[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, CANISIUS COLLEGE]

Schmidt Reactions in Polyphosphoric Acid. II Abnormal Rearrangements of Ketones[1,2]

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The abnormal Schmidt reactions of four spiroketones in polyphosphoric acid are described. The reaction products isolated indicate that ketones having the spiro-atom *alpha* to the carbonyl group rearrange in polyphosphoric acid medium in a manner similar to the abnormal Beckmann rearrangement of the corresponding ketoximes. The proposed mechanism for this transformation is substantiated by isolation of the unsaturated nitriles postulated as reaction intermediates and their corresponding cyclization in polyphosphoric acid to yield bicyclic, α,β-unsaturated ketones.

Recently, it has been reported that polyphosphoric acid is an excellent solvent and catalyst for the Schmidt reaction of ketones.[4] In the original investigation of the application of this method to a variety of compounds in order to determine the scope and limitations of rearrangements in this medium, a series of α-substituted alicyclic ketones were observed to rearrange by the normal reaction path to yield the expected lactams. It was desirable to extend the study to compounds having a completely substituted carbon *alpha* to the carbonyl group of the ketone since it has been shown that ketoximes of compounds of this type usually rearrange abnormally under acid catalyzed Beckmann rearrangement conditions.[5] Moreover, Barton[6] has reported that sulfuric acid catalyzed Schmidt reaction of 3-beta-acetoxyandrostane-11,17-dione, an example of an α-disubstituted carbonyl compound, yields an unsaturated nitrile presumably arising from a cleavage reaction similar to that observed in the abnormal, second-order Beckmann transformation.[7] Hill and Conley[8] have found that the oxime of spiro[4,4]nonanone-1 and related spiroketoximes having the spiro-atom *alpha* to the oximino-group rearrange in polyphosphoric acid to yield bicyclic, α,β-unsaturated ketones along with other products arising from abnormal rearrangement reaction. In no case was any of the expected lactam observed. These authors proposed as intermediates in these reactions, the unsaturated nitriles obtained by a second-order cleavage process observed under other acid catalyzed conditions. Cyclization of the unsaturated nitriles by polyphosphoric acid under the conditions used for ketoxime rearrangement yield the same bicyclic, α,β-unsaturated ketones by an unusual type of Ritter reaction[9] in which carbon is added across the olefinic linkage rather than the usual nitrogen addition to produce secondary amides.

It was, therefore, desirable to investigate the Schmidt rearrangement of a series of spiro ketones under polyphosphoric acid catalyzed conditions in an effort to correlate the abnormal Schmidt reaction to the abnormal Beckmann rearrangement. In addition, by using the same series of spiro ketones, it was felt that it would be possible, at least in the cases under study, to distinguish experimentally between the proposed mechanism for the Schmidt reaction formulated by Newman[10] and Smith.[11] The extension of these mechanisms to the abnormal rearrangement is shown in Fig. 1.

Since in polyphosphoric acid, amides such as the amide derived from cyclopentylidenebutyronitrile have been shown to yield the lactams anticipated

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(3) Abstracted, in part, from the thesis of B.E.N. submitted to the Department of Chemistry, Canisius College, in fulfillment of the requirements for the Bachelor of Science degree.

(4)(a) R. T. Conley, *Chem. Ind. (London)*, 438 (1958). (b) R. T. Conley, *J. Org. Chem.*, **23**, 1330 (1958).

(5)(a) R. Leuckart and E. Bach, *Ber.*, **20**, 104 (1887); (b) G. Schroeter, *Ber.*, **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, *J. Am. Chem. Soc.*, **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, *J. Org. Chem.*, **18**, 1058 (1953); (i) R. E. Lyle, H. L. Fielding, G. Canquil, and J. Rouzand, *J. Org. Chem.*, **20**, 623 (1955). For exceptions, see: (j) B. M. Regan and F. N. Hayes, *J. Am. Chem. Soc.*, **78**, 639 (1956); (k) S. Kaufmann, *J. Am. Chem. Soc.*, **73**, 1779 (1951); (l) W. D. Burrows and R. H. Eastman, *J. Am. Chem. Soc.*, **79**, 3756 (1957); (m) H. A. Bruson, F. W. Grant, and E. Bobko, *J. Am. Chem. Soc.*, **80**, 3633 (1958); (n) R. T. Conley, L. F. Frainier, and B. E. Nowak, Absts. of Papers, Am. Chem. Soc., 136th Meeting, Atlantic City, September 1959.

(6) D. H. R. Barton, A. da. S. Campos Neves, and A. I. Scott, *J. Chem. Soc.*, 2698 (1957).

(7) For other examples of abnormal Schmidt reactions arising from a second-order cleavage process see: P. A. S. Smith and J. P. Horowitz, *J. Am. Chem. Soc.*, **72**, 3718 (1950).

(8)(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).

(9) J. J. Ritter and P. P. Minieri, *J. Am. Chem. Soc.*, **70**, 4045 (1948).

(10) M. S. Newman and H. Gildenhorn, *J. Am. Chem. Soc.*, **70**, 317 (1948).

(11) P. A. S. Smith, *J. Am. Chem. Soc.*, **70**, 320 (1948).

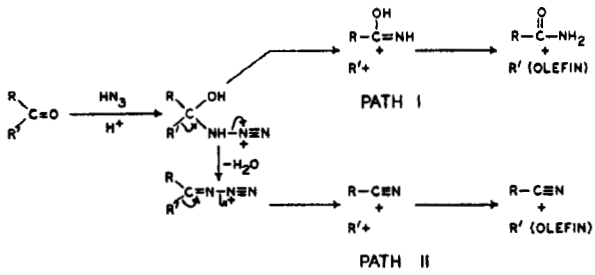

Fig. 1. Abnormal rearrangement of ketones

from a normal rearrangement of the spiro ketones,[12] reactions proceeding *via* the amide intermediate (Reaction Path I. Fig. 1) would be anticipated to yield a lactam. Alternately, if the hydroxyl-carbonium ion[10] was not the reaction intermediate, but rather a Beckmann type intermediate[11] was produced by dehydration of the ketone-hydrazoic acid adduct prior to rearrangement, on nitrogen elimination a nitrile would be produced. Under polyphosphoric acid catalysis the unsaturated nitrile would be expected to yield a bicyclic, α,β-unsaturated ketone as the reaction product.[8]

It can now be reported, at least in the cases studied, that ketones having the spiro-atom *alpha* to the carbonyl group rearrange in polyphosphoric acid medium, first to the unsaturated nitriles, which are cyclized to bicyclic, α,β-unsaturated ketones. Spiro[4,4]nonanone-1,spiro[4,5]decanone-1, spiro[4,5]decanone-5, and spiro[5,5]undecanone-1 on treatment with hydrazoic acid in polyphosphoric acid at 60–70° for eight hours yield $\Delta^{8,9}$-hydrindenone-4, $\Delta^{9,10}$-octalone-1, cyclopentylidenecyclopentanone, and cyclohexylidenecyclopentanone, respectively. In none of these cases was any of the "normal" lactam isolated.

Synthesis of the spiro ketones followed standard routes. Spiro[4,5]decanone-5 was prepared by the pinacol rearrangement of 1,1′-dihydroxybicyclopentyl. Contraction of the ketone ring by nitric acid oxidation and barium oxide pyrolysis of the diacid yielded spiro[4,4]nonanone-1. Spiro[5,5]-undecanone-1 was prepared by a modification of the method described by Mousseron, Jacquier, and Christol[13] utilizing the alkylation of cyclohexanone with 1,5-dibromopentane in the presence of potassium *t*-butoxide. Spiro[4,5]decanone-1 was prepared from spiro[5,5]undecanone-1 by contraction of the ketone ring as described above. All of the ketones were carefully purified and the physical properties of the oxime derivatives found in agreement with reported values.

The rearrangement of spiro[4,4]nonanone-1 was studied most extensively. Rearrangement with polyphosphoric acid at room temperature for two hours resulted in the formation of γ-cyclopentylidenebutyronitrile in low yield. The cyano group was distinguished by its infrared absorption at 4.3 μ and the compound was identified by hydrolysis to the corresponding acid, which took up one mole of hydrogen upon catalytic reduction to yield γ-cyclopentylbutyric acid, identified by mixed melting point determination of its *p*-bromophenacyl ester with a synthetic sample. The position of the unsaturation was determined by ozonolysis of the unsaturated acid and identification of cyclopentanone among the products, thus establishing the structure, γ-cyclopentylidenebutyronitrile for the initial cleavage reaction.[14]

At higher temperatures (60–70°), and longer reaction times (eight hours), $\Delta^{8,9}$-hydrindenone-4 was obtained and identified by its infrared and ultraviolet spectral characteristics and the physical constants of its derivatives.

A reasonable mechanism for the rearrangement is illustrated in Fig. 2. As in the mechanism proposed by Smith,[11] (Reaction Path II, Fig. 1) the reaction is initiated by protonation of the carbonyl group by polyphosphoric acid followed by the addition of hydrazoic acid to the carbonium ion to produce the ketone-hydrazoic acid adduct. Dehydration of the adduct forms a Beckmann type intermediate which on loss of nitrogen leaves an electron deficient nitrogen atom. In the normal rearrangement, the loss of the nitrogen is accompanied by simultaneous migration of the α-carbon *trans* to the eliminating species, leading to lactam formation. The presence of two substituents on the α-carbon permits a second path to compete

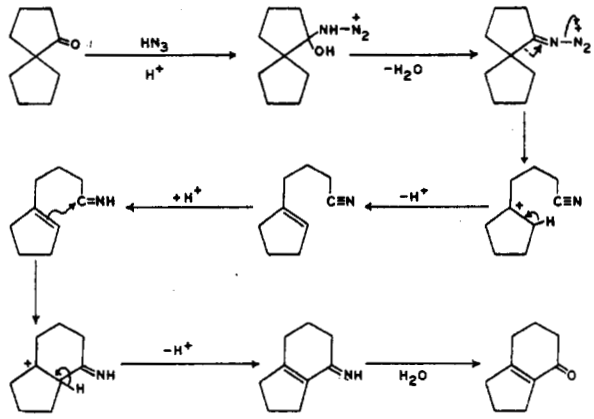

Fig. 2. Rearrangement of spiro[4,4]nonane-1

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

(13) M. Mousseron, R. Jacquier, and H. Christol, *Compt. rend.*, **239**, 1805 (1954).

(14) It is unexpected to observe formation of the double bond *exo* to the five membered ring rather than in the more stable *endo* position.[15] The probable explanation is that the reaction conditions are such not to allow equilibrium between the two isomers, and therefore the more stable product is not formed preferentially. Compare the dehydration of a steroid, 1-alkylcyclopentanol, which leads to an alkylidene, cyclopentane.[16]

(15) R. B. Turner and R. H. Garner, *J. Am. Chem. Soc.*, 80, 1424 (1958).

(16) A. Butenandt, J. Schmidt-Thome, and H. Paul, *Ber.*, **72**, 1112 (1939).

with bond migration: bond cleavage, in which only the bonding electrons move to satisfy the electron-deficient nitrogen, leaving a stable tertiary carbonium ion. Loss of a proton from this ion forms the unsaturated nitrile.

Polyphosphoric acid as a strong protonating medium presents the opportunity for the nitrile to react further. Protonation of the cyano group produces an imino-carbonium ion which may undergo cyclization *via* electrophilic attack on a suitably situated double bond, yielding after proton elimination and hydrolysis of the imine, a bicyclic, α,β-unsaturated ketone. The proof of the correctness of this proposed step in the mechanism was confirmed by subjecting the reaction mixture obtained after two hours at room temperature to elevated temperatures (60–80°) and on hydrolysis isolating the unsaturated ketones.

The possibility that the reaction proceeds through an amide intermediate or that the nitrile is first hydrated to the amide, which then cyclizes by direct loss of ammonia is excluded by the finding of Hill[12] that polyphosphoric acid converts the amide to the lactam. This is further exemplified in this investigation, as δ-cyclopentylidenevaleronitrile, obtained from rearrangement of spiro[4,5]-decanone-5, was converted to the amide, and treated under the reaction conditions (60–80°) in polyphosphoric acid for eight hours to yield the expected lactam rather than the α,β-unsaturated ketone.

Spiro[4,5]decanone-1 and spiro[4,5]decanone-5 on rearrangement gave $\Delta^{9,10}$-octalone-1 and cyclopentylidenecyclopentanone, respectively. However, in the former case appreciable tarring of the reaction mixture occurred and only 56% of the ketonic product could be isolated. Attempted separation of the residual material was unsuccessful. In the latter, case 82% of the ketone was obtained as the only identifiable product of the reaction. At room temperature, spiro[4,5]decanone-5 gave cyclopentylidenevaleronitrile which could be converted to cyclopentylidenecyclopentanone by the action of polyphosphoric acid in a fashion analogous to that described above. The nitrile was identified by conversion to the amide through hydrolysis to the acid, followed by standard conversion procedures to the amide, and comparison with an authentic sample of δ-cyclopentylidenevaleramide.

Spiro[5,5]undecanone-1 presents the only wide divergence from the results reported for ketone formation on ketoxime rearrangements with polyphosphoric acid. On rearrangement of spiro[5,5]-undecanone-1, a 22% yield of cyclohexylidenecyclopentanone was obtained. The structure of cyclohexylidenecyclopentanone was established by the reduction to 2-cyclohexylcyclopentanone by the method of Cornubert[17] and by its ultra violet spectrum. The corresponding oxime has been reported to yield bicyclo[5,4,0]undec-10-en-5-one. The reason for this difference in unsaturated ketone is not well understood, at present, but it is possible that the differences in rearrangement conditions used in each study may be an important factor in the rate of isomerization of the double bond of the nitrile intermediate prior to the cyclization process. In the Beckmann rearrangement the double bond was in the expected *endo* position; in the case presented here the double bond undoubtedly was *exo* to the cyclohexane ring during the cyclization process. Formation of cyclohexylidenecyclopentanone as in the formation process to form cyclopentylidenecyclopentanone requires cyclization of the cyano group with the double bond in the *exo* position. It is presumed that although this *endo-exo* pair is interconvertible in polyphosphoric acid and in spite of the preference for the *endo* position in each case, cyclization occurs at a more rapid rate to form a five-membered ring than to form a seven-membered ring.[18]

Further examples of the abnormal Schmidt reaction to show the generality of these reactions in α,α-disubstituted alicyclic system will be reported in the near future.

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 2-B, double beam recording spectrophotometer. The ultraviolet spectra were determined using a Carey, model 11, recording spectrophotometer.

Reactants. Spiro[4,5]decanone-5 was prepared by the method described by Zelinski and Elagina.[19] Spiro[4,4]-nonanone-1 was obtained by ring contraction of spiro[4,5]-decanone-5 according to the procedure of Cram and Steinberg.[20] Spiro[5,5]undecanone-1 was prepared by a modification of the method of Mousseron, Jacquier, and Christol.[18] Spiro[4,5]decanone-1 was obtained by the application of the ring contraction procedure of Cram and Steinberg,[20] used to obtain spiro[4,4]nonanone-1.

Products: $\Delta^{8,9}$-Hydrindenone-4,[21] $\Delta^{9,10}$-octalone-1[22], and cyclopentylidenecylopentanone[23] were prepared by reported procedures.

$\Delta^{8,9}$-Hydrindenone-4 from spiro[4,4]nonanone-1. To a mixture of 13.8 g. (0.1 mole) of spiro[4,4]nonanone-1 in 150 g. of polyphosphoric acid, 6.80 g. (0.1 mole) of sodium azide was added in small portions over 1 hr. with constant agitation. After stirring for 7 hr. at 60–70°, the mixture was hydrolyzed in 1000 ml. of crushed ice and water. The solution was made alkaline in the cold with 10% sodium hydroxide solution. The resulting solution was extracted seven

(17) R. Cornubert and H. G. Eggert, *Bull. soc. chim. Franc.*, 522 (1954).

(18) W. S. Johnson, *Org. Reaction*, 2, 117 (1944).

(19) N. D. Zelinski and H. V. Elagina, *Compte, rend. acad. sci., U.S.S.R.*, 49, 568 (1945); *Chem. Absir.*, 40, 6058 (1946).

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

(21) V. Prelog, K. Schenker, and W. Kung, *Helv. Chem. Acta*, 36, 471 (1953).

(22) C. D. Nenitzescu and V. Przemetzky, *Ber.*, 74, 676, 686 (1941).

(23) J. Stanek, *Chem. Listy*, 46, 110 (1952); *Chem. Abstr.*, 47, 8024 (1953).

times with 150-ml. portions of chloroform. The chloroform extracts were combined, dried over anhydrous sodium sulfate, filtered, and evaporated to yield 13 g. of a black, viscous, tarry residue. After elution in 1:1 ether–petroleum ether (b.p. 60–70°) mixture from an alumina column, 4.5 g. (33%) of $\Delta^{8,9}$-hydrindenone-4 was obtained. Ultraviolet absorption (ethanol): λ_{max} 249.5 mμ, ϵ_{max} 9120 (lit.,[21] λ_{max} 250 mμ, log ϵ 3.95).

No other products could be isolated from the remainder of the material on the alumina column on successive elution with polar solvent mixtures.

The oxime after isolation and air drying was recrystallized twice from petroleum ether to yield a white solid, m.p. 135.5–136.5°. Mixed melting point with an authentic sample showed no depression, m.p. 136–136.5°.

The semicarbazone obtained on filtration of the derivatization mixture was twice recrystallized from methanol-water, then methanol alone, m.p. 244° dec. Mixed melting point showed no depression, m.p. 245° dec.

The 2,4-dinitrophenylhydrazone derivative was recrystallized four times from chloroform-methanol, m.p. 252.5° dec. Mixed melting point showed no depression, m.p. 252.5° dec. Ultraviolet absorption (ethanol) λ_{max} 386 mμ, ϵ_{max} 14,360.

Anal. Calcd. for $C_{15}H_{16}N_4O_4$: C, 56.96; H, 5.10; N, 17.71. Found: C, 57.04; H, 5.30; N, 17.96.

α-Cyclopentylidenebutyronitrile from spiro[4,4]-nonanone-1: To a mixture of 13.8 g. (0.1 mole) of spiro[4,4]nonanone-1 in 156 g. of polyphosphoric acid, 6.80 g. (0.1 moles) of sodium azide was added in small portions over 1 hr. with slow agitation. After 2 hr. at room temperature, the mixture was hydrolyzed with 1000 ml. of crushed ice and water. The aqueous solution was extracted five times with 100-ml. portions of ether. The ether extracts were combined, dried over anhydrous magnesium sulfate, filtered, and evaporated. On chromatography over an alumina column, two fractions were obtained: 8.28 g. (60%) of spiro[4,4]nonanone-1 was recovered along with 2.43 g. (18%) of α-cyclopentylidenebutyronitrile.

Anal. Calcd. for $C_9H_{13}N$: C, 79.95; H, 9.69; N, 10.36. Found: C, 80.15; H, 9.69; N, 10.34.

γ-Cyclopentylidenebutyric acid from γ-cyclopentylidenebutyronitrile: A 1.0-g. sample of nitrile was refluxed with 2.5 g. of sodium hydroxide in 5 ml. of water and 20 ml. of ethanol for 8 hr. On cooling, an equal volume of water was added and the alcohol evaporated. The alkaline solution was thoroughly extracted with ether, then acidified with cold, dilute hydrochloric acid. The acidic solution was extracted three times with 25-ml. portions of ether. The ether extracts were combined, dried over anhydrous magnesium sulfate, filtered, and evaporated to yield 1.0 g. of γ-cyclopentylidenebutyric acid. The acid was purified by passing it in ether solution over activated alumina.

Anal. Calcd. for $C_9H_{14}O_2$: C, 63.62; H, 9.15. Found: C, 63.58; H, 9.04.

The *p*-bromophenacyl ester was prepared by standard procedure and after two recrystallizations from ethanol yielded a white crystalline solid, m.p. 65–66°.

Anal. Calcd. for $C_{17}H_{19}O_3Br$: C, 58.13; H, 5.45. Found: C, 58.01; H, 5.38.

γ-Cyclopentylbutyric acid from γ-cyclopentylidenebutyric acid: A 0.5-g. sample of γ-cyclopentylidenebutyric acid was dissolved in 100 ml. of sodium hydroxide solution and hydrogenated in a Paar hydrogenation apparatus for 4 hr. at 6 p.s.i.g. of hydrogen using Raney nickel as a catalyst. The solution was filtered, acidified with dilute hydrochloric acid, then extracted four times with 50-ml. portions of ether. After the usual workup, 0.44 g. of a colorless oil was obtained.

The *p*-bromophenacyl ester was prepared from the crude acid after two recrystallizations from ethanol, a white crystalline derivative, the *p*-bromophenacyl ester of γ-cyclopentylbutyric acid, was obtained, m.p. 80–81°. Mixed melting point with an authentic sample[6b] showed no depression, m.p. 80.5–81.5°.

Ozonolysis of γ-cyclopentylidenebutyric acid: The position of the double bond was established by ozonolysis of γ-cyclopentylidenebutyric acid using standard procedures. After the usual workup, the ketone was isolated as the 2,4-dinitrophenylhydrazone derivative, m.p. 143–144° which did not depress the melting point of the corresponding derivative obtained from cyclopentanone, m.p. 143–144°.

Cyclization of γ-cyclopentylidenebutyronitriles: A mixture of 0.5 g. of γ-cyclopentylidenebutyronitrile and 40 g. of polyphosphoric acid were heated at 60–70° with constant stirring for 4 hr. After hydrolysis and evaporation of the ether extracts, the crude residue was converted to the 2,4-dinitrophenylhydrazone derivative. After recrystallization from chloroform-methanol a red crystalline solid was obtained, m.p. 251.5° dec. No depression of the mixed melting point with the 2,4-dinitrophenylhydrazone of $\Delta^{8,9}$-hydrindenone-4 was observed, m.p. 252° dec.

A similar experiment performed directly on a mixture of spiro[4,4]nonanone-1, polyphosphoric acid, and sodium azide after 2 hr. at room temperature was known to contain the unsaturated nitrile; it gave $\Delta^{8,9}$-hydrindenone-4 after subsequent temperature increase to 60–70° for 4 hr.

Cyclopentylidenecyclopentanone from spiro[4,5]decanone-5: To a mixture of 5.0 g. (0.033 mole) of spiro[4,5]decanone-5 in 100 g. of polyphosphoric acid, 2.14 g. (0.033 mole) of sodium azide was added over a period of 30 min. with constant stirring. After 6.5 hr. at 60–70°, the mixture was hydrolyzed in 600 ml. of crushed ice and water. After the solution was made alkaline with cold 10% sodium hydroxide, the aqueous mixture was extracted five times with 150-ml. portions of chloroform. The chloroform extracts were combined, dried over anhydrous sodium sulfate, filtered, and evaporated to yield 4.90 g. of a reddish oil. Chromatography of the red oil in 1:1 petroleum ether–ether mixture yielded 4.06 g. (82%) of cyclopentylidenecyclopentanone. Ultraviolet absorption (ethanol); λ_{max} 256 mμ, ϵ_{max} 8710.

The oxime of cyclopentylidenecyclopentanone was isolated as a yellow solid. After repeated recrystallization from ethanol, a white crystalline derivative was obtained, m.p. 122–123°. The mixed melting point with an authentic sample[23] showed no depression, m.p. 122–123.5°.

The semicarbazone after a single recrystallization from methanol was a white crystalline solid, m.p. 214.5–215°. No depression on mixed melting point was observed 214.5–215°.

The 2,4-dinitrophenylhydrazone was recrystallized from chloroform-methanol to give a deep red solid, m.p. 237° dec. Mixed melting point was not depressed with an authentic sample, 237.5° dec. Ultraviolet absorption (ethanol); λ_{max} 393 mμ, ϵ_{max} 7870.

δ-Cyclopentylidenevaleronitrile from spiro[4,5]decanone-5: To a mixture of 5.0 g. (0.033 mole) of spiro[4,5]decanone-5 in 123 g. of polyphosphoric acid, 2.14 g. (0.033 mole) of sodium azide was added over a 20 min. period with constant agitation. After 3 hr. at room temperature, the mixture was hydrolyzed with 600 ml. of crushed ice and water. The solution was made alkaline with cold dilute sodium hydroxide then extracted eight times with 100-ml. portions of chloroform. The chloroform extracts were combined, dried over anhydrous sodium sulfate, filtered, and evaporated to yield an oily semisolid mass. Column chromatography over alumina yielded three fractions: Elution of the column with 1:1 petroleum ether-ether yielded first, 1.0 g. (25%) of unchanged spiro[4,5]decanone-5 identified as its oxime derivative, m.p. 64.5–65.5° (mixed melting point with the oxime of the starting ketone showed no depression, 64.5–65.5°) and second, 2.5 g. (51%) of δ-cyclopentylidenevaleronitrile.

Anal. Calcd. for $C_{10}H_{15}N$: C, 80.61; H, 10.06; N, 9.32. Found: C, 80.37; H, 9.97; N, 9.00.

Further elution of the column with chloroform yielded 0.5 g. (9%) of δ-cyclopentylidenevaleramide, m.p. 100–101°. Mixed melting point with an authentic sample[6b] showed no depression, m.p. 100.5–101°.

Conversion of δ-cyclopentylidenevaleronitrile to δ-cyclopentylidenevaleramide: A 0.5-g. sample of δ-cyclopentylidenevaleronitrile was refluxed for 8 hr. with 3 g. of potassium hydroxide in 30 ml. of 50% aqueous alcohol solution. On cooling, the alcohol was evaporated and an equal volume of water added. The aqueous solution was extracted twice with 25-ml. portion of chloroform, then acidified with cold, dilute hydrochloric acid. The acidic solution was extracted three times with 25 ml.-portions of chloroform. The chloroform extracts were combined, dried over anhydrous magnesium sulfate, filtered, and evaporated. The residual oil, 0.45 g. of δ-cyclopentylidenevaleric acid, was distilled in a micro apparatus for an analytical sample.

Anal. Calcd. for $C_{01}H_{16}O_2$: C, 72.15; H, 9.53. Found: C, 72.27; H, 9.61.

A 0.3-g. sample of the crude δ-cyclopentylidenevaleric acid obtained from the chloroform washings of the micro distillation apparatus was refluxed for 45 min. with 1 g. of oxalyl chloride in 20 ml. of anhydrous benzene. The resulting mixture was evaporated to remove the excess oxalyl chloride and the benzene replaced by 30 ml. of anhydrous benzene and cooled in an ice bath. Anhydrous ammonia was bubbled through the cooled solution for 10 min. Evaporation of the solvents deposited a white solid (0.2 g.) which after recrystallization from ethyl acetate–petroleum ether followed by recrystallization from ethanol-water yielded white crystalline plates, m.p. 100–101°. Mixed melting point with authentic sample[8b] showed no depression, m.p. 100.5–101.5°.

Cyclization of δ-cyclopentylidenevaleronitrile: Using the procedures described for the cyclization of γ-cyclopentylidenebutyronitrile, cyclopentylidenecyclopentanone could be isolated in high yield as the 2,4-dinitrophenylhydrazone derivative, m.p. 237° dec. Mixed melting point with an authentic sample showed no depression, m.p. 237° dec.

Cyclization of δ-cyclopentylidenevaleramide: A 0.20-g. sample of δ-cyclopentylidenevaleramide in 2.5 g. of polyphosphoric acid was heated at 70–73° for 6 hr. with intermittent stirring. The mixture was hydrolyzed by the addition of ice and extracted three times with 20-ml. portions of chloroform. The chloroform extracts were combined, dried over anhydrous sodium sulfate, filtered, and evaporated to yield 1.7 g. of 5-azaspiro[6,4]undecanone-6 which after a single sublimation melted at 112.5–113.5°. Mixed melting point with an authentic sample[12] showed no depression, m.p. 112.5–113.5°.

$\Delta^{9,10}$-Octalone-1 from spiro[4,5]decanone-1: To a mixture of 5.0 g. (0.033 mole) of spiro[4,5]decanone-1, 92 g. of polyphosphoric acid and 2.14 g. (0.033 mole) of sodium azide was added over a 10-min. period with constant agitation. After 6 hr. at 65–70°, the lemon yellow mixture was hydrolyzed in 250 ml. of 15% sodium hydroxide solution and ice. Additional 15% sodium hydroxide solution was added in the cold until the hydrolysis mixture was definitely basic. The aqueous solution was extracted six times with 150-ml. portions of chloroform. The chloroform extracts were combined, dried over anhydrous magnesium sulfate, filtered, and evaporated to yield 4.4 g. of a black, viscous tarry mass. Steam distillation of residue, yielded 2.75 g. (56%) of $\Delta^{9,10}$-octalone-1 after the usual workup of the distillate. Ultraviolet absorption (ethanol) λ_{max} 244 mμ ϵ_{max} 10,500 (lit.[24] λ_{max} 243 mμ, log ϵ 4.0).

The 2,4-dinitrophenylhydrazone derivative was twice recrystallized from chloroform-methanol, m.p. 264.5–265° dec.

The mixed melting point with an authentic sample[8b,22] showed no depression, m.p. 264° dec. Ultraviolet absorption (ethanol) λ_{max} 385 mμ, ϵ_{max} 13,420.

Cyclohexylidenecylopentanone from spiro[5,5]undecanone-1: To a mixture of 7.6 g. (0.045 mole) of spiro [5,5] undecanone-1 in 130 g. of polyphosphoric acid, 2.93 g. (0.045 mole) of sodium azide was added over a 15-min. period with constant stirring. After 6 hr. at 65–75° it was hydrolyzed with 500 ml. of 15% sodium hydroxide and ice. Additional sodium hydroxide was added until the hydrolysis mixture was definitely basic. After chloroform extraction and steam distillation of the residual tarry mass, 1.40 g. (22%) of cyclohexylidenecyclopentanone was obtained.

Anal. Calcd. for $C_{11}H_{16}O$: C, 80.44; H, 9.82. Found: C, 80.19; H, 9.63. Ultraviolet absorption (ethanol) λ_{max} 255 mμ, ϵ_{max} 8940.

The deep red, 2,4-dinitrophenylhydrazone derivative was recrystallized four times from chloroform-methanol, m.p. 213° dec.

Anal. Calcd. for $C_{17}H_{20}N_4O$: C, 59.25; H, 5.85; N, 16.27. Found: C, 59.01; H, 5.49; N, 12.24. Ultraviolet absorption (ethanol), λ_{max} 392 mμ, ϵ_{max} 7520. (*cf.*, ultraviolet absorption of cyclopentylidenecyclopentanone).

2-Cyclohexylcyclopentanone from cyclohexylidenecyclopentanone: A 1-g. sample of cyclohexylidenecyclopentanone was reduced by the method of Cornubert[17] using hydrogen and Raney nickel catalyst in dichloroethane medium. On isolation of the product and conversation to the semicarbazone derivative, 1.3 g. of the 2-cyclohexylcyclopentanone-semicarbazone was obtained, m.p. 206.5–207°. Mixed melting point with an authentic sample prepared according to the procedure of Mitter and Dutta[25] showed no depression, m.p. 206.5–207°.

Anal. Calcd. for $C_{12}H_{21}N_3O$: C, 64.53; H, 9.48; N, 18.82. Found: C, 64.51; H, 9.41; N, 18.80.

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