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

Treatment of Cyclooctenimine with Hot, Aqueous Sodium Hydroxide.[11]—A mixture of 0.11 g. of cyclooctenimine 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 cyclooctenimine and, in particular, showed no absorption in the carbonyl region characteristic of cyclooctanone.

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[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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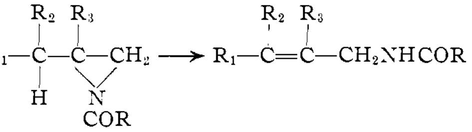
Refluxing a solution of 1-(*p*-nitrobenzoyl)-2-benzylaziridine in toluene for twenty-four hours gave a 91% yield of N-(*trans*-cinnamyl)-*p*-nitrobenzamide. The observation is best explained in terms of an intramolecular reaction mechanism in which the *cis*-elimination of a proton is concerted with 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.



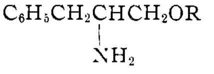
Ia, $R_1 = R_2 = R_3 = H$ II

Ib, $R_1 = R_2 = H$; $R_3 = CH_3$

Ic, $R_1 = H$; R_2 and $R_3 = -(CH_2)_4-$

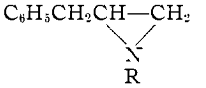
The same type of rearrangement occurred on heating a 2,3-dialkyl-1-acylaziridine, N-(*p*-nitrobenzoyl)-cyclooctenimine, to give *cis*-N-(*p*-nitrobenzoyl)-3-cyclooctenylamine, although in this instance the yield was only 37%.[4]

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]



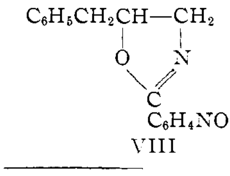
IIIa, R = H

IIIb, R = SO_3H



IVa, R = H

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-

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

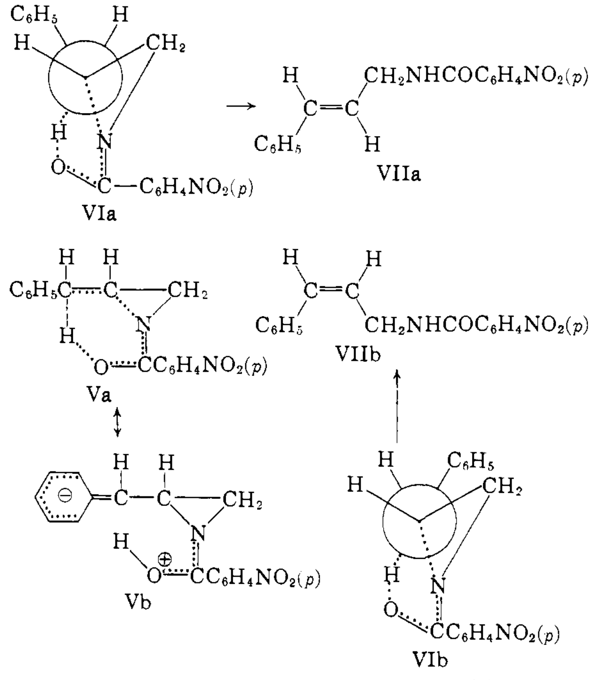
[2] To whom inquiries regarding this paper should be sent.

[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.

benzylaziridine to N-(*trans*-cinnamyl)-*p*-nitrobenzamide is an intramolecular rearrangement involving a *cis*-elimination similar in facility and stereospecificity to the Cope reaction of tertiary amine oxides.



Va,b are transition states in plane projection

VIa,b are transition states in Newman projection

Experimental[6]

(±)-**Phenylalaninol** (IIIa) was prepared as previously described.[7] Treatment of the amino alcohol with phenyl isothiocyanate gave the **N-phenylthiocarbamyl derivative**, shining, colorless plates from ethanol, m.p. 170–171°.

Anal. Calcd. for $C_{16}H_{18}N_2OS$: C, 67.10; H, 6.33; N, 9.78. Found: C, 67.18; H, 6.80; N, 9.82.

(±)-**Phenylalaninyl Hydrogen Sulfate** (IIIb).—To a cold suspension of phenylalaninol (12.0 g.) in 30 ml. of water was added 10.0 g. of cold 95% sulfuric acid. The light yellow solution was heated in a metal-bath at 120° to remove water, first at atmospheric pressure and finally at 130–140° (15 mm.). The brown residue was recrystallized from 100 ml. of 40% aqueous ethanol with concentration of the mother liquors to give a total crop of 14.5 g. (79%) of shining, elongated needles. An additional recrystallization from 95% ethanol gave the analytical sample, m.p., becomes brown at 250° and decomposes at 265–270° (uncor.).

Anal. Calcd. for $C_9H_{13}NO_4S$: C, 46.74; H, 5.66; N, 6.06. Found: C, 46.84; H, 5.63; N, 5.66.

(±)-**2-Benzylaziridine** (IVa).—A solution of 11.0 g. of the sulfate ester and 10.0 g. of sodium hydroxide in 35 ml. of water was heated in a distilling flask, and the distillate was collected in a cooled receiver containing 50 ml. of ether over sodium hydroxide pellets. During the distillation, water was added intermittently to the distilling flask whenever the residue began to crystallize. When the condensate no longer contained oily drops, the ether layer was separated and the aqueous layer was extracted with three 30-ml. portions of ether. The combined ether solution was dried over sodium hydroxide pellets, concentrated, and distilled through a short column, giving 4.8 g. (76%) of colorless imine with a characteristic sharp odor, b.p. 73–75° (1 mm.), $n^{20}D$ 1.5431, λ_{max} 3.1μ (N-H band).

Anal. Calcd. for $C_9H_{11}N$: C, 81.15; H, 8.33; N, 10.52. Found: C, 81.03; H, 8.75; N, 10.05.

(±)-**1-(*p*-Nitrobenzoyl)-2-benzylaziridine** (**IVb**).—To a solution of 2-benzylaziridine (3.85 g.) and triethylamine (2.93 g.) in 30 ml. of dry benzene was added a suspension of 5.38 g. of *p*-nitrobenzoyl chloride in 80 ml. of dry benzene while the mixture was stirred and maintained at 0–5°. After 2 additional hours of stirring, triethylamine hydrochloride was removed by filtration and the colorless filtrate was concentrated *in vacuo* to a solid, crystalline residue. Recrystallization from hexane gave 6.7 g. (82%) of colorless product. An additional recrystallization from hexane gave an analytically pure sample, m.p. 85.5–86.5°, no N-H band in the infrared spectrum.

Anal. Calcd. for $C_{16}H_{14}N_2O_3$: C, 68.07; H, 5.00; N, 9.93. Found: C, 68.13; H, 5.20; N, 9.84.

N-(*trans*-Cinnamyl)-*p*-nitrobenzamide (**VIIa**).—A solution of 550 mg. of IVb in 50 ml. of dry toluene was refluxed for 24 hours. Removal of the toluene *in vacuo* and recrystallization of the residue from 15 ml. of benzene gave 500 mg. (91%) of product in the form of colorless, pointed needles. The analytical sample was obtained by two further recrystallizations from benzene, m.p. 131–132°, $\lambda_{max}^{CH_2Cl_2}$ 3.1μ (N-H), 6.0μ (amide C=O) and strong band at 10.3μ (*trans*-CH=CH—).[8]

Anal. Calcd. for $C_{16}H_{14}N_2O_3$: C, 68.07; H, 5.00; N, 9.93. Found: C, 68.28; H, 4.98; N, 9.76.

2-(*p*-Nitrophenyl)-5-benzyl-2-oxazoline (VIII).—The amide VIIa (1.0 g.) was added to 10 ml. of cold 95% sulfuric acid and the reaction mixture was stirred while the temperature was maintained below 30°. After 3 hours the solution was poured onto 70 g. of ice and the resulting solution was made neutral by careful addition of aqueous sodium hydroxide solution. The crude product, which was precipitated in almost quantitative yield, melted at 110–115°. Recrystallization from aqueous ethanol gave an analytical sample, m.p. 114–115°, no N-H band in the infrared absorption spectrum.

Anal. Calcd. for $C_{16}H_{14}N_2O_3$: C, 68.07; H, 5.00; N, 9.93. Found: C, 68.10; H, 5.26; N, 9.86.

Hydrolysis of the Amide VIIa.—A solution of 0.3 g. of the amide VIIa in 20 ml. of 5 *N* hydrochloric acid was refluxed for 5 hours. Cooling gave a fine, crystalline precipitate of *p*-nitrobenzoic acid, m.p. 240° (lit. 240°), which was removed by filtration. The filtrate was made alkaline by addition of concentrated aqueous sodium hydroxide solution and extracted with three 25-ml. portions of ether. The combined ethereal extracts were dried over anhydrous sodium sulfate and concentrated to an oily residue of cinnamylamine, which was identified by preparation of the **picrate**, yellow needles from water or aqueous alcohol, m.p. 181–182° (lit.[9] 179–180°).

Anal. Calcd. for $C_{15}H_{14}N_4O_7$: C, 49.72; H, 3.89; N, 15.47. Found: C, 50.02; H, 4.13; N, 15.49.

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

[7] P. Karrer, P. Portmann and M. Suter, *Helv. Chim. Acta*, **31**, 1617 (1948).

[8] L. J. Bellamy, "The Infra-red Spectra of Complex Molecules," 2nd Ed., John Wiley and Sons, Inc., New York, N. Y., 1958, p. 45.

[9] R. E. Lutz, *et al.*, *J. Org. Chem.*, **12**, 96 (1947).