Beckmann Rearrangements in Alicyclic Systems. II. 2,2-Diphenylcycloalkanone Oximes[1]

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The Beckmann rearrangement of 2,2-diphenylcyclopentanone, 2,2-diphenylcyclohexanone, and 2,2-diphenylcycloheptanone oximes using phosphorus pentachloride, thionyl chloride, and polyphosphoric acid as catalysts is described. The rearrangements conducted in phosphorus pentachloride and thionyl chloride lead to the formation of the ring-opened unsaturated nitriles from the typical hindered ketoxime fragmentation reaction. Using polyphosphoric acid, however, unexpected results were obtained. 2,2-Diphenylcyclopentanone oxime was cleaved to 5,5-diphenyl-4-pentenonitrile in high yield. None of the unsaturated amide from hydration of the nitrile group was observed among the reaction products. 2,2-Diphenylcyclohexanone oxime yielded 2-benzhydrylidene cyclopentanone imine in good yield. The basic hydrolysis of the imine resulted in the formation of the corresponding ketone in low yield. In contrast, 2,2-diphenylcycloheptanone oxime was rearranged to 7,7-diphenylheptanamide analogous to previously reported saturated amide formation in certain spiroketoxime rearrangements in polyphosphoric acid.

Recently, the abnormal rearrangement of a series of spiroketoximes in polyphosphoric acid has been reported.[2] On heating in polyphosphoric acid at 120 to 130°, these ketoximes were rearranged to α,β-unsaturated ketones and/or saturated amides. It was also observed that rearrangements carried out using phosphorus pentachloride or thionyl chloride as catalysts resulted in the formation of unsaturated nitriles from oxime cleavage. These latter results are consistent with the reported fragmentation reactions observed for ketoximes having fully substituted α-positions.[3,4] Heating the unsaturated nitriles in polyphosphoric acid, at rearrangement temperatures, resulted in the cyclization of the nitrile and olefinic linkage to form the same α,β-unsaturated ketones isolated from oxime rearrangement.

In view of the abnormal results obtained in the spiroketoxime series in polyphosphoric acid medium, it was of interest to examine the behavior of other 2,2-disubstituted cycloalkanone oxime systems in polyphosphoric acid. The cyclization of olefins and nitriles to give α,β-unsaturated ketones was of further interest since it represents a little known example of a limitation of the Ritter reaction.[5,6] It was desirable, also, to contrast the results of aromatic and aliphatic 2,2-disubstituted cycloalkanone oxime rearrangements in order to gain information regarding the effect of varying ring size and substituents on the course of the reaction. These data should assist in the eventual elucidation of a more complete reaction mechanism for the Beckmann rearrangement.

This report deals primarily with the rearrangement of 2,2-diphenylcyclopentanone, 2,2-diphenylcyclohexanone, and 2,2-diphenylcycloheptanone oximes in polyphosphoric acid as compared with other rearrangement catalyst systems. The ketones used in this study were all prepared in good yield by the pinacol rearrangement of the appropriate 1-(1′-hydroxycycloalkyl)diphenylcarbinol using reported methods.[7]

The rearrangement of the three cycloalkanone oximes using either thionyl chloride or phosphorus pentachloride proceeded in high yield to the ring cleavage products, unsaturated nitriles. For example, 2,2-diphenylcyclohexanone oxime was readily cleaved to 6,6-diphenyl-5-hexenonitrile in 96% yield after twenty-four hours at room temperature in ethereal phosphorus pentachloride solution. None of the normal Beckmann rearrangement product, the lactam, was observed in the product mixture. This result is in good agreement with rearrangement data already reported for several members of this series. Graham and Williams[8] observed that the product of the phosphorus pentachloride-catalyzed rearrangement of 2,2-diphenylcyclopentanone oxime was 5,5-diphenyl-4-pentenonitrile. Lyle and Lyle[3h] report the almost quantitative cleavage of 2,2-diphenylcycloheptanone oxime to the unsaturated nitrile, 7,7-diphenyl-6-heptenonitrile, using thionyl chloride. In these reports also, none of the lactam

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[1] This investigation was supported by a Frederick Gardner Cottrell Grant the Research Corporation and by Grants #B-2239 and B-3628 from the Department of Health, Education, and Welfare, Public Health Service.

[2] (a) R. K. Hill and R. T. Conley, *J. Am. Chem. Soc.*, **82**, 645 (1960); (b) R. T. Conley and M. C. Annis, *J. Org. Chem.*, **27**, 1961 (1962).

[3] For examples see: (a) R. Leuckart and E. Bach, *Ber.*, **20**, 104 (1887); (b) G. Schroeter, *ibid.*, **44**, 1201 (1911); (c) O. Wallach, *Ann.*, **259**, 309 (1890); (d) W. H. Glover, *J. Chem. Soc.*, **93**, 1285 (1908); (e) C. C. Price and C. P. Mueller, *J. Am. Chem. Soc.*, **66**, 634 (1934); (f) P. D. Bartlett and M. Stiles, *ibid.*, **77**, 2806 (1955); (g) W. L. Bencze and M. J. Allen, *J. Org. Chem.*, **22**, 352 (1957); (h) R. E. Lyle and G. G. Lyle, *ibid.*, **18**, 1058 (1953); (i) R. E. Lyle, H. L. Fielding, G. Cauquil, and J. Rouzaud, *ibid.*, **20**, 623 (1955).

[4] For exceptions see: (a) B. M. Regan and F. N. Hayes, *J. Am. Chem. Soc.*, **78**, 639 (1956); (b) S. Kaufmann, *ibid.*, **73**, 1779 (1951); (c) W. D. Burrows and R. H. Eastmann, *ibid.*, **79**, 3756 (1957); (d) H. A. Bruson, F. W. Grant, and E. Bobko, *ibid.*, **80**, 3633 (1958).

[5] J. J. Ritter and P. P. Minieri, *ibid.*, **70**, 4045 (1948).

[6] For exceptions see: (a) ref. 2a; (b) F. H. Howell and D. A. H. Taylor, *J. Chem. Soc.*, 3011 (1957).

[7] (a) R. T. Conley, *Rec. trav. chim.*, in press; (b) A. Burger and W. B. Bennet, *J. Am. Chem. Soc.*, **72**, 5414 (1950); (c) R. E. Lyle and G. G. Lyle, *ibid.*, **74**, 4059 (1952).

[8] S. H. Graham and A. J. S. Williams, *J. Chem. Soc.*, 4066 (1959).

seems to have been isolated from the rearrangement mixtures. In this study, re-examination of these examples indicate that oxime fragmentation is the exclusive reaction course in either phosphorus pentachloride or thionyl chloride in these hindered ketoximes.

Using polyphosphoric acid, the results indicate that a marked difference exists in the behavior of the respective oximes as the ring size is increased from five through seven. 2,2-Diphenylcyclopentanone oxime was rearranged smoothly in polyphosphoric acid to yield the same unsaturated nitrile as isolated in the thionyl chloride and phosphorus pentachloride rearrangements. This was unexpected since polyphosphoric acid is an excellent medium for the hydration of nitriles to amides.[9] It is rather interesting that this nitrile survived the temperatures of the rearrangement reaction without hydration. As far as can be determined this is the first example using polyphosphoric acid as a Beckmann rearrangement catalyst in which the nitrile from fragmentation has been observed.[10] This is apparently an interesting example of a system following the rule of six,[11] in which the rate of nitrile hydration is markedly decreased due to proximity of the benzhydrylidene group. This result is even more reasonable if the hydration proceeds *via* phosphorylization by a bulky polyphosphate species causing crowding in the transition state. From the rearrangements carried out in the spiroketoxime system,[2] it was expected that the rearrangement of 2,2 - diphenylcyclopentanone would yield the ring-opened saturated amide. In general, it was shown that in those cases where cyclization of the unsaturated nitrile intermediate was not the preferred reaction, a saturated amide was observed among the reaction products. Since the cyclization of 5,5-diphenyl-4-pentenonitrile would proceed with formation of 2-benzhydrylidenecyclobutanone, an energetically unfavored reaction, it was anticipated that saturated amide formation would be the favored reaction product. These data indicate that the formation of saturated amides in polyphosphoric acid does not follow from the unsaturated nitrile intermediate obtained by oxime cleavage.

The rearrangement of 2,2-diphenylcyclohexanone oxime, however, yielded the expected α,β-unsaturated ketone initially in low yield. Re-examination of the isolation method, indicated that extensive tarring occurred during the isolation of the products. By rapid isolation of the rearrangement products, 2-benzhydrylidene cyclopentanone imine could be obtained in 87% yield as its hydrochloride. Attempted isolation of the ketone by hydrolysis in dilute sodium hydroxide solution resulted in extensive tar formation. From the resulting product mass only a small quantity of the α,β-unsaturated ketone could be isolated by chromatographic techniques. The structure of the ketone was established by both permanganate oxidation and ozonolysis to yield benzophenone as the isolated product and by the typical α,β-unsaturated carbonyl infrared characteristics of purified product. The unsaturated nitrile, 6,6 - diphenyl - 5 - hexenonitrile was readily cyclized to the imine under conditions similar to those used in the oxime rearrangement. The major products of the polyphosphoric acid rearrangements are shown in Fig. 1.

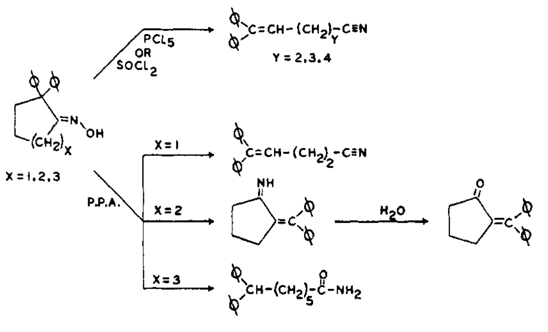

Figure 1

In contrast to the products isolated in the five- and six-membered ring ketoximes, 2,2-diphenylcycloheptanone oxime exhibited the most anomalous behavior. Polyphosphoric acid-catalyzed rearrangement of this oxime resulted in the formation of at least three products. No unsaturated nitrile, unsaturated amide from nitrile hydration, or α,β-unsaturated ketone were among these three products. 2,2-Diphenylcycloheptanone was isolated in small amounts, undoubtedly formed by the partial hydrolysis of the oxime. In addition, a lactam whose structure, although not unequivocally established, appears to be 2-keto-8,8-diphenylheptamethylene imine (Fig. 2). This

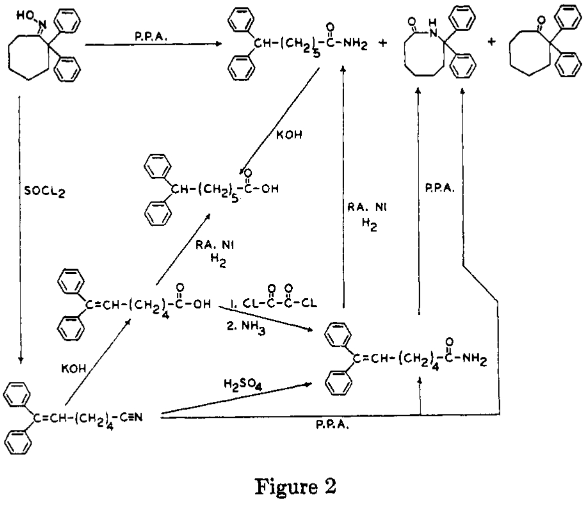

Figure 2

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[9] H. R. Snyder and C. T. Elston, *J. Am. Chem. Soc.*, **76**, 3039 (1954).

[10] A similar observation, however, has been made in the abnormal Schmidt reaction in polyphosphoric acid, R. T. Conley and B. E. Nowak, *J. Org. Chem.*, **26**, 692 (1961).

[11] M. S. Newman, "Steric Effects in Organic Chemistry," J. Wiley and Sons, Inc., New York, N. Y., 1956, pp. 203–248.

structure is postulated from the infrared and ultraviolet spectral properties of the compound and its combustion analysis data. Although present in small amounts, it was shown that this product resulted from treating either 7,7-diphenyl-6-heptenonitrile or its hydration product, 7,7-diphenyl-6-heptenamide with polyphosphoric acid. This product is apparently formed *via* an intramolecular Ritter addition of the unsaturated nitrile and/or unsaturated amide in polyphosphoric acid to form the lactam. The major product of the rearrangement, isolated in 66.8%, was identified as 7,7-diphenylheptanamide. The structure of the amide was established by comparison with an authentic sample. The unsaturated nitrile on treatment with sulfuric acid or polyphosphoric acid gave the unsaturated amide. Catalytic reduction of the unsaturated amide gave 7,7-diphenylheptanamide. Although the mechanism for the formation of this product is not clear, it is apparently a rather general product from rearrangements in polyphosphoric acid in which the hindered oximino compound cannot readily undergo rearrangement cyclization to the α,β-unsaturated ketone. It may well be that the saturated amide is derived from the reductive cleavage of a rearrangement intermediate prior to dissociation to the unsaturated nitrile. Further work toward the elucidation of the reaction route for saturated amide formation is presently in progress.

Experimental

All melting points were taken using the capillary method and are uncorrected. The infrared spectra used for comparison were recorded using a Baird, Model AB-2 or a Beckman IR-4, recording spectrophotometer with sodium chloride optics. The ultraviolet spectra were obtained using a Beckman DK-2A recording spectrophotometer. All ultraviolet spectra were determined on samples in ethanol solution.

Reactants.—2,2-Diphenylcyclopentanone was prepared from 1-(1-hydroxycyclobutyl)diphenylcarbinol by the pinacol rearrangement.[7a] 2,2-Diphenylcyclohexanone and 2,2-diphenylcycloheptanone were prepared from the corresponding pinacols by the methods described by Burger and Bennet[7b] and Lyle and Lyle,[7c] respectively. The oximes were prepared by the pyridine–ethanol procedure described by Cram.[12]

Beckmann Rearrangements I. 2,2-Diphenylcyclopentanone Oxime. (a) In Polyphosphoric Acid.—In a 50-ml. beaker, 0.68 g. (0.0027 mole) of 2,2-diphenylcyclopentanone oxime and 6.5 g. of polyphosphoric acid were heated at 110–120° for 10 min. The mixture was stirred manually during the reaction period. After cooling, the mixture was hydrolyzed over 16 g. of ice and neutralized with 10% aqueous sodium hydroxide solution. The aqueous layer was extracted four times with 40-ml. portions of ether. The ether extracts were combined, dried over anhydrous magnesium sulfate, filtered, and evaporated to yield 0.61 g. of a solid melting at 62–64.5°. An infrared spectrum indicated a strong absorption at 4.45 μ, indicative of the nitrile stretching vibration. Recrystallization of the crude product from methanol yielded 0.60 g. (95%) of 5,5-diphenyl-4-pentenonitrile, m.p. 66–67.5°. Mixed melting point with an authentic sample prepared by the method described by Graham and Williams[8] showed no depression, m.p. 66.5–67.5°.

(b) With Phosphorus Pentachloride.[13]—To a mixture of 1.6 g. (0.0076 mole) of phosphorus pentachloride and 32 ml. of anhydrous ether, 0.68 g. (0.0027 mole) of 2,2-diphenylcyclopentanone oxime was slowly added with external cooling of the reaction mixture. The mixture was slowly warmed to room temperature. After 24 hr., 50 ml. of ice–water mixture was cautiously added to the reaction mixture. The ether layer was separated and the remaining aqueous solution thoroughly extracted four times with 50-ml. portions of ether. The ethereal solution and extracts were combined, dried over anhydrous magnesium sulfate, filtered, and evaporated to obtain 0.61 g. (96%) of crude 5,5-diphenyl-4-pentenonitrile, m.p. 63.0–65.5°. Examination of the infrared spectrum did not indicate the presence of any normal rearrangement product, the lactam. After a single recrystallization from methanol, the product melted at 66.5–67.5° (lit.,[8] m.p. 68°).

(c) Using Thionyl Chloride.—In a 25-ml. Erlenmeyer flask, a mixture of 10 ml. of anhydrous, thiophene-free benzene, and 1.00 g. (0.004 mole) of 2,2-diphenylcyclopentanone oxime was treated with 1.00 g. of freshly distilled thionyl chloride. The mixture was allowed to stand at room temperature for 24 hr. The reaction mixture was diluted with 20 ml. of benzene and evaporated *in vacuo* to remove any unchanged thionyl chloride. The residue was cooled and treated with 20 ml. of water. The aqueous solution was extracted five times with 25-ml. portions of ether. The ether extracts were combined, dried over anhydrous magnesium sulfate, filtered, and evaporated to yield 0.88 g. (95%) of 5,5-diphenyl-4-pentenonitrile, m.p. 62.5–65.5°. No indication of a lactam by-product could be detected in the infrared spectrum of the crude nitrile. After a single recrystallization from methanol, the product melted at 66.5–67.5° and showed no depression in melting point when mixed with an authentic sample.

II. 2,2-Diphenylcyclohexanone Oxime. (a) In Polyphosphoric Acid.—In a 125-ml. Erlenmeyer flask, 5.00 g. (0.019 mole) of 2,2-diphenylcyclohexanone oxime and 751 g. of polyphosphoric acid were heated at 120–125° for 10 min. On cooling, the reaction mixture was hydrolyzed in 400 ml. of water containing 250 g. of ice and 65 g. of sodium hydroxide. During the hydrolysis, the odor of ammonia was definitely detectable. The aqueous solution was extracted five times with 175-ml. portions of chloroform. The chloroform extracts were combined, dried over anhydrous magnesium sulfate, filtered, and evaporated to yield 5.60 g. of a viscous, black oil. The crude product mixture was chromatographed over an ether packed, alumina column to yield only one isolable product. On removal of the ether eluent, 0.76 g. (15.2%) of 2-benzhydrylidene cyclopentanone, m.p. 114–115°, was obtained. The melting point was unaffected by sublimation *in vacuo* for further purification. The infrared spectrum of the ketone exhibited characteristic intense bands at 5.90 and 6.12 μ for an α,β-unsaturated ketone having the carbonyl group in a five-membered ring.

Anal. Calcd. for $C_{18}H_{16}O$: C, 87.05; H, 6.44. Found: C, 86.92; H, 6.47.

The 2,4-dinitrophenylhydrazone derivative was prepared using the sulfuric acid–ethanol procedure.[14] The resulting deep red solid was collected by filtration and twice recrystallized from chloroform–methanol mixture. The 2,4-dinitrophenylhydrazone derivative melted at 219–219.5° dec.

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[12] D. J. Cram and H. Steinberg, *J. Am. Chem. Soc.*, **76**, 2753 (1954).

[13] This experiment was conducted in a fashion similar to that reported by Graham and Williams, ref. 8, with the exception that the product mixture was examined for the presence of the lactam and the yield of the unsaturated nitrile.

[14] R. L. Shriner, R. C. Fuson, and D. Y. Curtin, "The Systematic Identification of Organic Compounds," 4th ed., J. Wiley and Sons, Inc., New York, N. Y., p. 219.

Anal. Calcd. for $C_{24}H_{20}N_4O_4$: C, 67.28; H, 4.71; N, 13.08. Found: C, 67.21; H, 4.69; N, 13.21.

Oxidation of 2-Benzhydrylidenecyclopentanone. (a) With Potassium Permanganate.—In a 25-ml. Erlenmeyer flask, 0.05 g. of 2-benzhydrylidenecyclopentanone, 6 ml. of saturated potassium permanganate and 4 *N* sulfuric acid were cautiously mixed together. An immediate exothermic reaction was observed. After 20 min., finely powdered oxalic acid was added until all the permanganate color had disappeared. To the resulting mixture, 10 ml. of 2,4-dinitrophenylhydrazine solution, prepared from 0.40 g. of 2,4-dinitrophenylhydrazine, 2 ml. of concd. sulfuric acid, 3 ml. of water, and 10 ml. of ethanol, was added. After several minutes of shaking, the mixture was chilled and the precipitate removed by filtration. After a single recrystallization from ethyl acetate–petroleum ether the benzophenone 2,4-dinitrophenylhydrazone derivative was obtained in high purity, m.p. 236–237°. Admixture with an authentic sample showed no depression, m.p. 236.5–237°.

(b) **Ozonolysis.**—A solution of 50 mg. of the unsaturated ketone in 20 ml. of glacial acetic acid was ozonized with a stream of oxygen containing 4% ozone. Water (10 ml.) was added and oxygen bubbled through the solution for 10 min. The solution was made alkaline with 10% sodium hydroxide solution and extracted with ether. The extracts were dried over anhydrous sodium sulfate, filtered, and concentrated. The residue was treated with 2,4-dinitrophenylhydrazine solution (prepared as described above). The precipitate was isolated and purified in the usual manner. Mixed melting point with an authentic sample of benzophenone 2,4-dinitrophenylhydrazone showed no depression, m.p. 236.5–237.5°.

Isolation of 2-Benzhydrylidenecyclopentanone Imine.—The rearrangement of 2,2-diphenylcyclohexanone oxime (1.0 g.) in 20 g. of polyphosphoric acid was carried out as previously described. The reaction mixture was cooled to room temperature and diluted with crushed ice. The resulting ice-acid solution was cautiously neutralized to pH 12 with chilled, 5% aqueous sodium hydroxide. The basic solution was immediately extracted five times with 100-ml. portions of ether. The ether extracts were dried over anhydrous magnesium sulfate, filtered, and concentrated to 100 ml. The ether solution was chilled in an ice–salt mixture and treated with anhydrous hydrogen chloride. An immediate precipitate formed which was filtered under dry nitrogen and dried *in vacuo* to yield 0.82 g. (87%) of 2-benzhydrylidenecyclopentanone imine hydrochloride, m.p. 169.5–171.5° dec.

Anal. Calcd. for $C_{18}H_{18}NCl$: C, 76.18; H, 6.39; N, 4.94; Cl, 12.49. Found: C, 75.92; H, 6.21; N, 4.95; Cl, 12.50.

Hydrolysis of the Imine Hydrochloride.—The imine hydrochloride (0.20 g.) in 10 ml. of 5% hydrochloric acid solution was chilled and treated with 5% aqueous sodium bicarbonate. The neutralized mixture was extracted twice with 15 ml. of ether. The extracts were combined, dried over anhydrous magnesium sulfate, filtered, and evaporated to yield a viscous, black tarry mass, similar to the original Beckmann rearrangement product mixture. The tar was sublimed *in vacuo* to yield 0.03 g. of 2-benzhydridenecyclopentanone, m.p. 114–115°. Admixture with the ketone obtained from the Beckmann rearrangement showed no depression.

Cyclization of 6,6-Diphenyl-5-hexenonitrile.—A mixture of 1.0 g. of 6,6-diphenyl-5-hexenonitrile and 18 g. of polyphosphoric acid was heated, with manual stirring of the viscous mass, at 120–130° for 15 min. The reaction mixture was carefully hydrolyzed and neutralized as described previously. After ether extraction, subsequent concentration and treatment with hydrogen chloride, 0.74 g. (85%) of 2-benzhydrylidenecyclopentanone imine hydrochloride was obtained, m.p. 169.5–171.5° dec.

(b) **With Thionyl Chloride.**—To a suspension of 3.00 g. (0.011 mole) of 2,2-diphenylcyclohexanone oxime in 36 ml. of anhydrous, thiophene-free benzene, 3 ml. of freshly distilled thionyl chloride was cautiously added. After standing for 18 hr. at room temperature, the benzene solvent was evaporated at reduced pressure. To the residue, 40 ml. of water was added and the product extracted from the aqueous solution with three 50-ml. portions of ether. The ether extracts were combined, dried over anhydrous magnesium sulfate, and evaporated to yield 2.80 g. (99%) of crude 6,6-diphenyl-5-hexenonitrile, m.p. 60–62°. After two recrystallizations from methanol, a white crystalline product was obtained, m.p. 62.5–63.0°.

Anal. Calcd. for $C_{18}H_{17}N$: C, 87.41; H, 6.93; N, 5.66. Found: C, 87.36; H, 6.90; N, 5.73.

Hydrolysis to 6,6-Diphenyl-5-hexenoic Acid.—A mixture of 2.65 g. (0.01 mole) of 6,6-diphenyl-5-hexenonitrile, 5.6 g. (0.1 mole) of potassium hydroxide, 28 ml. of water, and 28 ml. of 95% ethanol was heated at reflux for 12 hr. The ethanol was evaporated at reduced pressure and the aqueous reaction mixture acidified with 10% hydrochloric acid. The precipitated solid was removed by filtration and, after air-drying, recrystallized from ethyl acetate to give 2.13 g. (80%) of 6,6-diphenyl-5-hexenoic acid, m.p. 112.5–113° (lit.,[15] m.p. 113–113.5°).

Preparation of 6,6-Diphenyl-5-heptanamide.—A mixture of 1.00 g. (0.0036 mole) of 6,6-diphenyl-5-hexenoic acid, 3 ml. of oxalyl chloride, and 25 ml. of anhydrous thiophene-free benzene was heated slowly to reflux on a steam bath. After 3 hr., the benzene was evaporated at reduced pressure to remove any excess oxalyl chloride. The residual oil was taken up in 25 ml. of anhydrous benzene and treated with anhydrous ammonia in the cold. After 15 min., the benzene solution was evaporated and the light brown solid recrystallized from ethyl acetate–petroleum ether to yield 0.62 g. (62%) of 6,6-diphenyl-5-hexenamide, m.p. 99.5–100.5° (lit.,[15] m.p. 100–101°).

(c) **With Phosphorus Pentachloride.**—To a mixture of 1.6 g. (0.0076 mole) of phosphorus pentachloride and 32 ml. of anhydrous ether, 1.00 g. (0.0036 mole) of 2,2-diphenylcyclohexanone oxime was slowly added in small portions. After standing at room temperature for 24 hr., 50 ml. of water was cautiously added to the chilled reaction mixture. The ether layer was separated and the aqueous solution extracted four times with 50-ml. portions of ether. The ethereal solution and extracts were combined, dried over anhydrous magnesium sulfate, filtered, and evaporated to yield 0.86 g. (96%) of 6,6-diphenyl-5-hexenonitrile, m.p. 61–63°. A single recrystallization of the nitrile from methanol produced a white crystalline product, m.p. 62.5–63°, the melting point of which was not depressed with a sample of the nitrile obtained from the thionyl chloride rearrangement of 2,2-diphenylcyclohexanone oxime.

III. 2,2-Diphenylcycloheptanone Oxime.[16] (a) Using Polyphosphoric Acid.—A mixture of 5.0 g. (0.019 mole) of 2,2-diphenylcycloheptenone oxime and 55.0 g. of polyphosphoric acid was heated at 125–130° for 10 min. On cooling, the reaction mixture was hydrolyzed in 650 ml. of ice-cold 10% sodium hydroxide. The alkaline solution was extracted four times with 50-ml. portions of chloroform. The chloroform extracts were combined over anhydrous magnesium sulfate, filtered, and evaporated at reduced pressure to yield 4.89 g. of a dark red viscous oil. The crude product mixture was dissolved in a minimum amount of chloroform and chromatographed over 210 g. of alumina, eluting successively with ether, 1:1 ether–chloroform and finally chloroform.

2,2-Diphenylcycloheptanone.—Fractions 1–8 yielded 0.30 g. (6.3%) of 2,2-diphenylcycloheptanone on evaporation of the ether eluents, m.p. 93.5–94°. The melting point was

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[15] C. Cauquil, J. Rouzaud, R. E. Lyle, H. L. Fielding, and G. G. Lyle, *Bull. soc. chim. France*, 513 (1955).

[16] These experiments were performed by R. T. C. during the course of the doctoral dissertation studies at Princeton University. It is a pleasure to thank Prof. R. K. Hill for permission to publish this work and for his interest and stimulating discussions.

not depressed on admixture with an authentic sample, m.p. 93.5–94°.

2-Keto-8,8-diphenylheptamethylene Imine.—Fractions 21–25 on evaporation of the chloroform eluents yielded 0.57 g. (11.5%) of a white crystalline product which gave a characteristic lactam spectrum in chloroform solution with a single N—H at 2.95 μ and Amide I band at 6.05 μ. The ultraviolet spectrum indicated typical weak, nonconjugated phenyl absorption at 240 mμ and 275 mμ. After four recrystallizations from ethyl acetate, the fine colorless needles, melted at 244–245°.

Anal. Calcd. for $C_{19}H_{21}NO$: C, 81.68; H, 7.58; N, 5.01. Found: C, 82.22; H, 7.06; N, 4.93.

7,7-Diphenylheptanamide.—Fractions 35–51 were combined and the chloroform evaporated to yield 3.34 g. (66.8%) of 7,7-diphenylheptanamide. After two recrystallizations from ethyl acetate–petroleum ether, the amide melted at 105–106°. Admixture with an authentic sample showed no depression, m.p. 105–106°. However, on admixture with a sample of 7,7-diphenyl-6-heptenamide a marked depression was observed, m.p. 84–91°.

Anal. Calcd. for $C_{19}H_{23}NO$: C, 81.10; H, 8.24; N, 4.98. Found: C, 81.25; H, 8.30; N, 5.03.

Hydrolysis to 7,7-Diphenylheptanoic Acid.—A mixture of 1.0 g. of 7,7-diphenylheptanamide, 4.8 g. of potassium hydroxide, and 25 ml. of diethylene glycol was heated under reflux for 4.5 hr. On cooling, an equal volume of water was added and the mixture extracted three times with 10-ml. portions of ether. The aqueous solution was then acidified with dilute hydrochloric acid. The acid solution was extracted ten times with 25-ml. portions of ether. The extracts of the acid solution were combined, dried over anhydrous magnesium sulfate, filtered, and evaporated under reduced pressure. The semisolid residue was crystallized from cyclohexane to yield 0.93 g. (93%) of 7,7-diphenylheptanoic acid, m.p. 104–105° (lit.,[15] m.p. 104–105°). The melting point was not depressed when mixed with an authentic sample.

(b) **Using Thionyl Chloride.**[3i]—A solution of 10 ml. of redistilled thionyl chloride in 10 ml. of anhydrous benzene was cautiously added to a suspension of 10 g. of 2,2-diphenylcycloheptanone oxime in 100 ml. of anhydrous benzene. The mixture was allowed to stand at room temperature for 24 hr. The solvents were removed at reduced pressure and the residue placed in a Soxhlet extractor. After 3.5 hr. of continuous extraction with petroleum ether, the solvent was removed and the residual oil cooled. The solid was examined in the infrared region and showed no indication of lactam formation as one of the reaction products. After recrystallization from ethanol (three times), 9.2 g. of 7,7-diphenyl-6-heptenonitrile was obtained, m.p. 59–59.5° (lit.,[3i] m.p. 59–59.5°); λ_{max} 250 mμ, log ϵ 4.13.

Preparation of 7,7-Diphenyl-6-heptenamide. (a).—The amide was prepared as described previously for the preparation of 6,6-diphenyl-5-hexenamide. Initial hydrolysis of 7,7-diphenyl-6-heptenonitrile yielded the acid, m.p. 74–74.5° (lit.,[3i] 70.5–71.5°); λ_{max} 250 mμ, log ϵ 4.12. The acid was converted to the amide using first oxalyl chloride followed by anhydrous ammonia. After two recrystallizations from ethyl acetate–petroleum ether, 7,7-diphenyl-6-heptenamide was isolated, m.p. 93.5–94.5°, λ_{max} 249 mμ, log ϵ 4.12.

Anal. Calcd. for $C_{19}H_{21}NO$: C, 81.68; H, 7.58; N, 5.01. Found: C, 81.57; H, 7.50; N, 5.01.

(b) **Hydration of the Nitrile Using Sulfuric Acid.**—To 5 ml. of concd. sulfuric acid cooled in an ice–salt mixture, 0.15 g. of 7,7-diphenyl-6-heptenonitrile was slowly added over a 15-min. period. The mixture was stirred until all of the solid dissolved. After 2 hr. at −5°, the mixture was hydrolyzed over crushed ice. The cold aqueous acid was thoroughly extracted with chloroform. The chloroform extracts were combined, dried over anhydrous magnesium sulfate, filtered, and evaporated. The residual solid was recrystallized five times from ethyl acetate-petroleum ether to yield a small amount of 7,7-diphenyl-6-heptenamide, m.p. 93.5–94.5° identical in all respects to the sample obtained from the unsaturated acid.

(c) **Hydration of the Nitrile Using Polyphosphoric Acid.**—A mixture of 1.0 g. of 7,7-diphenyl-6-heptenonitrile and 10.5 g. of polyphosphoric acid was heated slowly to 125–130°. After 10 min., the reaction mixture was poured into 150 ml. of crushed ice and water. The aqueous solution was extracted three times with 50-ml. portions of chloroform. The chloroform extracts were combined dried over anhydrous magnesium sulfate, filtered, and evaporated. On recrystallization of the solid residue from ethyl acetate–petroleum ether, 0.6 g. of 7,7-diphenyl-6-heptenamide was obtained, m.p. 93.5–95°.

The filtrate from the crystallization was evaporated to yield 0.1 g. of a yellow-white solid. After a single recrystallization and sublimation, 2-keto-8,8-diphenylheptamethylene imine was obtained, m.p. 243–244.5°. Mixed melting point determined by admixture with Beckmann rearrangement product did not depress, m.p. 243–245°.

Reduction of 7,7-Diphenyl-6-heptenamide.—A mixture of 1.0 g. of 7,7-diphenyl-6-heptenamide and 50 ml. of absolute ethanol was hydrogenated at 70 p.s.i.g. for 18 hr. using Raney nickel catalyst. The hydrogenation mixture was vented, filtered, then evaporated to yield 0.9 g. of 7,7-diphenylheptanamide, m.p. 105–106°. Admixture with the amide obtained from the polyphosphoric acid, Beckmann rearrangement did not depress the melting point.

Reduction of 7,7-Diphenyl-6-heptenoic Acid.—Using the procedure described for reduction of the unsaturated amide, 1.0 g. of 7,7-diphenyl-6-heptenoic acid was hydrogenated to yield 0.9 g. of 7,7-diphenylheptanoic acid, m.p. 104–105°.

Cyclization of 7,7-Diphenyl-6-heptenamide in Polyphosphoric Acid.—A mixture of 0.5 g. of 7,7-diphenyl-6-heptenamide and 8.0 g. of polyphosphoric acid was heated to 120–130°. After 25 min., the mixture was poured over crushed ice. The aqueous acid was made basic with 10% sodium hydroxide solution and then extracted four times with 50-ml. portions of chloroform. The chloroform extracts were combined, dried over anhydrous sodium sulfate, filtered, and evaporated under reduced pressure. The residual red oil was chromatographed over alumina in chloroform. Fractions 3–9, eluted with chloroform, were evaporated and the residue triturated with petroleum ether to yield 0.40 g. of a white solid. After a single recrystallization followed by sublimation, 2-keto-8,8-diphenylheptamethylene imine was obtained, m.p. 243–244.5°. Admixture with the Beckmann rearrangement product did not depress the melting point.