Tetrahedron Letters No.33, pp. 3935-3938, 1966. Pergamon Press Ltd.
Printed in Great Britain.

REACTIONS OF gem-CHLORONITROCYCLOALKANES WITH TRIPHENYLPHOSPHINE

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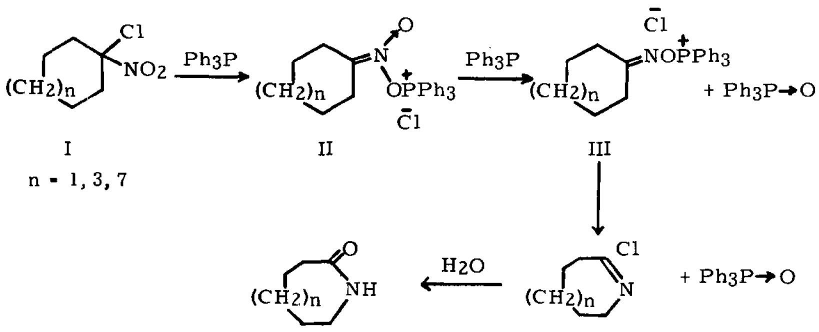
(Received 23 May 1966; in revised form 9 June 1966)

The reaction of 2-chloro-2-nitropropane with two moles of triethyl phosphite afforded diethyl isopropylideneamino phosphate, but no Beckmann rearrangement product was able to isolate by its pyrolysis1). The reaction of bromonitromethane and triphenylphosphine smoothly forms a phosphonium salt that with aqueous alkali at 0° gives triphenylphosphine oxide and fulminic acid2) and it has been shown that the treatment of 1-bromo-1-nitroalkanes with triphenylphosphine in general gives nitriles3). However, no attempt has been carried out to investigate Perkov type reaction of gem-halonitrocycloalkanes with trivalent organophosphorus compounds4). We have recently shown that the reaction of gem-halonitrosocycloalkanes with triphenylphosphine affords the corresponding lactams in excellent yields under mild conditions5). In this report, we wish to report a new Beckmann rearrangement of gem-chloronitrocycloalkanes with triphenylphosphine.



gem-Chloronitrocyclohexane was prepared by the reaction of sodium salt of nitrocyclohexane and chlorine according to Robertson's method6). gem-Chloronitrocycloalkanes of 8- and 12-membered rings, which are new compounds, were prepared by the oxidation of gem-chloronitrosocycloalkanes5) with nitric acid according to Iffland's method7). 1-Chloro-1-nitrocyclooctane (I, n=3) is a colorless liquid, b.p. 74°/0.6 mm Hg and the infrared spectrum showed absorptions at 1563 and 1333 cm^{-1} characteristic of the nitro group8). 1-Chloro-1-nitrocyclododecane (I, n=7) is a colorless solid, m.p. 49.5 - 50.5°, b.p. 118 - 119°C/0.2 mmHg, and the infrared spectrum showed absorptions at 1556 and 1348 cm^{-1} characteristic of the nitro group8).

1-Chloro-1-nitrocyclohexane was treated with two moles of triphenylphosphine in benzene under reflux for 5 hours. After treating the reaction mixture with 2N hydrochloric acid, the benzene solution afforded triphenylphosphine oxide in 86% yield and the aqueous solution afforded ε-caprolactam in 58% yield. The treatments with one mole and three moles of triphenylphosphine gave ε-caprolactam in 34 and 77% yields, respectively. From these results, it seems reasonable to assume that two moles of triphenylphosphine are required to remove two oxygen atoms of the nitro group. The same reaction of 1-chloro-1-nitrocyclooctane and 1-chloro-1-nitrocyclo-dodecane with two moles of triphenylphosphine afforded azacyclononane-2-on in 43% yield and azacyclotridecane-2-on in 32% yield, respectively.

The reaction of gem-chloronitrocycloalkanes with triphenylphosphine is very different from that of gem-chloronitrosocycloalkanes in many respects. The former is endothermic and requires more drastic conditions, but the latter is exothermic and is carried out smoothly at room temperature. These evidences combined with no observation of blue color during the reaction suggest that the reaction mechanism is not through gem-chloronitrosocycloalkane, but most reasonably explained by the formation of Perkov type intermediate (II) followed by transformation into a phosphonium salt (III) and then Beckmann rearrangement as shown above successive formula.

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