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Reactions of gem-Halonitrosocycloalkanes with Triphenylphosphine. A New Synthesis of Lactams

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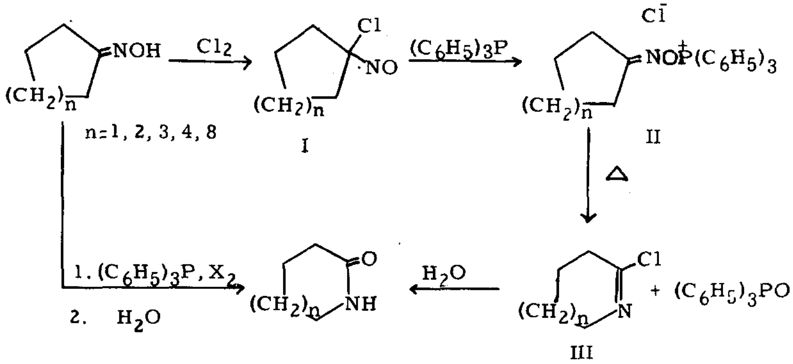
Although a considerable amount of work has been carried out on the Perkov reaction since 1955[1], little is known about the reaction of gem-halonitrosoalkanes with trivalent organophosphorus compounds. The reaction of 2-chloro-2-nitrosopropane with triethyl phosphite afforded diethyl isopropylideneamino phosphate, but no Beckmann rearrangement product was obtained by its pyrolysis[2]. We wish to report the first successful Beckmann rearrangement of gem-halonitrosocycloalkanes with triphenylphosphine.



gem-Chloronitrosocycloalkanes[3)] were dissolved in nonpolar solvents such as benzene, toluene, ether, or tetrahydrofuran, and treated with one mole equivalent of triphenylphosphine at room temperature. The reaction was found to be exothermic and the deep blue color of nitroso group disappeared immediately. After 30 - 60 minutes, the reaction mixture was hydrolysed and the corresponding lactams were obtained in moderate to excellent yields. When the temperature was kept at 0 - 10°, a very hygroscopic precipitate (I. R., 1655 cm^{-} characteristic of C=N group) was formed, which was heated in dry benzene at 60° and the infrared spectrum of the benzene solution showed the presence of triphenylphosphine oxide. From the observations on this new reaction, the mechanism seems to include initial attack of phosphorus on oxygen to give phosphonium salts (II) directly followed by thermal rearrangement to chlorimine (III), and is resonably consistent with the present understanding of the reactions of α-bromoketones with triphenylphosphine[4)].

In a typical example, a benzene solution (100 ml.) of triphenylphosphine (0.068 mole) was slowly added to a benzene solution (100 ml.) of 1-chloro-1-nitrosocyclohexane (0.068 mole) at room temperature. The deep blue color of the solution disappeared within 15 minutes and the temperature rose as high as 70°. After 30 minutes, the reaction mixture was treated with 1N hydrochloric acid. Triphenylphosphine oxide was obtained in 95% yield from the organic layer and ε-caprolactam was obtained in 96% yield from the aqueous fraction. The results of reactions of other gem-chloronitrosocycloalkanes with triphenyl-

Table I

Starting material	Reagent	Product*	Yield(%)
1-chloro-1-nitroso-cyclopentane	$(C_6H_5)_3P$	δ -valerolactam	57
1-chloro-1-nitroso-cyclohexane	$(C_6H_5)_3P$	ε-caprolactam	96
1-chloro-1- nitroso-cycloheptane	$(C_6H_5)_3P$	azacyclooctane-2-one	76
1-chloro-1-nitroso-cyclooctane	$(C_6H_5)_3P$	azacyclononane-2-one	83
1-chloro-1-nitroso-cyclododecane	$(C_6H_5)_3P$	azacyclotri-decane-2-one	78
cyclopentanone oxime	$(C_6H_5)_3P$ Cl_2	δ -valerolactam	76
cyclohexanone oxime	$(C_6H_5)_3P$ Cl_2	ε-caprolactam	85
cyclohexanone oxime	$(C_6H_5)_3P$ Br_2	ε-caprolactam	74
cyclohexanone oxime	$(C_6H_5)_3P$ I_2	ε-caprolactam	39
cyclooctanone oxime	$(C_6H_5)_3P$ Br_2	azacyclononane-2-one	74
cyclooctanone oxime	$(C_6H_5)_3P$ I_2	azacyclononane-2-one	60
cyclododecanone oxime	$(C_6H_5)_3P$ Br_2	azacyclotri-decane-2-one	81
cyclododecanone oxime	$(C_6H_5)_3P$ I_2	azacyclotri-decane-2-one	48

* All lactams were confirmed to be identical with authentic samples prepared by usual Beckmann rearrangement[5].

phosphine are summarized in Table I.

In order to apply the reaction more easily, cycloalkanone oximes were directly treated with halogens in the presence of equivalent amount of triphenylphosphine. The corresponding lactams were obtained in good yields in case of chlorine and bromine, and in fair yields in case of iodine. The results are summarized in Table I.

References

1) F. W. Lichtenthaler, Chem. Rev., 61, 607 (1961).
2) J. F. Allen, J. Am. Chem. Soc., 79, 3071 (1957).
3) All gem-chloronitrosocycloalkanes were prepared according to Piloty's method. O. Piloty and A. Stork, Ber., 35, 3093 (1902).
4) I. J. Borowitz and R. Virkhaus, J. Am. Chem. Soc., 85, 2183 (1963).
5) L. G. Donaruma and W. Z. Heldt, Organic Reactions Vol. XI, p. 55, John Wiley & Sons, Inc., New York, 1960.