m.p. 147–149°.[19] After recrystallization from acetone–hexane and ethyl acetate–hexane, the product was sublimed at 125° (0.07 mm.) to give the analytical sample, m.p. 151–152°.

Anal. Calcd. for $C_{10}H_{13}NO_4S$: C, 49.40; H, 5.36; N, 5.77; S, 13.21. Found: C, 49.33; H, 5.42; N, 5.79; S, 13.19.

Acknowledgment.—We are indebted to Messrs. D. L. Rogerson and J. D. Link for the processing of plant material and to Mrs. L. C. Warren for the instrumental aspects of the work.

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Beckmann Rearrangements in Alicyclic Systems. V. Evidence for Carbonium Ion Intermediates in Acid-catalyzed Oxime Rearrangements[1,2]

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The Beckmann reactions of several 1,1-disubstituted 2-tetralone oximes in phosphorus pentachloride are shown to result in the formation in high yield of unsaturated nitriles from typical α-trisubstituted oxime fragmentation. Rearrangement of these oximes in polyphosphoric acid and the cyclization of the unsaturated nitriles in this medium are shown to proceed in such a fashion as to yield identical products, the expected lactam and α,β-unsaturated ketone. In each case studied, the ratio of lactam to unsaturated ketone was found to be identical to that obtained from the independent nitrile cyclizations under comparable conditions of temperature and time. It is concluded from these data that the lactam, although the expected product of Beckmann rearrangement, is produced *via* a Ritter cyclization of the nitrile intermediate from initial fragmentation of the oxime. These data support a mechanism for these reactions involving ionic intermediates in α-trisubstituted oxime rearrangements.

Recently,[3] the Beckmann rearrangements of 2,2-disubstituted 1-indanone oximes and related tetralone and benzosuberone oximes were reported to rearrange in the normal fashion to 3,3-disubstituted hydrocarbostyrils and homologous products. These reactions did not follow the same course of rearrangement as previously observed in other spiro-[4] and 2,2-disubstituted cycloalkanone oximes.[5] The literature indicates that the cleavage of an oxime which is completely substituted at the α-carbon is a rather general process.[6,7] Compounds of this class, together with certain bridged bicyclic ketoximes[8] and compounds bearing a β-hetero atom adjacent to the oximino group[9] follow the cleavage reaction rather than the normal course of rearrangement to an amide or a lactam. The structural features of these systems, in general, indicate that this process involves the ejection of a positive fragment from the β-position of an electron-deficient intermediate. Our interest in these processes has been centered about the examination of the rearrangement behavior of α-trisubstituted oximes, particularly, in cyclic systems. These studies have indicated that it may be possible to have more than one mechanistic route followed in the rearrangement of hindered ketoximes. In extending these studies, it was of interest to investigate model systems potentially capable of fragmentation but in which the previously reported α,β-unsaturated ketone formation from the unsaturated nitrile intermediate would compete with a second potential cyclization reaction through the Ritter reaction[10] involving the nitrile addition to the double bond to form an amide, identical in type to the expected product of Beckmann rearrangement. This second route would yield the normal Beckmann rearrangement product, but, *via* a reaction course which would be expected to proceed through such intermediate carbonium ion steps as to yield, in the case of an asymmetric α-carbon, a racemic product.[11] It is the purpose of this paper to show that this second mechanistic route is followed, at least, with a number of hindered ketoximes. This observation together with previous observations in rearrangements in cyclic systems adds additional information to the fundamental mechanistic processes involved in group migration from carbon to nitrogen and also indicates a similarity to analogous carbon–carbon rearrangement processes.

One of the most frequently quoted exceptions[12] to the generality of oxime fragmentation in the α-trisubstituted class of oximes is the polyphosphoric acid rearrangement of 1,1,4,4-tetramethyl-2-tetralone oxime. This oxime has been reported to rearrange normally to the expected lactam in 24% yield. The remaining products of the reaction were not characterized. Since the course of reaction in this case could follow either normal rearrangement or a fragmentation–recombination route, it was of interest to examine carefully the

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[2] This study was presented at the Metropolitan Regional Meeting, American Chemical Society, New York, N. Y., January 22, 1962.

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rearrangement of this system and related ketoximes for both lactam and α,β-unsaturated ketonic products. In addition, it was of further interest to contrast the independent cyclization of the unsaturated nitrile intermediates in polyphosphoric acid medium under the conditions used to effect oxime rearrangement.

The ketones used in this study were prepared using reported methods. 1,1,4,4-Tetramethyl-2-tetralone was prepared from 2,2,5,5-tetramethyltetrahydrofuranone by the procedure described by Bruson, Grant, and Bobko.[12] 1,1-Dimethyl- and 1,1-pentamethylene-2-tetralone were prepared by the alkylation of 2-tetralone with methyl iodide or pentamethylene dibromide, respectively, using potassium *t*-butoxide.[13] The oxime derivatives were prepared from the purified ketones using hydroxylamine hydrochloride and the pyridine–ethanol solvent system.[14]

Rearrangement Studies.—The rearrangement of 1,1-dimethyl-, 1,1,4,4-tetramethyl- and 1,1-pentamethylene-2-tetralone oximes using phosphorus pentachloride resulted in almost quantitative yields (93–96%) of the unsaturated nitriles (Figure 1) expected from oxime fragmentation. In the case of 1,1-dimethyl- and 1,1,4,4-tetramethyl-2-tetralone oxime cleavage, small amounts (3–4%) of the lactams, 2-aza-1,1-dimethyl-3-benzosuberone and 2-aza-1,1,5,5-tetramethyl-3-benzosuberone, respectively, were isolated during the chromatographic separation of the reaction products. The structure of the lactams was established unequivocally in further studies of the reactions of the unsaturated nitriles and their respective amides. Heating the unsaturated nitrile or amide in polyphosphoric acid resulted in the formation of identical lactams, characterized by their infrared spectrum and mixed melting point determinations. These cyclizations will be discussed later in this report in some detail.

Treatment of 1,1-dimethyl-2-tetralone oxime with hot polyphosphoric acid resulted in the formation of two major reaction products: the lactam, 2-aza-1,1-dimethyl-3-benzosuberone (24%) and an α,β-unsaturated ketone, 4,5-benzo-3-methylcyclohepta-2,4-dien-1-one (71%). The structure of this ketone was established by its characteristic substituted cinnamaldehyde ultraviolet spectrum with an intense maxima at 288 mμ and elemental analysis of the ketone and its 2,4-dinitrophenylhydrazone derivative. In addition, the structure could be readily deduced from previous studies[4,5] on α,β-unsaturated ketone formation under Beckman rearrangement conditions in polyphosphoric acid. The final confirmation of structure was obtained, again in light of previous work, by the polyphosphoric acid cyclization of the unsaturated nitrile, obtained in the phosphorus pentachloride oxime fragmentation reaction, to the lactam and the identical α,β-unsaturated ketone. In analogous fashion 1,1,4,4-tetramethyl-2-tetralone oxime gave 2-aza-1,1,5,5-tetramethyl-3-benzosuberone (24%) and 4,5-benzo-3,6,6-trimethylcyclohepta-2,4-dien-1-one (72%). Examination of the course of rearrangement of 1,1-pentamethylene-2-tetralone in polyphosphoric acid resulted in the isolation of 4,5-benzo-2,3-pentamethylenecyclohepta-2,4-dien-1-one also in 72% yield. In this latter case, the lactam although identified in the crude reaction product mixture by infrared analysis was not isolated.

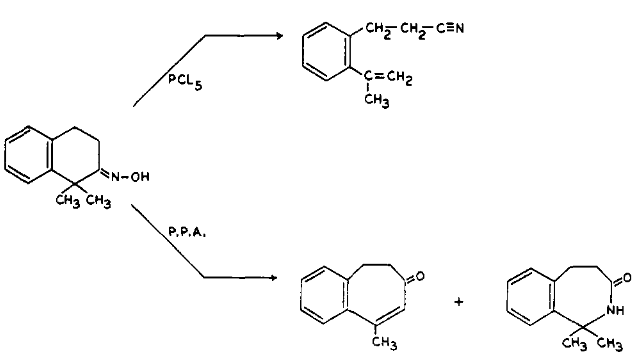

Figure 1

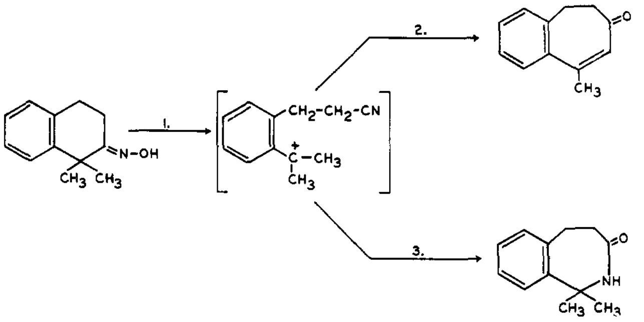

Fig. 2.—The fragmentation–recombination mechanism: step 1, fragmentation of the oxime to carbonium ion–nitrile intermediate; step 2, α,β-unsaturated ketone formation *via* the Hoesch reaction; step 3, lactam formation *via* the Ritter reaction.

Noticeable in each of the above rearrangement cases in polyphosphoric acid was the remarkable consistency in yields and the ratio of unsaturated ketone to lactam, approximately 3:1 as determined by column chromatography. Further rearrangements were carried out at successively shorter time intervals of eight, five, and three minutes although the yields diminished as expected the ratio of ketone to lactam remained constant. The possibility occurred to us that the immediate precursor responsible for ketone formation might also be responsible for lactam formation *via* the Ritter cyclization of the unsaturated nitrile. In previous studies,[4b,5] we have shown that the nitrile intermediate must be essentially free after fragmentation, since the size of the new ring formed was consistent with existing thought on ring cyclization processes. In the cases studied here Hoesch cyclizations[15] to form the ketone and Ritter cyclization[10] to form the lactam result in seven-membered ring formation and therefore these processes would be expected to be competitive. It was felt that this postulate could readily be confirmed by studying the cyclization process of the unsaturated nitriles under conditions of time and temperature used in the oxime rearrangement studies. Typical results were obtained in the cyclization of 3-(2′-isopropenylphenyl)propionitrile. In runs of three, five, eight and ten minutes, the ratio of ketone to lactam was found to be identical to that observed in the oxime rearrangements. In the normal cyclization reaction of ten minutes at 125°, 4,5-benzo-3-methylcyclohepta-2,4-dien-4-one was isolated in 73% yield and the lactam, 2-aza-1,1-dimethyl-3-benzosuberone in 24% yield.

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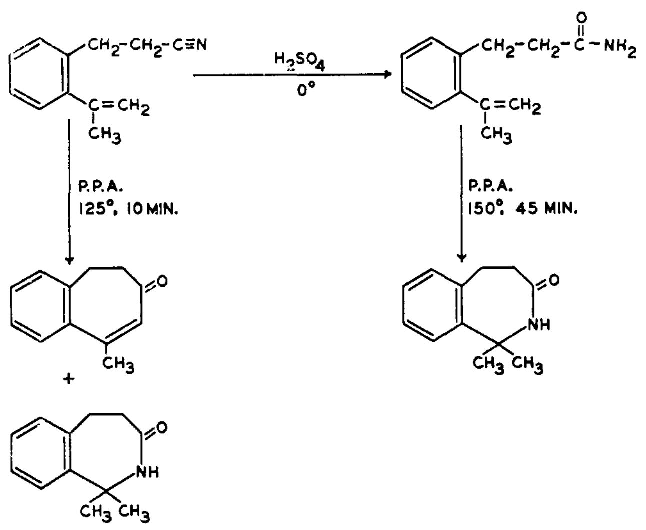

Figure 3

Similar results were obtained from the corresponding unsaturated nitriles obtained from phosphorus pentachloride fragmentation of 1,1,4,4-tetramethyl-2-tetralone oxime and 1,1-pentamethylene-2-tetralone oxime. The lactams and unsaturated ketones produced by nitrile cyclizations were identical in all respects to the Beckmann rearrangement products.

It was of further interest to attempt the cyclization of the unsaturated amide to the lactam under the rearrangement conditions since it remained a possibility that a portion of the nitrile was hydrated to amide prior to cyclization to the lactam. 3-(2′-Isopropenylphenyl)propionitrile was hydrated in cold concentrated sulfuric acid to 3-(2′-isopropenylphenyl)propionamide. Attempted cyclization of the unsaturated amide at 125° for ten minutes resulted in 96% recovery of starting amide. However, at 150° for forty-five minutes it was possible to isolate the lactam in good yield. This evidence, therefore, negates the possible formation of the lactam through an initial hydration to amide followed by cyclization route (Figure 3).

From these data it can be concluded that the lactam expected from the Beckmann rearrangement, although isolated, is not produced in the initial reaction step. Rather, the lactam and ketone are produced competitively by Ritter and Hoesch type cyclizations of the nitrile intermediate.

In contrast to existing thoughts on the Beckmann rearrangement involving concerted group migration, these studies support a two-step rearrangement mechanism,[11b] involving a oxime fragmentation followed by recombination of the fragments intramolecularly to produce the lactam product. These results point toward the necessity of modifying the present approach used in describing carbon–nitrogen rearrangement processes and interpreting data therefrom to include a more detailed analysis of the structural features of molecules thought to exhibit normal as well as anomalous behavior. Group migration of mono- and disubstituted α-carbon atoms with retention of configuration seems unquestionably the case. However, in trisubstituted α-carbon migration cases ionic intermediates may well be the most commonly found mode of group migration in oxime rearrangement in strong acid media.

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, Beckman IR-4 or IR-5 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-Tetralone was prepared by the method of Soffer, Bellis, Gallerson, and Stewart.[16]

I. **Beckmann Rearrangements. 1,1-Dimethyl-2-tetralone Oxime.** (A) **With Phosphorus Pentachloride.**—To a cold solution of 1.00 g. (0.0053 mole) of 1,1-dimethyl-2-tetralone oxime in 40 ml. of anhydrous, thiophene-free benzene, 1.00 g. of phosphorus pentachloride was added slowly in small amounts. The mixture was allowed to warm slowly to room temperature. After 24 hr., the reaction mixture was cautiously hydrolyzed by the dropwise addition of 30 ml. of water. The benzene layer was decanted and washed successively with 20 ml. of water, 20 ml. of 10% sodium bicarbonate and 20 ml. of saturated sodium chloride solution. The benzene layer was separated and evaporated to yield 0.91 g. of a light tan oil. The oil was transferred to a micro distillation tube and the distillable portion removed as a light yellow oil, b.p. 87–91°/0.6 mm. After a single separation over alumina in ether solution, 0.84 g. (93%) of the unsaturated nitrile, 3-(2′-isopropenylphenyl)propionitrile was obtained. The nitrile group showed a characteristic infrared absorption for the nitrile group at 4.45 μ.

Anal. Calcd. for $C_{12}H_{13}N$: C, 81.17; H, 7.65; N, 8.18. Found: C, 81.31; H, 7.77; N, 8.03.

The residue from the microdistillation was transferred to a sublimation apparatus. After 2 hr. at 100° and 0.01 mm., 0.034 g. (3.4%) of 2-aza-1,1-dimethyl-3-benzosuberone was obtained, m.p. 113–114.5°. The infrared spectrum indicated a single N—H vibration at 2.95 μ and a 6.05 μ Amide I band (chloroform solution).

Anal. Calcd. for $C_{12}H_{15}NO$: C, 76.15; H, 7.99; N, 7.40. Found: C, 76.20; H, 8.01; N, 7.32.

Hydration of 3-(2′-Isopropenylphenyl)propionitrile.—To 5 ml. of concentrated sulfuric acid cooled in an ice–salt bath, 0.15 g. (0.00088 mole) of 3-(2′-isopropenylphenyl)propionitrile was slowly added. The mixture was stirred until all of the nitrile had dissolved in the cold acid solution. After 2 hr. at 0.5°, the mixture was poured over crushed ice. The cold aqueous solution was extracted three times with 20-ml. portions of chloroform. The chloroform extracts were combined, dried over anhydrous magnesium sulfate, filtered, and evaporated *in vacuo*. The solid residue was recrystallized five times from an ethyl acetate–petroleum ether mixture to yield 0.08 g. (50.5%) of the unsaturated amide, m.p. 131–132.5°.

Anal. Calcd. for $C_{12}H_{15}NO$: C, 76.15; H, 7.99; N, 7.40. Found: C, 75.92; H, 7.78; N, 7.51.

(B) **Using Polyphosphoric Acid.**—A mixture of 1.00 g. (0.0053 mole) of 1,1-dimethyl-2-tetralone oxime and 16.8 g. of polyphosphoric acid was heated at 125–130° for 10 min. On cooling, the mixture was hydrolyzed over crushed ice. The aqueous solution was treated with 10% sodium hydroxide solution until it was definitely alkaline. The alkaline solution was extracted four times with 60-ml. portions of chloroform. The chloroform extracts were combined dried over anhydrous magnesium sulfate, filtered, and evaporated. The residue, a dark brown oil, was chromatographed over alumina in ether to yield two components.

Evaporation of the ether eluents yielded 0.65 g. (71%) of 4,5-benzo-3-methylcyclohepta-2,4-dien-1-one; λ_{max} 288 mμ, log ϵ 3.41.

Anal. Calcd. for $C_{12}H_{12}O$: C, 83.69, H, 7.02. Found: C, 83.72; H, 7.23.

The 2,4-dinitrophenylhydrazone was prepared by the method in the usual fashion.[5] After three recrystallizations from ethanol, scarlet plates of the 2,4-dinitrophenylhydrazone derivative were obtained, m.p. 156–156.5°.

Anal. Calcd. for $C_{18}H_{16}N_4O_4$: C, 61.36; H, 4.58; N, 15.90. Found: C, 61.47; H, 4.67; N, 15.71.

Further elution of the alumina column with 1:1 ether–chloroform yielded, on evaporation of the solvents, 0.24 g. (24%) of 2-aza-1,1-dimethyl-3-benzosuberone, m.p. 113–114.5°.

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[16] M. D. Soffer, M. P. Bellis, H. E. Gallerson, and R. A. Stewart, *Org. Syn.*, **32**, 97 (1952).

Similar runs of shorter durations (3, 5, and 8 min.) resulted in the isolation of unsaturated ketone and lactam in the ratio of yields of 3:1 on column chromatographic separation of the reaction mixtures.

Cyclization of 3-(2′-Isopropenylphenyl)propionitrile.—A mixture of 0.6 g. of 3-(2′-isopropenylphenyl)propionitrile and 12.9 g. of polyphosphoric acid was heated at 125–130° for 10 min. On cooling, the mixture was hydrolyzed over crushed ice. The aqueous mixture was made alkaline with 10% sodium hydroxide and the alkaline solution thoroughly extracted with chloroform. The extracts were combined, dried over anhydrous magnesium sulfate, filtered, and evaporated to yield a light brown oil.

Chromatographic separation of the oil in a manner identical with that described for the isolation of the polyphosphoric acid rearrangement products yielded 0.40 g. (73%) of 4,5-benzo-3-methylcyclohepta-2,4-dien-1-one which was characterized by mixed melting point determination of its 2,4-dinitrophenylhydrazone derivative with that obtained from oxime rearrangement, m.p. 156–156.5°. Further elution of the column yielded 0.14 g. (24%) of 2-aza-1,1-dimethyl-3-benzosuberone, m.p. 113–114.5°. Mixed melting point determination with the lactam obtained from oxime rearrangement showed no depression, m.p. 113–114.5°.

Cyclization of 3-(2′-Isopropenylphenyl)propionamide.—A mixture of 0.50 g. of the unsaturated amide and 2.4 g. of polyphosphoric acid was heated at 150–155° for 45 min. The reaction mixture was worked up in the usual manner. The infrared spectrum of the crude solid residue obtained on evaporation of the solvent was identical to that of the lactam isolated from phosphorus pentachloride oxime rearrangement. After a single sublimation, the colorless crystalline lactam, 2-aza-1,1-dimethyl-3-benzosuberone, melted at 113–114°. Mixed melting point with the Beckmann product did not depress, m.p. 113–114.5°.

A similar experiment carried out at 125° for 10 min. resulted in the recovery of 0.48 g. of the unsaturated amide.

II. 1,1-Pentamethylene-2-tetralone Oxime. (A) With Phosphorus Pentachloride.—To a cold solution of 0.23 g. (0.001 mole) of 1,1-pentamethylene-2-tetralone oxime in 10 ml. of anhydrous, thiophene-free benzene, 0.25 g. of phosphorus pentachloride was added slowly in small amounts. The mixture was allowed to slowly warm to room temperature. After 24 hr., the reaction mixture was hydrolyzed by the addition of 10 ml. of water. The benzene layer was separated and the aqueous portion extracted once with 10 ml. of benzene. The benzene layer and extract were combined and washed with 5 ml. of water, 5 ml. of 10% sodium carbonate and 5 ml. of saturated sodium chloride solution. The benzene solution was evaporated to yield a light yellow oil. The oil was chromatographed over alumina in ether solution to give on evaporation of the ether eluents 0.20 g. (96%) of an unsaturated nitrile, 3-(2′-cyclohexenylphenyl)propionitrile. The nitrile group showed a characteristic infrared absorption at 4.45 μ. A portion of the sample was rechromatographed in ether for elemental analysis.

Anal. Calcd. for $C_{15}H_{17}N$: C, 85.26; H, 8.11; N, 6.63. Found: C, 85.39; H, 8.00; N, 6.50.

(B) Using Polyphosphoric Acid.—A mixture of 0.75 g. (0.003 mole) of 1,1-pentamethylene-2-tetralone oxime and 12.4 g. of polyphosphoric acid was heated at 125–130° for 10 min. On cooling the mixture was hydrolyzed over crushed ice. The aqueous solution was treated with 10% sodium hydroxide solution until definitely alkaline. The alkaline solution was extracted three times with 50-ml. portions of chloroform. The chloroform extracts were combined dried over anhydrous magnesium sulfate, filtered, and evaporated. The residue, a light brown, viscous oil, was chromatographed over alumina in ether to yield in the ether eluents, 0.45 g. (72%) of 4,5-benzo-2,3-pentamethylene-2,4-dien-1-one; λ_{max} 287.5 mμ, log ϵ 3.48.

Anal. Calcd. for $C_{15}H_{16}O$: C, 84.87; H, 7.60. Found: C, 84.89; H, 7.57.

The 2,4-dinitrophenylhydrazone was prepared by the method in the usual fashion.[5] After two recrystallizations from ethanol scarlet plates of the 2,4-dinitrophenylhydrazone derivative were obtained, m.p. 193–193.5°.

Anal. Calcd. for $C_{21}H_{20}N_4O_4$: C, 64.27; H, 5.14; N, 14.28. Found: C, 64.23; H, 5.37; N, 14.54.

Cyclization of 3-(2′-cyclohexenylphenyl)propionitrile.—A mixture of 0.42 g. of 3-(2′-cyclohexenylphenyl)propionitrile and 11.6 g. of polyphosphoric acid was heated at 125–130° for 12 min. The reaction mixture was hydrolyzed, made alkaline, and extracted with chloroform in the usual manner. Conversion of the crude reaction product, from chloroform evaporation, to the 2,4-dinitrophenylhydrazone derivative yielded after two recrystallizations from ethanol, the 2,4-dinitrophenylhydrazone derivative of 4,5-benzo-2,3-pentamethylene-2,4-dien-1-one, m.p. 193–193.5°. No depression was observed on admixture of the sample from the ketone isolated in the Beckmann rearrangement in polyphosphoric acid.

III. 1,1,4,4-Tetramethyl-2-tetralone Oxime. (A) With Phosphorus Pentachloride.—To a cold solution of 1.50 g. (0.0069 mole) of 1,1,4,4-tetramethyl-2-tetralone in 60 ml. of anhydrous thiophene-free benzene, 1.50 g. of phosphorus pentachloride was added slowly in small amounts. After warming to room temperature, the mixture was allowed to stand for 24 hr. The mixture was hydrolyzed by the cautious addition of 50 ml. of water. The benzene layer was separated and washed successively with 25 ml. of water, 25 ml. of 10% sodium carbonate, and 25 ml. of saturated sodium chloride solution. The benzene was evaporated to yield 1.38 g. of a light tan oil. The oil was transferred to a micro distillation tube and the mixture distilled at reduced pressure. A light yellow liquid, b.p. 98–102°/0.6 mm., was obtained. The infrared spectrum indicated the characteristic infrared absorption at 4.45 μ for the nitrile group. The crude nitrile was purified over alumina in ether to yield 1.30 g. (94%) of 3-methyl-3-(2′-isopropenylphenyl)butyronitrile.

Anal. Calcd. for $C_{14}H_{15}N$: C, 85.23; H, 7.67; N, 7.10. Found: C, 85.20; H, 7.69; N, 6.85.

The solid, tar-like residue from the micro distillation was crushed and transferred to a sublimation apparatus. After two sublimations at 0.01 mm., 0.06 g. (4%) of 2-aza-1,1,5,5-tetramethyl-3-benzosuberone was obtained, m.p. 144–145° (lit.,[12] m.p. 144–145°).

Hydration of 3-Methyl-3-(2′-isopropenylphenyl)butyronitrile.—To 5 ml. of concentrated sulfuric acid cooled in an ice–salt bath, 0.20 g. of 3-methyl-3-(2′-isopropenylphenyl)butyronitrile was slowly added. The mixture was stirred until all the nitrile had dissolved in the cold acid solution. After 2 hr. at 0–5°, the mixture was poured over crushed ice. A semisolid mass separated which was isolated by decantation of the aqueous acid solution. The wet mass was dissolved in 20 ml. of chloroform. The chloroform solution was washed with 10 ml. of saturated sodium bicarbonate solution followed by 10 ml. of water. The chloroform was dried by passing the solution through a layer of anhydrous magnesium sulfate. After evaporation, the solid residue was recrystallized from ethyl acetate–petroleum ether mixture to yield 0.13 g. of the unsaturated amide, m.p. 158.5–160.5°.

Anal. Calcd. for $C_{14}H_{19}NO$: C, 77.38, H, 8.81; N, 6.45. Found: C, 77.24, H, 8.71; N, 6.49.

(B) Using Polyphosphoric Acid.—A mixture of 1.50 g. (0.0069 mole) of 1,1,4,4-tetramethyl-2-tetralone oxime and 22.0 g. of polyphosphoric acid was heated at 125–130° for 10 min. On cooling, the mixture was hydrolyzed over crushed ice. The aqueous solution was extracted three times with 60-ml. portions of ether. The ether extracts were combined, dried over anhydrous magnesium sulfate, filtered, and evaporated to yield a viscous oil which could be crystallized from petroleum ether to give 0.36 g. (24%) of 2-aza-1,1,5,5-tetramethyl-3-benzosuberone, m.p. 144–145°. No depression was observed on admixture with a sample of the lactam obtained in the phosphorus pentachloride rearrangement of the oxime.

The aqueous solution was made alkaline with 10% sodium hydroxide. The alkaline solution was extracted four times with 75-ml. portions of chloroform. The chloroform extracts were combined, dried over anhydrous magnesium sulfate, filtered, and evaporated to yield 1.00 g. (72%) of 4,5-benzo-3,6,6-trimethyl-cyclohepta-2,4-dien-1-one, λ_{max} 288 mμ, log ϵ 3.70 (after purification over alumina in ether).

Anal. Calcd. for $C_{14}H_{16}O$: C, 83.96; H, 8.05. Found: C, 83.72; H, 7.87.

The 2,4-dinitrophenylhydrazone was prepared by the method in the usual fashion.[5] After three recrystallizations from ethanol scarlet crystals of the 2,4-dinitrophenylhydrazone were obtained, m.p. 226–227.5°.

Anal. Calcd. for $C_{20}H_{20}N_4O_4$: C, 63.15; H, 5.30; N, 14.73. Found: C, 63.10; H, 4.98; N, 14.70.

In similar runs for 3, 5, and 8 min. the ratio of ketone to lactam (3:1) was found to be constant in all experiments. Column chromatographic separation of the reaction mixture gave comparable results.

Cyclization of 3-Methyl-3-(2′-isopropenylphenyl)butyronitrile.—The cyclization of 3-methyl-3-(2′-isopropenylphenyl)butyronitrile in polyphosphoric acid was carried out as previously described. The yield of ketone and lactam were found to be identical to that obtained in the Beckmann rearrangement of the parent oxime.

Cyclization of 3-Methyl-3-(2′-isopropenylphenyl)butyramide.—The cyclization of 0.10 g. of 3-methyl-3-(2′-isopropenylphenyl)-butyramide using the procedure described previously for 3-(2′-isopropenylphenyl)propionamide at 150–155° for 45 min. resulted in the isolation of the lactam, 2-aza-1,1,5,5-tetramethyl-3-benzosuberone, m.p. 144–145°.

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Notes

A Rapid, Precise Procedure for the Quantitative Determination of Unsaturation in Organic Compounds *via* Hydrogenation

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We wish to report a simple procedure which permits the rapid, quantitative determination of unsaturation in representative organic compounds. The method utilizes the new active platinum metal catalysts prepared by the *in situ* treatment of platinum metal salts with sodium borohydride,[1] the *in situ* generation of hydrogen from sodium borohydride, and a modification of the valve[2] which automatically introduces sodium borohydride solution into the reaction mixture as the hydrogenation is proceeding. With these modifications, hydrogenation[3] becomes a rapid, precise tool for the determination of unsaturation.

The apparatus is shown in Fig. 1. In this device, the buret ends in a capillary tube which dips into a mercury well to a depth sufficient to support the column of solution (sodium borohydride in ethanol). As hydrogen is utilized in the hydrogenation flask, the pressure drops 5 to 10 mm. below atmospheric, drawing a small quantity of the borohydride solution through the mercury seal, where it rises to the top of the mercury and runs into the flask through the small vent holes located just above the mercury interface. The acidic solution in the flask converts the borohydride into hydrogen and the resulting increase in pressure seals the valve. The addition proceeds smoothly and automatically to the completion of the hydrogenation, with the amount of borohydride solution corresponding quantitatively to the amount of unsaturated compound contained in the flask.

The procedure was tested by hydrogenating 20.0, 10.0, and 5.00 mmoles of 1-octene, introduced as the pure liquid, and 5.00, 2.50, 2.00 and 1.00 mmoles of 1-octene, introduced as a standard solution in ethanol, using 1.00 M, 0.250 M, and 0.100 M sodium borohydride in ethanol. The procedure was extended to the hydrogenation of 4-methylcyclohexene, 1,5,9-cyclododecatriene, and ethyl oleate, as well as to a mixture of the above four unsaturated compounds. The results are summarized in Table I.

TABLE I

HYDROGENATION OF VARIOUS UNSATURATED COMPOUNDS

Compound	Amt., mmoles	$NaBH_4$ soln. M	Volume of $NaBH_4$ solution	Av.	F.S.E.[c]	Olefin found, mmoles
1-Octene	20.0[a]	1.00	4.95, 4.94, 4.90, 4.96, 4.95	4.94 ± 0.02	0.32	20.08 ± 0.020
	10.0[a]	1.00	2.46, 2.44, 2.48, 2.44, 2.42	2.45 ± 0.02	.16	9.96 ± 0.018
	5.00[a]	1.00	1.23, 1.22, 1.22, 1.24, 1.20	1.22 ± 0.02	.08	4.96 ± 0.016
	5.00[b]	0.250	4.57, 4.59, 4.62, 4.56 4.63	4.97 ± 0.03	.38	4.97 ± 0.030
	2.50[b]	.250	.27, 2.06, 2.24, 2.25, 2.25	2.26 ± 0.02	.19	2.45 ± 0.015
	1.00[b]	.250	0.92, 0.91, 0.90, 0.92, 0.91	0.91 ± 0.01	.08	0.99 ± 0.010
	2.00[b]	.100	4.31, 4.39, 4.30, 4.32, 4.30	4.32 ± 0.03	.25	1.98 ± 0.030
	1.00[b]	.100	2.18, 2.15, 2.20, 2.15, 2.20	2.18 ± 0.03	.13	1.00 ± 0.025
4-Methylcyclohexene	2.00[b]	.100	4.32, 4.35, 4.38, 4.36, 4.32	4.35 ± 0.03	.25	1.99 ± 0.025
1,5,9-Cyclododecatriene	0.67[b]	.100	4.32, 4.33, 4.37, 4.35, 4.35	4.34 ± 0.02	.25	1.99 ± 0.025
Ethyl oleate	2.00[b]	.100	4.35, 4.39, 4.32, 4.35, 4.37	4.36 ± 0.02	.25	2.00 ± 0.020
Mixture[d]	2.00[b]	.100	4.37, 4.39, 4.40, 4.37, 4.38	4.38 ± 0.10	.25	2.01 ± 0.012

[a] Introduced as the pure liquid. [b] Introduced as a 1.00 M solution in ethanol. [c] mmoles of hydrogen displaced by the volume of olefin or olefin solution introduced plus volume of sodium borohydride introduced (total volume in cc./25.0). [d] A mixture of 1-octene, 4-methylcyclohexene, 1,5,9-cyclododecatriene, and ethyl oleate, prepared by mixing aliquots of the 1 N ethanolic solutions.

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