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THE ATTEMPTED BECKMANN REARRANGEMENT OF 2,2-DIPHENYL-1-CYCLOHEPTANONE OXIME[1]

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The reaction of several oximes under conditions which usually cause the Beckmann rearrangement has been shown to result in carbon to carbon bond cleavage forming a nitrile and an unsaturated hydrocarbon (1). These oximes were derivatives of either *tert*-alkyl phenyl ketones or bicyclo-systems, and since 2,2-diphenyl-1-cycloheptanone oxime (I) (2) was not related to either of these systems the formation of the cyclic amide, an aza-octanone derivative, (II or III) was expected as a product of the Beckmann rearrangement.

The reaction of I with thionyl chloride gave as product a low-melting solid (IVa) which contained nitrogen and gave no reaction with bromine in carbon tetrachloride or dilute potassium permanganate. On saponification, however, ammonia was evolved and an acid (IVb) which contained no nitrogen was obtained. Despite the lack of reaction of IVa with double-bond reagents, cleavage of the ring in the oxime I apparently occurred forming an unsaturated nitrile. The confirmation of this conclusion was achieved by the oxidation of the acid IVb with chromic acid to benzophenone and adipic acid, thus indicating that IVa was 7,7-diphenyl-6-heptenonitrile and IVb was 7,7-diphenyl-6-heptenoic acid. The slight possibility that the double bond had been formed during the saponification reaction was eliminated by an examination of the ultraviolet absorption spectra of IVa and IVb. Both of these compounds clearly contain the 1,1-diphenylethylene chromophoric system, for a maximum absorption occurred at 250 mμ with a molecular extinction of 1.45×10^4. These values are almost identical with those reported for other 1,1-diphenylethylene systems (3, 4).

The oxidation of the acid (IVb) with potassium permanganate did not give adipic acid but yielded benzophenone and a new acid (V) resulting from the hydroxylation of the double bond. 6,7-Dihydroxy-7,7-diphenylheptanoic acid (V) was also formed by the reaction of 7,7-diphenyl-6-heptenoic acid (IVb) with peroxyacetic acid. On oxidation of V with lead tetraacetate benzophenone and adipic hemialdehyde were isolated.

In a further attempt to form the cyclic amide (II or III) hydrogen chloride in acetic acid and sulfuric acid were used to effect the Beckmann rearrangement of the oxime I. The former conditions led to the formation of the unsaturated nitrile (IVa) and the latter conditions gave no reaction.

Although 2,2-diphenyl-1-cycloheptanone oxime (I) is the only oxime of a monocyclic ketone that has been recorded as not giving a Beckmann rearrangement on treatment with acid, it would appear that the electronic or steric effects

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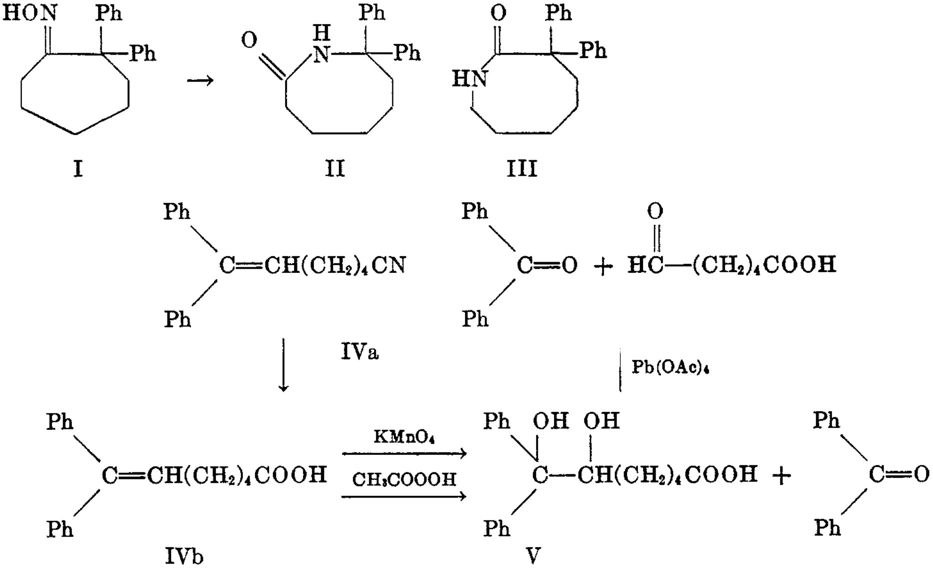
of the two α-phenyl substituents do alter the course of the reaction regardless of the absence of a phenyl ketone linkage.



EXPERIMENTAL

2,2-Diphenyl-1-cycloheptanone oxime (I). Following a modified procedure of Bachmann and Barton (5) 52.8 g. (0.20 mole) of 2,2-diphenyl-1-cycloheptanone, 50.0 g. (0.72 mole) of hydroxylamine hydrochloride, 165 ml. of anhydrous methanol, and 500 ml. of anhydrous β,γ-picoline were heated under reflux for 36 hours. After removal of the solvents by distillation under reduced pressure, the residue was washed with water, dried, and triturated three times with 200 ml. of boiling ethanol to give 36.3 g. of oxime I, m.p. 189–190°, lit. m.p. 190.5–192.0° (2). Distillation of the alcohol extracts gave 18.4 g. of recovered ketone.

Reactions of 2,2-diphenyl-1-cycloheptanone oxime (I). (*a*). *With thionyl chloride.* A solution of 30 ml. of thionyl chloride in 25 ml. of dry benzene was added to a suspension of 30.0 g. of 2,2-diphenylcycloheptanone oxime (I) in 250 ml. of dry benzene. After standing for 24 hours, the solvent was removed by distillation under reduced pressure, and the residue was extracted with petroleum ether in a Soxhlet extractor for 3.5 hours. Evaporation of the petroleum ether gave 27.2 g. (96.8%) of 7,7-diphenyl-6-heptenonitrile (IVa) m.p. 56–58°, which, after recrystallization from ethanol melted 59.0–59.5°.

Anal. Calc'd for $C_{19}H_{19}N$: C, 87.30; H, 7.33.

Found: C, 87.30; H, 7.34.

(*b*). *With hydrogen chloride in acetic acid.* Dry hydrogen chloride was passed into a suspension of 2,2-diphenyl-1-cycloheptanone oxime (I) in 25 ml. of glacial acetic acid until the solid dissolved (30 minutes). The solution was heated under reflux for two hours, poured into 150 ml. of water, and extracted with four 20-ml. portions of ether. The ether solution was extracted with three 20-ml. portions of water and dried over sodium sulfate. Removal of the solvent by evaporation gave a mixture of the oxime I and the unsaturated nitrile (IVa) which was separated by extraction with petroleum ether. The insoluble material consisted of 2.4 g. of unreacted 2,2-diphenyl-1-cycloheptanone oxime (I), m.p. 185–189°, and from the petroleum ether solution there was isolated 3.0 g. (46%) of 7,7-diphenyl-6-heptenonitrile (IVa), m.p. 59.5–61.5°.

(*c*). *With sulfuric acid.* From the treatment of 1.0 g. of 2,2-diphenyl-1-cycloheptanone oxime (I) with 20 ml. of concentrated sulfuric acid for 12 hours there was recovered 0.9 g. (90%) unreacted I (m.p. 185–190°).

7,7-Diphenyl-6-heptenoic acid (IVb). A mixture of 10.0 g. (0.038 mole) of 7,7-diphenyl-6-heptenonitrile (IVa), 48.0 g. of potassium hydroxide, and 200 ml. of diethylene glycol was heated under reflux for 4.5 hours. The solution was cooled below 100°, an equal volume of water was added, and the solution was extracted with three 20-ml. portions of ether. The water solution was acidified with dilute hydrochloric acid and extracted with ten 30-ml. portions of ether. The extracts were dried over sodium sulfate and distilled to give 10.5 g. (98%) of 7,7-diphenyl-6-heptenoic acid (IVb), m.p. 70.5–71.5° after recrystallization from cyclohexane.

Anal. Calc'd for $C_{19}H_{20}O_2$: C, 81.37; H, 7.18.
Found: C, 81.64, 80.66; H, 7.60, 6.95.

Oxidation of 7,7-diphenyl-6-heptenoic acid (IVb). (*a*). *With chromic acid.* A solution of chromic acid prepared by mixing equal volumes of water and sulfuric acid saturated with potassium dichromate was added to 1.0 g. of 7,7-diphenyl-6-heptenoic acid (IVb) at 70–80° until the chromic acid color remained in the mixture. The excess chromic acid was destroyed by the addition of sodium bisulfite and the reaction mixture was extracted with four 40-ml. portions of benzene. On removal of the benzene by distillation 0.5 g. (85%) of benzophenone was obtained.

The aqueous layer was saturated with sodium chloride and extracted with nine 50-ml. portions of ether. The ether extracts were concentrated to 10 ml. and then they deposited 0.01 g. (2%) of adipic acid, m.p. and mixture m.p. with authentic sample 151–152° lit. m.p. 152° (6), after seeding with a very small crystal.

(*b*). *With potassium permanganate.* A solution of 10.0 g. of 7,7-diphenyl-6-heptenoic acid in 400 ml. of water was effected by the addition of dilute sodium hydroxide. The solution was warmed to 65–70° and 15.0 g. of solid potassium permanganate was added in portions over a period of 20 minutes. The reaction mixture was filtered and the residue was washed well with hot water, dried, and extracted with three 20-ml. portions of ether. The basic filtrate was also extracted with ether and the ether extracts were combined, dried, and distilled giving 2.1 g. (32%) of benzophenone, m.p. 46–48° which did not lower the melting point of an authentic sample on mixing. The 2,4-dinitrophenylhydrazone derivative melted at 241°, lit. m.p. for benzophenone 2,4-dinitrophenylhydrazone, 239° (6).

The basic filtrate was acidified, extracted with ether, and the ether extracts were dried over sodium sulfate. Distillation of the ether gave 1.8 g. (16%) of *6,7-dihydroxy-7,7-diphenylheptanoic acid* (V), m.p. 165–166° after recrystallization from acetone-petroleum ether.

Anal. Calc'd for $C_{19}H_{22}O_4$: C, 72.57; H, 7.06; N. E., 316.
Found: C, 72.46; H, 6.90; N. E., 314.

The p-bromophenacyl ester of V was prepared and after recrystallization from benzene melted 164–165°.

Anal. Calc'd for $C_{27}H_{27}BrO_5$: C, 63.42; H, 5.32.
Found: C, 63.23; H, 5.23.

(*c*). *With peroxyacetic acid.* A solution containing 10.0 g. of 7,7-diphenyl-6-heptenoic acid (IVb), 16.0 g. of 25% peroxyacetic acid in acetic acid, and 2.0 g. of sodium acetate in 250 ml. of glacial acetic acid was allowed to stand for 36 hours. The solution was poured into 800 ml. of water and the solid which precipitated was removed by filtration and dissolved in aqueous alcohol containing 10 g. of potassium hydroxide. The solution was heated under reflux for five hours, cooled, diluted with water, filtered, and acidified. The solid acid was separated by filtration and triturated with petroleum ether to give 7.8 g. (67%) of 6,7-dihydroxy-7,7-diphenylheptanoic acid (V), m.p. 165–166°. Mixture melting points of this acid with V from Part *b* and of the corresponding *p*-bromophenacyl esters gave no depression.

Starting material could be recovered on evaporation of the petroleum ether extracts of crude V.

The oxidation of 6,7-dihydroxy-7-7-diphenylheptanoic acid (V) *with lead tetraacetate.* A solution of 0.85 g. of lead tetraacetate in 50 ml. of glacial acetic acid was added slowly to 0.6 g. of the acid V dissolved in 70 ml. of acetic acid. The reaction mixture stood for 10 hours and 5 ml. of a saturated solution of sodium sulfate was added. The precipitated lead sulfate was removed by filtration, and the filtrate was evaporated under reduced pressure. The residue was treated with 40 ml. of ether and 50 ml. of sodium carbonate solution. The ether layer was separated and the aqueous layer extracted with ether. From the ether extracts there was isolated 0.3 g. (86%) of benzophenone, m.p. 47–48°; 2,4-dinitrophenylhydrazone, m.p. 235–237°.

The aqueous solution was acidified, and an excess of 2,4-dinitrophenylhydrazine in 7% hydrochloric acid was added. The solution was heated for 30 minutes and cooled to give 0.25 g. of adipic hemialdehyde 2,4-dinitrophenylhydrazone, m.p. 135–136°, lit. m.p. 140–141° (7).

SUMMARY

1. The reaction of 2,2-diphenyl-1-cycloheptanone oxime with acidic reagents did not give the expected Beckmann rearrangement but resulted in rupture of the ring forming 7,7-diphenyl-6-heptenonitrile.

2. The hydrolysis of the above nitrile to the corresponding acid and the oxidation reactions of this acid are described.

3. The ultraviolet spectra of 7,7-diphenyl-6-heptenonitrile and 7,7-diphenyl-6-heptenoic acid are shown to be related to that of 1,1-diphenylethylene.

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