(a) *1,1-Dinitroethane ammonium salt,* m.p. 116° dec., lit., m.p. 90–93° dec.,[9] 127–128°.[10]

Anal. Calcd. for $C_2H_7N_3O_4$: C, 17.53; H, 5.14. Found: C, 17.53; H, 5.07.

(b) *1,1-Dinitropropane ammonium salt,* m.p. 117° dec.

Anal. Calcd. for $C_3H_9N_3O_4$: C, 23.84; H, 6.00; N, 27.81. Found: C, 23.38, 23.97; H, 5.25, 5.53; N, 27.68, 27.18.

(c) *1,1-Dinitrobutane ammonium salt,* m.p. 128° dec.

Anal. Calcd. for $C_4H_{11}N_3O_4$: C, 29.09; H, 6.71; N, 25.45. Found: C, 29.30, 29.47; H, 7.03, 6.71; N, 25.67.

(d) *1,1-Dinitropentane ammonium salt,*[11] m.p. 131–132° dec.

Anal. Calcd. for $C_5H_{13}N_3O_4$: C, 33.52; H, 7.31; N, 23.46. Found: C, 33.30; H, 7.51; N, 23.66.

Infrared absorption spectra were determined with a Perkin-Elmer Model 21 spectrophotometer.

LOS ALAMOS, N. M.

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[9] T. S. Belew, C. E. Grabiel, and L. B. Clapp, *J. Am. Chem. Soc.,* **77,** 1110 (1955).

[10] M. F. Hawthorne, *J. Am. Chem. Soc.,* **78,** 4980 (1956).

[11] This salt was prepared from the dinitroparaffin and ammonia in chloroform.

[CONTRIBUTION FROM THE CAROTHERS RESEARCH LABORATORY, TEXTILE FIBERS DEPARTMENT, E. I. DU PONT DE NEMOURS AND CO., INC.]

The Beckmann Rearrangement of Fenchone Oxime

R. W. COTTINGHAM

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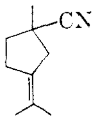
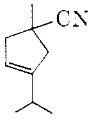
The Beckmann rearrangement of fenchone oxime has been carried out under a variety of conditions to give apparently exclusive formation of products arising from scission of the bridgehead bond. It would appear that both the normal and anomalous products are derived from the concerted *anti*-migration process generally accepted as the initial step in the Beckmann rearrangement, and that the stability of the incipient carbonium ion adjacent to the oximino function is of importance only in determining the relative amounts of the two products.

The literature of the Beckmann rearrangement contains numerous examples of a competitive reaction in which an unsaturated nitrile rather than the usual amide is produced by treatment of a ketoxime with a strong acid.[1–3] Notable among compounds undergoing this anomalous reaction are the oximes of bicyclic ketones having bridgeheads adjacent to the oximino functions. The oximes of camphor,[4] verbanone,[5] and various norcamphane derivatives[6,7] give, under conditions commonly employed for the Beckmann rearrangement, mixed products to which the competitive reaction contributed appreciably. The rearrangement of fenchone oxime (I) is of particular interest in this connection, for despite the ditertiary structure of the oxime, both the normal and anomalous rearrangements proceeded exclusively *via* scission of the bridgehead bond.

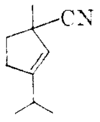
Treatment of the sharp melting oxime with *p*-toluenesulfonyl chloride and pyridine, phosphorus pentachloride, or sulfuric acid lead in all cases to the formation of a single lactam which was isomeric with the oxime and a liquid which from its infrared spectrum was obviously an unsaturated nitrile (—C≡N stretching 4.50 μ, C=C stretching 6.03 μ, vinyl C—H stretching 3.32 μ).[8] The inference from infrared data of the presence of a single vinyl hydrogen in this nitrile was confirmed by the ratio of vinyl to total hydrogen as determined by proton magnetic resonance, thus eliminating the possibility that the product might be the isopropylidenecyclopentanonitrile, VI, or any of the three isomeric structures possessing two vinyl hydrogens.



VI



VII



VIIa

From further consideration of the proton resonance data which are summarized in Table I, it appears that the unsaturated nitrile must have the

TABLE I

PROTON RESONANCE DATA

Group	Cps. from H_2O at 56.4 Mc.	Chemical Shift	
		Observed	Accepted[9]
$-\underset{CH_3}{\overset{\vert}{\underset{\vert}{C}}}-CH_3$	214	3.8	4.1 ± 0.6
$=\overset{\vert}{\underset{\vert}{C}}-CH_3$	183	3.2	3.3 ± 0.5
$=\overset{\vert}{\underset{\vert}{C}}-CH_2-$	148	—	—
$-\overset{\vert}{\underset{\vert}{C}}-H$	127	—	—
$=\overset{\vert}{\underset{\vert}{C}}-H$	−23	−0.4	−0.6 ± 0.7

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[1] A. H. Blatt, *Chem. Revs.,* **12,** 215 (1933).

[2] B. Jones, *Chem. Revs.,* **35,** 335 (1944).

[3] L. G. Donaruma and W. Z. Heldt, *Org. Reactions,* (in press).

[4] J. Bredt and W. Holz, *J. prakt. Chem.,* **95,** 133 (1917).

[5] H. Wienhaus and P. Schumm, *Ann.,* **439,** 38 (1924).

[6] M. Gates and S. P. Malchick, *J. Am. Chem. Soc.,* **79,** 5546 (1957).

[7] H. K. Hall, Jr., *J. Am. Chem. Soc.,* **82,** 1209 (1960).

[8] L. J. Bellamy, *The Infrared Spectra of Complex Molecules,* Methuen and Co., Ltd., London, 1956.

[9] J. D. Roberts, *Nuclear Magnetic Resonance,* McGraw-Hill, New York, 1959, p. 23.

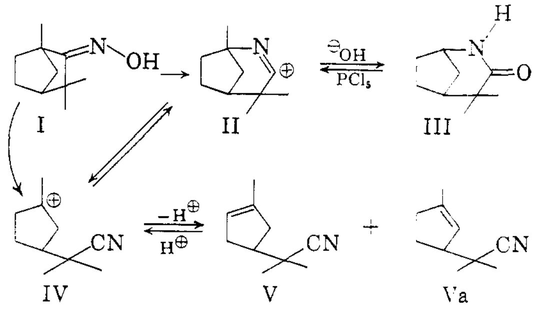
structure V or Va rather than the possible, albeit less likely, isomeric structures VII or VIIa, as the major peak attributed to the *gem* methyls was extremely sharp and devoid of any indication of the splitting expected of the isopropyl group common to the latter pair. Moreover, the band at 183 cps. appears to require the presence of the allylic methyl group of the structures V and Va.

As a mixture of α- and β-fencholenonitriles (V and VI) has been reported to arise from the treatment of fenchone oxime with boiling 5% sulfuric acid,[10] repetition of the work was undertaken for the purpose of comparing the mixed product with that obtained under dehydrating conditions. The nitrile obtained from the dilute acid treatment of the oxime was indistinguishable in infrared and proton resonance spectra from a sample of the product of the reaction with *p*-toluenesulfonyl chloride in pyridine. Vapor phase chromatography[11] showed no separation of the product isomers despite the fact that they are reported to differ in boiling point by 7°. Moreover, alkaline hydrolysis under conditions reported by Cockburn to give good conversion of V to α-fencholenamide of VI to β-fencholenic acid yielded largely amide and recovered nitrile with a total crude acidic product which accounted for only 10% of the theoretical amount. That this product was largely α-fencholenic acid was shown by a strong proton resonance band for vinyl hydrogen, vapor phase chromatography which gave one peak accounting for at least 80% of the crude mixture, and conversion of the crude acid to an amide identical with that obtained in the hydrolysis step by treatment with oxallyl chloride and ammonia.

The disparity between the results of the present and earlier studies may be attributable to a difference in isomeric purity of the starting materials. The assumption that the oxime employed in the earlier work contained an appreciable amount of the low melting isomer described by Delepine[12] would account for the formation of mixed rearrangement products. As the low melting oxime is unstable with respect to the high melting isomer in alcohol solution, it would appear that the alcohol-recrystallized starting material employed in the present work contained little if any of the unstable isomer. From the present data it may be concluded that the nitrile produced from the high melting isomer of fenchone oxime arises preponderantly if not exclusively from cleavage of the bridgehead bond even in dilute aqueous acid.

The identity of the lactam was established as 1,4,4-trimethyl-2-azabicyclo[3.2.1]octan-3-one (III) by interconversion with the nitrile. Treatment of the lactam with phosphorus pentachloride under the same conditions as were employed in the Beckmann rearrangement produced an unsaturated nitrile identical in infrared spectrum with that obtained from the rearrangement; moreover, a mixture of the two nitriles was inseparable by vapor phase chromatography.[11] Conversion of the original nitrile to the lactam was effected by the Ritter reaction[13] with sulfuric acid, and the lactam formed in this manner was shown to be identical with that produced directly from the oxime in melting point, mixed melting point, and infrared spectrum. While the yield of lactam derived from the Ritter reaction was poor, these interconversions determine unequivocally that both of the isolated products (accounting in one case for 96% of the theoretical total) arise from cleavage of the bridgehead bond.

This unidirectional rearrangement would appear to imply that the initial step in both the normal and anomalous reactions involves a concerted cleavage of the N—O bond and migration of either the bridgehead atom or the electrons involved in the bridgehead bond to form the intermediate ions II or IV respectively. That either of these processes is compatible with the generally accepted *trans*-migration mechanism of the Beckmann rearrangement is apparent from a consideration of the steric relationships in the oxime. The coplanarity of the bridgehead methyl group with the oximino function should sterically favor the oxime isomer having the hydroxyl group *syn* to the *gem* methyls which are located symmetrically on opposite sides of the oximino plane; hence the high melting compound which was obtained should have the configuration depicted in I with the bridgehead bond *trans* to the hydroxyl function.



That the ion II rather than IV is the initial intermediate in the formation of the lactam may be inferred from the relative amounts of lactam obtained from the rearrangement and the Ritter reaction. As the ion IV must be the precursor of II in the latter reaction, which produces much less lactam than is derived directly from the oxime under the same conditions, IV must not be involved in the major reaction path leading to the lactam. The assumption that both of the rearrangement products arise *via* the initial formation of

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[10] G. B. Cockburn, *J. Chem. Soc.*, 501 (1899).

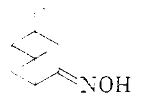
[11] Twelve-foot helical column packed with silicone grease on Chromasorb, elution with helium at *ca.* 10 p.s.i. 80 ml./min.

[12] (a) M. Delepine, *Compt. rend.*, **178**, 1721 (1924). (b) J. L. Simonsen, *The Terpenes*, Cambridge University Press, London, 1932, vol. II, page 473.

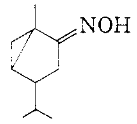
[13] J. J. Ritter and J. Kalish, *J. Am. Chem. Soc.*, **70**, 4048 (1948).

the bicyclic ion II followed by the product-forming steps which have been shown to be reversible is compatible with the generally accepted mechanism of the Beckmann rearrangement and is attractive but for the fact that a competitive path leading to the unsaturated nitrile through the direct formation of IV may exist.

Irrespective of which of these species is the initial intermediate in the formation of the nitrile, it may be concluded that the direction of the anomalous reaction like that of the normal process is determined by the configuration of the oxime and that the stability of the incipient carbonium ion *trans* to the hydroxyl group is of importance only in determining the relative amounts of nitrile and lactam in the products. This latter conclusion is in at least qualitative agreement with the results of the rearrangements of a number of closely related oximes. Camphor[4] and fenchone oximes yielded unsaturated nitriles as the major products of this reaction; verbanone oxime[5] (VIII) gave only a small amount of the corresponding product; and β-dihydroumbellulone oxime[14] (IX) produced only lactam in excellent yield in keeping with the diminishing stability of the substituted cyclopentyl, cyclobutyl, and cyclopropyl carbonium ions as evidenced by the relative rates of solvolysis of the cycloalkyl halides.[15]



VIII



IX

EXPERIMENTAL[16]

Fenchone oxime. Commercial racemic fenchone was distilled at atmospheric pressure through a 90 cm. packed column and a fraction boiling at 195° was collected. Vapor phase chromatography of samples immediately preceding and following the product fraction showed them to be of at least 99% purity.

A mixture of 90 g. of fenchone purified in this manner, 78 g. of hydroxylamine hydrochloride, 70 ml. of 30% sodium hydroxide, 110 ml. of water, and 375 ml. of 95% ethanol was heated under reflux for 20 hr. and then cooled in an ice bath.[17] The crystalline product which precipitated was filtered, washed with water, recrystallized from ethanol, and air dried to give 93.0 g. (94%) of fenchone oxime, m.p. 162–163° (previously published value 158–160°).[12b]

The Beckmann rearrangement. (a) *With p-toluenesulfonyl chloride.* A modification of the method of Burrows and Eastman[14] gave excellent conversion of the oxime to rearranged products. Ice cold solutions of 14.4 g. (0.086 mole) of fenchone oxime in 30 ml. of dry pyridine and 25 g. of *p*-toluenesulfonyl chloride in 30 ml. of the same solvent were mixed and the resultant solution was allowed to warm to room temperature. After the vigorously exothermic reaction subsided, the bright yellow solution was allowed to stand overnight. It was then warmed on the steam bath for 30 min. and poured into a mixture of 30 ml. of 36*N* sulfuric acid and 125 g. of ice.

The acidic suspension was extracted with three 100-ml. portions of ether; the ethereal solution was washed with 5% aqueous sodium bicarbonate and dried over anhydrous magnesium sulfate. Removal of the solvent from the dried ether solution left a two-phase residue which was shown to contain three volatile components separable by vapor phase chromatography. Two of these were later identified as water and the unsaturated nitrile described below. The third component was not found in the crude product when phosphorus pentachloride was used to effect the rearrangement, and no attempt at its identification was made.

The crude product was triturated with 50 ml. of petroleum ether (b.p. 30–60°) and the hydrocarbon solution was distilled through a 45-cm. spinning band column to give, after removal of the solvent, 10.1 g. of a colorless liquid, b.p. 100–102°/19.5 mm. which was shown by infrared analysis to be an unsaturated nitrile. Elemental analysis and proton magnetic resonance data (Table I) indicated that this product was one of the cyclopentenylisobutyronitriles V or Va, or a mixture of the two.

Anal. Calcd. for $C_{10}H_{15}N$: C, 80.58; H, 10.13. Found: C, 80.70, 80.80; H, 10.13, 10.25.

The petroleum ether insoluble material from the above step was combined with the residue in the still pot, and this mixture was recrystallized from the minimal amount of 95% alcohol which would dissolve it at the boil (*ca.* 20 ml.) to give 4.7 g. of fine needles, m.p. 163–164°. An analytical specimen of this product was sublimed at reduced pressure (130°/10 mm.), and the product so obtained was shown by elemental analysis, infrared spectrum, and interconversion with the nitrile described above to be 1,4,4-trimethyl-2-azabicyclo[3.2.1]octan-3-one.

Anal. Calcd. for $C_{10}H_{17}NO$: C, 71.84; H, 10.25. Found: C, 71.64, 71.72; H, 10.00, 10.19.

The total isolated products of this reaction accounted for 96% conversion of the oxime to what appeared to be a single nitrile and a single lactam.

(b) *With phosphorus pentachloride.*[18] Fenchone oxime (16.7 g., 0.1 mole) was added slowly with stirring to a suspension of 17 g. of phosphorus pentachloride in 175 ml. of petroleum ether (b.p. 30–60°) at a rate which maintained vigorous boiling of the solvent. When the reaction had subsided, the mixture was allowed to stand overnight and the solvent was removed by evaporation on the steam bath. Ice (200 g.) was added to the residue, the aqueous suspension was extracted with three 100-ml. portions of ether, and the products were isolated in the manner described above to give 10.5 g. of the unsaturated nitrile and 1.3 g. of the lactam (total yield 78%).

(c) *With concentrated sulfuric acid.*[3] Fenchone oxime (16.7 g., 0.1 mole) was added portionwise to 20 ml. of cold 36*N* sulfuric acid with stirring and ice cooling to maintain the reaction temperature below 25°. When the addition was completed, the mixture was allowed to stand in a water bath at 25° for *ca.* 5 min., whereupon the temperature rose spontaneously to 55° and the solution became dark red and then brown.

After neutralization with ice cold aqueous sodium hydroxide, the mixture was ether extracted and the products were isolated in the manner described above to give 5.6 g. of the nitrile and 1.2 g. of the lactam. The considerable amount of resinous material which remained after the isolation of these products was assumed to be a mixture of a low molecular weight polyamide[19] and hydrolysis products derived from the nitrile and lactam.

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(14) W. D. Burrows and R. H. Eastman, *J. Am. Chem. Soc.*, **79**, 3756 (1957).

(15) A. Streitwieser, Jr., *Chem. Rev.*, **56**, 667 (1956).

(16) Melting points were taken in a stirred oil bath with no correction for stem emergence. Microanalyses were conducted by Miss V. Jean Carrier.

(17) J. Cologne, *Bull. soc. chim. France*, **5**, 98 (1938).

(18) H. Rupe and I. Splittgerber, *Ber.*, **40**, 4313 (1907).

(19) C. J. Albisetti, U. S. Patent 2,620,327.

(d) *With dilute sulfuric acid.*[10] The oxime (25 g.) was boiled for 1 hr. with a solution of 5 ml. of 36N sulfuric acid in 125 ml. of water and worked up in the manner of the reference cited to give a nitrile indistinguishable in its infrared and proton resonance spectra from that described above. No attempt at isolation of the lactam was made.

Hydrolysis of the nitrile. A mixture of 10 g. of the nitrile derived from the reaction of fenchone oxime with dilute sulfuric acid, 10 g. of potassium hydroxide, 25 ml. of methanol, and 10 ml. of water was heated under reflux for 60 hr. The methanol was removed by distillation at reduced pressure, water (50 ml.) was added, the mixture was cooled to 0°, and the oily solid which precipitated was filtered and recrystallized from benzene–petroleum ether (b.p. 30–60°) to give 4.8 g. (43%) of *dl*-α-fencholenamide as white platelets, m.p. 85–86.5°. An analytical specimen was prepared by sublimation at 100°/1 mm.

Anal. Calcd. for $C_{10}H_{17}NO$: C, 71.84; H, 10.25; N, 8.38. Found: C, 71.71, 71.75; H, 10.22, 10.43; N, 8.42, 8.51.

Evaporation of the mother liquor from the recrystallization of the amide produced a liquid residue (3.2 g.) which was shown by its infrared spectrum to be largely unchanged starting material containing a small amount of the amide as evidenced by the amide carbonyl band.

The alkaline solution from the hydrolysis was cooled in ice and acidified with hydrochloric acid. The amber liquid which separated was removed and the aqueous phase was extracted with ether. The organic solutions were combined, dried with anhydrous magnesium sulfate, and the solvent was removed by distillation from a steam bath at 10 mm. The crude acidic product obtained in this manner was a viscous yellow-brown oil which was identified as containing largely α-fencholenic acid by the presence of a band for vinyl hydrogen in its proton resonance spectrum and vapor phase chromatography which indicated the crude acid was at least 80% one component.

The crude acid (0.8 g.) was heated under reflux for 2 hr. with 15 ml. of oxallyl chloride. The mixture was concentrated by distillation from the steam bath, and the brown oily residue was treated with 30 ml. of 30% aqueous ammonia to produce a brown solid. This product was twice recrystallized from benzene-petroleum ether (b.p. 30–60°) to give 0.3 g. of slightly yellow platelets identical in infrared spectrum, melting point and mixed melting point with the amide obtained directly from hydrolysis of the nitrile.

The Ritter reaction of the unsaturated nitrile.[13] The nitrile obtained from the above reactions (50 g., 0.33 mole) was added cautiously, with stirring, to 50 ml. of 36N sulfuric acid. The mixture was cooled in an ice bath throughout the addition to maintain the reaction temperature below 25°. When the addition of the nitrile was completed, the reaction mixture was allowed to stand in the ice bath for an additional 0.5 hr. and then warmed to room temperature, whereupon the temperature rose spontaneously to 60° and the mixture turned red and foamed slightly. The flask was then stoppered loosely and allowed to stand overnight.

The dark brown resinous mixture was poured into an ice cold solution of 80 g. of sodium hydroxide in 500 ml. of water and the aqueous suspension was extracted four times with a total of 1 l. of ether. The ethereal extract was dried over anhydrous magnesium sulfate and concentrated to dryness to give an oily brown residue which was triturated with petroleum ether (b.p. 30–60°) to remove the unsaturated nitrile.

The crude product was worked up in the usual manner to give 10 g. of unchanged nitrile and *ca.* 0.5 g. of lactam which was shown to be identical with the product obtained directly from the oxime in melting point, mixed melting point, and infrared spectrum. (As in the sulfuric acid catalyzed rearrangement, a large amount of resinous material was formed.)

Dehydration of the lactam.[20] A mixture of 3.24 g. of the lactam, 3.4 g. of phosphorus pentachloride and 35 ml. of petroleum ether (b.p. 30–60°) was allowed to stand for 48 hr. with periodic shaking and then heated for 1 hr. on a steam bath. The mixture was worked up in the manner described for the Beckman rearrangement with phosphorus pentachloride to give 1.9 g. of nitrile which was identical with that derived directly from the oxime in infrared spectrum and inseparable from the latter in vapor phase chromatography.

Acknowledgment. The author wishes to express his thanks to Mr. John A. Ray for assistance with the experimental work, Miss Ruth A. Staszesky for infrared spectra, and Dr. W. D. Phillips for assistance in the interpretation of the proton magnetic resonance data.

WILMINGTON, DEL.

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[20] G. Schroeter, *Ber.*, **44**, 1201 (1911).

[CONTRIBUTION FROM THE DEPARTMENT OF AGRICULTURAL CHEMISTRY, KYOTO UNIVERSITY]

Synthesis of Two Isomeric *p*-Menthane-3,4-diols and Their Pinacolic Dehydration to a Menthone Mixture[1]

WAICHIRO TAGAKI AND TETSUO MITSUI

Received January 13, 1960

Two isomeric *p*-menthane-3,4-diols, (+)-*cis*-4-hydroxymenthol (VIa) and (−)-*trans*-4-hydroxyneoisomenthol (VIb), were prepared by lithium aluminum hydride reduction of two isomeric *p*-menthane-4,8-epoxy-3-ols (Va) and (Vb) which were derived from (+)-pulegone. With 10% sulfuric acid, VIa and VIb were dehydrated to a menthone mixture (VII) which was composed of 65% (−)-menthone and 35% (+)-isomenthone.

The pinacolic dehydration of *p*-methane-3,4-diol (VI) to a menthone mixture[2-4] appears to be significant for the industrial production of synthetic menthol, because VI can be easily prepared from

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[1] Presented at the meeting of the Kansai Branch of the Agricultural Chemical Society of Japan, Nara, Japan, October 17, 1959.

[2] S. Tanaka, *J. Chem. Soc. Japan*, **53**, 668 (1932); *Mem. Coll. Sci. Kyoto Univ.*, 22A, 97 (1939).

[3] Y. Ogata, *J. Soc. Chem. Ind. Japan*, **45**, 1157 (1942).

[4] Y. R. Naves, *Helv. Chim. Acta*, **42**, 1174 (1959).