Chromatographic separation on acid-washed alumina gave *trans*-1,2-dibenzoylcyclohexane and *o*-dibenzoylbenzene, m.p. 144.5–146°, yield 44 mg. (13%). The aromatized compound was identified by a mixture melting point with an authentic specimen.

1,2-Bis(3,4-dimethylbenzoyl)-1-cyclohexene, made in a similar way in 87% yield, was purified by successive recrystallization from high-boiling petroleum ether–chloroform, ethanol, and methanol, m.p. 137–138°.

Anal. Calcd. for $C_{24}H_{26}O_2$: C, 83.20; H, 7.56. Found: C, 83.28; H, 7.74.

The infrared spectrum shows one carbonyl group at 1655 cm.$^{-1}$ and a peak at 829 cm.$^{-1}$, assignable to the two adjacent hydrogen atoms of the 3,4-dimethylphenyl radical. The NMR spectrum is consistent only with a 1,2-diaroyl-1-cyclohexene structure.

trans-**1,2-Bis(3,4-dimethylbenzoyl)cyclohexane.**—To an ice-cold mixture of *trans* hexahydrophthaloyl chloride (86.2 g., 0.412 mole), 200 ml. of *o*-xylene, and 500 ml. of methylene chloride was added over a 50-min. period 137.4 g. (1.030 moles) of aluminum chloride. The mixture was stirred for 1 hr. in an ice–salt bath, then warmed slowly and heated under reflux for 3 hr. By conventional procedures two products were isolated one of which separated from ethanol as colorless crystals, m.p. 166.5–167.5°.

Anal. Calcd. for $C_{24}H_{28}O_2$: C, 82.72; H, 8.10. Found: C, 82.51; H, 8.13.

That this compound is **2,2-bis(3,4-dimethylphenyl)hexahydrophthalide** is indicated by its infrared spectrum, which has a carbonyl band at 1775–1785 cm.$^{-1}$.

The second product, also recrystallized from ethanol, was identified as *trans*-1,2-bis(3,4-dimethylbenzoyl)cyclohexane, m.p. 107.5–109°. The yield of crude product was 21%.

Anal. Calcd. for $C_{24}H_{28}O_2$: C, 82.72; H, 8.10. Found: C, 82.87; H, 8.13.

The assigned structure is supported by a peak in the infrared spectrum for a carbonyl group (1670 cm.$^{-1}$) and peaks for a 1,2,4-trisubstituted aryl group (900, 834, and 823 cm.$^{-1}$).

2-Duroylcyclohexane-1-carboxylic Acid.—A solution of 16.2 g. (0.105 mole) of *cis* hexahydrophthalic anhydride and 14.1 g. (0.105 mole) of durene in 200 ml. of dry methylene chloride was stirred at 0° while 33.4 g. (0.250 mole) of aluminum chloride was added during a 15-min. period. The reaction mixture, after being allowed to come to room temperature, was heated under reflux for 4 hr. with continued stirring and poured into a mixture of ice and 10 ml. of concentrated hydrochloric acid. 2-Duroylcyclohexane-1-carboxylic acid, recrystallized from ethyl acetate, melted at 194–195°, yield 19.5 g. (65%).

Anal. Calcd. for $C_{18}H_{24}O_3$: C, 74.97; H, 8.39. Found: C, 74.84; H, 8.42.

The infrared spectrum shows adsorption in the 2500–3400-cm.$^{-1}$ region (hydroxyl group), at 1705–1710 cm.$^{-1}$ (aliphatic acid carbonyl group), at 1690 cm.$^{-1}$ (hindered ketone carbonyl group), and at 865 cm.$^{-1}$ (carbon-hydrogen deformation characteristic of the duryl group).

Beckmann Rearrangements in Alicyclic Systems. I. Spiro[5.6]dodecan-7-one Oxime[1]

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The Beckmann rearrangement of spiro[5.6]dodecan-7-one oxime under a variety of catalyic conditions is reported. Using polyphosphoric acid, 6-cyclohexylcaproamide was isolated as the only product af the rearrangement. Phosphorus pentachloride rearrangement yielded 6-(1′-cyclohexenyl)capronitrile, while concentrated sulfuric acid gave the corresponding amide, 6-(1′-cyclohexenyl)caproamide as the major reaction product. Benzenesulfonyl chloride and sodium hydroxide treatment of the oxime resulted in the formation of 7-azaspiro[5.7]tridecan-8-one rather than the expected nitrile from abnormal cleavage. Attempted Ritter reaction of the unsaturated nitrile using either concentrated sulfuric acid or polyphosphoric acid resulted in amide formation rather than cyclization to the lactam or α,β-unsaturated ketone as observed in other spiroketoxime systems.

Recently, the Beckmann rearrangement of several spiroketoximes in polyphosphoric acid leading to unusual products has been reported.[2] With the oximino group in a five-membered ring, rearrangement usually proceeded in high yield to an α,β-unsaturated ketone. However, with the oximino group in a six-membered ring, the yield of the unsaturated ketone sharply decreased and a second product, a saturated amide was also isolated in reasonable yield from the reaction mixtures.

The mechanism proposed for this reaction was initially identical to the course of rearrangement followed by a large number of α,α-disubstituted ketoximes[3] in that it was proposed that bond cleavage took place to produce an unsaturated nitrile. Such reactions have been observed in various nonprotonating media and in certain cases in protonating media to yield amides instead of the nitrile group through hydration. Indeed, this course for the rearrangement has been reported for such systems as the Beckmann rearrangement of α-keto and α-hydroxy ketoximes[4] and also reported in the low temperature Schmidt reactions

(1) This work was supported by a Frederick Gardner Cottrell Grant from the Research Corporation and 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, *Chem. Ind.* (London), 1314 (1956); (b) R. K. Hill and R. T. Conley, *J. Am. Chem. Soc.*, **82**, 645 (1960).

(3) For review see: L. G. Donaruma and W. Z. Heldt, *Org. Reactions*, **11**, 1 (1960).

(4) (a) R. T. Conley and F. A. Mikulski, *Tetrahedron*, **3**, 90 (1958); (b) R. T. Conley and F. A. Mikulski, *J. Org. Chem.*, **24**, 97 (1959).

of a series of spiroketones in polyphosphoric acid.[5] Polyphosphoric acid, however, presents the opportunity for the unsaturated nitrile to react further. Protonation of the nitrile group would give an ion which could undergo cyclization with a double bond suitably situated. Subsequent ejection of a proton followed by hydrolysis would yield an α,β-unsaturated ketone.

In the course of a number of concurrent studies concerned with Beckmann rearrangements in alicyclic systems, it became of interest to investigate further the effect of enlarging the size of the spiro-ring containing the oximino group. Examples of the rearrangement of 2,2-disubstituted cycloheptanone oximes have been reported. Lyle, Fielding, Canquil, and Rouzaud[6] found that treatment of 2,2-diphenylcycloheptanone oxime with thionyl chloride cleaved the ring to yield 7,7-diphenyl-6-heptenonitrile. These investigators also reported the failure of sulfuric acid to promote rearrangement of this oxime. Hill and Conley[2a] have observed the formation of 7,7-diphenylheptanamide on treatment of this oxime with hot polyphosphoric acid. This latter reaction was analogous to the saturated amide formation observed in several spiroketoxime rearrangements in polyphosphoric acid. In order to contrast these results with the seven-membered oximino compound of the spiroketoxime series, the rearrangement of spiro[5.6]dodecan-7-one oxime was investigated.

Rearrangement of spiro[5,6]dodecan-7-one oxime would be expected to yield an unsaturated nitrile by the typical oxime cleavage process. The unsaturated nitrile should have the double bond in either the *endo* or *exo* position to the cyclohexane ring. With the double bond in the favored *endo* position, cyclization of the nitrile to form an α,β-unsaturated ketone would necessitate the formation of the energetically unfavored eight-membered ring system. However, isomerization of the double bond to the *exo* position would on cyclization form a six-membered ring. This situation is also unfavorably due to the stability of the double bond in the *endo* position. Since these cyclization routes are not favored, it would be anticipated that saturated amide formation as a secondary process would occur to an appreciable extent.

Spiro[5,6]dodecan-7-one was prepared by the very convenient route described by Mousseron, Jacquier, and Christol[7] by the direct alkylation of cycloheptanone with pentamethylene dibromide in 41% yield. Oximation using the pyridine–ethanol solvent system and hydroxylamine hydrochloride[8] resulted in the near quantitative (94%) isolation of the desired oxime.

Rearrangement Studies.—The reaction of spiro[5.6]dodecan-7-one oxime using phosphorus pentachloride cleaved the oxime in nearly quantitative yield to 6-(1′-cyclohexenyl)capronitrile. The cyano group was distinguished by its infrared absorption. The compound was identified by hydrolysis to 6-(1′-cyclohexenyl)caproamide and the comparison of the amide with an authentic sample prepared independently from 5(1′-cyclohexenyl)-valeric acid by the Arndt-Eistert synthesis. Using thionyl chloride for the rearrangement yielded a large amount of tarry material. Column chromatography over alumina yielded only trace amounts of the nitrile which was identified as 6-(1′-cyclohexenyl)capronitrile by its spectral identity with the phosphorus pentachloride rearrangement product. Benzenesulfonyl chloride in sodium hydroxide, investigated as typical of rearrangements taking place in alkaline medium, yielded the lactam, 7-azaspiro[5.7]tridecan-8-one, identified as a lactam by its typical infrared spectrum. In carbon tetrachloride solution, the infrared spectrum showed a single band at 2.93 μ for the N—H stretching vibration and a single amide band at 6.05 μ indicative of the amide I band. As typical of lactams, no amide II band was found in the 6-μ region of the spectrum. The compound was identified by comparison with an authentic sample prepared by the method described by Hill.[9] When the oxime was treated with concentrated sulfuric acid only a single product could be isolated from the product mixture which was badly charred. The compound was identified as 6-(1′-cyclohexenyl)caproamide by comparison with a synthetic sample. Using polyphosphoric acid at 120°, rearrangement resulted in the formation again of only a single product, 6-cyclohexylcaproamide, in 46% yield. The compound was identified by comparison with an authentic sample prepared by the reduction of 6-(1′-cyclohexenyl)-caproamide. The remainder of the reaction mixture was carefully examined for ketonic components without avail. All attempts to isolate additional products by chromatographic techniques failed. The infrared spectrum of the remaining black material was typical of an amide, although no monomeric material could be withdrawn from it. These rearrangements are summarized in Fig. 1.

Extending the study, it was of interest to attempt the cyclization of the unsaturated nitrile, 6-(1′-cyclohexenyl)capronitrile, to an α,β-unsaturated ketone using polyphosphoric acid. Isolation of the reaction product yielded only the corresponding amide from nitrile hydration. It has been postulated[2] that the reason similar unsaturated nitriles do not undergo the Ritter reaction may be that the shorter methylene chains connecting the cyano

(5) R. T. Conley and B. E. Nowak, *J. Org. Chem.*, **26**, 692 (1961).

(6) R. E. Lyle, H. L. Fielding, G. Canquil, and J. Rouzaud, *ibid.*, **20**, 623 (1955).

(7) (a) M. Mousseron, R. Jacquier, and H. Christol, *Compt. rend.*, **239**, 1805 (1954); (b) M. Mousseron, R. Jacquier, and H. Christol, *Bull. soc. chim. France*, 346 (1957).

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

(9) R. K. Hill, *J. Org. Chem.*, **22**, 830 (1957).

group to the double bond may not be long enough to permit the nitrogen of the linear cyano group to approach the carbonium ion. Apparently, this is not the case here. Neither ketone nor lactam could be formed under the reaction conditions utilized in smaller methylene chain systems. Attempts to cyclize the amide as previously described for shorter chained species[9] failed even at temperatures up to 180°. It must be concluded, therefore, that once the ring is opened to the unsaturated nitrile or unsaturated amide, the cyclization reactions to form larger ring unsaturated ketones or lactams are not favored. These data add support to the postulated mechanism for the unsaturated ketone formation[2] since the primary reaction step must be the cleavage reaction of the oxime to the unsaturated nitrile. This process is followed by secondary reactions promoted by the solvent-catalyst medium.

Since it has also been shown that the formation of saturated amides is not a result of the reaction of polyphosphoric acid and an unsaturated nitrile,[2] experiments were conducted in which added hydroxylamine, a potential reducing agent,[10] was present in excess. On rearrangement of the oxime under these conditions no increased yield of the saturated amide was noted. Therefore, it must be concluded that either some third compound is required (as yet unknown) to act as a reducing agent or that the reaction product is formed directly from the oxime. It was also thought possible that the lactam might be cleaved reductively in polyphosphoric acid by a disproportionation reaction of the reagent. This route of reduction was also negated in this study since heating the lactam in polyphosphoric acid for thirty minutes at 130° resulted in the near quantitative recovery of the starting material on isolation of the products from the reaction mixture.

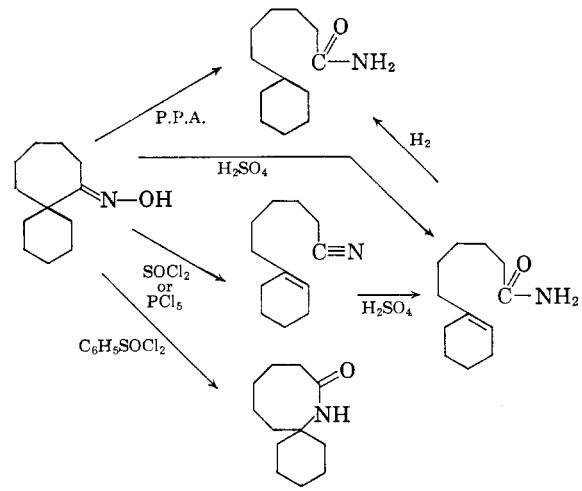

Figure 1

Experimental

All melting points were determined using a Hoover-Thomas Unimelt apparatus and are corrected. The infrared spectra used for comparison were determined using a Baird, Model AB-2, double beam recording spectrophotometer.

Spiro[5.6]dodecan-7-one was prepared by the method described by Mousseron, Jacquier, and Christol.[7] The oxime derivative (m.p. 103.5–104°, lit.,[7b] m.p. 101–102°) was obtained using the method outlined by Cram[8]; 7-aza-spiro[5.7]tridecan-8-one was prepared by the procedures outlined by Hill[9] from nitrocyclohexane. 5-(1′-Cyclohexenyl)valeric acid was obtained by the procedure described by Hill and Conley.[2]

Beckmann Rearrangements of Spiro[5,6]dodecan-7-one Oxime. (a.) **With Phosphorus Pentachloride.**—To a solution of 1.0 g. of spiro[5.6]dodecan-7-one oxime in 20 ml. of anhydrous benzene 1.68 g. of phosphorus pentachloride was added in small portions. When the exothermic reaction ceased, the flask was stoppered and kept overnight. The benzene solution was washed successively with water, dilute sodium carbonate, and saturated salt solution, then filtered and evaporated. The infrared spectrum of the crude product after solvent removal showed a strong nitrile band at 4.45 μ and the noticeable absence of any bands attributable to a lactam. A sample was obtained for analysis by chromatography over alumina in ether. From the ether eluents 0.84 g. (92%) of the colorless 6-(1′-cyclohexenyl)-capronitrile was isolated.

Anal. Calcd. for $C_{12}H_{19}N$: C, 81.30; H, 10.80; N, 7.90. Found: C, 81.52; H, 10.91; N, 7.82.

Hydrolysis of 6-(1′-Cyclohexenyl)capronitrile to 6-(1′-Cyclohexenyl)caproamide.—A mixture of 0.45 g. of 6-(1′-cyclohexenyl)capronitrile and 2.0 g. of concd. sulfuric acid was allowed to stand for 24 hr. after mixing at 0°. The reaction mixture was poured into 25 g. of crushed ice and water. After two extractions of the aqueous solution with 25-ml. portions of chloroform, drying of the combined extracts over anhydrous magnesium sulfate, filtration, and evaporation, 0.38 g. (76%) of 6-(1′-cyclohexenyl)-caproamide, m.p. 98.5–99° (lit.,[11] m.p. 98–99°), was isolated by sublimation at 95°/0.05 mm.

Anal. Calcd. for $C_{12}H_{21}NO$: C, 73.80; H, 10.85; N, 7.17. Found: C, 73.79; H, 10.83; N, 7.02.

Synthesis of 6-(1′-Cyclohexenyl)caproamide.—5-(1′-Cyclohexenyl)valeric acid[2] (2.0 g.) was treated in the cold with 2.5 g. of oxalyl chloride, slowly warmed to room temperature, then refluxed on a steam bath for 2 hr. The excess oxalyl chloride was evaporated at reduced pressure, the residue was taken up in anhydrous ether, and added to an ice-cold etheral solution of diazomethane from 3.0 g. of nitrosomethylurea. The solution was allowed to stand for 4 hr., concentrated, and the solid residue refluxed for 3 hr. with a solution of 10 ml. of dioxane, 4 ml. of concd. ammonium hydroxide, and 1 ml. of aqueous, 10% silver nitrate solution. The solution was decolorized, warmed, and diluted with water to the cloud point. After standing for 18 hr. in the refrigerator, the crystals which had separated were collected and sublimed, yielding 1.34 g. of 6-(1′-cyclohexenyl)caproamide, m.p. 98.5–99°.

Mixed melting point determination with the product obtained from the phosphorus pentachloride rearrangement followed by sulfuric acid hydration showed no depression, m.p. 98–99°.

(b). **Using Thionyl Chloride.**—A solution of 1.0 g. of the oxime in 10 ml. of dry benzene was cooled in an ice bath and 2 ml. of redistilled thionyl chloride added dropwise. After standing 24 hr. at room temperature, the solution was concentrated under reduced pressure. The black, semisolid residue was dissolved in petroleum ether (b.p. 60–70°)

(10) (a) E. Wenkert, B. S. Bernstein, and J. H. Udelhofen, *J. Am. Chem. Soc.*, **80**, 4899 (1958); (b) R. E. Steiger, *Org. Syntheses*, Coll. Vol. III, 91 (1955).

(11) J. Plesek, *Chem. Listy*, **49**, 1844 (1955).

and chromatographed over alumina. The ether eluents yielded a light yellow oil, 0.02 g. which on rechromatographing over alumina was spectrally identical to 6-(1′-cyclohexenyl)capronitrile. Further identification was not attempted. The remainder of the reaction mixture either remained on the column or was eluted with ethanol as a black, viscous oil which could not be further purified.

(c). **With Benzenesulfonyl Chloride and Alkali.** A mixture of 1.0 g. of spiro[5,6]dodecan-7-one oxime, 1.1 g. of benzenesulfonyl chloride, 0.25 g. of sodium hydroxide, 20 ml. of acetone, and 5 ml. of water was refluxed on a steam bath for 4 hr. Water (50 ml.) was added, the acetone removed at reduced pressure, and the aqueous solution remaining extracted three times with 50-ml. portions of ether. The ether extracts were combined, dried over anhydrous magnesium sulfate, filtered, and evaporated to yield 0.92 g. of a semisolid material. The infrared spectrum of the crude product indicated that no nitrile was present and the product was almost exclusively a lactam. After recrystallization from ethyl acetate–petroleum ether and a single sublimation at 85°/0.05 mm., 0.73 g. (73%) of 7-azaspiro[5.7]tridecan-8-one, m.p. 91.5–92° was obtained.

Anal. Calcd. for $C_{12}H_{21}NO$: C, 73.80; H, 10.85; N, 7.17. Found: C, 73.56; H, 10.78; N, 7.21.

Admixture with an authentic sample showed no depression in the melting point, m.p. 91.5–92°.

(d). **Using Concd. Sulfuric Acid.**—The oxime (0.5 g.) was slowly added to 15 g. of concd. sulfuric acid. The mixture was slowly heated on an oil bath. At 40° an exothermic reaction occurred and the temperature rose sharply to 70°. After several minutes, the reaction mixture was hydrolyzed over 30 g. of crushed ice. The aqueous solution was neutralized with 10% sodium hydroxide solution. The aqueous mixture was extracted four times with 20-ml. portions of ether. The extracts were combined, dried over anhydrous magnesium sulfate, filtered, and evaporated to 0.35 g. of a dark brown, viscous oil. The oil was sublimated at 95°/0.05 mm. to yield 0.05 g. (10%) of 6-(1′-cyclohexenyl)caproamide, m.p. 98–99°, not depressed by admixture with an authentic sample.

(e). **In Polyphosphoric Acid.**—A mixture of 2.0 g. of spiro[5,6]dodecan-7-one oxime and 22.5 g. of polyphosphoric acid was slowly heated, with stirring, to 120–125°. After 10 min., the reaction mixture was worked up as described in (d) to yield 1.9 g. of a dark brown solid. Infrared examination of the crude product showed the absence of any functional groups other than an amide (3.1, 5.95, and 6.2 μ). The product was passed through an alumina column in ether to yield only 0.93 g. (46%) of 6-cyclohexylcaproamide. After a single sublimation at 95°/0.05 mm. the product showed a melting point of 109.5–110°. When admixed with an authentic sample no depression in melting point was observed, m.p. 109.5–110°.

Anal. Calcd. for $C_{12}H_{23}NO$: C, 73.04; H, 11.75; N, 7.10. Found: C, 72.94; H, 11.61; N, 7.02.

Examination of the eluents from the alumina column as well as the crude reaction mixture using 2,4-dinitrophenylhydrazine reagent failed to indicate the presence of ketonic components among the reaction products.

Preparation of 6-Cyclohexylcaproamide.—The unsaturated amide, 6-(1′-cyclohexenyl)caproamide, (0.10 g.) was hydrogenated at 4 atm. in ethanol using Raney nickel. Evaporation of the filtered solution and sublimation of the product at 95°/0.05 mm. gave 6-cyclohexylcaproamide, m.p. 109.5–110° (lit.,[11] m.p. 114–115°).

Attempted Ritter Reaction of 6-(1′-Cyclohexenyl)capronitrile.—A mixture of 0.5 g. of the unsaturated nitrile and 8.7 g. of polyphoshoric acid was heated to 120–130°. After 20 min., the reaction mixture was worked up as previously described. The infrared spectrum of the crude product was identical to that of 6-(1′-cyclohexenyl)caproamide. The solid reaction product was sublimated at 95°/0.05 mm. to yield 0.46 g. (84%) of the unsaturated amide, m.p. 98–99°, not depressed by admixture with an authentic sample.

Attempted Cyclization of 6-(1′-Cyclohexenyl)caproamide.—A mixture of 0.5 g. of the unsaturated amide and 10.5 g. of polyphosphoric acid was heated at 150–155° for 30 min. After work-up of the reaction mixture and isolation of the product, infrared examination and attempted chromatographic separation over alumina indicated only the starting-material was present, m.p. 98–99°, not depressed by admixture with an authentic sample. A similar experiment at 175–180° gave identical results.

Polyphosphoric Acid Rearrangement with Added Hydroxylamine.—A mixture of 2.0 g. of the oxime, 19.0 g. of polyphosphoric acid, and 0.1 g. of hydroxylamine hydrochloride was heated to 120–125°. After 10 min. the reaction mixture was hydrolyzed and worked up as before to yield 0.95 g. (47%) of 6-cyclohexylcaproamide, m.p. 109–110°. Mixed with an authentic sample, no depression was observed, m.p. 109.5–110°.

Attempted Lactam Cleavage with Polyphosphoric Acid.—7-Azaspiro[5,7]tridecan 8-one (0.25 g.) and 5.0 g. of polyphosphoric acid were heated at 130–135° for 30 min. After hydrolysis and isolation of the crude product in the usual manner, 0.24 g. of the lactam was recovered, m.p. 90.5–92°, not depressed by admixture with the starting material.