Chemistry of Spiropentane. III. The Synthesis and Deamination of Spiropentylamine

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Spiropentylamine has been synthesized from chlorospiropentane by reaction of the Grignard reagent with ethyl chloroformate, followed by a Curtius degradation. Reaction of the amine with aqueous nitrous acid gives a mixture of 2- and 3methylenecyclobutanols, the latter predominating. The implications of these results with regard to the structures of nonclassical carbonium ions are discussed.

The spiropentyl cation I is a species of particular interest because of the possibility that the instability normally associated with cyclopropyl cations² might be in part or in whole overcome by the stabilization associated with cyclopropylcarbinyl cations,³ depending upon the geometrical requirements for such stabilization.



The recently-described synthesis of chlorospiropentane $(II)^4$ makes several potential routes to I available. Unusual stabilization of I might be revealed by enhancement of rates of solvolysis reactions leading to it or by formation of unusual products from it. Direct solvolysis studies on the chloride II were discouraged by the finding that it does not react appreciably with refluxing aqueous silver nitrate in twelve hours. Other derivatives of spiropentane will no doubt be easier subjects for solvolysis studies, and such experiments are in progress. This research deals with the synthesis of spiropentylamine (VI) from II and the reaction of VI with nitrous acid to determine the products formed from the carbonium ion I under one set of conditions.

The chloride II was converted to ethyl spiropentanecarboxylate (III) in 49% yield by reaction of the Grignard reagent with ethyl chloroformate. Attempts to employ the lithium reagent instead of the Grignard reagent were failures. In the case of tetrahydrofuran solvent at -45 to -50° this failure was apparently due to reaction of the lithium reagent with the solvent, since spiropentane (32%)yield) was formed before any water was added. The structure of III was confirmed by the n.m.r. spectrum, which showed a typical quartet and triplet for the ethyl group at 0.70 and 3.47 p.p.m. from water, respectively, a quartet at 2.83 p.p.m. for the proton alpha to the carboxylate function,⁴ a strong, sharp peak for the unsubstituted ring at 3.84 p.p.m., and some partially obscured peaks near 3.29 p.p.m. for the methylene of the substituted ring.

The hydrazide IV was prepared in 80% yield from III by reaction with hydrazine hydrate. The n.m.r. spectrum showed signals at 2.89 p.p.m. (quartet) for the proton alpha to the carbonyl, at

(1) Abstracted from the Ph.D. Thesis of George F. Fanta, University of Illinois, 1960.

(2) J. D. Roberts and V. C. Chambers. This Journal, 73, 5034 (1951).



3.39–3.52 p.p.m. for the β -hydrogens, and at 3.94 p.p.m. for the unsubstituted ring. The deuterium oxide solvent removed the N-H protons by exchange, so only a water signal was observed for them. Compound IV was converted to the azide, which was not isolated but was decomposed directly in a benzene-heptane solvent to the isocyanate, which was in turn directly converted to β -naphthyl spiropentylcarbamate (V) in 75% yield with β -naphthol. The structure of V was supported by its basic hydrolysis to give β -naphthol, its lack of unsaturation and its n.m.r. spectrum, which again showed a multiplet at 1.96 p.p.m. for the hydrogen alpha to the nitrogen, a series of signals at 3.63–3.83 p.p.m. for the β -hydrogens, and a series of signals with prominent maxima at 4.02 and 4.14 p.p.m. for the unsubstituted ring. An attempt to prepare the ethyl carbamate by decomposition of the azide in the presence of ethanol failed to give more than a 24% yield of nitrogen gas, presumably due to simple acylation of ethanol by the azide. Decomposition of the azide in benzeneheptane followed by addition of ethanol gave a mixture of liquids which probably contained the ethyl carbamate, but it was not easily purified. The β naphthyl carbamate V was therefore used as a source of spiropentylamine (VI).

The amine VI was never isolated as such in pure form, because the small quantities of materials available made such isolation inconvenient. It was shown that basic hydrolysis of V at room temperature generated VI by preparation of the phenylthiourea derivative VII of VI with phenyl isothiocyanate. A 55% yield of VII was obtained

⁽³⁾ R. H. Mazur, W. N. White, D. A. Semenow, C. C. Lee, M. S. Silver and J. D. Roberts, *ibid.*, **81**, 4390 (1959).

⁽⁴⁾ D. E. Applequist, G. F. Fanta and B. W. Henrikson, *ibid.*, 82, 2368 (1960).



Fig. 1.—Infrared spectra: 1, 3-methylenecyclobutanol (VIII), 98.4% pure, 5% in carbon tetrachloride; 2, 2-methylenecyclobutanol (IX), 94.1% pure, 5% in carbon tetrachloride.

from V. The preservation of the spiropentane structure in VII was again supported by the n.m.r. spectrum, which was nearly identical in appearance with that of V. The signal for the α -hydrogen appeared at 1.68 p.p.m., those for the β -hydrogens at 3.49–3.68 p.p.m., and those for the unsubstituted ring at 3.92 and 4.04 p.p.m. from water. The structures of II–V and VII were also sup-

The structures of 11–V and V11 were also supported by the infrared spectra, which showed no sign of unsaturation and which consistently showed a typical medium to strong cyclopropane (?) absorption at 1000 to 1015 cm.^{-1.5}

A basic aqueous solution of spiropentylamine (VI) prepared by saponification of V was acidified with perchloric acid, the resulting β -naphthol was removed with ether, and sodium nitrite was added to the aqueous solution to give a nitrous acid-nitrite system at about the optimum pH of 3.4. After 41 hours at room temperature, the neutral products consisted of 32 and 6.7% yields of alcohols assigned the structures VIII and IX, respectively, and a 3% total yield of two other products detected by vapor chromatography but not identified.



The remainder of the amine was presumably unreacted, but the scale of operation was too small to permit isolation of it. The alcohol VIII was isolated by vapor chromatography in 98.4% purity and analyzed as the pure substance and as the 3,5dinitrobenzoate. Alcohol IX was separated from VIII in a purity of 94%, but the amount obtained was sufficient only for infrared and n.m.r. spectral examination. The infrared spectra of VIII and IX were nearly the same (Fig. 1) and showed the strong C==C stretch at 1678 cm.⁻¹ and the C==CH₂ out of plane deformation at 880 and 885 cm.⁻¹, respectively, characteristic of methylenecyclobutanes.⁶



Fig. 2.—N.m.r. spectra: 1, 3-methylenecyclobutanol (VIII), 98.4% pure, 216 mg./ml. in carbon tetrachloride, with acetic acid added to move OH proton (-0.11 p.p.m.) off scale; 2, 2-methylenecyclobutanol (IX), 94.1% pure, 60 mg./ ml. in carbon tetrachloride.

Very strong OH absorptions at about 3300 cm.⁻¹ were also observed in both spectra. The infrared spectra did not appear to offer any way of assigning the positions of the hydroxyls, but the n.m.r. spectra (Fig. 2) provided the basis for a tentative assignment. The olefinic protons and the proton alpha to OH appeared as two symmetrical quintets (at 0 and 0.51 p.p.m., respectively) in the spectrum assigned to VIII, as if the four ring methylene protons were all identical, and as if there were only one type of olefinic proton. Such a spectrum is reasonable for VIII if the coupling constant between the two protons of a ring methylene group is greater than the chemical shift difference between them. The spectrum of the substance assigned structure IX, on the other hand, appeared to show two separate olefinic signals at -0.23 and 0.02 p.p.m. and two separate ring methylene signals at 2.52 and 2.67 p.p.m., as expected for IX. The proton alpha to OH was probably represented by the broad signal at 0.20 p.p.m., and the OH proton appeared at 0.75 p.p.m. (identified by its disappearance upon addition of acetic acid).

The formation of VIII and IX in the reaction of spiropentylamine with nitrous acid suggests that neither the spiropentyl cation (I) nor a nonclassical modification of it (such as X or XI) is stable enough to prevent



rapid rearrangement to other cations, as yet undefined. Two possible paths for the rearrangement are shown in Fig. 3, but these (and other possibilities) cannot be distinguished without further experimentation. If the initially formed cation has

⁽⁵⁾ C. F. H. Allen, T. J. Davis, W. J. Humphlett and D. W. Stewart, J. Org. Chem., 22, 1291 (1957).

^{(6) (}a) D. E. Applequist and J. D. Roberts, THIS JOURNAL, 78, 4012
(1956); (b) H. N. Cripps, J. K. Williams and W. H. Sharkey, *ibid.*, 81, 2723 (1959).

structure X instead of I, cation XII might be omitted as a discrete intermediate. The conversion of XIII to XIV, for which there appears to be no



easy alternative,⁷ is of special interest in that it suggests unusual stabilization of the homoallylic cat-



ion XIV compared with the allylic cation XIII. The geometry of XIV probably favors transannular participation of the double bond.⁸ The conversion of XIII to XIV is formally a hydride shift, but the



existing analogies³ suggest that skeletal rearrangement of the sort observed in cyclobutyl cations is a more probable mechanism.

The qualitative indications from the products observed (VIII and IX rather than XV, XVI and XVII or decomposition products thereof) and from the unreactivity of chlorospiropentane with aqueous silver nitrate suggest that the initially formed carbonium ion (possibly I or X or XI) does not have much of the stabilization associated with cyclopropylcarbinyl cations.³ Quantitative information is



still needed, but it is of interest that reasonable extrapolations of the known solvolysis rates of cyclopropyl derivatives,² using the Winstein mYtreatment⁹ for solvent corrections, leads to calculated half-lives for the hydrolysis of cyclopropyl chloride in water at 100° of about 100 hours. Any strong enhancement of this reactivity in chlorospiropentane would presumably have resulted in reaction with refluxing aqueous silver nitrate under the conditions reported here. It is tempting to conclude that some distortion of the carbon skeleton is necessary to obtain substantial participation of the cycloproylcarbinyl type and that this distortion is inhibited by the strain which it would introduce, certainly in the bicyclobutonium ion X and possibly in the homoallylic ion XI. Non-classical participation of type XI, which is probably also important in the nortricyclyl-dehydronorbornyl and cholesteryl-cyclocholestanyl systems,¹⁰ would appear to be quite favorable stereoelectronically in the spiropentyl cation if no geometrical change were required. Further experiments will be required to reconcile the results reported here with observations of others which are most easily interpreted in terms of relatively minor disturbances of the cyclopropane ring in cyclopropylcarbinyl cations.¹¹

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Experimental¹²

Attempted Preparation of Spiropentyllithium.—Spiropentyl chloride (1.8 g., 0.0176 mole, 90.9% pure by vapor chromatography) was added to a suspension of 0.3 g. of lithium in tetrahydrofuran (THF) which had been cooled to -76° , and the resulting mixture was stirred for 22 hr. at this temperature. Since reaction at this temperature was negligible, the mixture was stirred at -45 to -50° for an additional 5.25 hr., and 2.97 g. (0.0175 mole) of 1-naphthyl isocyanate in 10 ml. of THF was then added. After this mixture had stood at room temperature for 19 hr., helium was bubbled through the reaction mixture to drive volatile materials into the cold trap. Vapor chromatographic analysis of the 5.92 g. of volatile liquid collected in 32% yield (spiropentane identified by comparison of retention time with that of a known sample). The remaining reaction mixture was poured into 200 ml. of ice-water and the resulting mixture evaporated to near dryness. The brown solid which formed was separated by filtration and dried (3.45 g.). Extraction with petroleum ether (b.p. 60–68°) yielded 1.58 g. of a brown insoluble powder. Chromatography on Florisil of the petroleum ether-soluble material gave as the only crystalline product 93 mg. of a solid, m.p. 158–159° (softened 144.5°), whose infrared spectrum was very similar to, although not quite superimposable, with that of an authentic sample of 1,1'-binaphthyl. None of the desired N-1-aphthyls.

hender sample of 1, 5 binaphilyt. Totice of the desired reference in th

(10) S. Winstein and E. M. Kosower, ibid., 81, 4399 (1959).

(11) (a) H. Hart and J. M. Sandri, *ibid.*, **81**, 320 (1959); (b) S. Borcic, M. Nikoletic and D. E. Sunko, *Chemistry & Industry*, 527 (1960).

(12) Melting points and boiling points are uncorrected. Infrared spectra were measured with a Perkin-Elmer model 21B spectrophotometer with sodium chloride optics. Gas chromatography was done with a Perkin-Elmer model 154B vapor fractometer, using helium as the carrier gas.

⁽⁷⁾ A direct conversion of I to XIV can be imagined, but does not appear favorable stereoelectronically.
(8) (a) J. C. Martin and D. J. Anderson have reported in a private

^{(8) (}a) J. C. Martin and D. J. Anderson have reported in a private communication that there is marked participation by sulfur in solvolysis of 3-thiacyclobutyl chloride. (b) K. B. Wiberg and R. P. Clula, THIS JOURNAL, **81**, 5261 (1959).

⁽⁹⁾ A. H. Fainberg and S. Winstein, ibid., 78, 2770 (1956).

phere) at a rate rapid enough to keep the reaction mixture at constant reflux. After addition was complete, the reaction mixture was heated at reflux temperature for 7.3 hr. and then cooled to room temperature. The inverse Grignard flask cooled to room temperature. The inverse Grignard flask was then transferred to one of the necks of a 500-ml. three-necked flask which had previously been charged with a solution of 39.3 ml. (0.412 mole) of ethyl chloroformate in 100 ml. of THF. After the ethyl chloroformate solution had been cooled to near 0°, the Grignard reagent was added to this rapidly stirred solution over a 2-hr. period (nitrogen atmosphere). The resulting reaction mixture was allowed atmosphere). The resulting reaction mixture was allowed to warm slowly to room temperature overnight and was then poured into approximately 1.51. of ice-water. The aqueous mixture was extracted with several portions of ether and the ether removed from the dried extracts by distillation through a 4.5-ft. spiral wire column. Fractionation of the residue from this distillation through a Holzman column¹³ afforded ethyl spiropentanecarboxylate of approximately 85% purity (b.p. 61-69°, 17 mm.) as determined by vapor chromatography (didecyl phthalate column). The yield of III, as calculated from vapor chromatograms of the several fractions obtained, was 49.3%. Pure ethyl spiropentanecarboxylate was isolated for n.m.r., infrared and elemental analyses by means of vapor chromatography.

Anal. Calcd. for $C_{s}H_{12}O_{2};\ C,\ 68.53;\ H,\ 8.63.$ Found: C, 68.21; H, 8.63.

The Grignard reagent from one run (diethyl ether solvent) was treated with 1-naphthyl isocyanate to obtain N-1-naphthylspiropentanecarboxamide, which was isolated in 6% yield (m.p. $164-167^{\circ}$) by chromatography on Florisil and recrystallization from benzene-petroleum ether. Several further recrystallizations raised the melting point to $167-169^{\circ}$.

Anal. Caled. for C₁₆H₁₅NO: C, 80.98; H, 6.37. Found: C, 80.79; H, 6.41.

Spiropentanecarboxylic Acid Hydrazide (IV).—A solution of 7.25 g. of ethyl spiropentanecarboxylate (purity approximately 85%) in 15 ml. of absolute ethanol was added dropwise to 30 ml. of stirred, refluxing 85% hydrazine hydrate over about a 50-min. period. The reaction mixture was then stirred for 2 hr. at reflux temperature and evaporated to dryness. The resulting white crystalline residue was recrystallized twice from benzene to yield 4.5 g. (80% yield) of IV, m.p. 115–117.5° (softened approximately 100°). The infrared spectrum of this material was identical to that of purified IV (m.p. 115.5-117°) obtained by sublimation and repeated recrystallization.

Anal. Calcd. for C₆H₁₀N₂O: C, 57.11; H, 7.99. Found: C, 56.96; H, 7.77.

 β -Naphthyl Spiropentylcarbamate (V).—To a solution of 2.929 g. (0.0232 mole) of spiropentanecarboxylic acid hydrazide in 54 ml. of water was added 13.5 ml. of 6 N hydrochloric acid and 60 ml. of a mixture of 5 parts benzene and 3 parts *n*-heptane (by volume). After this mixture was cooled to -5 to -10° , a solution of 3.00 g. (0.0435 mole) of sodium nitrite in 6 ml. of water was added to the rapidly stirred mixture over approximately a 20-min. period. The mixture was then stirred for 10 min. at -5 to -10° and the organic layer separated. The aqueous solution was extracted with 4 portions of benzene-heptane mixture and the combined organic extracts washed with 5% sodium bicarbonate solution and with water. The solution was then dried for 5 min. in the cold over calcium chloride. The dried solution of the azide was heated under reflux for 5 hr. A solution of 8.65 g. (0.0600 mole) of β -naphthol in 60 ml. of hot benzene plus 0.1 ml. of a 10% solution of triethylamine in n-heptane14 was then added and the resulting solution heated under reflux for 91 hr. Evaporation of the reaction mixture to dryness afforded 11.228 g. of crystalline solid. Excess β -naphthol was easily removed by sublimation from this crude mixture at approximately 60° under reduced pressure. The residue from this sublimation was recrystallized from benzene-petroleum ether to yield 3.992 g. of β -naphthyl spiropentylcarba-mate, m.p. 117–118.5°. An additional 0.434 g. of V was obtained by concentration of the mother liquors and recrystallization of the crude material so obtained. The total yield of V was 75%.

Anal. Caled. for C₁₆H₁₅NO₂: C, 75.86; H, 5.97. Found: C, 75.91; H, 5.95.

Basic Hydrolysis of β -Naphthyl Spiropentylcarbamate (V). Isolation of 1-Spiropentyl-3-phenyl-2-thiourea (VII). A mixture of 0.103 g. (0.000407 mole) of V and 5 ml. of 1 Nsodium hydroxide was shaken in a sealed flask at room temperature for 47.5 hr. The reaction mixture was made strongly acid with 3 N perchloric acid and the precipitate of β -naphthol removed by extraction with ether. From this ether solution, 56.0 mg. (95%) of crude β -naphthol having a melting point of 114–121.5° (softened at approximately 90°; melt cloudy) was isolated. After traces of ether had been removed, the pH of the extracted aqueous solution was adjusted to about 8, and 0.49 ml. (0.00408 mole) of phenyl isothiocyanate was added. This mixture was shaken at room temperature for about 1 hr. (pH kept at approximately 8). An excess of 1 N sodium hydroxide was then added and the reaction mixture shaken for an additional hour. Extraction of the basic solution with ether and evaporation of the ether extracts to dryness yielded an oil which deposited 59.8 mg. of crude VII, m.p. 102.5–107° (melt cloudy), upon addition of petroleum ether. Recrystallization of this material from petroleum ether afforded 49.2 mg. (55.4%) of VII, m.p. 104-107°; n.m.r. analysis was obtained on this material. A pure sample of VII (m.p. 105.5-107.5°, shrinking slightly at 103°) was obtained for infrared and carbon-hydrogen analyses by repeated recrystallization from both benzenepetroleum ether and ethanol-petroleum ether.

Anal. Calcd. for $C_{12}H_{14}N_2S$: C, 66.01; H, 6.46. Found: C, 66.16; H, 6.27.

Attempted Hydrolysis of Spiropentyl Chloride (II).-To a solution of 35 g. (0.206 mole) of silver nitrate in a minimum amount of water was added 12 g. (0.3 mole) of sodium hydroxide also dissolved in a small amount of water. The mixture was shaken and the resulting brown precipitate of silver oxide washed with distilled water until the wash solution tested neutral with pH paper. To the moist, freshly prepared silver oxide was added 50 ml. of water and 5.01 g. (0.0489 mole) of spiropentyl chloride. The resulting mixture was shaken at room temperature for approximately 17 hr. Since it appeared that reaction had not occurred, 8.3 g. (0.0489 mole) of silver nitrate was added and the mixture shaken for an additional 1.5 hr. Sodium nitrate was then added to salt out any water-soluble alcohols, and the reaction mixture was centrifuged. A permanganate test run on a portion of the resulting organic layer indicated no unsaturation, and a vapor chromatogram (didecyl phthalate column) of this substance showed starting material as the only product (identified by comparison of retention times). The reaction mixture was then allowed to stand at about 10° for approximately 8 months. At the end of this time, infrared analysis of a portion of the organic layer indicated it to be chiefly starting material.

In another experiment, 66.4 mg. of spiropentyl chloride was heated under reflux with a solution of 0.48 g. of silver nitrate in 8 ml. of water. After 12.25 hr. at reflux temperature and 2 days at room temperature, only about 3 mg. (approximately 3% of theoretical) of a darkened precipitate of silver chloride was isolated.

Diazotization of Spiropentylamine.—A mixture of 2.004 g. (0.00793 mole) of β -naphthyl spiropentylcarbamate (V) and 108 ml. of 1 N sodium hydroxide was shaken in a sealed flask for 42 hr. The reaction mixture was then acidified with 3 N perchloric acid and the precipitate of β -naphthol removed by extraction with ether. After traces of ether were removed, the acidic, aqueous solution was diluted in a volumetric flask to 200 ml. and the β H adjusted to 1.23 with perchloric acid. The solution was transferred to a flask connected to a Dry Ice trap and the apparatus swept with nitrogen. A solution of 2.202 g. (0.0319 mole) of sodium nitrite in 50 ml. of water was then added and the resulting mixture allowed to stand at room temperature for 41 hr. At the end of this time, the cold trap contained what appeared to be only a minute quantity of water which was undoubtedly carried over by the nitrogen evolved during the reaction. The reaction products were then salted out with sodium perchlorate and extracted from the aqueous solution with several portions of ether. The ether extracts were dried over magnesium sulfate and the ether removed by distillation through a 4.5-ft. spiral wire column. The residue

⁽¹³⁾ C. W. Gould, Jr., G. Holzman and C. Niemann, Anal. Chem., 20, 361 (1948).

⁽¹⁴⁾ N. D. Cheronis and J. B. Entriken, "Semimicro Qualitative Organic Analysis," Interscience Publishers, Inc., New York, N. Y., 1957, p. 516.

4.311 g.) from this distillation gave a positive permanganate test for unsaturation. Vapor chromatographic analysis of this residue (didecyl phthalate column) indicated two major components (VIII and IX) formed in 32.5 and 6.7% yield, respectively. Two minor components were also observed, but these were formed in only about 3% total yield and were therefore not investigated further. By means of vapor chromatography, components VIII and IX were isolated for infrared and n.m.r. analyses in purities of 98.4 and 94.1%, respectively (determined by vapor chromatography of VIII in ether and IX in carbon tetrachloride solution). In both cases, the only contaminant observed was the other isomer. An analytical sample of VIII was obtained by refractionation of an ether solution of 98.4% pure material by vapor chromatography.

Anal. Caled. for C₅H₈O: C, 71.39; H, 9.59. Found: C, 71.00; H, 10.04.

3-Methylenecylobutyl 3,5-Dinitrobenzoate.—A solution of approximately 70 mg. of 3-methylenecyclobutanol (VIII) in a mixture of carbon tetrachloride and ether, which contained 49 mg. of acetic acid as an impurity, was combined with 0.394 g. of 3,5-dinitrobenzoyl chloride and 1 ml. of pyridine and the resulting mixture heated under reflux for 55 min. The dark brown mixture was then cooled and poured into ice-water. The aqueous mixture was filtered and the precipitate and filtrate extracted separately with ether. The ether extracts were combined and washed first with saturated

sodium bicarbonate solution and then with water. Evaporation of the ether solution to dryness yielded a red oil which deposited 76 mg. of pink crystals, m.p. $100-103.5^{\circ}$ (softened 94°), upon addition of petroleum ether. An analytical sample (white crystals, m.p. $102-105^{\circ}$) was obtained by chromatography on Florisil, recrystallization from benzenepetroleum ether and sublimation under reduced pressure. The infrared spectrum of the material so obtained was identical in every respect with the spectrum of the crude product.

Anal. Caled. for $C_{12}H_{10}N_2O_6$: C, 51.80; H, 3.62. Found: C, 51.99; H, 3.74.

Nuclear Magnetic Resonance Spectra.—The n.m.r. spectra were measured with a Varian high resolution spectrometer (model V-4300B with super stabilizer). The spectra of III and IV were measured at 40 mc. with external methylene chloride as standard. Compound III was examined as a carbon tetrachloride solution containing 235 mg./ml. and IV as a deuterium oxide solution containing 200 mg./ml. The signal of the methylene chloride standard was taken to be at -0.65 p.p.m. from water. The spectra of the other substances were measured at 60 mc. with tetramethylsilane as an internal standard using the following solutions: V, 104 mg./ml. in carbon disulfide-phenol; VIII, 164 mg./ml. in carbon disulfide-phenol; VIII, 216 mg./ml. in carbon tetrachloride; IX, approx. 60 mg./ml. in carbon tetrachloride. The signal of the tetramethylsilane standard was taken to be at 4.78 p.p.m. from water.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF CALIFORNIA, LOS ANGELES 24, CALIF.]

The Addition of Hydrogen Chloride to Aliphatic Allenic Hydrocarbons¹

By Thomas L. Jacobs and Robert N. Johnson

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The addition of hydrogen chloride to allene and 1,2-butadiene at -78° involves attack at a terminal methylene group of the allenic system. Allene requires a catalyst such as bismuth trichloride and yields a mixture of 2-chloropropene and 2,2-dichloropropane. Slight rearrangement to propyne occurs during the addition. 1,2-Butadiene yields a mixture of *trans*-and *cis*-2-chloro-2-butene in the ratio 87/13; 2-butyne is also formed but does not add hydrogen chloride under the conditions. The orientation of addition of hydrogen chloride to the allenic system is reversed when one end of the system is disubstituted; attack occurs at the middle carbon. At -78° 3-methyl-1,2-butadiene gives a mixture of 3-chloro-3-methyl-1-butene in the ratio 64/36; rearrangement to isoprene also occurs. It was shown that these allylic chlorides do not rearrange under the conditions employed. Hydrogen chloride adds to isoprene more rapidly under the same conditions to give the same products but the ratio is 83/17. This shows that not all of the addition to the allene occurs through inspected if present to the extent of 0.1%. The principal product of the addition products were absent; they could have been detected if present to the extent of 0.1%. The principal product of the addition of 2,4-dinitrobenzene-sulfenyl chloride to allene is 2-(2,4-dinitrobenzenethio)-3-chloro-1-propene which represents the opposite orientation to that observed with hydrogen chloride. This reagent gives mixtures with 1,2-butadiene and 3-methyl-1,2-butadiene; pure addition products were not isolated.

The ionic addition of unsymmetrical reagents HA to allenic systems has not been studied extensively and some uncertainty remains about even the orientation in such reactions. Hydration of allene itself in the presence of sulfuric acid was shown to yield acetone in the first definitive paper on this compound² and aliphatic monosubstituted allenes $RCH=C=CH_2$ yield methyl ketones.^{3–5} This orientation for the addition of reagents HA as H and A appears to be general for these classes of allenes. Other examples include the addition of

(1) Taken from a dissertation submitted by Robert N. Johnson in partial fulfillment of the requirements for the Ph.D. degree, University of California, Los Angeles, February, 1960. Most of this work was carried out under a contract with the Office of Ordnance Research, U. S. Army. Reproduction in whole or in part is permitted for purposes of the U. S. Government.

(2) G. Gustavson and N. Demjanoff, J. prakt. Chem., [2] 38, 201 (1888).

hydrogen fluoride to allene to yield 2,2-difluoropropane⁶ and of methyl alcohol to 1,2-hexadiene in the presence of boron trifluoride and mercuric oxide to yield the dimethyl ketal of 2-hexanone.⁵ None of these reactions establishes which double bond is attacked first.

The reaction of 1,2-hexadiene with dry hydrogen chloride in the presence of bismuth trichloride gives a mixture of 2-chloro-2-hexene and 2,2-dichlorohexane.⁵ This establishes that reaction can occur first at the terminal double bond, but attack at the secondary carbon is not excluded because the dichloride may have arisen mainly from 2-chloro-1hexene which could react with hydrogen chloride more rapidly than its isomer.

A single example of the addition of hydrogen chloride to a tertiary allene has been reported⁷;

⁽³⁾ M. Bouis, Ann. chim. (Paris), [10] 9, 402 (1928).

⁽⁴⁾ W. H. Carothers and G. J. Berchet, THIS JOURNAL, **55**, 1628 (1933).

⁽⁵⁾ G. F. Hennion and J. J. Sheehan, ibid., 71, 1964 (1949).

⁽⁶⁾ P. R. Austin, U. S. Patent 2,585,529, Feb. 12, 1952; C.A., 46, 3799 (1952).

⁽⁷⁾ I. W. Kondakov, J. Russ. Phys.-Chem. Soc., 21, 36 (1889); Chem. Zentr., 61, I, 311 (1890).