The formation of vinyl bromides **3** and **5** from **2** and **4**, respectively, is undoubtedly related to the facile alkaline decomposition of dibromophosphonic acids to vinyl bromides, first discovered by Conant and coworkers[10] in 1924 and recently reinvestigated by Kenyon and Westheimer.[11] The latter investigators found that the reaction is completely stereospecific, and hence, *if* the present reaction goes by way of the sodium salt of the dibromophosphonic acid, the configuration about the double bond must be the same in **2** and **3**.

Experimental Section[12]

Chlorofenchenephosphonic acid (**2**) was prepared according to the procedure of Gardner and Cockburn.[4a] Indene-2-phosphonic acid (**4**) was synthesized by the method of Bergmann and Bondi.[7]

Chlorobromofenchene (**3**).—This compound was prepared by a variation on the method of Gardner and Cockburn.[4b] A suspension of 1.25 g (0.005 mole) of chlorofenchenephosphonic acid (**2**) in 50 ml of water containing 1 drop of phenolphthalein solution was neutralized with dilute base. Dropwise addition of saturated bromine water was accompanied by immediate decolorization and separation of a milky precipitate. Addition of bromine water was continued until a light orange color persisted. The mixture was then treated with sodium bisulfite solution and extracted with ether. The ether solution was washed with water and dried over sodium sulfate. Distillation of the ether afforded 1.15 (92%) of **3**, homogeneous by vpc (15% SE-30 on Fluoropack 80, 3-ft column, 170°).

2-Bromoindene (**5**).—This compound was prepared in 85% yield from indene-2-phosphonic acid (**4**) in the same manner as chlorobromofenchene. Its melting point of 34–36° compares with a literature[8] value of 38–39°. Its nmr spectrum consists of a complex aromatic multiplet from τ 2.6 to 3.1, a triplet at τ 3.22 (J = 1.7 cps), and a doublet at τ 6.59 (J = 1.7 cps), relative areas 4:1:2, respectively.

Registry No.—**2**, 10485-07-1; **3**, 10485-08-2; **5**, 10485-09-3.

Acknowledgment.—This research was supported by the Petroleum Research Fund of the American Chemical Society. We thank Dr. T. W. Rave for a helpful discussion.

(10) J. B. Conant and A. A. Cook, *J. Am. Chem. Soc.*, **42**, 830 (1920).
(11) G. L. Kenyon and F. H. Westheimer, *ibid.*, **88**, 3561 (1966).
(12) Nmr spectra were measured on a Varian A-60A spectrometer relative to tetramethylsilane (τ 10.00) as external standard. Vapor phase chromatography (vpc) was carried out on a Varian Aerograph model A-90P. Infrared spectra were measured in carbon tetrachloride on a Perkin-Elmer Model 237 spectrophotometer.

Transannular Cyclization Reactions in Medium-Sized Ring Amino Alcohols

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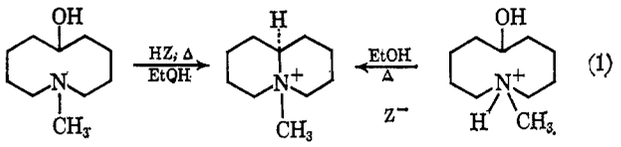
While investigating possible transannular[2] cyclization reactions with olefinic amine oxides contained in medium-sized ring systems, we had occasion to attempt a dehydration of N-methyl-1-azacyclodecan-6-ol (**1**) by conventional procedures. In no instance during the latter treatment were we able to isolate the anticipated olefin, but instead products produced from a novel and rapid transannular cyclization reaction (eq 1). Compound **1** yielded normal salts (**2**) as

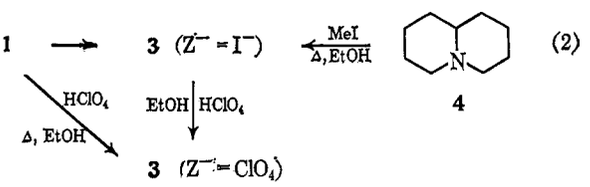


(1)

1 **3** **2**

$Z^- = ClO_4^-, I^-$, picrate

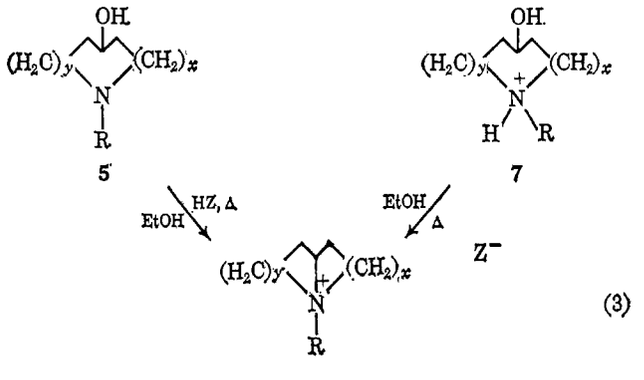
ascertained by infrared and elemental analysis, which upon heating in ethanol also resulted in the cyclization products, **3** (eq 1). Unequivocal structure proof of **3** was obtained by the treatment of quinolizidine[3] (**4**) with methyl iodide[4] producing **3** ($Z^- = I^-$) identical (mixture melting point, infrared, and nmr) with the compound produced upon treatment of **1** with hydrogen iodide in refluxing ethanol (eq 2). In addition, **3**



(2)

($Z^- = I^-$), obtained from **4**, when treated with excess perchloric acid yielded the perchlorate, **3** ($Z^- = ClO_4^-$), identical (mixture melting point and infrared) with the product obtained from **1** when treated with perchloric acid in refluxing ethanol (eq 2).

An obvious extension of this type of transannular cyclization reaction to other medium-sized ring systems was undertaken for the purpose of determining the generality of the reaction. Accordingly, the amino alcohols, **5a** and **b**, were prepared and upon direct treatment with monoprotic acids in refluxing ethanol resulted in the formation of **6a** and **b**, as a consequence of transannular cyclization reactions (eq 3). The



(3)

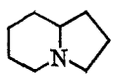
5 **7**

6

a, $x = y = 2$; R = cyclohexyl
b, $x = 2$; $y = 3$; R = methyl
$Z^- = ClO_4^-, I^-$, picrate

(1) Taken in part from the Ph.D. thesis of D. Lohner, Adelphi University, 1966.
(2) For a recent review, see A. C. Cope, M. M. Martin, and M. A. Mckervey, *Quart. Rev.* (London), **20**, 119 (1966).
(3) N. J. Leonard, A. S. Hay, R. W. Fulmer, and V. W. Gash, *J. Am. Chem. Soc.*, **77**, 439 (1955).
(4) The product from the reaction of quinolizidine (**4**) with methyl iodide, **3** ($Z^- = I^-$), was shown to be the *trans* isomer by comparison with an authentic sample graciously supplied by K. Winterfield.

normal salts, **7a** and **b**, when heated in ethanol, produced identical ring-closure products, **6a** and **b** (eq 3). Our structural assignment for **6b** was substantiated by synthesis. When indolizidine[5] (**8**) was treated with



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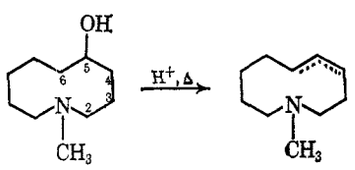
methyl iodide, the methiodide obtained was identical (infrared and mixture melting point) with **6b** ($Z^- = I^-$). The latter was then treated with excess perchloric acid yielding a perchlorate salt which was identical with **6b** ($Z^- = ClO_4^-$). The assignment for **6a** was based on infrared and elemental analysis.

The amino alcohols, **1**, **5a**, and **b**, were easily prepared by the reduction of the corresponding ketones which were obtained by the procedures of Leonard[6] and Reinecke.[7] The procedure of Reinecke was employed for the first time for the synthesis of N-methyl-1-azacyclodecan-6-one in excellent yield.

The driving force for the observed acid-catalyzed transannular reactions appears to be due to a proximity of the atoms involved (nitrogen and hydroxyl carbon). The latter is borne out by the examination of Dreiding models.

It is noteworthy to mention that the acid treatment of N-methyl-1-azacyclodecan-5-ol (**9**) yielded only product(s) characteristic of a dehydration reaction[8] (eq 4). However, **1** only undergoes a transannular



(4)

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cyclization reaction indicating that an olefinic intermediate is not involved, but, rather, a nucleophilic attack by nitrogen on the 6 position with the expulsion of water seems more likely. Finally, these results further substantiate Leonard's observations that, with N-methyl-1-azacyclodecan-5-one and -6-one, only the latter underwent a transannular cyclization reaction with monoprotic acids[6] indicating that interactions between the nitrogen and the 5 position are virtually absent.

Experimental Section[9]

N-Cyclohexyl-1-azacyclooctan-5-ol (5a) was prepared by the reduction of N-cyclohexyl-1-azacyclooctan-5-one[6] with lithium aluminum hydride. Five grams (0.035 mole) of amino ketone dissolved in 50 ml of tetrahydrofuran was added over a 3-min period to 5 g (0.14 mole) of lithium aluminum hydride in 200 ml of tetrahydrofuran at 0°. The mixture was then allowed to warm to room temperature and refluxed for 1 hr. The solution was cooled and then decomposed by the addition of 5 ml of water followed by 5 ml of 15% sodium hydroxide and 15 ml of water. The thick slurry was filtered and washed with 10 ml of tetrahydrofuran. The solution was dried with anhydrous magnesium sulfate and filtered and the tetrahydrofuran was removed under reduced pressure. Distillation of the residue yielded 4.8 g (0.022 mole) of an oil: bp 115° (0.5 mm) 96%); ν 3600, 3075 cm^{-1} (chloroform).

N-Cyclohexyl-1-azacyclooctan-5-ol iodide (7a, $Z^- = I^-$) was prepared with 0.084 g (0.0004 mole) of **5a** in 5 ml of absolute ethanol and 0.57 g of 57% hydriodic acid in 1 ml of absolute ethanol at 0°. There was obtained 0.128 g (0.0004 mole) of salt, mp 280° dec, after recrystallization from ethanol–ether at room temperature (*ca.* quantitative): ν 3225, 2480 cm^{-1} (chloroform.)

Anal. Calcd for $C_{13}H_{26}INO$: C, 46.02; H, 7.67; N, 4.13. Found: C, 45.92; H, 7.64; N, 4.09.

The picrate of 5a was prepared with 0.11 g (0.00054 mole) of **5a** in 2 ml of absolute ethanol and 10 ml of a saturated ethanolic solution of picric acid at room temperature. After recrystallization from ethanol–ether at room temperature there was obtained 0.214 g (0.00048 mole) of picrate: mp 116–117° (90%); ν 3140, 2450 cm^{-1} (chloroform).

Anal. Calcd for $C_{10}H_{28}N_4O_8$: C, 51.95; H, 6.19; N, 12.75. Found: C, 52.09; H, 6.34; N, 12.41.

The perchlorate of 5a was prepared with 0.15 g (0.00071 mole) of **5a** in 5 ml of ether and 0.12 g of 70% perchloric acid in 0.5 ml of absolute ethanol at 0°. After recrystallization from ethanol–ether at room temperature, there was obtained 0.154 g (0.0005 mole) of salt, mp 140° (71%): ν 3380, 2600 cm^{-1} (chloroform).

Anal. Calcd for $C_{13}H_{26}ClNO_5$: C, 50.10; H, 8.31; N, 4.49. Found: C, 50.11; H, 8.41; N, 4.48.

N-Cyclohexyl-1-azabicyclo[3.3.0]octane Iodide (6a).—A solution of 0.115 g (0.00055 mole) of **5a** in 5 ml of absolute ethanol was treated with 0.69 g of 57% hydriodic acid in 1 ml of absolute ethanol and refluxed for 20 hr. After recrystallization from ethanol there was obtained 0.137 g (0.00042 mole) of solid, mp 292–295° dec (82%).

Anal. Calcd for $C_{13}H_{24}IN$: C, 48.60; H, 7.48; N, 4.36. Found: C, 48.54; H, 7.39; N, 4.34.

N-Cyclohexyl-1-azabicyclo[3.3.0]octane Picrate (6a).—A saturated ethanolic solution of picric acid (30 ml) and 0.5 g (0.0023 mole) of **5a** in 2 ml of absolute ethanol were combined and refluxed for 5 hr. After recrystallization from ethanol there was obtained 0.9 g (0.0021 mole) of picrate, mp 78° (93%).

Anal. Calcd for $C_{19}H_{26}N_4O_7$: C, 54.02; H, 6.16; N, 13.27. Found: C, 53.71; H, 6.20; N, 12.96.

N-Cyclohexyl-1-azabicyclo[3.3.0]octane Perchlorate (6a).—A solution of 0.15 g (0.00071 mole) of **5a** in 25 ml of absolute ethanol was treated with 0.712 g of 70% perchloric acid dissolved in 0.5 ml of absolute ethanol and refluxed for 5 hr. The volume of the solution was reduced to approximately 10 ml (reduced pressure) and 5 ml of ether was added to precipitate the salt. After recrystallization from ethanol there was obtained 0.185 g (0.0006 mole) of solid, mp 242–243° (87%).

Anal. Calcd for $C_{13}H_{24}ClNO_4$: C, 53.20; H, 8.17; N, 4.77. Found: C, 53.11; H, 8.09; N, 4.77.

1-Azabicyclo[4.3.0]nonane (indolizidine, **8**) was prepared according to the procedure of Reinecke[10] with the following changes. Active Raney nickel catalyst no. 28 in water was substituted for W-5 Raney nickel. In addition, to the mixture of 500 ml of water, 60 g of wet catalyst and 25 g of 3-(2-piperdyl)-1-propanol[10] was added 50% sodium hydroxide until the solution was basic to litmus paper, bp 160° (lit.[10] bp 156–160° 745 mm).

N-Methyl-1-azabicyclo[4.3.0]nonane iodide (6b, $Z^- = I^-$) was prepared with 0.55 g (0.004 mole) of **8** in 25 ml of absolute ethanol and excess methyl iodide. The solution was refluxed for 30 min and cooled and the solvent was removed under reduced pressure. The solid was recrystallized from acetone–ether and there was obtained 0.9 g (0.0034 mole), mp 328–329° dec (75%).

Anal. Calcd for $C_9H_{18}IN$: C, 40.36; H, 6.79; N, 5.24. Found: C, 40.11; H, 6.68; N, 5.15.

N-Methyl-1-azacyclononan-5-ol (5b) was prepared as previously described for **5a** with 5 g (0.032 mole) of N-methyl-1-azacyclononan-5-one,[7] 50 ml of tetrahydrofuran, and 5 g (0.14 mole) of lithium aluminum hydride in 200 ml of tetrahydrofuran. The resulting oil was distilled, bp 50° (0.05 mm). There was obtained 4.7 g (0.30 mole) of the alcohol (98%): ν 3600, 3080 cm^{-1} (chloroform).

(5) N. L. Leonard and W. E. Goode, *J. Am. Chem. Soc.*, **72**, 5404 (1950).
(6) N. J. Leonard, M. Oki, and S. Chivaraelli, *ibid.*, **77**, 6234 (1955).
(7) M. G. Reinecke, L. R. Kray, and R. F. Francis, *Tetrahedron Letters*, No. 40, 3549 (1965).
(8) N. J. Leonard, S. Swan, Jr., and J. Figueras, Jr., *J. Am. Chem. Soc.*, **74**, 4620 (1952).
(9) All melting points and boiling points are uncorrected. Microanalyses were performed by Spang Microanalytical Laboratory, Ann Arbor, Mich. Infrared spectra were determined with a Perkin-Elmer Spectrocord infrared spectrophotometer. Nmr spectra were determined with a Varian A-60 instrument.
(10) M. G. Reinecke and L. R. Kray, *J. Org. Chem.*, **29**, 1736 (1964).

N-Methyl-1-azacyclononan-5-ol Iodide (7b).—A solution of 0.11 g (0.0007 mole) of **5b** in 5 ml of absolute ethanol was treated with 0.115 g (0.0009 mole) of 57% hydriodic acid in 1 ml of absolute ethanol at 0°. Ether was then added to precipitate the salt. There was obtained 0.16 g (0.00056 mole) of the iodide salt, mp 145° (80%).[11] The salt was recrystallized at room temperature from ethanol–ether: ν 3220, 2500 cm^{-1} (chloroform).

Anal. Calcd for $C_9H_{20}INO$: C, 37.90; H, 7.07; N, 4.91. Found: C, 37.86; H, 6.96; N, 5.00.

The **picrate** of **5b** (**7b**) was prepared with a solution of 0.094 g (0.0006 mole) of **5b** in 1 ml of absolute ethanol and 10 ml of a saturated ethanolic solution of picric acid at room temperature. There was obtained 0.23 g (0.0006 mole): mp 150° (recrystallized from acetone–ether)[12] (90%); ν 3275, 2450 cm^{-1} (KBr pellet).

Anal. Calcd for $C_{15}H_{22}N_4O_8$: C, 46.62; H, 5.74; N, 14.50. Found: C, 46.57; H, 5.66; N, 14.39.

N-Methyl-1-azabicyclo[4.3.0]nonane Iodide (6b).—A solution of 0.15 g (0.0009 mole) of **5b** in 10 ml of absolute ethanol was refluxed for 8 hr with 0.128 g (0.001 mole) of 57% hydriodic acid. There was obtained, after recrystallization from ethanol–ether, 0.19 g (0.0007 mole), mp 328 (82%). Comparison of the infrared spectrum and mixture melting point with an authentic sample [indolizidine (**8**) and methyl iodide] confirmed the structural assignment.

N-Methyl-1-azabicyclo[4.3.0]nonane Picrate (6b).—A solution of 0.157 g (0.001 mole) of **5b** in 2 ml of absolute ethanol was refluxed for 3 hr with 20 ml of a saturated ethanolic solution of picric acid. There was obtained 0.31 g (0.00089 mole) of picrate, mp 318° dec (89%).

Anal. Calcd for $C_{15}H_{20}N_4O_7$: C, 49.28; H, 5.47; N, 15.21. Found: C, 49.24; H, 5.42; N, 15.18.

N-Methyl-1-azabicyclo[4.3.0]nonane Perchlorate (6b).—A solution of 0.3 g (0.0019 mole) of **5b** in 8 ml of absolute ethanol was refluxed with 0.348 g (0.038 mole) of 70% perchloric acid in 1 ml of absolute ethanol for 4 hr. The volume was then reduced to about 2 ml under reduced pressure and then ether was added to effect precipitation. After recrystallization from ethanol there was obtained 0.4 g (0.0017 mole) of a solid, mp 308–309° (90%).

Anal. Calcd for $C_9H_{18}ClNO_4$: C, 45.09; H, 7.57; N, 5.84. Found: C, 45.27; H, 7.39; N, 5.88.

N-Methyl-1-azabicyclo[4.3.0]nonane Perchlorate from N-Methyl-1-azabicyclo[4.3.0]nonane Iodide.—A solution of 0.21 g (0.0008 mole) of **6b** (Z^- = I^-) dissolved in 10 ml of absolute alcohol was treated with 0.5 ml of 70% perchloric acid and then stirred for 15 min at room temperature. The perchlorate was precipitated by the addition of ether and there was obtained 0.17 g (0.00064 mole) of a white solid, mp 309° (80%). The latter compound and the one prepared from **5b** with perchloric acid were identical by mixture melting point and infrared spectra.

1-Aza-6-benzylbicyclo[4.4.0]decane was prepared according to the procedure of Reinecke.[7] The following quantities were employed: 4 g (0.151 g-atom) of magnesium, 400 ml of anhydrous ether, 19.11 g (0.151 mole) of benzyl chloride, and 11.94 g (0.054 mole) of Δ^5-dehyroquinolizindinium perchlorate.[3,10] There was obtained 11.1 g (0.048 mole) of a pale yellow oil (89%).

The **picrate**, recrystallized from ethanol, had a melting point of 201–202°.

Anal. Calcd for $C_{22}H_{26}N_4O_7$: C, 57.63; H, 5.71; N, 12.20. Found: C, 57.96; H, 5.76; N, 12.40.

1-Aza-6-benzylbicyclo[4.4.0]decane Methiodide.—A solution of 6.2 g (0.27 mole) of 1-aza-6-benzylbicyclo[4.4.0]decane in 54 ml of absolute methanol was refluxed for 1 hr with 7.66 g (0.054 mole) of methyl iodide. The volume was then reduced to approximately 25 ml under reduced pressure and the resultant white solid was filtered and recrystallized from ethanol. There was obtained 9.2 g (0.24 mole) of salt, mp 261° dec (92%).

Anal. Calcd for $C_{17}H_{26}IN$: C, 54.98; H, 7.05; N, 3.77. Found: C, 54.73; H, 7.01; N, 3.98.

N-Methyl-1-aza-6-benzylidenecyclodecane was prepared by treating 7 g (0.019 mole) of 1-aza-6-benzylbicyclo[4.4.0]decane methiodide with a sodium ethoxide solution prepared with 2.6 g (0.114 mole) of sodium in 100 ml of absolute ethanol. After refluxing the mixture for 48 hr, 200 ml of water was added followed by ether extraction. Distillation afforded 4.2 g (0.017 mole, 91%) of the benzylidene compound as a colorless oil, bp 122° (0.2 mm); nmr indicated one vinyl proton (a singlet at τ 2.8).

The **picrate** prepared with a saturated ethanolic solution of picric acid and recrystallized from ethanol melted at 168–169°.

Anal. Calcd for $C_{23}H_{28}N_4O_7$: C, 58.59; H, 5.77; N, 11.88. Found: C, 58.65; H, 5.83; N, 11.85.

N-Methyl-1-azacyclodecan-6-ol (**1**) was prepared as previously described for **5a** with 2 g (0.0118 mole) of N-methyl-1-azacyclodecan-6-one,[13] 150 ml of tetrahydrofuran, and 3 g (0.085 mole) of lithium aluminum hydride. The resulting oil was distilled, bp 74° (0.15 mm), yielding 1.8 g (0.0106 mole) of a colorless oil (90%) that solidified at room temperature: ν 3625, 3400^{-1} (chloroform).

N-Methyl-1-azacyclodecan-6-ol Iodide (**2**).—A solution of 0.153 g (0.0009 mole) of **1** in 5 ml of absolute alcohol was treated with 0.3 ml of 57% hydriodic acid in 1 ml of absolute ethanol at 0°. Ether was added until the salt precipitated and there was obtained, after recrystallization, 0.2 g (0.0007 mole) of the iodide salt: mp 128–129° (80%); ν 3310, 2800 cm^{-1} (KBr pellet).

Anal. Calcd for $C_{10}H_{22}INO$: C, 40.14; H, 7.41; N, 4.68. Found: C, 40.09; H, 7.25; N, 4.72.

The Picrate of 1 (**2**).—A solution of 0.15 g (0.0009 mole) of **1** and 2 ml of absolute ethanol was added to 10 ml of a saturated picric acid solution (ethanol) at room temperature. There was obtained, after recrystallization from ethanol–ether at room temperature, 0.31 g (0.0008 mole) of solid: mp ≅150° (88%); ν 3550, 2725^{-1} (KBr pellet).[14]

Anal. Calcd for $C_{16}H_{24}N_4O_8$: C, 47.99; H, 6.04; N, 13.50. Found: C, 48.06; H, 5.94; N, 13.44.

N-Methyl-1-azabicyclo[4.4.0]decane Iodide (**3**).—A solution of 0.153 g (0.0009 mole) of **1** in 9 ml of absolute ethanol was treated with 0.3 ml of 57% hydriodic acid in 1 ml of absolute ethanol and refluxed for 5 hr. Ether was added to the cooled solution and there was obtained 0.28 g (0.0008 mole) of the salt after recrystallization from ethanol, mp 339° (lit.[15] mp 339°) (89%). A comparison of this compound with an authentic sample of *trans*-N-methyl-1-azabicyclo[4.4.0]decane iodide (from quinolizidine[10] and methyl iodide)[4] showed them to be identical (mixture melting point and infrared and nmr spectra).

N-Methyl-1-azabicyclo[4.4.0]decane Picrate (**3**).—A solution of 0.15 g (0.0009 mole) of **1** in 2 ml of absolute ethanol added to 15 ml of a saturated ethanol solution of picric acid was refluxed for 5 hr. Ether was added until the picrate precipitated and there was obtained, after recrystallization from ethanol, 0.29 g (0.0008 mole) of solid, mp 239° dec (91%).

Anal. Calcd for $C_{16}H_{22}N_4O_7$: C, 50.25; H, 5.80; N, 14.65. Found: C, 50.25; H, 5.86; N, 14.79.

N-Methyl-1-azabicyclo[4.4.0]decane Perchlorate (**3**).—A solution of 0.15 g (0.0009 mole) of **1** in 10 ml of absolute ethanol was added to 0.348 g (0.038 mole) of 70% perchloric acid dissolved in 1 ml of absolute ethanol and refluxed for 5 hr. The volume was then reduced to 2 ml and ether was added until the salt crystallized. There was obtained 0.19 g (0.0008 mole) of solid after recrystallization from ethanol, mp 284–285° (89%).

Anal. Calcd for $C_{10}H_{20}ClNO_4$: C, 47.33; H, 7.95; N, 5.52. Found: C, 47.46; H, 8.02; N, 5.64.

N Methyl-1-azabicyclo[4.4.0]decane Perchlorate (**3**) **from N-Methyl-1-azabicyclo[4.4.0]decane Iodide** (**3**).—A solution of 0.15 g (0.0005 mole) of **3** (Z^- = I^-) dissolved in 20 ml of absolute ethanol was treated with 0.5 ml of 70% perchloric acid and the reaction mixture was stirred for 15 min at room temperature. The volume was reduced to 8 ml and ether was added to precipitate the salt. There was obtained 0.9 g (0.00045 mole) of the perchlorate salt, mp 284–286° (89%). The latter compound and the perchlorate from the reaction of **1** and perchloric acid were identical in mixture melting point and infrared spectra.

Registry No.—**1**, 10478-87-2; **2** (Z^- = I^-), 10478-69-0; **2** (Z^- = picrate), 10478-70-3; **3** (Z^- = I^-), 4820-38-6; **3** (Z^- = picrate), 10478-72-5; **3** (Z^- = ClO_4^-), 10478-73-6; **5a**, 10478-74-7; **5b**, 10498-

(11) This melting point is approximate. The salt turned to a waxy solid at 145° but true melting did not occur until 328° dec. This higher melting compound was shown to be N-methyl-1-azabicyclo[4.3.0]nonane iodide (**6b**).

(12) This melting point is approximate. The salt turned to a waxy solid at 150° but melting did not occur until 318° dec.

(13) The ketone was prepared by the oxidation of N-methyl-1-aza-6-benzylidenecyclodecane according to the procedure of Reinecke[7] (90% yield).

(14) This melting point is approximate. The salt turned to a waxy solid at 150° but melting did not occur until 239° dec. The latter compound was shown to be **3** (Z^- = picrate).

(15) K. Schofield and R. J. Wells, *Australian J. Chem.*, **18**, 1423 (1965).

53-0; **6a** (Z^- = I^-), 10478-75-8; **6a** (Z^- = picrate), 10478-76-9; **6a** (Z^- = ClO_4^-), 10478-77-0; **6b** (Z^- = I^-), 10478-78-1; **6b** (Z^- = picrate), 10482-27-6; **6b** (Z^- = ClO_4^-), 10478-79-2; **7a** (Z^- = I^-), 10478-80-5; **7a** (Z^- = picrate), 10478-81-6; **7a** (Z^- = ClO_4^-), 10478-82-7; **7b** (Z^- = I^-), 10501-30-1; **7b** (Z^- = picrate), 10478-83-8; 1-aza-6-benzylbicyclo[4.4.0]decane, 10498-54-1; 1-aza-6-benzylbicyclo[4.4.0]decane picrate, 10482-28-7; 1-aza-6-benzylbicyclo[4.4.0]decane methiodide, 10478-84-9; N-methyl-1-aza-6-benzylidenecyclodecane, 10478-85-0; N-methyl-1-aza-6-benzylidenecyclodecane picrate, 10478-86-1.

The Nitration of 2-Nitro-1,4-dialkylbenzenes

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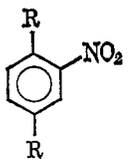
Previous workers[1] have shown that 2-nitro-1,4-dimethylbenzene nitrates predominantly in the 3 position. This somewhat surprising conclusion was based entirely on the orientation assignments of Lellman,[2] which appeared equivocal. It was therefore decided to reinvestigate this nitration, using nmr techniques for analysis, and to extend the results to the 2-nitrodiethyl-, -diisopropyl-, and -di-*t*-butylbenzenes. 2-Nitrodi-*t*-butylbenzene had previously been reported to nitrate in the 5 position,[3] but in these experiments the yields were low.

The mononitrodialkylbenzenes (I) were prepared by the methods given by Franck and Williamson;[4] final purification was found to be best effected by preparative vpc on an Apiezon L–Chromosorb P column at 180°. The nmr spectra of these compounds were measured, and our results matched those of Franck and Williamson,[4] whose work appeared while ours was in progress. We measured the ultraviolet spectra of these compounds, together with that of nitrobenzene in cyclohexane solution and calculated the apparent angle of twist (φ) by the method of Wepster[5] (I).



I

R = CH_3, φ = 35°
R = CH_2CH_3, φ = 42°
R = $CH(CH_3)_2$, φ = 48°
R = $C(CH_3)_3$, φ = 65°

The second nitration of these compounds was carried out in sulfuric acid, and the crude material, obtained by pouring onto ice, was examined directly by nmr.

(1) K. A. Kobe and T. B. Hudson, *Ind. Eng. Chem.*, **42**, 356, 19 (1950).
(2) E. Lellman, *Ann.*, **228**, 250 (1885).
(3) F. Bell and K. R. Buck, *J. Chem. Soc.*, 1890 (1956).
(4) R. W. Franck and M. A. Williamson, *J. Org. Chem.*, **31**, 2420 (1966).
(5) B. M. Wepster, "Progress in Stereochemistry," W. Klyne and P. B. D. de la Mare, Ed., Academic Press Inc., New York, N. Y., 1958, p 110.

TABLE I

ISOMER PROPORTIONS OBTAINED BY NITRATION OF 2-NITRO-1,4-DIALKYLBENZENES

Compd I, R	Over-all yield (calcd as dinitro product)	II, %	III, %	IV, %	*ortho/para* ratio
H[a]		6.12	2.06	91.8	1.5 ($^1/_2$ *o/p*)
Me	97	48	12	40	4.0
Et	80	52	19	29	2.7
i-Pr	60	Complex aromatic region in nmr spectrum			
t-Bu	70	Predominantly III			

[a] A. D. Mesuré and J. G. Tillet, *J. Chem. Soc., B*, 669 (1966).

TABLE II

NMR SPECTRA OF THE DINITRO-1,4-DIALKYLBENZENES

(A) Aromatic Proton Resonances[a,b]

R	II, τ	III, τ	IV, τ
Me	2.62, 2.17[c]	2.12, 1.93[c]	2.22, 2.02[c]
Et	2.46, 2.58[d]	2.10, 2.23[d]	2.17, 2.30[d]
t-Bu		2.47, 2.31[c]	

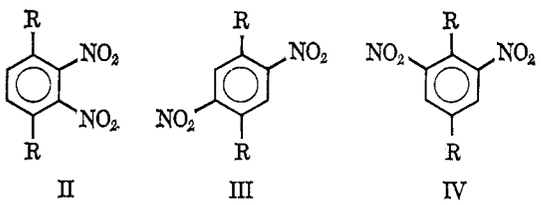
(B) Alkyl Proton Resonances[a,b]

Me	7.56, 7.39[c]	7.37, 7.18[c]	7.48, 7.12, 7.46[c]
Et			
CH_3CH_2	8.70, 8.72[d] (triplet)	8.67, 8.67[d] (triplet)	8.67, 8.68[d] (triplet)
CH_3CH_2	7.24, 7.03[d] (quartet)	7.09[d,e] (quartet)	7.14, 7.20[d,e] (quartet)
t-Bu		8.56, 8.46[c]	8.52, 8.26, 8.36[c]

[a] Taking tetramethylsilane as standard. [b] Solvent $CDCl_3$ unless otherwise indicated. [c] Solvent pentafluoropyridine. [d] Solvent CCl_4. [e] Unresolved peaks in $CDCl_3$.

The results are given in Table I, and nmr data are given in Table II.

For all three possible dinitro isomers (II, III, and IV), the two remaining aromatic protons are equivalent: of these the protons in II would be expected to resonate at higher field than those of III or IV.[6] The protons of the alkyl groups are equivalent in II and III, but not in IV.



II III IV

Considerable difficulty was encountered in resolving the two methyl peaks expected for the 2,6-dinitro-1,4-dimethylbenzene, which was obtained in pure form from the reaction product. It yielded only a single peak for the alkyl region in $CDCl_3$, CF_3COOH, and CCl_4, but the expected, well-separated peaks in 1,3-dichlorobenzene and pentafluoropyridine.

An isomer of dinitro-*p*-diethylbenzene (mp 84°) was obtained from the reaction product. This was assigned the 2,5-dinitro configuration, from the fact that the aromatic protons resonated at lowest field, and only a single quartet was produced in the alkyl region. Accidental coincidence of the chemical shift positions of the two quartets in the 2,6-dinitro isomer does not occur in this case; two methylene peaks of equal intensity, due to the 2,6-dinitro isomer, can be detected

(6) L. M. Jackman, "Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry," Pergamon Press Inc., New York, N. Y., (1959) p 63.