms *cis*) than for the corresponding *cis* isomer. The chemical shift differences at 60 Mc were 35.1, 5.9, and 1.4 cps for the 1-fluoro-, 1-chloro-, and 1-bromopropenes, respectively. Richards and Beach[10] found that the vinyl proton of *cis*-2-bromo-2-butene (vinyl proton and bromine atom *cis*) has a chemical shift that is 2 cps (60 Mc) downfield from the vinyl proton of *trans*-2-bromo-2-butene. The *trans*-1,2,3-trichloropropene[7] (vicinal vinyl hydrogen and chlorine atoms *cis*) has its vinyl proton resonance downfield from that of the *cis* isomer by 11.8 cps (40 Mc).

The evidence, therefore, suggests that *cis*-2,3-dibromocyclononene (vinyl proton and vinyl bromine atom *cis*) is the isomer with the lowest field vinyl proton resonance. On this basis the isomer with its vinyl proton resonance at τ 3.89 and gas chromatographic retention time of 28.0 min is assigned the *cis* structure (**1**), and the isomer having its vinyl proton resonance at τ 4.11 with a retention time of 30.5 min is assigned the *trans* structure (**2**). Consistent with this assignment, 2,3-dibromocyclohexene, 2-bromo-3-hydroxycyclohexene, and 2-bromo-2-cyclohepten-1-yl acetate, which are all constrained, due to ring size, to have their double bonds in the *cis* configuration, have their vinyl proton resonances at τ 3.84, 3.93, and 3.67, respectively. As these cyclic compounds would be restricted in their rotation and would have conformational relationships similar to *cis*-2,3-dibromocyclononene (**1**), field effects due to bond anisotropy should be very comparable in these molecules and in **1**, and they would, perhaps, be better model compounds than the open-chain examples for comparison with **1**. The nearly identical chemical shift values observed for the 28.0-min isomer and these compounds, therefore, give strong support to the stereochemical assignments.

The apparent lack of any observable allylic (1,3) coupling in either the *cis* or *trans* isomer suggests that the predominant conformation or conformations in both isomers have a geometry in which the methine carbon–hydrogen bond and the plane of the double bond form an angle, θ, such that θ will be greatly displaced from 90°.[11] Molecular models (Coutauld) indicate that both isomers are surprisingly crowded and are quite restricted in the conformations that they can assume. In the model of neither isomer does it appear possible to have θ anywhere near 90° (most favorable for $\sigma-\pi$ overlap) in any reasonably stable conformation. In fact, from these models it appears that θ will be either near 0 or 180°.

The formation of both *cis*-2,3-dibromocyclononene (**1**) and *trans*-2,3-dibromocyclononene (**2**) by the addition of 1 mol of bromine to 1,2-cyclononadiene is an interesting result. In contrast, Moore and Bertelson[12] have reported that 1,2-cyclononadiene adds 2,-4-dinitrobenzenesulfenyl chloride to apparently give only one of the isomeric 3-(2,4-dinitrobenzenethio)-2-chloro-1-cyclononenes. The addition of 2,4-dinitrobenzenesulfenyl chloride has been postulated to involve a cyclic sulfonium ion intermediate.[13] The ionic[14,15] and quite probably the free-radical[16] addition of bromine to simple alkenes involve a similar type of bridged intermediate. Assuming that this type of bridged intermediate is involved in the bromination of an allene,[17] it is striking that the additions of bromine and 2,4-dinitrobenzenesulfenyl chloride to 1,2-cyclononadiene give rather different results.

Although no significant isomerization of **2** to **1** at room temperature during the course of several days was observed, it is still an open question as to whether the relative amounts of **1** and **2** formed (about 40% of **1** and 60% of **2**) represent a kinetically or a thermodynamically controlled product distribution. This matter is currently under investigation.

Experimental Section

General Procedure.—Infrared spectra were measured with a Perkin-Elmer Model 337 spectrophotometer. Nmr spectra were

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[6] N. S. Bhacca, L. F. Johnson, and J. N. Shoolery, "High Resolution Nuclear Magnetic Resonance Spectra Catalog," Varian Associates, Palo Alto, Calif., 1962.

[7] F. S. Mortimer, *J. Mol. Spectrosc.*, **3**, 340 (1959).

[8] E. B. Whipple, J. H. Goldstein, and G. R. McClure, *J. Amer. Chem. Soc.*, **82**, 3811 (1960).

[9] M. Y. De Wolf and J. D. Baldeschwieler, *J. Mol. Spectrosc.*, **13** (3), 344 (1964).

[10] J. H. Richards and W. F. Beach, *J. Org. Chem.*, **26**, 623 (1961).

[11] N. S. Bhacca and D. H. Williams, "Applications of NMR Spectroscopy in Organic Chemistry," Holden-Day, Inc., San Francisco, Calif., 1964.

[12] W. R. Moore and R. C. Bertelson, *J. Org. Chem.*, **27**, 4182 (1962).

[13] N. Kharasch and S. J. Assony, *J. Amer. Chem. Soc.*, **75**, 1081 (1953); *ibid.*, **77**, 3390 (1955); N. Kharasch, *J. Chem. Educ.*, **33**, 585 (1953); A. J. Havlik and N. Kharasch, *J. Amer. Chem. Soc.*, **78**, 1207 (1956).

[14] J. Hine, "Physical Organic Chemistry," 2nd ed, McGraw-Hill Book Co., Inc., New York, N. Y., 1962, p 214 ff.

[15] E. L. Eliel, "Stereochemistry of Carbon Compounds," McGraw-Hill Book Co., Inc., New York, N. Y., 1962, p 355.

[16] P. L. Abell and L. H. Piette, *J. Amer. Chem. Soc.*, **84**, 916 (1962); P. S. Skell and P. D. Readio, *ibid.*, **86**, 3334 (1964); W. Thaler, *ibid.*, **85**, 2607 (1963); P. S. Skell, D. L. Tuleen, and P. D. Readio, *ibid.*, **85**, 2849 (1963).

[17] See ref 3 for evidence for this. However, for evidence inconsistent with nucleophilic attack occuring on a bromonium ion intermediate see T. L Jacobs, R. Macomber, and D. Zunker, *ibid.*, **89**, 7001 (1967).

obtained at 60 Mc on a Varian Associates A-60 spectrometer[18] using carbon tetrachloride containing tetramethylsilane as solvent. Chemical shifts are reported in τ units.[19a] An Aerograph 90-P3 gas chromatograph[19b] was used. The columns were 5 ft × 0.25 in., and unless otherwise specified Pyrex glass injector inserts and Pyrex glass columns containing hexamethyldisilazane-treated Chromosorb P (80–100 mesh) as the solid support were used. Elemental analyses were performed by Dr. A. Bernhardt, Max Planck Institute, Mulheim (Ruhr), Germany. All melting points are corrected. Boiling points are uncorrected.

1,2-Cyclononadiene.—This compound was prepared by reacting 9,9-dibromobicyclo[6.1.0]nonane[20] with methyllithium according to the procedure of Moore and Ward[21] [bp 58° (6 mm), $n^{22}\text{D}$ 1.5061; lit.[22] bp 62° (16 mm), $n^{20}\text{D}$ 1.5060].

2,3-Dibromocyclononene.—To a stirred solution of 12.22 g (0.100 mol) of 1,2-cyclononadiene in 45 ml of carbon tetrachloride at −20° under a nitrogen atmosphere was added dropwise a solution of 16.22 g (0.102 mol) of bromine in 45 ml of carbon tetrachloride. The addition took place over a period of 40 min. The mixture was then stirred an additional 5 min at 20° after which 50 ml of a 20% sodium thiosulfate solution was added. The aqueous layer was removed, and the carbon tetrachloride solution was washed with two 50-ml portions of water, dried ($MgSO_4$), filtered, and vacuum evaporated leaving 28.50 g of crude product. Distillation through a small Vigreux column gave a considerable forerun of a smelly, pale yellow liquid, bp 65–100° (2 mm), which quickly turned black and was discarded, and 8.72 g (31%) of a main fraction: bp 106–110° (2 mm); $n^{23}\text{D}$ 1.5698. The combined yields of several preparations were redistilled [bp 84° (0.2 mm), $n^{23}\text{D}$ 1.5671] with good recovery. The liquid gave a positive test for bromine after being fused with sodium;[23] treatment with both alcoholic and aqueous silver nitrate resulted in an immediate precipitate. Analysis by gas chromatography using the following columns was tried without successful resolution of the major peak into its two components: 20% Apiezon L on 30–60 mesh Chromosorb P, 2% Apiezon L on Teflon 6, 10% SE-30, and a stainless steel column with 10% PDEAS on HMDS-treated 60–80 mesh Chromosorb P. In each case the conditions were as follows: helium flow 120 cc/min, injector and detector 210°, and column 150°. With all of the columns listed above, decomposition of samples injected into the gas chromatograph was noted. A 10% Carbowax 20M column (helium flow 300 cc/min, injector and detector 210°, column 152°) was finally found to partially resolve the major peak into two components with a minimum of decomposition. Two overlapping peaks, approximately equal in area, with retention times of 28.0 and 30.5 min accounted for 85% of the total peak area. Five small peaks were observed between 0.0 and 5.0 min retention time. The retention times for the other minor peaks were 20.2, 33.2, and 39.2 min. The two major peaks (retention times of 28.0 and 30.5 min) were collected by preparative gas chromatography as a single fraction. Reinjection of a portion of this material into the gas chromatograph showed, in addition to the two major peaks, a trace amount of material between 0 and 5 min indicating that a small amount of decomposition had occurred in the detector during the collection of the sample or upon rechromatographing. The following data were obtained from this gas chromatography purified material: the ir spectrum showed absorption at 1635 cm^{-1} (C=C); the nmr showed two overlapping triplets at τ 3.89 (J = 8.8 cps) and 4.11 (J = 8.8 cps) with a total relative area of 1.0, a quartet at 4.86 (J = 5.3 cps), a quintet at 5.84 (J = 5.8 cps) with a total relative area of 1.0, and a broad poorly resolved multiplet at 7.05–8.90 with a relative area of 12.0.

Anal. Calcd for $C_9H_{14}Br_2$: C, 38.33; H, 5.00; Br, 56.67. Found: C, 38.47, 38.56; H, 5.08, 5.05; Br, 56.57.

An attempt was made to obtain the compound giving the 28.0-min peak and the compound giving the 30.5-min peak by preparative gas chromatography. The center portion of each peak was collected during several successive runs. Each fraction was rechromatographed and collected as before. The fraction obtained from the center portion of the 28.0-min peak gave a gas chromatogram that showed no substantial enrichment in the 28.0-min peak. The failure to obtain this component free from the material giving the 30.5-min peak is explained by the observation that the 30.5-min peak tails toward short retention times and overlaps the 28.0-min peak. The fraction obtained from the 30.5-min peak gave only the 30.5-min peak plus a trace of material at short retention times when its gas chromatogram was obtained. Its nmr spectrum showed a triplet (J = 8.8 cps) at τ 4.11 (area 1.0), a quintet (J = 5.8 cps) at 5.84 (area 1.0), and a multiplet at 7.05–8.90 (area 12.1). The above nmr spectrum of the isomer having a retention time of 30.5 min showed no peaks uniquely attributable to the other isomer. The isomer having a retention time of 28.0 min has been assigned the *cis* structure (**1**), and the isomer having a retention time of 30.5 min has been assigned the *trans* structure (**2**). From the relative areas of the vinyl and methine protons in the nmr spectrum of the mixture of both isomers, it was estimated that the bromination product consists of about 40% of **1** and 60% of **2**.

Debromination of 2,3-Dibromocyclononene with Magnesium in Tetrahydrofuran.—A solution of 1.00 g (3.55 mmol) of 2,3-dibromocyclononene (an 85% pure sample of **1** and **2**) in 15 ml of tetrahydrofuran was added to 0.86 g (35.5 mmol) of magnesium powder. The mixture was stirred and kept under a nitrogen atmosphere at room temperature. An exothermic reaction began about 3 min after the reagents were mixed. About 1.5 hr after the reaction had begun, a sample was removed and injected into the gas chromatograph (10% Carbowax 20M column, helium flow 120 cc/min, injector 155°, detector 150°, and column 102°). A peak with a retention time (5.1 min) identical with that of an authentic sample of 1,2-cyclononadiene was observed to be the major component. The two partially resolved major peaks corresponding to **1** and **2** were completely absent. After standing for 24 hr it was filtered, and excess solvent was removed under reduced pressure. Despite the care employed, much of the 1,2-cyclononadiene dimerized[24] and precipitated. However, there was sufficient remaining 1,2-cyclononadiene to permit the collection of a sample by gas chromatography. The ir spectrum of this sample was identical with that of authentic 1,2-cyclononadiene.

Essentially the same result was observed when the debromination was carried out with magnesium in ether or zinc in tetrahydrofuran.

2-Bromo-3-hydroxycyclohexene.—The method of Sonnenberg and Winstein[25] was used to prepare 2-bromo-3-hydroxycyclohexene: mp 38–40°; $n^{20}\text{D}$ 1.5424 on melted sample (lit.[25] mp 38.2–40.2°, $n^{25}\text{D}$ 1.5404).

2,3-Dibromocyclohexene.—A mixture of 35.42 g (0.200 mol) of 2-bromo-3-hydroxycyclohexene and 9.0 ml of dry pyridine in 85 ml of dry ether was placed in a 250-ml three-neck flask equipped with a reflux condenser with a calcium chloride guard tube, a stirrer, and a dropping funnel. The mixture was kept at 0° while 27 g (0.10 mol) of phosphorus tribromide was added dropwise with stirring over a period of 40 min. The reaction mixture was stirred an additional 5 min at 0° and then refluxed for 5 hr. After being cooled to 0°, it was poured into about 100 ml of ice–water. The ether layer was removed and washed with water. The reaction flask was rinsed with water and with ether. The combined washings and the aqueous layer were washed with three 100-ml portions of ether. The combined ether extract was washed with 100 ml of water, 100 ml of 10% sodium bicarbonate, and 100 ml of water, dried ($MgSO_4$), filtered, and vacuum evaporated leaving 43.42 g. This crude product was fractionally distilled through a 6-in. column packed with Raschig rings yielding 34.72 g (72.3%) of 2,3-dibromocyclohexene: bp 50–52° (0.4 mm); $n^{24}\text{D}$ 1.5770 (lit.[25] bp 94–95° (4.5 mm); $n^{25}\text{D}$ 1.5764); ir absorption at 1625 cm^{-1} (C=C); nmr multiplet centered at τ 3.84 (area 0.9), multiplet at 5.28 (area 0.9), multiplet at 7.3–8.5 (area 6.1).

2-Bromo-2-cyclohepten-1-yl Acetate.—The silver ion assisted solvolysis of 7,7-dibromobicyclo[4.1.0]heptane[26] in acetic acid was used to prepare 2-bromo-2-cyclohepten-1-yl acetate.[27]

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[18] The authors wish to express their gratitude to Dr. G. E. Pollard and Shell Development Co., Modesto, Calif., for the nmr spectra.

[19] (a) G. V. D. Tiers, *J. Phys. Chem.*, **62**, 1151 (1958). (b) We are deeply indebted to the American Philosophical Society for a grant (No. 3729, Penrose Fund) for the gas chromatograph.

[20] L. Skattebol, *Acta Chem. Scand.*, **17**, 1683 (1963).

[21] W. R. Moore and H. R. Ward, *J. Org. Chem.*, **25**, 2073 (1960).

[22] L. Skattabøl, *Tetrahedron Lett.*, 167 (1961).

[23] R. L. Shriner, R. C. Fuson, and D. Y. Curtin, "The Systematic Identification of Organic Compounds," 5th ed, John Wiley and Sons, Inc., New York, N. Y., 1964, p 62 ff.

[24] K. G. Untch and D. J. Martin, *J. Amer. Chem. Soc.*, **87**, 4501 (1965); L. Skattebøl and S. Soloman, *ibid.*, **87**, 4506 (1965).

[25] J. Sonnenberg and S. Winstein, *J. Org. Chem.*, **27**, 748 (1962).

[26] P. S. Skell and A. Y. Garner, *J. Amer. Chem. Soc.*, **78**, 5430 (1956).

[27] S. S. Sandler, *J. Org. Chem.*, **32**, 3876 (1967).

Registry No.—**1**, 17206-75-6; **2**, 17202-30-1; 1,2-cyclononadiene, 1123-11-1; 2,3-dibromocyclohexene, 17202-32-3.

New Synthesis of Some 1,5-Diazacyclooctanes

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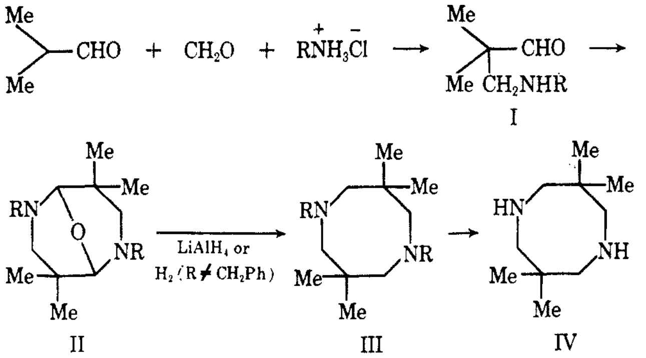
This is to report a new synthesis of 1,5-diazacyclooctanes substituted in the 3 and 7 positions (III). The sequence involves reductive cleavage of the oxygen bridge of a 9-oxa-2,6-diazabicyclo[3.3.1]nonane II, which is readily formed by condensation of the secondary β-amino aldehyde I obtained in the Mannich reaction of an α,α-disubstituted aldehyde, formaldehyde, and a primary amine hydrochloride. When R = benzyl, further hydrogenolysis of III leads to the disecondary amine IV.



The condensation of secondary β-amino aldehydes of type I was first observed by Mannich and Wieder,[1] who postulated structure II for these products on the basis of elemental analysis. This structure has now been verified by nmr spectroscopy. It has also been found that the rate of condensation is greatly increased by acid catalysis. Reduction of the 9-oxa-2,6-diazabicyclo[3.3.1]nonane II (R = Me) was effected in high yield (~80%) by lithium aluminum hydride or quantitatively by catalytic hydrogenolysis, using rhodium-on-alumina catalyst in acetic acid solvent. 3,3,7,7-Tetramethyl-1,5-diazacyclooctane (IV) was obtained by a two-stage reduction of II (R = CH_2Ph): lithium aluminum hydride reduction to III (R = CH_2Ph) in 78% yield, followed by quantitative catalytic reduction of III (R = CH_2Ph) using Pd–C in ethanol as solvent.[2]

The rate of the condensation reaction is dependent upon the nature of the substituent group R. Mannich and Wieder[1] reported that, when R = Me, a 40% yield of the 9-oxa-2,6-diazabicyclo[3.3.1]nonane accompanies the β-amino aldehyde (35%) during the distillation of the crude reaction product, and that condensation occurs rapidly upon allowing the β-amino aldehyde to stand at room temperature. When R = CH_2Ph, we found that little 9-oxa-2,6-diazabicyclo[3.3.1]nonane was formed during the distillation of the crude β-amino aldehyde, but it was obtainable readily upon heating to 50° in the presence of a catalytic amount of methanesulfonic acid. A 50% yield was obtained overnight.

Experimental Section

β-Methylamino-α,α-dimethylpropionaldehyde (I, R = Me) and 2,4,4,6,8,8-hexamethyl-9-oxa-2,6-diazabicyclo[3.3.1]nonane (II, R = Me) were obtained, as described by Mannich and Wieder, as a colorless liquid, bp 45° (11 mm), in 30–35% yield, and a white crystalline solid, mp 68°, in 40% yield, respectively.

Nmr Data for 2,4,4,6,8,8-Hexamethyl-9-oxa-2,6-diazabicyclo[3.3.1]nonane (II, R = Me).—Peaks were observed at δ 0.80 (s), 1.30 (s), 2.80 (s), 2.85 (q, J_{AB} = 14 cps), and 3.90 (s) in the ratio of 3:3:3:2:1; δ, in parts per million, refers to TMS (internal).

1,3,3,5,7,7-Hexamethyl-1,5-diazacyclooctane (III, R = Me).—2,4,4,6,8,8-Hexamethyl-9-oxa-2,6-diazabicyclo[3.3.1]nonane (106 g) was added in portions over a period of 15 min to a suspension of lithium aluminum hydride (35 g) in ether (600 ml). The mixture was refluxed for 1 hr and cooled; excess reagent was decomposed by addition of ethyl acetate (~200 ml), followed by water, until a pale gray precipitate was formed (~200 ml). The ether solution was decanted, dried over $MgSO_4$ and stripped. Distillation of the residue gave 78 g (79% yield) of product, bp 96° (25 mm). Nmr peaks were at δ 0.80 (s), 2.31 (s), and 2.40 (s) in the ratio of 6:3:4. *Anal.* Calcd for $C_{12}H_{26}N_2$: C, 72.6; H, 13.1. Found: C, 72.5; H, 13.1.

1,3,3,5,7,7-Hexamethyl-1,5-diazacyclooctane (III, R = Me).—Microhydrogenation of 2,4,4,6,8,8-hexamethyl-9-oxa-2,6-diazabicyclo[3.3.1]nonane (II, R = Me) gave a hydrogen number 114 using Rh-Al_2O_3 catalyst in acetic acid as solvent (theoretical value for uptake of 2 mol of H_2 = 106). In another determination 1.95 mol of H_2 was taken up. (Rh-Al_2O_3 in ethanol caused no uptake.) 1,3,3,5,7,7-Hexamethyl-1,5-diazacyclooctane, identified by its nmr spectrum, was obtained.

β-Benzylamino-α,α-dimethylpropionaldehyde (I, R = CH_2Ph).—Isobutyraldehyde (81 g; 1.125 mol), paraformaldehyde (42 g; 1.40 mol), and benzylamine hydrochloride (150 g; 1.08 mol) were stirred vigorously and heated at 100° for 4 hr. After cooling, water (200 ml) was added and the mixture extracted with ether (200 ml). The aqueous solution was made alkaline with a solution of 100 g of KOH in 100 ml of water and extracted into three 200-ml portions of ether. The combined ether extracts of the alkaline solution were dried over $MgSO_4$ and stripped; 103 g (51% yield) of product, bp 93–100° (0.75 mm), was obtained by distillation. It was redistilled at 74° (0.25 mm), $n^{24}{}_D$ 1.5113. *Anal.* Calcd for $C_{12}H_{17}NO$: C, 75.4; H, 8.9; N, 7.3. Found: C, 75.5; H, 8.9; N, 7.1.

2,6-Dibenzyl-4,4,8,8-tetramethyl-9-oxa-2,6-diazabicyclo[3.3.1]nonane (II, R = CH_2Ph).—β-Benzylamino-α,α-dimethylpropionaldehyde (85 g) was heated to 50° overnight in the presence of a catalytic amount of methanesulfonic acid. Hexane (100 ml) was added, and the mixture was filtered. The solid was washed with hexane and dried to yield 40 g (50%). Recrystallization from ethyl acetate gave a product melting at 155–157.5°. Nmr peaks appeared at δ 0.85 (s), 1.30 (s), 3.08 (q, J_{AB} = 14.5 cps), 4.05 (s), 4.15 (s), 4.25 (s), and 7.30 (s) in the ratio of 3:3:2:1:1:1:5. *Anal.* Calcd for $C_{24}H_{32}N_2O$: C, 79.1; H, 8.8; N, 7.7. Found: C, 79.1; H, 8.7; N, 7.6.

1,5-Dibenzyl-3,3,7,7-tetramethyl-1,5-diazacyclooctane (III, R = CH_2Ph).—2,6-Dibenzyl-4,4,8,8-tetramethyl-9-oxa-2,6-diazabicyclo[3.3.1]nonane (36.1 g; 0.1 mol) was added portionwise over 5 min to a well-stirred suspension of lithium aluminum hydride (20 g; 0.6 mol) in ether (800 ml). The mixture was refluxed for 1 hr and then cooled. Excess reagent was decomposed using ethyl acetate followed by water. The ether solution was decanted, dried, and stripped, leaving a syrup which rapidly crystallized, 27.5 g (78% yield). Recrystallization from ethanol gave a product melting at 49–50°. Nmr peaks appeared at δ 0.70 (s), 2.50 (s), 3.75 (s), and 7.25 (s) in the ratio of 6:4:2:5. *Anal.* Calcd for $C_{24}H_{34}N_2$: C, 82.3; H, 9.7; N, 8.0. Found: C, 82.2; H, 9.8; N, 7.9.

3,3,7,7-Tetramethyl-1,5-diazacyclooctane (IV).—1,5-Dibenzyl-3,3,7,7-tetramethyl-1,5-diazacyclooctane (17.5 g; 0.05 mol), dissolved in ethanol (120 ml), was hydrogenated using 10% Pd-C (5 g) as a catalyst. Hydrogen uptake was completed in

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[1] C. Mannich and H. Wieder, *Ber.*, **65**, 385 (1932).

[2] W. H. Harteung and R. Simonoff, *Org. Reactions*, **7**, 263 (1953).