yellow band was observed to pass down the column, and was preceded by a very slight second band. When the leading band was about 2 cm. from the bottom of the column, collection of the effluent in 5-ml. portions was started. Titration of the effluent fractions gave the values plotted in Fig. 1. The minor band evidently was formed by too small an amount of acid to be detected by the titration procedure used, which in control experiments[3] has been found adequate to reveal the presence of 7% or more of a second acid. Total recovery of the acid placed on the column was 92.2%, which corresponds to an over-all yield of 71.4% of *n*-heptanoic acid.

In a second experiment a similar solution of degradation acid from another portion of the above crude dihydroxy acid was used for a mixed chromatogram. An aliquot containing 0.0286 milliequivalent of acid was mixed with 0.0197 milliequivalent of *n*-heptanoic acid, and the mixture subjected to partition chromatography as before. The results are given in Fig. 2. Total recovery from the column in this case was 96%, and only one band could be detected.

A sample of *trans*-11-octadecenoic acid obtained by selenium isomerization of the *cis* acid at 180° was carried through an exactly similar degradation process, and the monocarboxylic acid fraction, which was obtained in 62% over-all yield, was shown by mixed chromatogram to be *n*-heptanoic acid. In this case also no trace of a second band could be seen on the column or detected by titration of the effluent fractions. Degradation of the *cis*-acid and chromatographic analysis was carried out in the same manner with similar results.

Summary

Since the X-ray diffraction pattern of synthetic *trans*-11-octadecenoic acid has been reported to differ from that of natural vaccenic acid and to resemble that of elaidic acid, the structure of the synthetic acid was re-examined. The identity of the synthetic product as a $\Delta^{11,12}$-octadecenoic acid was definitely established.

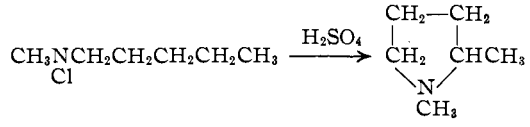
MADISON, WIS. RECEIVED OCTOBER 24, 1949

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, STATE UNIVERSITY OF IOWA]

Preparation of N-Methylgranatanine

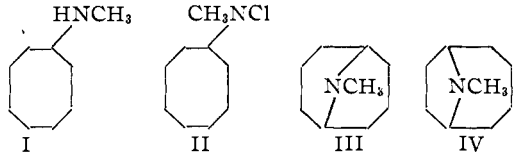
BY STANLEY WAWZONEK AND PAUL J. THELEN[1]

N-Haloamines are converted by heat in sulfuric acid solution into N-substituted pyrrolidines.[2] N-Chloroamines have been found by



Coleman and co-workers[3] to be more applicable under these conditions than the N-bromoamines and to be suitable for preparing bicyclic compounds like tropane.[4]

The cyclization of the N-chloroamine (II) derived from N-methylcycloöctylamine (I) has now been studied in order to determine whether N-methylgranatanine (III) or 9-azabicyclo[4,2,1]-nonane (IV) would be produced. The reaction leading to the latter (IV) would be similar to that involved in the formation of pyrrolidines, whereas a reaction leading to the former (III)



would constitute a new cyclization method for bridged piperidine structures (III) and would be a new synthesis of N-methylgranatanine (III). Fisher–Hirschfelder models favored the formation of N-methylgranatanine (III). During the course of this work sufficient evidence was obtained to propose a mechanism for the reaction.

N-Chloro-N-methylcycloöctylamine (II) was converted in sulfuric acid into varying yields of N-methylgranatanine (III) under conditions which are summarized in Table I. The cyclization was found to proceed consistently in best yields in sulfuric acid at 0–8° in the presence of ultraviolet light and chlorine. The structure of the product was demonstrated by the formation of a picrate and a chloroplatinate which did not

TABLE I

RING CLOSURES OF N-CHLORO-N-METHYLCYCLOÖCTYLAMINE (55.7 MILLIMOLES)

Run	Chlorination, %	H_2SO_4 concn., %	Temp., °C.	Time, hours	Yield, % Granatanine picrate	Yield, % II° Amine recovered as sulfonamide
1	97	84	65	0.5	15	64
2	97	84	65	0.25	22	55
3	91.5	84	65	0.25	10	42.8
4	46.5	84	65	0.5	23	54.5
5	91.7	84[a]	25	22.0	15.3	34
6	87.8	84[b]	25	22.0	3.3	50.4
7	93.5	84[a]	65	.5	10.4	45.4
8	83.6	87[c]	5–8	22.0	24.4	35.8
9	94.2	84[d]	5–8	8.0	11.9[e]	23.7
10	79.7	84[c]	0–8	18.0	22.6	33.3

[a] Irradiated with ultraviolet light. [b] Carried out in complete darkness. [c] Irradiated with ultraviolet light in the presence of chlorine. [d] Carried out in complete darkness in the presence of 6.6 ml. of 30% H_2O_2. [e] 19.1% of the N-chloroamine was recovered.

(1) Abstracted from a thesis by Paul J. Thelen presented to the Graduate College of the State University of Iowa in partial fulfillment of the requirements for the Ph.D. degree, January, 1948.

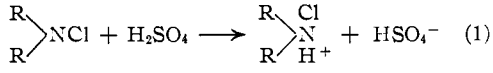
(2) Britton, U. S. Patent 1,607,605; *C. A.*, **21**, 249 (1927).

(3) (a) Coleman and Goheen, THIS JOURNAL, **60**, 730 (1938); (b) Coleman, Nichols and Martens, *Org. Syn.*, **25**, 14 (1945); (c) Coleman, U. S. Patent No. 2,285,413 (1942).

(4) Coleman and Carnes, *Proc. Iowa Acad. Sci.*, **49**, 288 (1942) [Abstract].

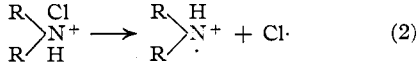
lower the melting point of similar derivatives of N-methylgranatanine (III) prepared from pseudopelletierene.[5] None of the 9-azabicyclo-[4,2,1]nonane derivative (IV) was isolated.

Examination of the results in Table I suggests the following possible mechanism for the cyclization. The first step is the formation of a salt between the chloroamine and the sulfuric acid and is borne out by the extraction of the N-chloroamine from ligroin by sulfuric acid. In the next step the cation is converted into a free radical (an aminium ion)[6] by either heat, hydrogen peroxide (Run 9) or irradiation with ultraviolet light alone



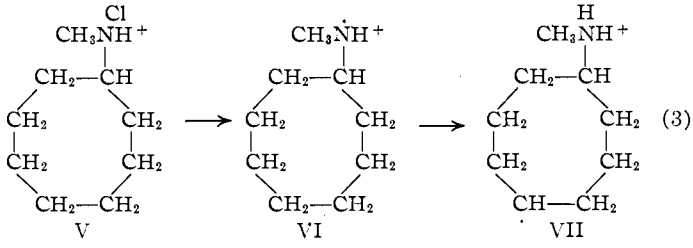
(1)

or in the presence of chlorine, since runs in complete darkness at room temperature gave very

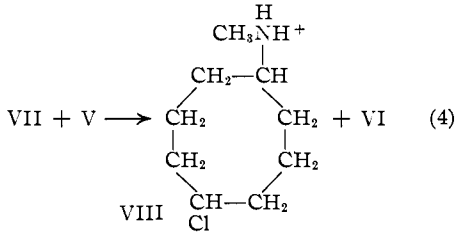


(2)

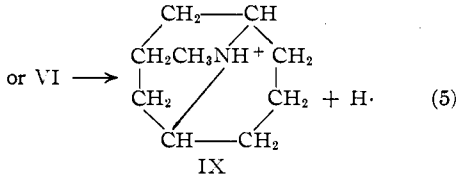
little ring closure (Run 6). The aminium ion thus formed keeps dimerization at a minimum and may undergo one of the following reactions.



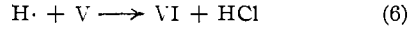
(3)



(4)

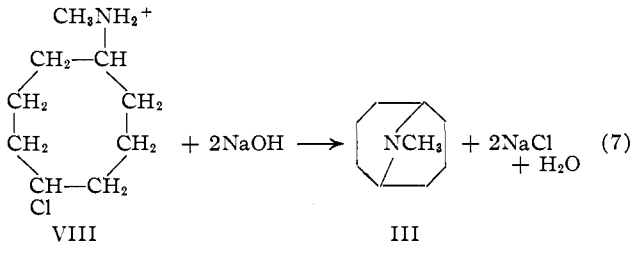


(5)



(6)

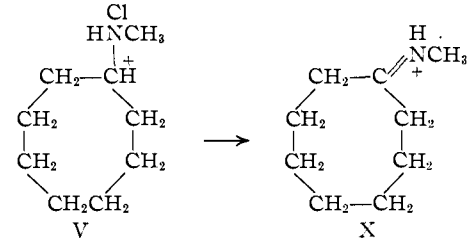
The aminium ion (VI) may abstract a hydrogen from a sterically favored carbon atom and form a new free radical (VII) which may start a chain reaction and form the chlorocycloöctylmethyl amine salt (VIII). The latter (VIII) is then cyclized during the neutralization of the reaction mixture with alkali. In the other possibility (equation 5) the aminium ion (VI) undergoes an



(7)

VIII III

intramolecular S_N2 type of attack on a sterically favored carbon atom and forms a ring together



V X

with a hydrogen atom which continues the reaction. Evidence for the first path is the formation of secondary amine and high molecular weight material in the cyclization. These products could arise from radical (VII) by disproportionation. The second mechanism represents a reaction which apparently only occurs in gas phase, free radical reactions. The liberation of hydrogen chloride which would be indicative of such a step, must be formed directly from the N-chloroamine salt (V) by involving the hydrogen in a manner similar to that observed with dibutyl chloroamine.[7] The mechanism is being investigated further with simpler compounds.

Experimental[8]

N-Methylcycloöctylamine.—Cycloöctanone (79 g.) was heated with 500 ml. of a 20% methanolic methylamine solution and sodium ethoxide (75 g.) in 425 ml. of ethanol in an iron bomb for six hours at 95°. After cooling the solution was added to one liter of absolute ethanol and treated with sodium (200 g.) at such a rate that reflux was maintained. Toward the end of the reaction, the solution had to be heated on a steam-bath to complete the reduction. The resulting solution was diluted with 500 ml. of water and steam distilled into excess hydrochloric acid. Evaporation of the distillate gave the amine hydrochloride. The amine was obtained by treating the salt in water (150 ml.) with 40% sodium hydroxide. Extraction with ether gave 69 g. (78%) of N-methylcycloöctylamine, b. p. 201–201.5°; 85–87° (14–15 mm.); $n^{26}D$ 1.4740; d^{34}_4 0.906. *Anal.* Calcd. for $C_9H_{19}N$: C, 76.52; H, 13.56. Found: C, 76.67; H, 13.66.

N-Methylcycloöctylamine was converted into the picrate by treating the amine in ether with a saturated ethanol solution of picric acid until the ether became acid to damp nitrazene paper. Upon removal of the solvent a yellow oil was obtained which crystallized from a water-alcohol mixture; m. p. 128–129°. *Anal.* Calcd. for C_{15}-

(5) Cope and Overberger, THIS JOURNAL, **70**, 1433 (1948).

(6) Sidgwick,'s "Organic Chemistry of Nitrogen," Oxford University Press, 1946, p. 64.

(7) Wright, THIS JOURNAL, **70**, 1958 (1948).

(8) Melting points and boiling points are not corrected.

$H_{22}O_7N_4$: C, 48.64; H, 5.99; N, 15.13. Found: C, 48.32; H, 5.93; N, 14.95. N-Methylcycloöctylamine gave an oily sulfonamide which could not be crystallized.

N-Methylgranatanine.—A mixture of N-methylcycloöctylamine (7.75 g.) in purified petroleum ether (30–38°) (50 ml.), ice (20 g.) and 12% sodium hydroxide (100 ml.) was treated in a pressure bottle with chlorine gas under 30 mm. of pressure until no more fuming was noticed. During the addition the bottle was cooled in an ice-bath. The petroleum ether solution of the chloroamine was separated and the aqueous layer extracted with two 20-ml. portions of cold petroleum ether. The extracts were combined, washed with 12% sodium hydroxide (50 ml.) and dried for one hour over anhydrous sodium carbonate in a flask immersed in an ice-bath. The solution was then analyzed for chloroamine by adding a cold sample (20 ml.) to a solution of potassium iodide (3 g.) in a mixture of acetic acid (10 ml.), distilled water (20 ml.) and acetone (20 ml.). The liberated iodine was titrated with standard 0.100 *N* sodium thiosulfate using the disappearance of iodine as an end-point. The cold petroleum ether solution containing 0.054 mole of chloroamine was extracted with two 30-ml. portions of cold 84% sulfuric acid (80 ml. of concentrated sulfuric acid, 20 ml. of water) and then analyzed for completeness of extraction of chloroamine. If this was incomplete a third extraction with cold 84% sulfuric acid (40 ml.) was made and the extract combined with the other two. If the extraction was complete, the two extracts were combined and added to 40 ml. of cold 84% sulfuric acid. The combined solutions were treated in various ways listed in Table I. At the end of the reaction the sulfuric acid solution was poured onto 400 g. of ice, diluted with water to 1000 ml. and extracted with 100 ml. of ligroin. The ligroin was tested for the presence of unreacted chloroamine.

The aqueous acid solution of the amine was placed in a 5-liter flask fitted for steam distillation and equipped with an addition funnel through which 300 ml. of 50% sodium hydroxide was added to make the solution basic. Steam distillation into dilute hydrochloric acid was continued until about 3–4 liters of distillate were obtained or until the distillate came over neutral to nitrazine paper. Evaporation of the distillate to dryness under reduced pressure (30–50 mm.) gave the amine hydrochloride. This salt was dissolved in water (100 ml.) in a Pyrex flask with a glass stopper, benzenesulfonyl chloride (20 g.) and 50% sodium hydroxide (30 ml.) were added and the resulting mixture shaken for thirty minutes. After cooling the mixture was made acid with concentrated hydrochloric acid and the N-benzenesulfonyl-N-methylcycloöctylamine which forms as a viscous oil was extracted with three portions each of 50 ml. of ether. The ether solution upon drying and removal of the solvent gave 8.7 g. of the sulfonyl derivative which is equivalent to 55.6% of the unchanged amine. The remaining aqueous acidic solution was made alkaline with 50% sodium hydroxide and extracted with three 50-ml. portions of ether. The ether solution after drying over potassium hydroxide was treated with a saturated ethanol solution of picric acid and gave 4.4 g. of N-methylgranatanine picrate. After one recrystallization from ethanol the picrate melted at 295–300°. Piccinini[9] reports a sample softening at 270° and melting at 300°. A mixture with a sample prepared from pseudopelletierene[5] melted without any lowering.

N-Methylgranatanine Chloroplatinate.—N-Methylgranatanine picrate (2.0 g.) was treated with excess sodium hydroxide and the liberated free amine was extracted with ether. The ether solution was extracted with 5 ml. of 6 *N* hydrochloric acid and the resulting acid solution of the amine was treated with the calculated amount of platinic chloride. The chloroplatinate precipitated immediately and was filtered. Recrystallization from water gave a product melting at 220–221°. Willstätter and Veraguth[10] report 220–221°. A mixture with a sample prepared from pseudopelletierene[5] melted with no lowering.

Acknowledgment.—The authors wish to thank Dr. A. C. Cope and Dr. C. G. Overberger of Massachusetts Institute of Technology for a sample of pseudopelletierine.

Summary

N-Methylgranatanine has been prepared by the irradiation with ultraviolet light of N-chloro-N-methylcycloöctylamine in sulfuric acid.

A mechanism has been proposed for the cyclization of N-haloamines in sulfuric acid.

(9) Piccinini, *Gazz. chim. ital.*, **32**, I, 260 (1902).

(10) Willstätter and Veraguth, *Ber.*, **38**, 1984 (1905).

IOWA CITY, IOWA RECEIVED NOVEMBER 28, 1949

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY AT THE OHIO STATE UNIVERSITY]

The Synthesis of Some 4-Alken-1-ols[1]

BY RICHARD C. BRANDON,[2] JOHN M. DERFER AND CECIL E. BOORD

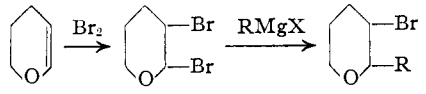
The β-bromoether synthesis has been highly developed as a method for preparing olefins.[3] The present paper describes a modification of this synthesis whereby unsaturated carbinols containing more than five carbon atoms can be prepared in acceptable yield from the commercially available 3,4-dihydro-1,2-pyran.

(1) This paper was abstracted from a dissertation presented by R. C. Brandon to the Graduate School of The Ohio State University in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

(2) Present address: Standard Oil Development Company, Elizabeth, New Jersey.

(3) (a) Swallen and Boord, THIS JOURNAL, **52**, 651 (1930); (b) Dykstra, Lewis and Boord, *ibid.*, **52**, 3396 (1930); (c) Shoemaker and Boord, *ibid.*, **53**, 1505 (1931); (d) Schmitt and Boord, *ibid.*, **54**, 751 (1932); (e) Soday and Boord, *ibid.*, **55**, 3293 (1933); (f) Schurman and Boord, *ibid.*, **55**, 4930 (1933).

Paul[4] found that with bromine 3,4-dihydro-1,2-pyran formed a very active addition product which condensed readily with ethyl and phenyl Grignard reagents according to the following equations. These reactions with a cyclic ether are analogous to those which take place with the open



chain compounds; in either type of α,β-dibromoether the α-bromine is many thousand times more reactive than the β-bromine.[3]

In the present work a series of 2-alkyl-3-

(4) Paul, *Compt. rend.*, **198**, 1246 (1934); *Bull. soc. chim.*, [5] **2**, 311 (1935).