163. *Reduction of Phenyl Vinyl Ketoxime with Lithium Aluminium Hydride.*

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Reduction of phenyl vinyl ketoxime with excess of lithium aluminium hydride in boiling ether yields *cis*-2-methyl-3-phenylaziridine.

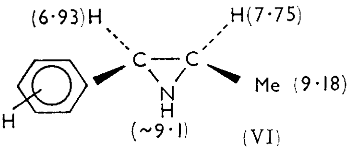
The reactivity of 1-phenylallylamine (III) is of interest in connection with the reaction of 1-phenylallyl chloride with amines.[1] The preparation of this amine by the following route has been claimed: [2]

$$\underset{\text{(I)}}{\mathrm{PhCO{\cdot}CH{:}CH_2}} \xrightarrow{\mathrm{NH_2{\cdot}OH}} \underset{\text{(II)}}{\mathrm{PhC({:}N{\cdot}OH){\cdot}CH{:}CH_2}} \xrightarrow{\mathrm{LiAlH_4}} \underset{\text{(III)}}{\mathrm{PhCH(NH_2){\cdot}CH{:}CH_2}}$$

Condensation of phenyl vinyl ketone (I) with hydroxylamine gave not the oxime (II) but the hydroxylamine (IV) as previously reported.[3] The desired oxime can, however, be prepared by treatment of the methiodide of β-dimethylaminopropiophenone oxime (V) with aqueous alkali: [4,5]

$$\underset{\text{(IV)}}{\mathrm{(PhCO{\cdot}CH_2{\cdot}CH_2{\cdot})_2N{\cdot}OH}} \qquad \underset{\text{(V)}}{\mathrm{PhC({:}NOH){\cdot}CH_2{\cdot}CH_2{\cdot}NMe_3^+\ I^-}}$$

Treatment [2] of the oxime (II) with a slight excess of lithium aluminium hydride at low temperature yielded unchanged starting material; however, with excess of the metal hydride in boiling ether, followed by decomposition of the complex with water, alkaline Rochelle salt, or a slight excess of ethereal hydrogen chloride, a solid product, $C_9H_{11}N$, was obtained which showed no infrared bands attributable to a vinyl group. The nuclear magnetic resonance spectrum confirmed the absence of vinylic protons and was compatible with the structure 2-methyl-3-phenylaziridine (VI) (τ-values in parentheses), the methyl peak being split as a doublet and the ring proton peaks as a doublet and a quintet, coupling constants being of the order of 6 c./sec. The *cis*-stereochemistry was confirmed by conversion of the product into *threo*-2-amino-1-chloro-1-phenylpropane hydrochloride with concentrated hydrochloric acid or excess of ethereal hydrogen chloride, and into *threo*-2-amino-1-phenylpropanol with dilute sulphuric acid. Final confirmation was obtained by synthesis of *cis*-2-methyl-3-phenylaziridine, from (±)-*erythro*-2-amino-1-phenylpropanol by way of *threo*-2-amino-1-chloro-1-phenylpropane,[6] which was identical with the reduction product.



(VI)

This reaction is reminiscent of the formation of aziridines by reaction of Grignard reagents with acetophenone and propiophenone oximes; [7] however, the latter compounds with lithium aluminium hydride under the same conditions as above give a mixture of the expected primary amine together with a secondary amine, as previously reported: [8]

$$\mathrm{PhC({:}N{\cdot}OH){\cdot}C_2H_5} \longrightarrow \mathrm{PhCH(NH_2){\cdot}C_2H_5 + PhNH{\cdot}C_3H_8}$$

Relatively few oximes of αβ-unsaturated carbonyl compounds have been reduced with metal hydrides.[9] We are carrying out further work to determine the generality of the

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[1] Valkanas and Waight, *J.*, 1964, 531.

[2] Pocker, *Chem. and Ind.*, 1959, 195.

[3] Casey and Marvel, *J. Org. Chem.*, 1959, **24**, 1022.

[4] Kyi and Wilson, *J.*, 1953, 798.

[5] Scott, Riordan, and Hegarty, *Tetrahedron Letters*, 1963, 537.

[6] Kojima, *J. Pharm. Soc. Japan*, 1959, **79**, 11.

[7] Hoch, *Compt. rend.*, 1934, **198**, 1865; Campbell, Campbell, McKenna, and Chaput, *J. Org. Chem.*, 1943, **8**, 103; Campbell, Campbell, Hess, and Schaffner, *ibid.*, 1944, **9**, 184.

[8] Smith, Maienthal, and Tipton, *J. Org. Chem.*, 1952, **17**, 294.

[9] Gaylord, " Reduction with Complex Metal Hydrides," Interscience, New York, 1956, p. 751.

aziridine-forming reaction and to clarify its mechanism; it seems possible that a reaction on the surface of undissolved reagent particles is involved.

EXPERIMENTAL

Microanalyses are by Miss J. Cuckney and the staff of the Organic Microanalytical Laboratory. N.m.r. spectra were determined, for carbon tetrachloride solutions using tetramethylsilane as an internal reference, by Mrs. A. I. Boston on a Varian A-60 instrument. Infrared spectra were determined with Unicam S.P. 200 or Grubb–Parsons DB2/S4 (fitted with fluorite optics) instruments.

β-*Dimethylaminopropiophenone Oxime*.—This, prepared from β-dimethylaminopropiophenone hydrochloride[10] and hydroxylamine hydrochloride in aqueous sodium carbonate, had m. p. 107° (lit.,[11] 108°).

Phenyl Vinyl Ketoxime.—A concentrated methanolic solution of the above oxime on treatment with methyl iodide afforded the methiodide, m. p. 191° (lit.,[4] 191—192°). The methiodide (6·3 g.) and N-sodium hydroxide (190 ml.) were kept at room temperature for 40 min. and then at 0° for 18 hr. The yellow solution was extracted with ether and the aqueous layer acidified (to pH 6) with concentrated hydrochloric acid. The ketoxime (1·24 g.), recrystallized from petroleum (b. p. 60—80°), had m. p. 112° (lit.,[4,5] 110°). The oxime is unstable and was immediately used in the next stage.

Reduction of Phenyl Vinyl Ketoxime with Lithium Aluminium Hydride.—The oxime (1·17 g., 0·008 mole) in dry ether (50 ml.) was added to a suspension of the metal hydride (1·7 g., 0·044 mole) in dry ether (150 ml.), and the mixture boiled under reflux for 3 hr. The complex was decomposed with either an aqueous alkaline solution of Rochelle salt or a slight excess of water,[12] or a slight excess of ethereal hydrogen chloride. Extraction with ether, in the latter case after first making the solution alkaline with aqueous sodium hydroxide, afforded, after distillation, a white slightly hygroscopic solid (0·53 g.), m. p. 46°, b. p. 85°/8 mm. (Found: C, 80·95; H, 8·45; N, 10·8%; *M*, 142. Calc. for $C_9H_{11}N$: C, 81·2; H, 8·35; N, 10·5%; *M*, 133), $\nu_{max.}$ (in CCl_4) 3360 cm.$^{-1}$ (free NH stretch). The product (0·2 g.) was heated on a steam-bath for 30 min. with concentrated hydrochloric acid (2 ml.). The crystals which separated on cooling had m. p. 200° (from concentrated hydrochloric acid) (Found: C, 52·9; H, 6·05; Cl, 34·7; N, 6·5. Calc. for $C_9H_{13}Cl_2N$: C, 53·0; H, 6·35; Cl, 34·4; N, 6·8%) and an infrared spectrum (Nujol) identical with that of *threo*-2-amino-1-chloro-1-phenylpropane hydrochloride (see below). The same compound was obtained by treatment of the reduction product with an excess of ethereal hydrogen chloride. The reduction product (1·0 g.) and N-sulphuric acid (50 ml.) were boiled under reflux (1 hr.). The solution was made alkaline with ammonium hydroxide and extracted with ether. On evaporation of the dried (Na_2SO_4) ethereal extract a solid, m. p. 72° (from petroleum, b. p. 60—80°), was obtained, which afforded a crystalline hydrochloride, m. p. 168° (from ethanol). (±)-*threo*-2-Amino-1-phenylpropanol has m. p. 71°; hydrochloride, m. p. 169°.[13]

cis-2-*Methyl*-3-*phenylaziridine*.[6]—Isonitrosopropiophenone[14] (10 g.) and lithium aluminium hydride (13 g.) in ether (500 ml.) were boiled under reflux for 3 hr. Water (30 ml.) was added and the precipitate removed by filtration and extracted well with ether. The combined ether solutions were dried (Na_2SO_4) and distilled. The residual *erythro*-2-amino-1-phenylpropanol (2·2 g.) had m. p. 104° (from ethanol) (lit.,[13] 104—105°); it was converted into its hydrochloride, m. p. 193° (from ethanol) (lit.,[13] 194°), with ethereal hydrogen chloride. To an ice-cold solution of the hydrochloride (1·6 g.) in chloroform (10 ml.) was added thionyl chloride (5 ml.) in chloroform (6 ml.) and the mixture was allowed to stand at room temperature for 18 hr. The crystalline *threo*-2-amino-1-chloro-1-phenylpropane hydrochloride (0·6 g.) which separated had m. p. 200° (from ethanol–acetone, 2·5 : 1) (lit.,[6] 200—201°); it was boiled under reflux for ½ hr. with water (3 ml.) and potassium hydroxide (0·6 g.), the solution extracted with ether, and the extract washed with water, dried ($MgSO_4$), and distilled. The product, b. p. 85°/8 mm., m. p. 43°, was incompletely soluble in carbon tetrachloride. Removal of the insoluble material by

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[10] *Org. Synth.*, Coll. Vol., III, 1955, p. 305.

[11] Mannich and Heilner, *Ber.*, 1922, **55**, 356.

[12] Lyle and Troscianiec, *J. Org. Chem.*, 1955, **20**, 1757.

[13] Nagai and Kanao, *Annalen*, 1929, **470**, 157.

[14] *Org. Synth.*, Coll. Vol. II, 1943, p. 363.

filtration followed by evaporation of the solvent gave *cis*-2-methyl-3-phenylaziridine (0·09 g.), m. p. 46° undepressed on admixture with the reduction product of phenyl vinyl ketoxime (lit.,[6] m. p. 45—46°). The infrared and n.m.r. spectra of the products obtained by the two routes were also identical.

We are indebted to Dr. J. A. Elvidge for assistance in interpreting the n.m.r. spectra, and to Mr. C. E. Boxer, B.Sc., A.R.C.S., for carrying out preliminary work on the preparation of phenyl vinyl ketoxime.

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[*Received, June* 30*th*, 1964.]