hydrofolic dehydrogenase system. This latter point is also demonstrated in Fig. 5. When the borohydride reduction product (curve 2) was treated with TPN and hydroxymethyl tetrahydrofolic dehydrogenase (containing cyclohydrolase[22]), the absorption spectrum changed to that of curve 3. The decrease in light absorption at 300 mμ and the increase in the region of 260 mμ are indicative of N^{10}-formyl tetrahydrofolate[46] formation, although the spectrum is obscured by the contribution due to the unreacted "active formaldehyde." Only 50% of the "active formaldehyde" would be reactive, due to the asymmetric carbon atom at the C^6-position. The appearance of the absorption band at 355 mμ, characteristic of N^5,N^{10}-methenyl tetrahydrofolate, after acidification of the cell contents (curve 4), confirmed that the product of the *enzymic* oxidation was N^{10}-formyl tetrahydrofolate. The above sequence of reactions is summarized in equation 4: steps (a) and (d) are non-enzymic, while (b) and (c) are enzymic.

The product of the borohydride reduction of N^5,-N^{10}-methenyl tetrahydrofolate was more conclusively identified as "active formaldehyde" by a detailed examination of its reactivity in the hydroxymethyl tetrahydrofolic dehydrogenase system at *p*H 9.5. As shown in Fig. 6, synthetic "active formaldehyde" was an effective substrate for TPN reduction, and the amount of TPNH produced (0.35 μmole) was equal to the theoretical maximum, *i.e.*, 50% of the "active formaldehyde"

(46) At the *p*H employed, the cyclohydrolase-catalyzed equilibrium of N^5,N^{10}-methenyl tetrahydrofolate and N^{10}-formyl tetrahydrofolate lies far in the direction of the latter compound (see ref. 22).

$$\text{N}^5,\text{N}^{10}\text{-methenyl tetrahydrofolate} \xrightarrow[(a)]{\text{NaBH}_4} \text{"active formaldehyde"} \xrightarrow[(b)]{\text{TPN}} \text{N}^5,\text{N}^{10}\text{-methenyl tetrahydrofolate} \xrightarrow[(c)]{\text{H}_2\text{O}} \text{N}^{10}\text{-formyl tetrahydrofolate} \xrightarrow[(d)]{\text{H}^+} \text{N}^5,\text{N}^{10}\text{-methenyl tetrahydofolate} \quad (4)$$

added (0.70 μmole). Under the same conditions, the borohydride reduction product was also quantitatively oxidized by TPN: 0.17 μmole of TPNH were formed after the addition of 0.35 μmole of borohydride-treated N^5,N^{10}-methenyl tetrahydrofolate to the reaction mixture, and the addition of a second, equal increment of the borohydride product led to the formation of a second equal increment of TPNH. A mixture of tetrahydrofolate and formaldehyde was, however, almost completely inactive, since the rate of adduct formation is low at this *p*H. It could be concluded, therefore, that "active formaldehyde" was formed *quantitatively* by the chemical reduction of N^5,N^{10}-methenyl tetrahydrofolate. Since $NaBH_4$ reduction was specific for N^5,N^{10}-methenyl tetrahydrofolate, additional evidence is provided for the contention that the N^5,N^{10}-bridge structure is retained during reduction to the formaldehyde level. A hydride-ion mechanism has been presented recently[42] for the enzymic or chemical interconversion of "active formaldehyde" and "active formate."

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, ILLINOIS INSTITUTE OF TECHNOLOGY]

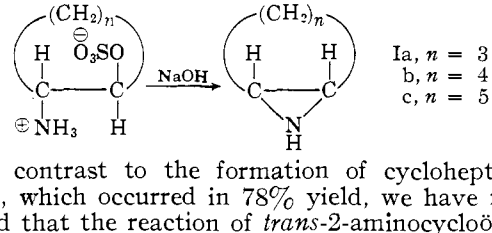
Chemistry of Ethylenimine. VII. Cycloöctenimine or 9-Azabicyclo[6.1.0]nonane[1]

BY D. V. KASHELIKAR AND PAUL E. FANTA[2]

RECEIVED JANUARY 29, 1960

Reaction of *trans*-2-aminocycloöctyl hydrogen sulfate with aqueous sodium hydroxide gives a mixture of cycloöctanone and the expected *cis*-cycloöctenimine. Formation of the two products is rationalized in terms of two alternative, energetically nearly equivalent transition states analogous to those proposed for the Hofmann elimination of cycloöctytrimethylammonium hydroxide. Pyrolysis of N-(*p*-nitrobenzoyl)-cycloöctenimine (IIc) in toluene yields *cis*-N-(*p*-nitrobenzoyl)-3-cycloöctenylamine (V) and an isomeric oxazoline (VII). Formation of V from IIc is sterically and mechanistically analogous to the formation of *cis*-cycloöctene by the pyrolysis of cycloöctyldimethylamine oxide.

Previous papers in this series have described the preparation of cyclopentenimine (Ia),[3] cyclohexenimine (Ib)[4] and cycloheptenimine (Ic)[5] by the treatment of the corresponding *trans*-2-aminocycloalkyl hydrogen sulfates with aqueous sodium hydroxide. Since these small carbocycles cannot accommodate a three-membered ring fused *trans*, the imines were assigned the *cis* configuration and the closure of the aziridine ring therefore must have occurred in each instance with inversion at the substituted carbon atom.



In contrast to the formation of cycloheptenimine, which occurred in 78% yield, we have now found that the reaction of *trans*-2-aminocycloöctyl hydrogen sulfate with aqueous sodium hydroxide gives a crude, volatile reaction product from which cycloöctenimine was isolated in only 33% yield, accompanied by 14% of cycloöctanone.

An analogous difference in the mode of an elimination reaction on going from the seven- to the eight-membered ring was reported by Cope,[6] who

(1) This research was supported by National Science Foundation Grant NSF-G6220 which provided a postdoctoral stipend for D. V. Kashelikar.

(2) To whom inquiries regarding this paper should be sent.

(3) P. E. Fanta, *J. Chem. Soc.*, 1441 (1957).

(4) O. E. Paris and P. E. Fanta, THIS JOURNAL, **74**, 3007 (1951).

(5) P. B. Talukdar and P. E. Fanta, *J. Org. Chem.*, **24**, 555 (1959).

(6) A. C. Cope, R. A. Pike and C. F. Spencer, THIS JOURNAL, **75**, 3212 (1953).

found that the pyrolysis of cycloheptyltrimethylammonium hydroxide gave an 87% yield of *cis*-cycloheptene, whereas cycloöctyltrimethylammonium hydroxide gave a mixture of olefins containing 60% of *trans*-cycloöctene and 40% of *cis*-cycloöctene. Since the Hofmann elimination is a concerted reaction requiring a backside attack on the carbon atom bearing the trimethylamino group,[7] it was concluded that the two conformations of the transition state which place either a *cis*-hydrogen or a *trans*-hydrogen in the same plane as the departing trimethylamino group have similar energies.[8] Thus the cycloöctane ring is sufficiently flexible to permit elimination of both *cis* and *trans* substituents on adjacent carbon atoms with backside attack.

In a similar way, the reaction of *trans*-2-aminocycloöctyl sulfate ion with base may proceed *via* transition state A in which the attack of the hydroxide ion on the amino group is concerted with the approach of the nitrogen atom to the backside of the carbon–oxygen bond, which ultimately yields the *cis*-imine IIa. Alternatively, in transition state B the electron pair of the *cis*-hydrogen accomplishes the displacement by backside attack at the carbon–oxygen bond, giving the vinylamine III which is hydrolyzed to cycloöctanone[9] under the conditions of the reaction.[10] It was also demonstrated in a separate experiment that under similar reaction conditions, cycloöctanone is not formed from cycloöctenimine.[11]

It is noteworthy that a third conceivable transition state C does not participate in the elimination reaction, since the allylamine IV is not found in the products. This may be explained on the grounds that the carbanion corresponding to transition state B is electrostatically stabilized by the polarization of the adjacent C–N bond, whereas no such stabilization is possible for the carbanion corresponding to transition state C.[12]

Cycloöctenimine was characterized further by the preparation of a picrate, the N-phenylthiocarbamyl derivative IIb and the N-*p*-nitrobenzoyl derivative IIc. Although IIc was recovered unchanged after refluxing for twenty-four hours in toluene solution, pyrolysis in toluene solution at 170–180° gave two products, both of which were found by elemental analyses to be isomeric with IIc.

The higher melting, less soluble isomer had an infrared spectrum with bands characteristic of the NH bond, amide C=O and *cis*-CH=CH—. Acid hydrolysis yielded an amine which was hydrogenated

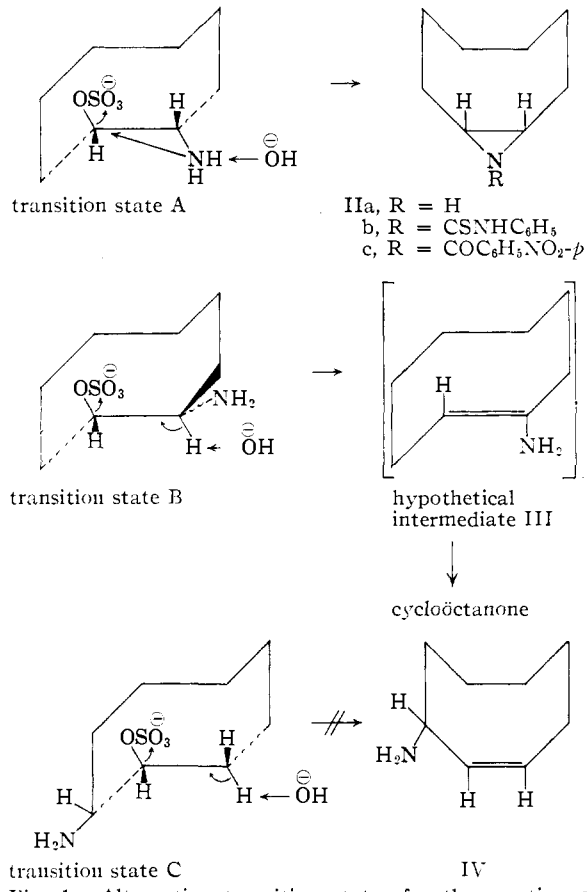
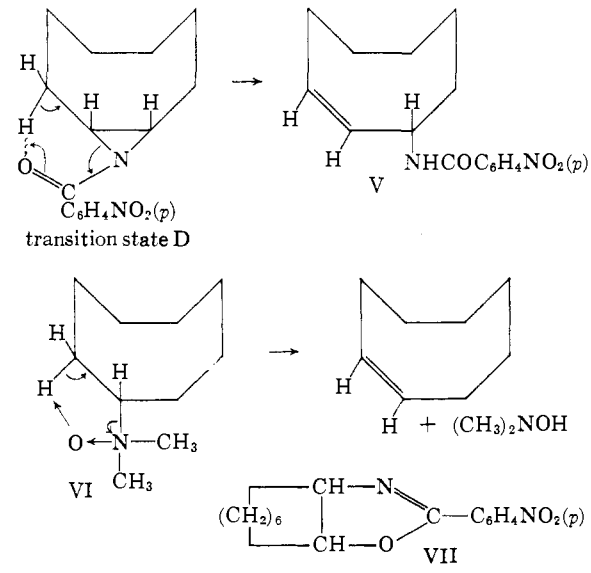


Fig. 1.—Alternative transition states for the reaction of *trans*-2-aminocycloöctyl sulfate ion with hydroxide ion.

to give cycloöctylamine. On the basis of these data, and in analogy with the previously observed rearrangements of N-acylaziridine derivatives to give unsaturated amides,[13] this product is assigned the structure *cis*-N-(*p*-nitrobenzoyl)-3-cycloöctenylamine (V). The formation of V may be rea-



(7) D. Y. Curtin, R. D. Stolow and W. Maya, THIS JOURNAL, **81**, 3330 (1959).

(8) A. C. Cope, D. C. McLean and N. A. Nelson, *ibid.*, **77**, 1628 (1955), give perspective drawings of the ball-and-stick models of the two conformations. This statement is somewhat ambiguous, and it would therefore be more precise to say that in certain cycloöctane derivatives, both *cis* and *trans* substituents on adjacent carbon atoms may assume the anti-parallel arrangement in the formation of a transition state involved in a concerted elimination reaction; *cf.* V. Prelog in "Perspectives in Organic Chemistry," ed. by A. Todd, Interscience Publishers, Inc., New York, N. Y., 1956.

(9) An analogous vinylamine intermediate has been proposed to account for the formation of cyclohexanone from the reaction of *cis*-2-chlorocyclohexylamine with aqueous sodium hydroxide, ref. 4.

(10) Transition states A and B may be demonstrated with Fisher-Hirschfelder scale atom models.

(11) This experiment was suggested by a referee.

(12) This explanation was suggested by Dr. S. I. Miller.

(13) P. E. Fanta and A. S. Deutsch, *J. Org. Chem.*, **23**, 72 (1958); P. B. Talukdar and P. E. Fanta, *ibid.*, **24**, 526 (1959).

sonably pictured as occurring by means of an intramolecular rearrangement *via* transition state D, which results in a *cis* elimination sterically and mechanistically analogous to the observed formation of *cis*-cycloöctene in 90% yield by the pyrolysis of the tertiary amine oxide VI.[6]

The lower-melting, more soluble isomer obtained from the pyrolysis of IVb had a characteristic C=N band and no NH band in the infrared absorption spectrum, and was sufficiently basic to form a picrate. On the basis of these data it is assigned the oxazoline structure VII, although it is not established whether the rings are fused *cis* or *trans*.[14]

Cycloöctenimine also differs from cycloheptenimine in being much more resistant to acid-catalyzed hydrolytic ring opening, since it was recovered unchanged after refluxing for one hour with dilute, aqueous perchloric acid.

Experimental[15]

(±)-*trans*-2-Aminocycloöctanol.—*cis*-Cycloöctene oxide[16] (10.5 g.) and 100 ml. of 28% aqueous ammonia were heated in a rocking steel bomb at 145° for 22 hr. The brown solution was boiled to remove ammonia, decolorized with Norit and concentrated by heating on a steam-bath at about 20 mm. pressure. Two recrystallizations of the residue from benzene–petroleum ether gave 6.0 g. (50%) of amino alcohol, m.p. 71–72° with previous sintering (lit.[17] 73–74°). Reaction of the amino alcohol with phenyl isothiocyanate gave the **N-phenylthiocarbamyl derivative**, m.p. 102–103° after recrystallization from ethanol.

Anal. Calcd. for $C_{15}H_{22}N_2OS$: C, 64.71; H, 7.97; N, 10.06. Found: C, 65.09; H, 7.85; N, 9.81.

(±)-*trans*-2-Aminocycloöctyl Hydrogen Sulfate.—The procedure described for the preparation of the homologous cycloheptyl compound was used.[5] The yield of product once recrystallized from water was 79%, and the analytical sample was obtained by a second recrystallization from water; long, glistening white needles, dec. without melting at 270–275° (uncor.).

Anal. Calcd. for $C_8H_{17}NO_4S$: C, 43.03; H, 7.67; N, 6.27. Found: C, 42.73; H, 7.54; N, 6.02.

Cycloöctenimine (IIa).—A solution of 12.0 g. of the sulfate ester and 12 g. of sodium hydroxide in 75 ml. of water was heated in a distilling flask, and the volatile product was collected in a cooled receiver containing sodium hydroxide pellets and 100 ml. of ether. Whenever the residue in the flask started to crystallize, more water was added and distillation was continued until no further oily drops appeared in the condensate. The aqueous portion of the distillate was further extracted with four 50-ml. portions of ether, and the combined ether solution was dried over sodium hydroxide pellets and distilled, giving 4.43 g. (65%) of colorless oil, b.p. 87–90° (19 mm.). The presence of a ketone in this material was indicated by a strong band at 6.0 μ in the infrared absorption spectrum.

The crude product was taken up in 50 ml. of 2 *N* hydrochloric acid and extracted with three 25-ml. portions of ether. The combined ether solution was dried over anhydrous magnesium sulfate and distilled, leaving a residue of 0.94 g. (14%) of crystalline **cycloöctanone**. Identity was confirmed by comparison of the infrared absorption spectrum with an authentic sample and preparation of the semicarbazone, lustrous plates, m.p. 171–172° (lit. 170–171).°[18]

The hydrochloric acid solution from this extraction was cooled and added to 50 ml. of cold 4 *N* aqueous sodium hydroxide covered with 50 ml. of ether. The aqueous portion was further extracted with three 25-ml. portions of ether and the combined ether solution was dried over sodium hydroxide pellets and distilled, giving 2.21 g. (33%) of colorless ***cis*-cycloöctenimine (IIa)**, which had the characteristic odor of an ethylenimine derivative, b.p. 94–97° (25 mm.), $n^{25}D$ 1.4949, λ_{max} 3.1μ (N—H band).

Anal. Calcd. for $C_8H_{15}N$: C, 76.73; H, 12.08; N, 11.19. Found: C, 76.90; H, 12.20; N, 10.98.

The picrate formed yellow needles from ethanol, m.p. 190–195° dec.

Anal. Calcd. for $C_{14}H_{18}N_4O_7$: C, 47.46; H, 5.12; N, 15.81. Found: C, 47.51; H, 5.24; N, 15.38.

Treatment of the imine with phenyl isothiocyanate gave the **N-phenylthiocarbamyl derivative IIb**, white plates from ethanol, m.p. 132–133°.

Anal. Calcd. for $C_{15}H_{20}N_2S$: C, 69.19; H, 7.74; N, 10.76. Found: C, 69.33; H, 7.81; N, 10.80.

N-(*p*-Nitrobenzoyl)-cycloöctenimine (IIc).—A suspension of 3.71 g. of *p*-nitrobenzoyl chloride in 75 ml. of benzene was added slowly with stirring and cooling to a solution of 2.37 g. of cycloöctenimine and 2.02 g. of triethylamine in 25 ml. of dry benzene. After 2 hours of stirring, the reaction mixture was filtered, and the filtrate was concentrated to a solid residue under reduced pressure. Recrystallization of the residue from 50 ml. of benzene gave 0.41 g. of a solid, m.p. 165–170°, which was not further identified. The benzene solution was again concentrated to a crystalline residue under reduced pressure, and the residue was recrystallized from hexane, giving 4.1 g. (79%) of IIc, m.p. 115–116°, λ_{max} 6.0μ (amide C=O, no NH band).

Anal. Calcd. for $C_{15}H_{18}N_2O_3$: C, 65.67; H, 6.61; N, 10.21. Found: C, 65.61; H, 6.65; N, 10.17.

Pyrolysis of N-(*p*-Nitrobenzoyl)-cycloöctenimine (IIc).—A solution of 1.74 g. of IIc in 60 ml. of toluene was heated in a steel bomb at 170–180° for 24 hours. The cold toluene then contained a crystalline solid which was removed by filtration and recrystallized from benzene (Norit), giving 0.65 g. (37%) of ***cis*-N-*p*-nitrobenzoyl-3-cycloöctenylamine (V)**, fine, white needles, m.p. 195–196°, $\lambda_{max}^{CH_2Cl_2}$ 3.1μ (N—H band), 6.0 (amide C=O) and 11.2μ (*cis*- CH=CH band). The latter band is also found in the spectrum of *cis*-cycloöctene.[6]

Anal. Calcd. for $C_{15}H_{18}N_2O_3$: C, 65.67; H, 6.61; N, 10.21. Found: C, 65.98; H, 6.57; N, 10.44.

The toluene filtrate was concentrated to a solid residue which was recrystallized from methanol, giving 0.40 g. (23%) of **4,5-hexamethylene-2-(*p*-nitrophenyl)-2-oxazoline (VII)**, pale yellow, irregular crystals, m.p. 134–135°, $\lambda_{max}^{CH_2Cl_2}$ 6.1μ (C=N), no NH band.

Anal. Calcd. for $C_{15}H_{18}N_2O_3$: C, 65.67; H, 6.61; N, 10.21. Found: C, 65.72; H, 6.42; N, 10.14.

The picrate of the oxazoline was prepared in ethyl acetate, yellow needles, m.p. 215.5–216.5°.

Anal. Calcd. for $C_{21}H_{21}N_5O_{10}$: C, 50.10; H, 4.21; N, 13.91. Found: C, 50.56; H, 4.64; N, 13.89.

Degradation of V to Cycloöctylamine.—Amide V (0.2 g.) was refluxed for 6 hours with 25 ml. of 5 *N* hydrochloric acid. Cooling gave a precipitate of *p*-nitrobenzoic acid, m.p. 240° (lit. 240°). The filtrate was made alkaline with sodium hydroxide, extracted with three 30-ml. portions of ether and the ethereal solution was dried and concentrated. The oily residue was taken up in absolute alcohol and shaken for 1 hour with a few mg. of platinum oxide catalyst under a hydrogen pressure of 1 atm. After removal of the catalyst, the solution was concentrated *in vacuo* to an oily residue, which on treatment with alcoholic picric acid gave a crystalline picrate, m.p. 192° (cycloöctylamine picrate reported[19] m.p. is 193–194°).

Attempted Hydrolysis of Cycloöctenimine.—A solution of 0.6 g. of cycloöctenimine and 1.5 ml. of 70% perchloric acid in 10 ml. of water was refluxed for 1 hour, made alkaline with sodium hydroxide and extracted with four 25-ml. portions of chloroform. Drying and evaporation of the chloroform left

(14) *d,l-trans*-2-Phenyl-4,5-tetramethylene-2-oxazoline was obtained in 20% yield by the pyrolysis of N-benzoyl-*cis*-cyclohexenimine; F. Winternitz, M. Mousseron and R. Dennilauler, *Bull. soc. chim. France*, 382 (1956).

(15) Melting points are corrected, unless otherwise stated. Infrared absorption spectra were determined with the Perkin-Elmer Infracord spectrophotometer, using sodium chloride disks. Analyses are by Micro-Tech Laboratories, Skokie, Ill.

(16) A. C. Cope, S. W. Fenton and C. F. Spencer, THIS JOURNAL, **74**, 5884 (1952).

(17) Obtained by a similar procedure, J. Sicher and M. Svoboda, *Collection Czechoslov. Chem. Commun.*, **23**, 1252 (1958).

(18) A. T. Blomquist and L. H. Liu, THIS JOURNAL, **75**, 2153 (1953).

(19) V. Prelog, M. Fausy El-Neweihy and O. Häfliger, *Helv. Chim. Acta*, **33**, 365 (1950).

an oil which was identified as cycloöctenimine by preparation of the phenylthiocarbamyl derivative, m.p. 133–134°.

Treatment of Cycloöctenimine with Hot, Aqueous Sodium Hydroxide.[11]—A mixture of 0.11 g. of cycloöctenimine and a solution of 1.6 g. of sodium hydroxide in 10 ml. of water was refluxed for 2 hours. The cooled reaction mixture was then extracted with three 10-ml. portions of chloroform and the combined extracts were dried and evaporated *in vacuo*. The infrared absorption spectrum of the oily residue (in carbon tetrachloride) was practically identical with that of cycloöctenimine and, in particular, showed no absorption in the carbonyl region characteristic of cycloöctanone.

CHICAGO 16, ILL.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, ILLINOIS INSTITUTE OF TECHNOLOGY]

Chemistry of Ethylenimine. VIII. Stereospecificity in the Pyrolytic Rearrangement of 1-(*p*-Nitrobenzoyl)-2-benzylaziridine[1]

BY D. V. KASHELIKAR AND PAUL E. FANTA[2]

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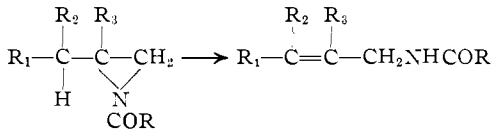
Refluxing a solution of 1-(*p*-nitrobenzoyl)-2-benzylaziridine in toluene for twenty-four hours gave a 91% yield of N-(*trans*-cinnamyl)-*p*-nitrobenzamide. The observation is best explained in terms of an intramolecular reaction mechanism in which the *cis*-elimination of a proton is concerted with the opening of the aziridine ring. The rearrangement is therefore analogous in facility and stereospecificity to the Chugaev reaction and the Cope reaction of tertiary amine oxides.

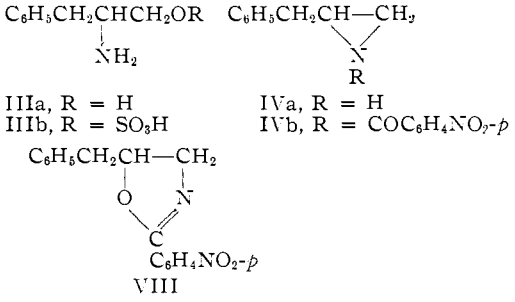
Previous papers in this series[3] described a novel pyrolytic rearrangement of suitably substituted 1-acylaziridines (I) to form unsaturated amides (II). The rearrangement failed with the monosubstituted 1-acylaziridine Ia, but occurred in excellent yield with the two 2,2-dialkyl derivatives Ib and Ic.



Ia, $R_1 = R_2 = R_3 = H$ II
Ib, $R_1 = R_2 = H$; $R_3 = CH_3$
Ic, $R_1 = H$; R_2 and $R_3 = -(CH_2)_4-$

The same type of rearrangement occurred on heating a 2,3-dialkyl-1-acylaziridine, N-(*p*-nitrobenzoyl)-cycloöctenimine, to give *cis*-N-(*p*-nitrobenzoyl)-3-cycloöctenylamine, although in this instance the yield was only 37%.[4]

The present paper provides further evidence that this rearrangement is a stereospecific elimination analogous to the Chugaev reaction and the Cope reaction of tertiary amine oxides.[5]



IIIa, R = H IVa, R = H
IIIb, R = SO_3H IVb, R = $COC_6H_4NO_2$-*p*

VIII

2-Benzylaziridine (IVa) was prepared *via* the conventional Wenker synthesis, *i.e.*, phenylalaninol (IIIa) was converted to the sulfate ester IIIb, which was cyclized by treatment with sodium hydroxide. The N-(*p*-nitrobenzoyl) derivative IVb was prepared by treatment of the imine with *p*-nitrobenzoyl chloride in the presence of triethylamine.

A solution of IVb in toluene on refluxing for twenty-four hours gave a 91% yield of N-(*trans*-cinnamyl)-*p*-nitrobenzamide (VIIa). The structure assigned to this amide was clearly indicated by the infrared absorption spectrum, which had a distinctive NH band at 3.0 μ, amide C=O at 6.0 μ, and *trans*-CH=CH— at 10.3μ.

Further evidence for the structure of VIIIa was provided by hydrolysis in hot, aqueous hydrochloric acid to give *p*-nitrobenzoic acid and cinnamylamine, and cyclization in concentrated sulfuric acid at room temperature to give the isomeric oxazoline VIII in almost quantitative yield.

These observations support the view that the rearrangement of IVb occurs *via* a transition state Va, in which the transfer of the proton from carbon to oxygen is facilitated by the adjacent phenyl group through the participation of resonance hydrid Vb. Transition state Va corresponds to two possible diastereomers, VIa and b, whose geometry is more clearly shown in the Newman projections. The formation of VIa should be greatly favored, since VIb requires eclipsing of the relatively bulky phenyl group and the methylene group of the aziridine ring.

Continued reaction of VIa should result exclusively in the formation of the *trans*-cinnamyl compound VIIa, as observed, whereas VIb should give the *cis* isomer VIIb. An alternative reaction path, involving the formation of VIIb, in a non-stereospecific rearrangement, followed by isomerization of VIIb to VIIa, appears much less likely in view of the mild conditions of the reaction (about 110° for 24 hours) and absence of reagents known to be effective in the *cis* → *trans* isomerization.

It is therefore reasonable to conclude that the pyrolytic rearrangement of 1-(*p*-nitrobenzoyl)-2-

(1) This research was supported by National Science Foundation Grant NSF-G6220 which provided a postdoctoral stipend for D. V. Kashelikar.

(2) To whom inquiries regarding this paper should be sent.

(3) (a) P. E. Fanta and A. S. Deutsch, *J. Org. Chem.*, **23**, 72 (1958); (b) P. B. Talukdar and P. E. Fanta, *ibid.*, **24**, 526 (1959).

(4) D. V. Kashelikar and P. E. Fanta, THIS JOURNAL, **82**, 4927 (1960).

(5) D. J. Cram in "Steric Effects in Organic Chemistry," ed. by M. Newman, John Wiley and Sons, Inc., New York, N. Y., 1956, p. 304. See also the comprehensive review of pyrolytic *cis*-eliminations, by C. H. DePuy and R. W. King, *Chem. Revs.*, in press.