of the *trans* absorption band at 965 cm.$^{-1}$ in 6.0 mmole % carbon disulfide solution of this compound was identical with that of 3.0 mmole % carbon disulfide solution of *cis,trans,trans*-1,5,9-cyclododecatriene.

Trimethylsilylcyclododecene.—A solution of 7 g. (0.029 mole) of 1-trimethylsilyl-4,8-cyclododecadiene in alcohol was stirred with 3 g. of 10% palladium–charcoal at 40° under atmospheric pressure of hydrogen. After 650 ml. (0.029 mole) of hydrogen was absorbed in the course of 2 hr., the catalyst was filtered and the solvent was removed to give a fraction boiling at 98–100° (1 mm.), n^{25}_{D} 1.4921, d^{25}_{4} 0.8909. It was determined by Wijs' method that the compound had one double bond. Absorbance of the *trans* absorption band at 965 cm.$^{-1}$ in 7.9 mmole % carbon disulfide solution of this compound was identical with that of 2.5 mmole % solution of *cis,trans,trans*-1,5,9-cyclododecatriene.

Anal. Calcd. for $C_{15}H_{30}Si$: C, 75.55; H, 12.68; Si, 11.77. Found: C, 75.75; H, 12.55; Si, 11.95.

Bis(trichlorosilyl)cyclododecene.—A mixture of 24 g. (0.15 mole) of *cis,trans,trans*-1,5,9-cyclododecatriene and 60 g. (0.45 mole) of trichlorosilane was heated with 0.20 ml. of 0.1 *N* chloroplatinic acid–propyl alcohol solution in a Carius tube at 180° for 80 hr. From the mixture, 30 g. of trichlorosilane and 4 g. of the cyclododecatriene were recovered. From reaction products, 13 g. (35%) of 1-trichlorosilyl-4,8-cyclododecadiene, 25 g. (46%) of a fraction boiling at 200–220° (6 mm.), and 8 g. of residue were obtained. The fraction was redistilled, giving a fraction boiling at 200–202° (5 mm.), d^{25}_{4} 1.322.

Anal. Calcd. for $C_{12}H_{20}Si_2Cl_6$: Cl, 49.2; Si, 12.96. Found: Cl, 49.0; Si, 12.69.

Bis(trimethylsilyl)cyclododecene.—With excess methylmagnesium chloride, 10 g. of bis(trichlorosilyl)cyclododecene was methylated, giving 5 g. (70%) of a fraction, b.p. 132–133° (1 mm.), n^{20}_{D} 1.4894, d^{25}_{3} 0.8818.

Anal. Calcd. for $C_{18}H_{38}Si_2$: C, 69.60; H, 12.33; Si, 18.07. Found: C, 69.32; H, 12.32; Si, 18.17.

It was determined by Wijs' method that the compound had one double bond. Absorbance of the *trans* absorption band at about 970 cm.$^{-1}$ in 6.6 mmole % carbon disulfide solution of this compound was identical with that of 2.2 mmole % carbon disulfide solution of *cis,trans,trans*-1,5,9-cyclododecatriene.

1-(Methyldichlorosilyl)-4,8-cyclododecadiene.—A mixture of 96 g. (0.57 mole) of *cis,trans,trans*-1,5,9-cyclododecatriene, 65 g. (0.57 mole) of methyldichlorosilane, and 0.20 ml. of 0.1 *N* chloroplatinic acid–propyl alcohol solution was heated in a Carius tube of about 200-ml. capacity at 185° for 60 hr. The mixture was distilled, giving 18 g. of methyldichlorosilane, 16 g. of cyclododecatriene, 91 g. of a fraction boiling at 165–175° (9 mm.), 66% based on the reacted cyclododecatriene, 16 g. of a fraction boiling at 195–215° (9 mm.), 8.5% based on the reacted cyclododecatriene, and 22 g. of residue. The fraction boiling at 165–175° (9 mm.) was redistilled, giving 1-(methyldichlorosilyl)-4,8-cyclododecadiene, b.p. 180–182° (15 mm.), n^{20}_{D} 1.511.

Anal. Calcd. for $C_{13}H_{22}SiCl_2$: Cl, 25.6; Si, 10.12. Found: Cl, 26.0; Si, 10.13.

Methylation of 9 g. of the compound gave 5 g. (63%) of 1-trimethylsilyl-4,8-cyclododecadiene, n^{25}_{D} 1.4957, which showed identical infrared absorption spectrum with that of the compound derived from 1-trichlorosilyl-4,8-cyclododecadiene.

The fraction boiling at 195–215° (9 mm.) was redistilled, giving a fraction boiling at 200–202° (5 mm.), chlorine content 32.0%. Methylation of the fraction gave bis(trimethylsilyl)-cyclododecene in 76% yields, n^{20}_{D} 1.4894. Its infrared spectrum was identical with that of the compound derived from bis(trichlorosilyl)cyclododecene.

Attempted Addition Reaction by Trimethylsilane.—A mixture of 49 g. (0.3 mole) of *cis,trans,trans*-1,5,9-cyclododecatriene and 30 g. (0.4 mole) of trimethylsilane was heated with 0.8 ml. of 0.1 *N* chloroplatinic acid–propyl alcohol solution in an autoclave at 250° for 48 hr. The mixture was distilled, recovering the starting material, *cis,trans,trans*-1,5,9-cyclododecatriene (92%). No adduct of trimethylsilane was obtained.

Hydrolysis of 1-trichlorosilyl-4,8-cyclododecadiene.—An ether solution of 1-trichlorosilyl-4,8-cyclododecadiene was poured into a mixture of ice and ether. The mixture was neutralized with aqueous ammonia and the ether layer was dried over anhydrous sodium sulfate. The solvent was removed *in vacuo* at room temperature and the residue was dried at room temperature *in vacuo* for a day, leaving white solid; content of OH group, 7.8% [calcd. for $(C_{12}H_{19}SiO)OH$, 7.6%]; molecular weight, 1300 [calcd. for $(C_{12}H_{19}SiOOH)_6$, 1344].

Hydrolysis of 1-(Methyl dichlorosilyl)-4,8-cyclododecadiene.—White solid was obtained by the method mentioned previously; content of OH group, 11.6% [calcd. for $C_{13}H_{22}Si(OH)_2$, 14.2%]; molecular weight, 330 [calcd. for $C_{13}H_{22}Si(OH)_2$, 240].

Deamination of 7-Aminobicyclo[4.1.0]heptane

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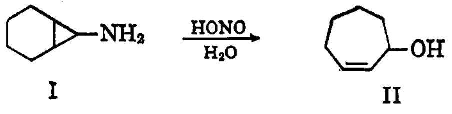
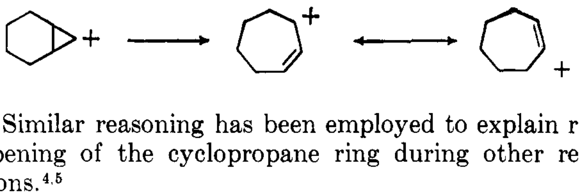
Nitrous acid deamination of 7-aminonorcarane leads, with ring expansion, to cyclohept-2-enol and not to 7-hydroxynorcarane as has been reported.

Deamination of small ring amines with nitrous acid usually leads to ring contraction or expansion or to ring opening. For example, cyclopropylamine yields allyl alcohol.[1] Deamination of either cyclobutylamine or cyclopropylcarbinylamine furnishes similar mixtures of cyclopropylcarbinol, cyclobutanol, along with some allylcarbinol.[2] Even in five- and six-membered ring systems the formation of some product, where possible, due to expansion of the ring during deamination is common.[3]

Considering these results one should expect the deamination of 7-aminonorcarane (7-aminobicyclo[4.1.0]-heptane, I) to lead to ring expansion and formation of cyclohept-2-enol (II). From a theoretical point of view, if an electron-deficient intermediate is involved in some stage of the reaction, then ring opening with formation of the symmetrical allylic ion should be energetically favored as shown.



I II



Similar reasoning has been employed to explain ring opening of the cyclopropane ring during other reactions.[4,5]

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(1) N. Kishner, *J. Russ. Phys. Chem. Soc.*, **37**, 316 (1905).

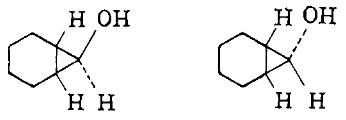
(2) J. D. Roberts and R. H. Mazur, *J. Am. Chem. Soc.*, **73**, 7509 (1951).

(3) W. Huckel, "Theoretical Principles of Organic Chemistry," Vol. 1, Elsevier Publishing Co., New York, N. Y., 1955, pp. 457–461, references cited.

(4) J. D. Roberts and V. C. Chambers, *J. Am. Chem. Soc.*, **73**, 5034 (1951).

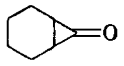
(5) K. L. Rinehart, Jr., S. I. Goldberg, C. L. Tarimu, and T. P. Culbertson, *ibid.*, **83**, 225 (1961).

Yet, I has been prepared and reported,[6,7] to yield both *exo*- and *endo*-7-hydroxynorcaranes (7-hydroxybicyclo[4.1.0]heptane, III) on nitrous acid deamination. This apparent contradiction to expected behavior seemed to demand duplication of these experiments as well as the reported[8] preparation of bicyclo[4.1.0]-heptanone-7 (IV) from III by Oppenauer oxidation.[9]



exo *endo*

III



IV

Results and Discussion

The synthetic scheme[3,5,10] for the preparation of I began with 7-carboethoxybicyclo[4.1.0]heptane (V). This ester was prepared by reaction of ethyl diazoacetate and cyclohexene (peroxide free) in the presence of a copper–bronze catalyst[11] in 48% yield. The n.m.r. spectra of the product showed no double bond hydrogen as well as no obvious cyclopropane hydrogen, possibly due to the opposing effects of the chemical shifts involved. The *exo* configuration of V is formed apparently to the exclusion of the *endo*, since on long equilibration of V with sodium ethoxide a small amount of isomeric ester is formed initially but does not increase beyond *ca.* 12% (gas chromatography). The side products of the diazo ester reactions, diethyl maleate and diethyl fumarate, are formed in equal amounts.

Saponification of V with potassium hydroxide lead to the acid VI which was converted to the acid chloride VII with thionyl chloride. The infrared spectra of VII showed the expected bands at 3.3, 5.6, and 9.8 μ for the acid chloride carbonyl and cyclopropane ring. Conversion of VII to 7-aminobicyclo[4.1.0]heptane (I) by the dry Curtius method[12] proceeded in 43% yield. The amine showed infrared bands at 3.0, 3.3, 6.2 (broad NH_2 closing), and 9.75 μ which are consistent with the structure I. The n.m.r. spectra showed no double bond hydrogen, the expected band at δ 2.15 for the amino hydrogen and a doublet at δ 0.75 probably due to the cyclopropane hydrogen in this molecule. Deamination of I in the cold (see Experimental method A) gave an alcohol (VIII) of doubtful purity which had phenylurethane m.p. 90–91°, in only 5% yield. This alcohol possibly corresponds to the minor alcohol (phenylurethane 95° obtained in trace amounts and assigned III *exo* structure) reported by the previous researchers.

Deamination of I by first adding silver nitrite in the cold, then heating the resulting solution to 70° (method B) until nitrogen evolution ceased, furnished an alcohol in 26% yield which had a phenylurethane derivative melting at 105.7°. This major product, apparently corresponding to the alcohol (30% yield) with phenylurethane m.p. 102–103° previously obtained and assigned structure *endo* III,[6,7] showed infrared bands more characteristic of structure II than of structure III. The n.m.r. spectrum showed two double bond hydrogens at δ 5.70, OH at δ 4.83, and single H at δ 4.32—also supporting structure II. The alcohol was proven to be cyclohept-2-enol (II) by direct comparison to an authentic sample prepared by brominating cycloheptene with N-bromosuccinimide followed by hydrolysis of the bromide with 5% aqueous carbonate. Mixture melting points of phenylurethane and *p*-nitrobenzoate derivatives of the synthetic and deamination alcohols were undepressed and their infrared spectra were identical. Thus, ring opening occurred during deamination to form the relatively strain-free alcohol as would be predicted.

The structure of the minor alcohol has not been established. Even after several preparations of the alcohol insufficient material was obtained for complete purification. The infrared spectra of the alcohol showed a great deal of contamination by the starting amine and the major alcohol. This minor alcohol (mixture) did not exhibit infrared bands characteristic of 2-methylcyclohexanol or cycloheptanol but that some of the product may have been cyclohex-1-ene carbinol or III cannot be excluded.

The reported[6,7] preparation of IV by Oppenauer oxidation from the mixture of alcohols obtained in the deamination reaction remains to be reinterpreted. The expected product of this reaction would be cyclohept-2-enone, but the 2,4-dinitrophenylhydrazone (DNP) of supposed IV was reported[7] to melt at 141° whereas the DNP of cyclohept-2-enone has been synthesized and melts at 122°.[13] In order to dispel this anomaly, cyclohept-2-enol was oxidized by the Oppenauer procedure using benzoquinone as the hydrogen acceptor.[3,5] The product showed infrared spectra and n.m.r. spectra expected of the cyclohept-2-enone structure and yielded an orange DNP which melted at 145° (eluted from alumina[13]). This DNP compares favorably in melting point with the DNP reported[7] for IV but not with the DNP for cyclohept-2-enone (red, m.p. 122°[13]) described by Braude and Evans. A repeat of the DNP procedure (no heat) gave an orange DNP in excellent yield which melted at 164°. The latter DNP had the correct analysis for the *double adduct* of 2,4-dinitrophenylhydrazine with cyclohept-2-enone. Thus, the first DNP of cyclohept-2-enone prepared in this work must either have been an impure preparation or a *syn* or *anti* isomer or eutectic composition of the double adduct. In any case, the DNP must be considered an unreliable derivative of cyclohept-2-enone. The previous report of formation of a DNP derivative of the *alcohol* III, melting at 170°, did not seem reasonable for that structure and would not immediately seem reasonable for the correct structure II. Cyclohept-2-enol is, however, both a secondary and allylic alcohol so that formation of a DNP, preceded by oxidation of the alcohol in the presence of DNPH,[14]

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[6] R. Jacquier and R. Fraisse, *Bull. soc. chim. France*, 766 (1955).

[7] R. Jacquier and R. Fraisse, *ibid.*, 108 (1957).

[8] R. Jacquier and R. Fraisse, *ibid.*, 559 (1956).

[9] For a critical review of reported cyclopropanone derivatives see E. L. Mitch, Ph.D. thesis, The Rice Institute, Houston, Tex., 1959. For a recent discussion of some norcarane alcohols, see W. G. Dauben and G. H. Berezin, *J. Am. Chem. Soc.*, **85**, 468 (1963).

[10] The over-all synthetic path was devised and performed by the previous researchers but no experimental details were given in the publications of the results.

[11] F. Ebel, R. Brunner, and P. Mangelli, *Helv. Chim. Acta*, **12**, 19 (1929).

[12] P. A. Smith, "Organic Reactions," Coll. Vol. III, John Wiley and Sons, Inc., New York, N. Y., 1946, pp. 337–449.

[13] E. H. Braude and E. H. Evans, *J. Chem. Soc.*, 607 (1954).

[14] E. A. Braude and W. F. Forbes, *ibid.*, 1762 (1951).

should not be completely unexpected. On treatment of the synthetic cyclohept-2-enol with Brady's reagent for one hour at 60° an orange DNP precipitated which was identical with the *double adduct* of cyclohept-2-enone (m.p. 164°).

An attempt was made to repeat the reported oxidation of II (then referred to as "III") to cyclohex-1-enyl aldehyde with manganese dioxide without success. The reported preparation[15] of 6-ketobicyclo[3.1.0]-hexane by the same reactions employed for the bicyclo-[4.1.0]heptane series may also be incorrect. The melting point of the DNP of 6-ketobicyclo[3.1.0]hexane is very close to that reported for cyclohex-2-enone. The ultraviolet spectra of this derivative suggests α,β unsaturation.

Experimental

The melting points and boiling points are uncorrected. Elution chromatography was done with activated alumina as absorbent and, unless otherwise specified, the eluting solvents were A. R. grade petroleum ether, benzene, ether, methanol—in that order. All gas chromatographs were done on a Perkin-Elmer vapor fractometer Model 154 or F & M 124 with helium as the carrier gas. The column which proved most satisfactory for the materials in this work was Apiezon-L on firebrick or Chromasorb. Infrared spectra were taken on a Perkin-Elmer Infracord spectrophotometer Model 137. N.m.r. spectra were taken with a Varian A-60 with tetramethylsilane as an internal reference. Ultraviolet spectra were taken on a Beckman DK-2.

Ethyl Diazoacetate.—Ethyl diazoacetate was prepared in accordance with the procedure of Womack and Nelson.[16]

Ethyl Ester of 7-Bicyclo[4.1.0]heptane Carboxylic Acid (Ethyl 7-Norcaranecarboxylate).—The following reaction was catalyzed by copper-bronze, prepared by adding 16 g. zinc dust over a 20-min. period into a stirred solution of 80 g. copper sulfate pentahydrate in 300 ml. of water. The precipitate was collected on a filter, washed well with water, then with three 20-ml. portions of absolute ethanol, and finally with ether. The dried catalyst was used within 1 to 4 hr. after preparation.

Ethyl 7-norcaranecarboxylate was prepared by adding dropwise 100 ml. of ethyl diazoacetate into a stirred suspension of the copper-bronze catalyst in 500 ml. of cyclohexene (freshly distilled from zinc dust) at reflux temperature. A 30-min. period was allowed to complete the reaction after addition. The excess cyclohexene was distilled and the residue fractionally distilled under vacuum. The preceding procedure was repeated a number of times, and those fractions boiling from 105–113° at 16 mm. (or equivalent) were combined and washed with a 3% aqueous solution of potassium permanganate. The ester layer was separated, washed with brine, and dried over sodium sulfate before redistillation under vacuum. Ethyl 7-norcaranecarboxylate boiled at 108–111° (16 mm.) [lit.[5] 110° (18 mm.)]. Direct yield from a reaction, calculated from gas chromatographic results before washing with permanganate and redistillation, was 48%. The preceding reaction also may be catalyzed in somewhat lower yield (43%) by a silver-copper catalyst (90–10 couple) prepared by slowly adding copper powder with stirring to a solution of silver nitrate, then washing with distilled water, ethanol, and ether in that order.

Curtius Reaction.[12]—The following Curtius reaction (preparation of 7-bicyclo[4.1.0]heptane hydrochloride) was repeated a number of times using varied quantities and techniques. The procedure described was found to give the best results.

7-Bicyclo[4.1.0]heptanecarboxylic Acid.—Ethyl 7-norcaranecarboxylate (61.9 g., 0.37 mole) was refluxed with a solution of 12 g. sodium hydroxide in 200 ml. of water until about half the ester layer had disappeared, then another 12 g. of sodium hydroxide in 200 ml. of water was added, and reflux was continued until the ester disappeared. The mixture was cooled and poured into 200 ml. of 4 *M* hydrochloric acid (0.8 mole). The precipitated acid was collected on a filter, washed well with water, and dried in a vacuum desiccator. The yield of 7-bicyclo[4.1.0]heptanecarboxylic acid melting at 98–99° (lit.[5] 97–98°), was 90%.

Acid Chloride of 7-Bicyclo[4.1.0]heptanecarboxylic Acid.—Thionyl chloride (40 ml.) reacted with 46.45 g. (0.332 mole) of 7-bicyclo[4.1.0]heptanecarboxylic acid. After the reaction had subsided, the flask was evacuated for 3 hr., then the solution was vacuum distilled. The yield of acid chloride, b.p. 108° (15 mm.) [lit.[5] 112° (25 mm.)], was 85%.

7-Aminobicyclo[4.1.0]heptane Hydrochloride.—The acid chloride of 7-bicyclo[4.1.0]heptanecarboxylic acid (21.78 g., 0.14 mole) was refluxed with 9.7 g. (15 moles) activated (with hydrazine) sodium azide in 125 ml. of benzene for 44 hr., after which the solution was cooled and filtered. The filtrate was washed into a 500-ml. flask with benzene and to it was added 60 ml. of concentrated hydrochloric acid, and the mixture refluxed gently for 3.5 hr. The cooled solution was separated and the benzene layer washed with a small amount of water. The combined aqueous solutions were evaporated to dryness on the steam bath and the residue was dissolved in absolute ethanol, swirled with Norit, filtered, and again evaporated to dryness. The amine hydrochloride was crystallized from a solution of benzene and absolute ethanol. The yield of 7-aminobicyclo[4.1.0]heptane hydrochloride, decomposing at 224–225° (lit.[5] 224–225° dec.), was 43%.

7-Aminobicyclo[4.1.0]heptane.—Into 15 ml. of water was dissolved 3.25 g. of 7-aminobicyclo[4.1.0]heptane hydrochloride and a solution of 1 g. of sodium hydroxide in 30 ml. of water was added dropwise until the mixture was basic. The amine was extracted with ether, the ether solution was dried over sodium sulfate, and then concentrated, and vacuum distilled. 7-Aminobicyclo[4.1.0]heptane boiled at 63° (17 mm.) [lit.[5] 72° (20 mm.)].

Nitrous Acid Deamination of 7-Aminobicyclo[4.1.0]heptane Hydrochloride.—Silver nitrite was prepared by precipitation from a solution of sodium nitrite by a solution of silver nitrate; the yellowish crystals were filtered and dried.

Method A.—A suspension of 11.55 g. (0.075 mole) of silver nitrite in 100 ml. of distilled water was mechanically stirred and cooled to 13–16° (maintained throughout the reaction). Into the stirred suspension, over a 20-min. period, was added dropwise a solution of 4 g. (0.0269 mole) of 7-aminobicyclo[4.1.0]heptane hydrochloride in 35 ml. of distilled water. Forty-five minutes were allowed after the addition was complete, then a solution of 8 ml. of hydrochloric acid in 10 ml. of water was added and 0.5 hr. was allowed to complete the reaction. The solution was filtered and the foamy silver chloride was washed with distilled water, and then with ether. The combined filtrates were extracted 12 times with ether; the extracts were combined and shaken with about 5 g. of potassium carbonate, then the solution was filtered and dried overnight over 3 g. of potassium carbonate. The ether solution was decanted and the solution was concentrated at low temperature under vacuum. The resulting liquid was light yellow which in a few minutes turned green and in an hour turned reddish orange and became viscous. Some of the product was eluted through an alumina column. The alcoholic fraction (by infrared spectra) was eluted only with methanol. A gas chromatography comparison of the eluted and noneluted product showed very little purification by elution chromatography. Attempts to vacuum distil the product at 13 mm. resulted in extensive decomposition. (Further details are given subsequently.)

Method B.—A suspension of 11.55 g. (0.075 mole) of silver nitrite in 100 ml. of distilled water was mechanically stirred and cooled to 0° whereupon a solution of 4 g. (0.0269 mole) of 7-aminobicyclo[3.1.0]heptane hydrochloride in 35 ml. of distilled water was added dropwise over a 1-hr. period. Another hour of stirring at 0° was allowed then the solution was gently heated and stirred at 75° for 3 hr. (The mixture turned black with application of heat.) The solution was then filtered, washed, extracted, dried, and concentrated as in procedure A. After concentration, there were 2.07 g. of products.

Derivatives were made (or the pure alcohol, from method B, could be isolated by chromatography on alumina) from the crude products from each method, by reaction with an excess of phenyl isocyanate on a 100° sand bath for 30 min., then purified by elution through an alumina column. From procedure A yield from amine hydrochloride to phenylurethane, m.p. 90–91°, was 5.3%. From procedure B, yield from amine hydrochloride to phenylurethane, m.p. 105.7°, was 26%. There may have been traces of phenylurethane of m.p. 90–91° from procedure B, which

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(15) R. Jacquier and P. Besinet, *Bull. soc. chim. France*, 988 (1957).

(16) E. B. Womack and A. B. Nelson, "Organic Syntheses," Coll. Vol. III, John Wiley and Sons, Inc., New York, N. Y., 1955, p. 392.

was concealed in elution fractions highly contaminated with diphenylurea.

Cycloheptene.—Cycloheptanol (67.13 g., 0.588 mole) and 14.7 ml. of 85% phosphoric acid were swirled together and heated under a 6-cm. column packed with wire gauze, above which was a cold finger condenser. Water and cycloheptene distilled together. When almost all the cycloheptene had distilled, the apparatus was cooled and 50 ml. of *o*-dichlorobenzene was added as a chaser solvent. The flask was reheated until dichlorobenzene began to distil. The wet solution was washed into a 500-ml. separatory funnel with dichlorobenzene and washed with an equal volume of a saturated salt solution. The upper layer was dried over sodium sulfate and distilled. Yield of cycloheptene, $n^{26}\text{D}$ 1.4552, b.p. 112–117° (lit.[17] 115–116°), was 88%.

3-Bromocycloheptene.—The procedure of Braude and Evans[13] was used to prepare 3-bromocycloheptene. Yield of 3-bromocycloheptene, $n^{27}\text{D}$ 1.5285, b.p. 64–71° (8 mm.) [lit.[13] 67° (8 mm.)], was 48.5%.

Cyclohept-2-enol.—Five grams (0.0286 mole) of 3-bromocycloheptene was gently refluxed with a solution of 4.1 g. of (0.033 mole) of sodium carbonate (monohydrate) in 100 ml. water. The heavy bromocycloheptene, which formed a pool at the bottom of the flask, gradually disappeared and in 30 min. was completely gone; whereupon the solution was cooled, 35 ml. of ether was added, and the aqueous layer was saturated with potassium carbonate. After the initial separation, the aqueous layer was extracted with five 20-ml. portions of ether. The combined ether solutions were dried over potassium carbonate, the solution was concentrated, and distilled under vacuum with dimethyl phthalate as a chaser solvent. Yield of cyclohept-2-enol, $n^{26}\text{D}$ 1.4892, b.p. 83–84 (13 mm.), was 27%. The *p*-nitrobenzoate derivative had m.p. 53.1–53.3°.

Anal. Calcd. for $C_{14}H_{15}NO_4$: C, 64.4; H, 5.75; N, 5.35. Found: C, 64.31; H, 5.79; N, 5.37.

A phenylurethane derivative was made in the usual way. Results of a mixture melting point taken with the phenylurethane of the aqueous deamination product of 7-aminobicyclo[4.1.0]-heptane hydrochloride (method B) are as follows: phenylurethane of cyclohept-2-enol, m.p. 102.5–103.5°; phenylurethane of product of nitrous deamination of 7-aminobicyclo[4.1.0]heptane, m.p. 105.5–105.7° (very pure); mixture of the two phenylurethanes, m.p. 103–105. The phenylurethane derivative was analyzed.

Anal. Calcd. for $C_{14}H_{17}O_2N$: C, 72.69; H, 7.36%. Found: C, 72.79; H, 7.31. Infrared spectra of cyclohept-2-enol and the alcohol (purified by elution chromatography) resulting from the nitrous deamination of 7-aminobicyclo[3.1.0]heptane hydrochloride (method B) were the same. Retention times of the same alcohols in a gas chromatography comparison were within 3 sec. and a mixture of the two showed no peak separation.

Oppenauer Oxidation of Cyclohept-2-enol.—In a 1-l. 4-neck flask equipped with a mechanical stirrer, a thermometer, a dropping funnel, and a condenser fitted with a calcium chloride tube was introduced 4.00 g. (0.0357 mole) of cyclohept-2-enol, 7.72 g. (0.0714 mole) of *p*-benzoquinone, 500 ml. of dry benzene, and 7.28 g. (0.0357 mole) of aluminum isopropoxide.[18] The dark violet mixture was stirred for 1 hr. at room temperature, then for 3 hr. at 70°, then overnight at room temperature. All but 150 ml. of the benzene solution was then distilled away, water was added, and the mixture was steam distilled. The distillate was saturated with sodium chloride and the upper layer was separated. The salt solution was extracted with 50 ml. of ether which was combined with the initial nonaqueous layer. The extracts were dried overnight over sodium sulfate. Benzene and ether were removed under vacuum and the residue was vacuum distilled, b.p. 73–74° (11 mm.), $n^{26}\text{D}$ 1.4925 (34% yield). A 2,4-DNP was made and purified by elution from alumina, m.p. 143–144°. The DNP of cycloheptanone is dark yellow, of cyclohept-2-enone, prepared as for the preceding, is orange. Braude and Evans[13] reported the DNP of cyclohept-2-enone as red plates, m.p. 122°. A second preparation of the DNP derivative employing Brady's reagent at room temperature yielded an orange compound melting at 164° (λ_{max} 352 mμ, log ϵ 4.96; shoulder at 422 mμ, log ϵ 3.65, ethylacetate) which analyzed correctly for the *double adduct*.

Anal. Calcd. for $C_{19}H_{18}N_8O_8$: C, 46.91; H, 3.73; N, 23.00; mol. wt., 450.9. Found: C, 46.87; H, 4.30; N, 22.56; mol. wt. (Rast), 421.

This same DNP was formed directly from cyclohept-2-enol by heating with Brady's reagent.

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Iodolactonization of 3-(3-Cyclohexenyl)propionic Acid[1a]

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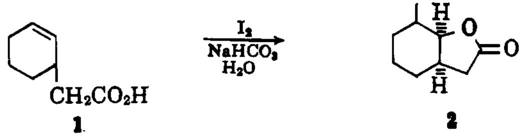
The reaction of the sodium salt of 3-(3-cyclohexenyl)propionic acid (**3**) with iodine in aqueous solution afforded the iodo-*cis*-δ-lactone **5**.

Previous studies[2] of the iodolactonization reaction have indicated that, when possible, a γ-lactone is formed in preference to a δ-lactone unless γ-lactone formation would be accompanied by the introduction of considerable strain.[2e] Furthermore, as illustrated by the conversion **1** → **2**, the formation of a *cis*-fused γ-lactone is the expected result when an appropriate cycloalkenylacetic acid is subjected to iodolactonization. In considering possible applications of this reaction to other synthetic problems, the question arose as to what would be the major course of the iodolactonization reaction with 3-(3-cyclohexenyl)propionic acid (**3**). Examination of molecular models suggested that three possible reaction paths (to form **4**, **5**, and **6**) might be possible (Chart I) with this system, whereas for the lower homologous acid **1** only the reaction path leading



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