Nitrations with Acetyl Nitrate. IV. The Formation and Reactions of β-Nitro Acetates from 1-Phenylcyclohexene and 1-Phenylcyclopentene[1]

FREDERICK G. BORDWELL AND EDGAR W. GARBISCH, JR.

Chemistry Department, Northwestern University, Evanston, Illinois

Received July 30, 1962

Of the two isomeric β-nitro acetates formed by nitration of 1-phenylcyclohexene, the major isomer was shown by reduction to have the NO_2 and OAc groups *trans* to one another. The more rapid rearrangement of the type, (NH_2, OAc) → (NHAc, OH), observed for the reduction product from the minor isomer supports the *cis* assignment made to it. Hydrogenolysis of the C–O bond in the amino alcohol derivatives with Raney nickel was found to occur with *inversion* of configuration for C–OAc compounds and with *retention* of configuration for C–OH compounds. Base-catalyzed elimination occurred more rapidly with the *trans* β-nitro acetate (*cis* elimination) than with the *cis* β-nitro acetate (*trans* elimination). This result is rationalized in terms of a carbanion mechanism. The nitration of 1-phenylcyclopentene led to a single β-nitro acetate which was shown to have the nitro and acetoxy groups in a *trans* configuration.

The study of the products formed in the reaction of alkenes with acetyl nitrate in acetic anhydride solution[2] now has been extended to 1-phenylcyclohexene and 1-phenylcyclopentene. When 1-phenylcyclohexene was nitrated under the usual conditions[3] and the products separated by chromatography, the successive fractions consisted of about 10% of nitroalkenes (mostly unconjugated), 49% of β-nitro acetate (I), and 16% of β-nitro acetate (II).

Electrolytic reduction of I gave a 75% yield of a β-amino acetate, isolated as its hydrochloride. A 53% yield of the same amine acetate hydrochloride was obtained in a reduction carried out with Raney nickel in absolute ethanol. Neutralization of this hydrochloride with aqueous potassium carbonate, followed by standing overnight in contact with the solvent, brought about a rearrangement of the amine acetate to an acetamido alcohol, m.p. at 164–165°; this is the melting point reported[4] for 2-acetamido-*trans*-1-hydroxy-1-phenylcyclohexane.[5] The same compound was obtained by acetylating the amine acetate hydrochloride to form the N-acetyl O-acetyl derivative followed by selective hydrolysis of the ester link. By benzoylation of the amine acetate hydrochloride the N-benzoyl O-acetyl derivative was obtained; this was then hydrolyzed to the N-benzoyl derivative, m.p. 155–156°. Curtin and Schmulker[4] report m.p. 157–158° for 2-benzamido-*trans*-1-hydroxy-1-phenylcyclohexane.

The infrared spectrum of II resembled that of I closely, but some differences were apparent (see Experimental). Treatment of either isomer with sulfuric acid in acetic anhydride or with alcoholic potassium hydroxide at room temperature resulted in the elimination of a molecular of acetic acid and the formation of 6-nitro-1-phenylcyclohexene (IV). These data indicate that isomers I and II are related as *cis–trans* isomers.

Reduction of II electrolytically, under the conditions used for I, gave a product that was difficult to characterize. Reduction with Raney nickel was successful, but the product proved to be the N-acetyl, rather than the O-acetyl derivative.

The results may be summarized as shown in Chart 1 in which structure assignments are given.

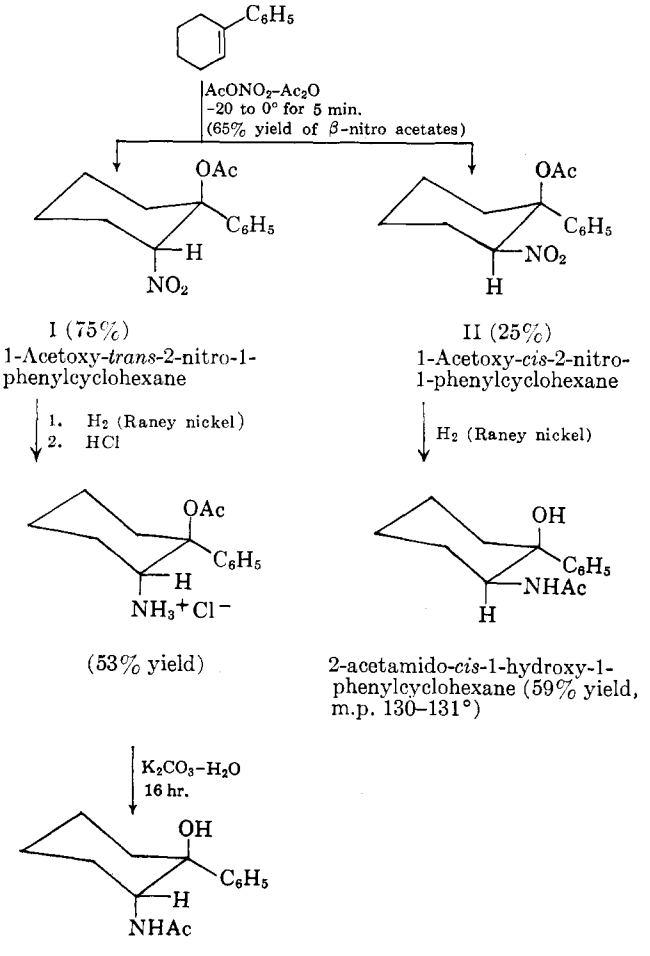


CHART 1

(1) Abstracted from the Ph.D. dissertation of Edgar W. Garbisch, Jr., submitted to Northwestern University, August, 1961.

(2) See F. G. Bordwell and E. W. Garbisch, Jr., *J. Org. Chem.*, **27**, 3049 (1962), for paper III in this series.

(3) F. G. Bordwell and E. W. Garbisch, Jr., *ibid.*, **27**, 2322 (1962).

(4) D. Y. Curtin and S. Schmulker, *J. Am. Chem. Soc.*, **77**, 1105 (1955).

(5) The terms *cis* and *trans* cannot be used unambiguously in such names unless some sort of convention is adopted. In this paper the first function mentioned in the name (as decided by the alphabetical order) is always used as the point of reference. The designation *cis* or *trans* refers to the relationship of the second function mentioned relative to this reference. The stereorelationship of the third function is also made obvious in this way. For example, the name 2-acetamido-*trans*-1-hydroxy-1-phenylcyclohexane shows that the acetamido and hydroxyl groups are *trans* to one another; it follows that the acetamido group is *cis* to the phenyl group. (The compound could also have been named 2-acetamido-*cis*-1-phenylcyclohexanol.) This convention is essentially that introduced by Epstein and Rossini for naming geometric isomers of polyalkyl monocycloalkanes [see the American Chemical Society Nomenclature Committee report in *Chem. Eng. News*, **28**, 1842 (1950)].

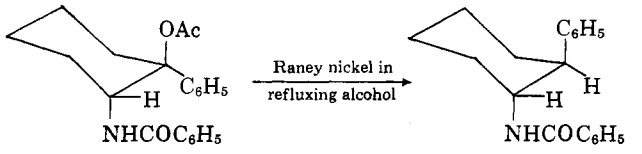
Since the amino and hydroxyl groups in the compound prepared by the action of ammonia on 1-phenylcyclohexene oxide[4] almost certainly bear a *trans* relationship to one another, the structure of the reduction product from I is established as having a *trans* configuration. Since reduction of the nitro group to amino under these conditions has been shown to occur with retention of configuration,[6] a *trans* relationship for the acetoxy and nitro group in I is established, and a *cis* relationship for these groups in II is indicated.

The rearrangements, (NH_2, OAc) → (NHAc, OH), observed with the reduction products from both isomers I and II, presumably both occur by intramolecular mechanisms. The rearrangement required several hours for the reduction product from I, whereas with the reduction product from II it was much more rapid, being complete by the end of the reduction. This difference in the ease of rearrangement is consistent with the structures assigned, since it is known that oxygen to nitrogen acyl migration is more rapid in *cis* (axial–equatorial) than in *trans* (equatorial–equatorial) systems of this type.[7]

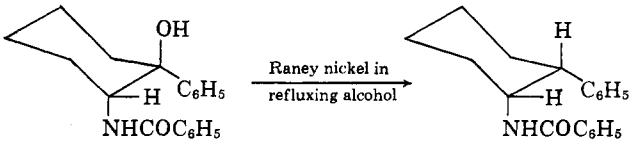
The nitration of 1-phenylcyclopentene gave 34% of nitro alkenes and 40% of a single β-nitro acetate. The latter was reduced electrolytically to an acetate amine hydrochloride in 68% yield. This was identified as 1-acetoxy-*trans*-2-amino-1-phenylcyclopentane hydrochloride by establishing the identity of its N-benzoyl amino alcohol derivative with a comparable derivative derived from the amino alcohol produced by the reaction of aqueous ammonia with 1-phenylcyclopentene oxide.

It is apparent from the previous discussion that the major isomer formed from the nitration of either 1-phenylcyclohexene or 1-phenylcyclopentene has the nitro and acetoxy groups in a *trans* relationship to one another. This corrects our earlier preliminary assignment,[8] which was based on what turned out to be an unjustified assumption with respect to the hydrogenolysis of the acetoxy group (following). It now appears that *trans* additions to C=C bonds, such as those reported here, are about as common in acetyl nitrate additions as are cis additions. The factors determining the stereochemistry in these reactions will be discussed further in a later paper.

Hydrogenolyses.—In an early attempt at structure assignment, I was hydrogenated in methanol containing sulfuric acid using a palladium-on-charcoal catalyst; these conditions led to hydrogenolysis of the acetoxy group. The product from the hydrogenolysis was identified as *trans*-2-phenylcyclohexylamine. Since previously recorded hydrogenolyses of C–O bonds were known to occur with retention of configuration,[9] including *a hydrogenolysis of the alcohol corresponding to one of the isomeric* acetates expected as a product,[4] retention of configuration was at first assumed to be the result in our experiments. This assumption proved to be an unfortunate one, since it led to incorrect structure assignments for the β-nitro acetates formed from 1-phenylcyclohexene and from 1-phenylcyclopentene.[8] The configurational assignments made show that hydrogenolysis of the C–O bonds in both 1-acetoxy-*trans*-1-phenyl-2-nitrocyclohexane and 1-acetoxy-*trans*-1-phenyl-2-nitrocyclopentane (or their reduction products) occurs with *inversion* of configuration. In checking into the matter further it was found that hydrogenolysis of 1-acetoxy-*trans*-2-benzamido-1-phenylcyclohexane with Raney nickel in refluxing ethanol gave *trans*-2-benzamido-1-phenylcyclohexane (inversion of configuration). It is remarkable that the corresponding alcohol undergoes hydrogenolysis with retention of configuration.[4] Similarly, it was observed that 1-acetoxy-*trans*-2-benzamido-1-phenylcyclopentane gave *trans*-2-benzamido-1-phenylcyclopentane with Raney nickel in refluxing alcohol (inversion).[10]

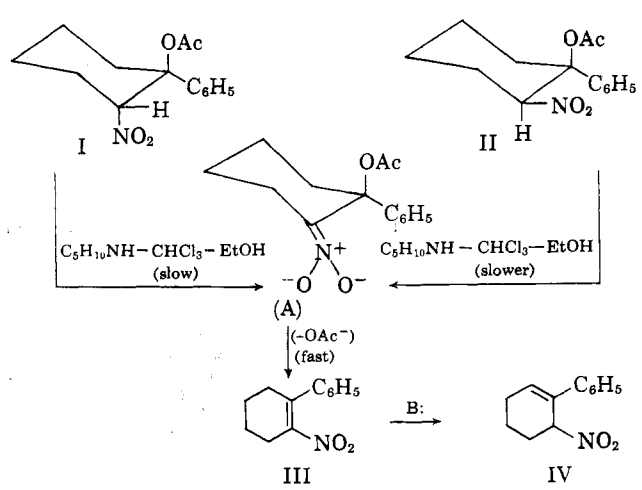


Hydrogenolysis with inversion (72%)



Hydrogenolysis with retention (78%)

Approximate pseudo first-order rates of elimination of acetic acid from I and II, as initiated by reaction with piperidine in chloroform–ethanol solution, were determined by following the disappearance of the 5.70-μ carbonyl stretching frequency. The rate of elimination from 1-acetoxy-*trans*-2-nitro-1-phenylcyclohexane (an apparent *cis* elimination) was found to be about four times as rapid as from 1-acetoxy-*cis*-2-nitro-1-phenylcyclohexane (a *trans* elimination). Since, when the hydrogen atoms involved in the elimination are of comparably acidity, *trans* elimination is usually much faster than *cis* elimination, this result suggests that elimination is proceeding by way of a carbanion intermediate wherein proton abstraction is the rate determining step. Assuming that the molecules react in the conformations shown, the lower reactivity of the *cis*



(6) F. G. Bordwell and R. L. Arnold, *J. Org. Chem.*, **27**, 4426 (1962).
(7) G. Fodor and J. Kiss, *J. Am. Chem. Soc.*, **72**, 3495 (1950).
(8) F. G. Bordwell and E. W. Garbisch, Jr., *ibid.*, **82**, 3588 (1960).
(9) W. A. Bonner, J. A. Zderic, and G. A. Casalette, *ibid.*, **74**, 5086 (1952); W. A. Bonner and J. A. Zderic, *ibid.*, **78**, 3218 (1956).

(10) S. Mitsui and S. Imaizumi, *Bull. Chem. Soc. Japan*, **34**, 774 (1961), recently also have observed hydrogenolyses of benzyl acetates which occur with inversion of configuration, whereas the corresponding alcohols undergo hydrogenolysis with retention of configuration.

isomer may be attributed to a relatively greater steric hindrance to the approach of the base to the axial hydrogen atom α to the nitro group during carbanion formation.

Zimmerman[11] has found recently in a study of the protonation of a carbanion intermediate identical in structure to (A), except that the OAc group was replaced by H, that proton donors approached preferentially so as to place the proton in an equatorial rather than an axial position. One would then expect, by the principle of microscopic reversibility, that proton abstraction to form the carbanion would also occur so as to remove an equatorial hydrogen atom in preference to an axial hydrogen atom. This is what we have observed.

Elimination of acetic acid from the nitro acetates could be effected with either acid or base catalysis. With sulfuric acid in acetic anhydride, either I or II gave 6-nitro-1-phenylcyclohexene (IV), and 2-nitro-1-phenylcyclopentyl acetate gave 5-nitro-1-phenylcyclopentene. With one mole of sodium methoxide in methanol, I gave a mixture of about 85% of 2-nitro-1-phenylcyclohexene (III) and 15% of 6-nitro-1-phenylcyclohexene (IV), judging from an infrared analysis. In the presence of 15% alkali, IV was the sole product. 2-Nitro-1-phenylcyclopentyl acetate gave 2-nitro-1-phenylcyclopentene with triethylamine in dioxane. Equilibration of this nitroalkene with triethylamine in chloroform gave 5-nitro-1-phenylcyclopentene. In both the cyclohexene and cyclopentene series the more stable nitrocycloalkene is that of the type $-C{=}C(C_6H_5)-C(NO_2)-$. The lesser stability of the isomer containing the $-C-C(C_6H_5){=}C-NO_2$ system is noteworthy. Evidently the steric interference between the nitro group and the phenyl group in the latter system is such that *neither* can conjugate effectively with the carbon–carbon double bond. As a result the preferred position for the double bond is that where conjugation is with phenyl alone.

Experimental[12]

Nitration of 1-Phenylcyclohexene. β-Nitro Acetates I and II.—The nitration reagent was prepared by adding 4.5 g. (0.05 mole) of 70% nitric acid to 35 ml. of acetic anhydride at 25–30°.[2,3,8] The resulting reagent was cooled to −20° and then 4.0 g. (0.025 mole) of 1-phenylcyclohexene in 10 ml. of acetic anhydride was added. The temperature rose to 0°; the solution was then recooled to −20° and maintained at this temperature for 5 min. After this time, the solution was poured into 200 ml. of water and the resulting mixture was stirred until the excess of acetic anhydride was hydrolyzed. The product then was extracted with ether, the extract was washed with dilute sodium bicarbonate and water, and finally dried over calcium chloride. The ether was evaporated under reduced pressure. The crude nitration product (infrared analysis gave the ratio of I to II as approximately 3 to 1 with about 7% contamination by nitrate ester[2]) was dissolved in a minimum amount of chloroform and the solution placed on a 3 × 70 cm. silica gel column slurry packed with 4% of ether in hexane. The product was eluted with ether in hexane solutions: 6200 ml. of 4%, 3000 ml. of 5%, and 3000 ml. of 15%. First collected were fractions containing 0.53 g. (10%) of a mixture of unconjugated and conjugated nitroalkenes with the former predominating (by infrared). Next were collected fractions containing a total of 3.24 g. (49%) of isomer I (melting between 130° and 137°). Fractions containing 1.05 g. (19%) of isomer II (melting between 132° and 137°) were collected last.

1-Acetoxy-*trans*-2-nitro-1-phenylcyclohexane (I) melted at 137–137.5° after three recrystallizations from ether in hexane; infrared maxima (chloroform): 8.05 (s), 9.04 (m), 10.20 (s), 10.95 (m), 11.55 (w), and 11.90 (m) μ.

Anal. Calcd. for $C_{14}H_{17}NO_4$: C, 63.86; H, 6.51; N, 5.32. Found: C, 63.48; H, 6.44; N, 5.55.

1-Acetoxy-*cis*-2-nitro-1-phenylcyclohexane (II) melted at 137–137.5° after three recrystallizations from ether in hexane; infrared maxima (chlorofrom): 8.80 (m), 10.24 (m), 10.34 (m), and 11.37 (m) μ.

Anal. Calcd. for $C_{14}H_{17}NO_4$: C, 63.86; H, 6.51; N, 5.32. Found: C, 63.77; H, 6.24; N, 5.57.

Reductions of I. (a) Palladium-on-Charcoal-Catalyzed Hydrogenation.—A mixture of 1.00 g. (0.0038 mole) of I, 35 ml. of methanol, 0.70 g. of concentrated sulfuric acid, and 0.60 g. of 10% palladium on charcoal was shaken under 40 p.s.i. of hydrogen at room temperature for 2.5 days. The mixture was then filtered into water (50 ml.) and the filtrate again filtered in order to remove a small amount of insoluble material. The resulting aqueous filtrate was extracted with 25 ml. of ether and the ether extract discarded. The aqueous layer was made basic with alkali and then extracted with 50 ml. of ether. The extract was dried over sodium sulfate and the ether then removed under reduced pressure to give 0.6 g. (86%) of *trans*-2-phenylcyclohexylamine melting at 54–56° (reported[13] m.p. 59–60°). The N-benzoyl derivative melted at 181° (reported[14] m.p. 181°).

(b) Electrolytic Reduction.—The procedure closely resembled that described by Bruckner and Fodor.[15] A solution of 2.63 g. 0.01 mole) of I in 20 ml. of acetic acid, and 40 ml. of absolute ethanol was placed in a 250-ml. beaker (7.5-cm. diameter), the bottom of which was covered with about 5 mm. of clean mercury (cathode compartment). Two and a half milliliters of concentrated hydrochloric acid was then added. A 4.5-cm. (inside diameter) porous cylinder was introduced and held about 1 cm. above the mercury surface. The porous cylinder was filled to approximately the level of the surrounding solution with 20% sulfuric acid. A lead plate 4.2 cm. wide was rested on the bottom of the cylinder and a current of 2.3 amp. was passed through the cell for 54 min., maintaining the reaction temperature at 50° by means of external cooling. After this time, the cathode solution was separated from the mercury. The reduction apparatus was washed with ethanol, and the washings added to the cathode solution. The solvent was removed under reduced pressure on the steam bath; the last traces of volatile material being removed under 1 mm. of pressure at 60°. The crude solid amine hydrochloride was digested with 20 ml. of ethyl acetate and then collected by filtration. The solid was washed with ethyl acetate and dried at 60° to give 2.01 g. (75%) of **1-acetoxy-*trans*-2-amino-1-phenylcyclohexane hydrochloride**, m.p 210–212° dec. After two recrystallizations, the amine hydrochloride melted at 215° dec.

Anal. Calcd. for $C_{14}H_{20}ClNO_2$: C, 62.33; H, 7.47; N, 5.19. Found: C, 62.26; H, 7.45; N, 5.29.

(c) Raney Nickel Hydrogenation.—A mixture of 1.32 g. (0.005 mole) of I, dissolved in 30 ml. of warm ethanol, and 4.0 g. of Raney nickel (W-2)[16] was shaken under 40 p.s.i. of hydrogen for 35 min. The mixture was then filtered and hydrochloric acid was added to the filtrate until acid to litmus. The solvent then was removed under reduced pressure and the semisolid residue digested with 15 ml. of ethyl acetate. Filtration gave 0.71 g. (53%) of 1-acetoxy-*trans*-2-amino-1-phenylcyclohexane hydrochloride, m.p. 208–209° dec. A mixture melting point with the amine hydrochloride of the electrolytic reduction was 208–209° dec.

1-Acetoxy-*trans*-2-acetamido-1-phenylcyclohexane.—Potassium bicarbonate (0.10 g.) was added to a stirred mixture of 0.27 g. (0.001 mol) of 1-acetoxy-*trans*-2-amino-1-phenylcyclohexane hydrochloride (dissolved in 5.0 ml. of water) and 6 drops of acetic anhydride. The oil which separated solidified slowly to give 0.25 g. (92%) of **1-acetoxy-*trans*-acetamido-1-phenylcyclohexane**, m.p. 60–63°. The melting point was not changed after three recrystallizations from ether–hexane.

Anal. Calcd. for $C_{16}H_{21}NO_3$: C, 69.79; H, 7.69; N, 5.09. Found: C, 69.74; H, 7.78; N, 5.29.

(11) H. E. Zimmerman and T. E. Nevins, *J. Am. Chem. Soc.*, **79**, 6559 (1957).

(12) Microanalyses were by Hilda Beck.

(13) R. T. Arnold and P. N. Richardson, *J. Am. Chem. Soc.*, **76**, 3649 (1954).

(14) D. V. Nightingale and W. Tweedie, *ibid.*, **66**, 1968 (1944).

(15) V. Bruckner and G. von Fodor, *Ber.*, **76**, 466 (1943); G. von Fodor, *ibid.*, **76**, 1216 (1943).

(16) R. Mozingo, "Organic Syntheses," Coll. Vol. III, John Wiley and Sons, Inc., New York, N. Y., 1955, p. 181.

2-Acetamido-*trans*-1-hydroxy-1-phenylcyclohexane.—A solution of 1.00 g. (0.0037 mole) of 1-acetoxy-*trans*-2-amino-1-phenylcyclohexane hydrochloride in 15 ml. of water was treated with an excess of potassmium carbonate and then left for 16 hr. After this time, the mixture was filtered and the solid recrystallized from ethyl acetate to give 0.56 g. (65%) of 2-acetamido-*trans*-1-hydroxy-1-phenylcyclohexane, m.p. 164–165°. Two further recrystallizations did not change the melting point (reported[4] m.p. 166.4–167°); infrared maxima (chloroform): 8.64 (m), 10.15 (m), and 11.27 (w) μ.

Treatment of 70 mg. of 1-acetoxy-*trans*-2-acetamido-1-phenylcyclohexane with 3.0 ml. of 90% methanol containing 2% of potassium hydroxide at 60° for 15 min. led to 2-acetamido-*trans*-1-hydroxy-1-phenylcyclohexane (60 mg.), m.p. 163.5–164° (crude).

1-Acetoxy-*trans*-2-benzamido-1-phenylcyclohexane.—This derivative was prepared from 1-acetoxy-*trans*-2-amino-1-phenylcyclohexane hydrochloride in 93% yield through treatment of a solution of the amine hydrochloride in pyridine with an excess of benzoyl chloride. The crude product melted at 168–168.5°, and the melting point was not changed by recrystallization from ethyl acetate–hexane.

Anal. Calcd. for $C_{29}H_{23}NO_3$: C, 74.75; H, 6.87; N, 4.15. Found: C, 75.07; H, 6.86; N, 4.32.

A mixture of 100 mg. of 1-acetoxy-*trans*-2-benzamido-1-phenylcyclohexane, 3 g. of W-2 Raney nickel,[16] and 10 ml. of ethanol was refluxed for 1 hr. The mixture was then filtered into water. The yield of *N*-*trans*-2-phenylcyclohexylbenzamide, m.p. 173–176°, was 72%. The melting point was raised to 178–179° after one recrystallization from methanol (reported[14] m.p. 181°).

2-Benzamido-*trans*-1-hydroxy-1-phenylcyclohexane.—This derivative was prepared by selective hydrolysis of the acetoxy function of 1-acetoxy-*trans*-2-benzamido-1-phenylcyclohexane through treatment with warm 90% methanol containing 2% of potassium hydroxide. The product melted at 155–156°. Repeated crystallizations did not raise the melting point (reported[4] m.p. 157–158°).

A mixture of 0.15 g. of 2-benzoylamino-*trans*-1-hydroxy-1-phenylcyclohexane, 3 g. of W-2 Raney nickel,[16] and 20 ml. of ethanol was refluxed for 25 min. The mixture was then filtered into water. The product which slowly solidified was collected by filtration to give 0.11 g. (78%) of *N*-*cis*-2-phenylcyclohexylbenzamide, m.p. 118–120°. Two crystallizations from aqueous methanol raised the melting point to 122.5–123.5° (reported m.p.[4] 126.5–127°).

Reduction of II. (a) Electrolytic Reduction.—The reduction, as described for I, did not lead to a product which could be characterized.

(b) Raney Nickel Hydrogenation.—A mixture of 0.66 g. (0.0025 mole) of II, 30 ml. of ethanol, and 3 g. of W-2 Raney nickel[16] was shaken under 40 p.s.i. of hydrogen for 1.5 hr. The mixture then was filtered and the ethanol removed under reduced pressure. The residue was dissolved in 10 ml. of ethyl acetate and the resulting solution filtered so as to remove a small amount of insoluble material. The ethyl acetate of the filtrate was evaporated and the residue solidified upon trituration with ether–hexane. Filtration gave 0.24 g. (59%) of 2-acetamido-*cis*-1-hydroxy-1-phenylcyclohexane, m.p. 130–131°. The melting point was not changed by three crystallizations from ether–hexane; infrared maxima (chloroform): 8.69 (m), 10.07 (m), 11.43 (w), and 11.81 (w) μ.

Anal. Calcd. for $C_{14}H_{19}NO_2$: C, 72.07; H, 8.21; N, 6.01. Found: C, 72.76; H, 8.36; N, 6.20.

6-Nitro-1-phenylcyclohexene.—A solution of 15 ml. of acetic anhydride containing 20 drops of sulfuric acid was added to 0.50 g. of I and the mixture stirred until the β-nitro acetate had dissolved and for 10 min. thereafter. About 50 ml. of ice–water then was added and the mixture was stirred until the acetic anhydride had hydrolyzed. The β-nitroalkene solidified upon cooling and was collected by filtration to give, after washing with dilute potassium bicarbonate and water, 0.36 g. (93%) of 6-nitro-1-phenylcyclohexene, m.p. 33–35°. After three crystallizations from pentane, the melting point was 37.5°; λ_{max}^{EtOH} 238–239 mμ, ϵ 11,300.

Anal. Calcd. for $C_{12}H_{13}NO_2$: C, 70.92; H, 6.45; N, 6.89. Found: C, 70.81; H, 6.22; N, 7.09.

Comparable results were obtained with isomer II; however, a longer reaction time was required (approximately fivefold).

The β-nitroalkene also was obtained by dissolving either I or II in an excess of 15% alcoholic alkali at room temperature and, after several minutes, acidifying with 20% acetic acid–alcohol. The resulting solution was left for several minutes and the product was then obtained after addition of water.

An attempt to prepare 1-nitro-2-phenylcyclohexene by titrating a warm methanolic solution of I with an equivalent amount of alcoholic sodium methoxide, led to an oily mixture of approximately 84% of 1-nitro-2-phenylcyclohexene and 16% of 6-nitro-1-phenylcyclohexene (by infrared). Chromatography failed to separate the isomers.

Equilibration of 6-Nitro-1-phenylcyclohexene.—A 2% (by weight) solution of both 6-nitro-1-phenylcyclohexene and triethylamine in chloroform was prepared and left at room temperature for 23 days. Periodically the infrared spectrum between 6.3 μ and 6.9 μ was measured. During this time, no absorption which could be attributed to 1-nitro-2-phenylcyclohexene was observed—the absorbance of the NO_2 absorption at 6.42 μ being the same after 23 days as compared with that initially.

Rates of Piperidine-Induced Elimination of Acetic Acid from I and II.—A solution of 105 mg. (4×10^{-4} mole) of I (or II) in 1.00 ml. of chloroform was prepared. To this was added 1.00 ml. of absolute ethanol followed by the addition of 1.00 ml. of freshly distilled piperidine. After mixing thoroughly, a sample of the resulting solution was transferred to a rock salt cell (73 μ) which then was placed in the sample beam of a Baird infrared spectrometer. A solution (in matched cell) of chloroform, ethanol, and piperidine (1:1:1 by volume) was placed in the reference beam. The absorbance at 5.07 μ was measured as a function of time. A plot of log (O.D. − O.D. ∞) 5.70 μ against time gave linear plots for I and II from which approximate pseudo first-order rate constants of 0.030 $min.^{-1}$ and 0.12 $min.^{-1}$, respectively, were determined. The temperature of the cell compartment was 35 ± 2°. Both runs were followed to approximately 80% completion (13 min. for I and 50 min. for II from the time mixing).

Nitration of 1-Phenylcyclopentene. 1-Acetoxy-*trans*-2-nitrophenylcyclopentane.—To a nitration reagent prepared from 4.5 g. (0.05 mole) of 70% nitric acid and 45 ml. of acetic anhydride, and then cooled to −20° was added 2 drops of sulfuric acid followed by the addition of 4.3 g. (0.03 mole) of 1-phenylcyclopentene. After the initial temperature rise, the solution was recooled to −20° and then poured into an excess of water. The product was processed as described for the nitration of 1-phenylcyclohexene. Chromatography of the crude nitration product (see 1-phenylcyclohexene) led to the isolation of 1.90 g. (34%) of a mixture of conjugated and unconjugated nitroalkenes with the latter predominating (by infrared), and 2.97 g. (40%) of *trans*-β-nitro acetate, m.p. 125–127°. The only other material obtained was 70 mg. of resinous oil which was eluted last. The 1-acetoxy-*trans*-2-nitro-1-phenylcyclopentane was recrystallized twice from ether–hexane and melted at 127–127.5°; infrared maxima (chloroform): 8.50 (w) μ and 10.20 (m) μ.

Anal. Calcd. for $C_{13}H_{15}NO_2$: C, 62.64; H, 6.07; N, 5.62. Found: C, 62.80; H, 6.12; N, 5.74.

Electrolytic Reduction of 1-Acetoxy-*trans*-2-nitro-1-phenylcyclopentane.—The procedure described for the reduction of I was followed with slight modification. A current of 2.3 amp. was passed through the electrolytic cell which contained in the cathode compartment a solution of 15 ml. of acetic acid, 30 ml of ethanol, and 2.0 ml. of concentrated hydrochloric acid. The cell was cooled to 30° and then 1.25 g. (0.005 mole) of coarsely ground 1-acetoxy-*trans*-2-nitro-1-phenylcyclopentane was added to the cathode compartment. The temperature was maintained at 40–45° for 35 min., during which time the β-nitro acetate gradually dissolved. The cathode solution then was processed as described earlier to give 0.87 g. (68%) of 1-acetoxy-*trans*-2-amino-1-phenylcyclopentane hydrochloride, m.p. 197–199° dec. (trituration of the crude product with ethyl acetate induced crystallization of the amine hydrochloride). Two recrystallizations from ethyl acetate–ethanol raised the melting point to 198–199° dec.

Anal. Calcd. for $C_{13}H_{18}ClNO_2$: C, 61.05; H, 7.09; N, 5.48. Found: C, 61.08; H, 7.19; N, 5.55.

Lower yields of amine hydrochloride were obtained when the reduction was conducted as described for I. This can be attributed to the apparent instability of 1-acetoxy-*trans*-2-nitro-1-phenylcyclopentane in the acidic reduction medium at 50°.

1-Acetoxy-*trans*-2-benzamido-1-phenylcyclopentane.—This derivative, m.p. 162.5–164°, was prepared from 1-acetoxy-*trans*-2-amino-1-phenylcyclopentane in 94% yield through the reaction with benzoyl chloride in pyridine.

Anal. Calcd. for $C_{20}H_{21}NO_3$: C, 74.28; H, 6.55; N, 4.33. Found: C, 74.85; H, 6.73; N, 4.54.

A mixture of 100 mg. of the N-benzoyl, O-acetyl derivative, 3 g. of W-2 Raney nickel.[16] and 10 ml. of ethanol was refluxed for 30 min. The mixture was filtered into water and the resulting solid product collected by filtration to give 60 mg. (73%) of N-*trans*-1-phenylcyclopentylbenzamide, m.p. 150–152°. Two recrystallizations raised the melting point to 156–156.5°. A mixture melting point with an authentic sample[17] was not depressed.

2-Benzamido-*trans*-1-hydroxy-1-phenylcyclopentane.—An 0.52-g. sample of 1-acetoxy-*trans*-2-benzamido-1-phenylcyclopentane was treated with 5.0 ml. of 4% methanolic potassium hydroxide for 5 min. on the steam bath. After addition of ice–water and filtration, 0.41 g. (91%) of 2-benzamido-*trans*-1-hydroxy-1-phenylcyclopentane, m.p. 96°, was obtained. After crystallization from chloroform–hexane, the derivative melted at 97.5–98°, resolidifying at this temperature and then remelting at 109.5–110.5°. The material was dried at 110° for analysis.

Anal. Calcd. for $C_{18}H_{19}NO_2$: C, 76.84; H, 6.81; N, 4.98. Found: C, 77.0; H, 6.63; N, 4.96.

1-Phenylcyclopentene Oxide.—The procedure was adopted from that of Curtin and Schmulker.[4] 1-Phenylcyclopentene, 24.5 g. (0.17 mole), was added to a solution of 23.2 g. (0.168 mole) of perbenzoic acid[18] in 280 ml. of chloroform at such a rate so as to maintain the reaction temperature below −15°. The reaction mixture was then left at −20° for 1 hr. and at −10° for 46 hr. After this time, iodometric titration showed only a trace of residual peroxide. The chloroform solution was then extracted with 11.0 g. of potassium hydroxide in 500 ml. of ice–water. The chloroform layer was dried over sodium sulfate and stored at −10°. Samples of the alkene oxide were obtained when needed by evaporation of the chloroform under reduced pressure at room temperature.

2-Amino-*trans*-1-hydroxy-1-phenylcyclopentane.—The procedure was patterned after that of Curtin and Schmulker.[4] A mixture of 10.0 g. (0.0575 mole) of 1-phenylcyclopentene oxide and 200 ml. of concentrated aqueous ammonia was heated at 145–150° for 19 hr. in a 450-ml. rotating autoclave (fitted with a glass liner) charged with 20 atm. of nitrogen. The reaction mixture then was cooled and slowly made acidic (to litmus) with concentrated hydrochloric acid. The solution was extracted four times with 300 ml. of ether and the ether extracts discarded. The aqueous layer was made basic with alkali and then extracted with three 300-ml. portions of ether. The ether extracts were combined and dried over sodium sulfate. The ether was evaporated under reduced pressure and the residue mixed with 15 ml. of ether and 5.0 ml. of hexane. The mixture was cooled, and scratching induced the crystallization of a mixture of amino alcohols. The solid was collected by filtration, and washed with 60% ether in hexane to give 5.86 g., m.p. 73–76°. An additional 0.83 g., m.p. 73–76°, was obtained from the filtrate and washings to bring the total of crude amino alcohols to 6.7 g. (62%).

The mixture of amino alcohols were partially separated by fractional crystallization from ether to give 0.56 g. of 2-amino-*trans*-1-phenylcyclopentane, m.p. 99–100°, and 0.18 g. of 2-amino-2-phenylcyclopentanol (?), m.p. 90°. The remaining material was chromatographed in a 2.5 × 70 cm. silica gel column slurry packed with 5% ether in hexane solution. The amino alcohols were eluted with 10% methanol–40% hexane in ether and 10% methanol in ether solutions. Fractions containing 1.09 g. of 2-amino-2-phenylcyclopentanol (?), m.p. 87–90°, were collected first. Fractions containing 0.51 g. of a mixture of amino alcohols, m.p. 69–73°, were collected next, and these were followed by fractions containing 0.79 g. of 2-amino-*trans*-1-hydroxy-1-phenylcyclopentane, m.p. 98–100°.

The 2-amino-*trans*-1-hydroxy-1-phenylcyclopentane, was recrystallized twice from ether and melted at 100.5°.

Anal. Calcd. for $C_{11}H_{15}NO$: C, 74.54; H, 8.53; N, 7.90. Found: C, 74.40; H, 8.57; N, 8.17.

A mixture of 30 mg. of 2-amino-1-phenylcyclopentanol (?) and 10 drops of acetic anhydride was heated on the steam bath for 15 min. After this time, 5.0 ml. of saturated sodium bicarbonate was carefully added. The resulting mixture then was filtered and the solid washed with water and dried to give 38 mg. (86%) of 2-acetoxy-1-N-acetyl-1-phenylcyclopentylamine (?), m.p. 156.5–157°. One crystallization from ethyl acetate–hexane raised the melting point to 157.5–158°.

Anal. Calcd. for $C_{15}H_{19}NO_3$: C, 68.95; H, 7.33; N, 5.36. Found: C, 68.80; H, 7.15; N, 5.60.

A similar treatment of 2-amino-*trans*-1-hydroxy-1-phenylcyclopentane with acetic anhydride led to an oily material which exhibited strong infrared absorptions at 6.02 and 6.60 μ, but no absorptions at near 5.7 and 8.0 μ indicative of the acetoxy function.

N-Benzoylation of 2-amino-*trans*-1-hydroxy-1-phenylcyclopentane with benzoyl chloride in pyridine at room temperature led to 2-benzamido-*trans*-1-hydroxy-1-phenylcyclopentane in 61% yield, m.p. 96–97°, resolidifying at this temperature and remelting at 108–109.5° (crude). A mixture melting point of this material with the N-benzoyl amino alcohol obtained *via* the electrolytic reduction of 1-acetoxy-*trans*-2-nitro-1-phenylcyclopentane was 109–110°.

1-Nitro-2-phenylcyclopentene.—A solution of 1.0 g. of 1-acetoxy-*trans*-2-nitro-1-phenylcyclopentane in 15 ml. of dioxane was treated with 1.0 g. of triethylamine.[3] The resulting solution was left for 1.5 hr. at room temperature and then poured into an excess of dilute acetic acid. The product which slowly solidified was collected by filtration to give 0.70 g. (95%) of crude 1-nitro-2-phenylcyclopentene which melted at 51° after one crystallization from methanol. Recrystallizations from hexane raised the melting point to 51.5–52°.

Anal. Calcd. for $C_{11}H_{11}NO_2$: C, 69.82; H, 5.86; N, 7.40. Found: C, 69.64; H, 5.87; N, 7.70.

Comparable results were obtained by stirring a solution of the β-nitro acetate in dimethylformamide with catalytic amounts of sodium nitrite.[3]

5-Nitro-1-phenylcyclopentene.—To a solution of 15 ml. of acetic anhydride and 10 drops of sulfuric acid was added 0.50 g. of 1-acetoxy-*trans*-2-nitro-1-phenylcyclopentane. The β-nitro acetate dissolved rapidly and the resulting solution was stirred for 30 sec. at room temperature and then poured into an excess of water. The aqueous mixture was stirred until the acetic anhydride had hydrolyzed and, after being cooled to *ca.* 10°, the remaining oily material solidified. The solid was collected by filtration to give 0.35 g. (93%) of 5-nitro-1-phenylcyclopentene, m.p. 33–34°. After two recrystallizations from hexane, the melting point was 34.0°; λ_{max}^{EtOH} 248–249 mμ, ϵ 13,700.

Anal. Calcd. for $C_{11}H_{11}NO_2$: C, 69.82; H, 5.86; N, 7.40. Found: C, 69.90; H, 5.85; N, 7.29.

Equilibration of 1-Nitro-2-phenylcyclopentene.—A solution of 24 mg. of 1-nitro-2-phenylcyclopentene, 0.6 ml. of chloroform, and 0.2 ml. of triethylamine was prepared and the infrared spectrum between 6.3 and 6.7 μ measured periodically over a period of 7 days. After this time, the initial conjugated nitro absorption at 6.60 μ had disappeared, being replaced by the unconjugated nitro absorption of 5-nitro-1-phenylcyclopentene at 6.42 μ. A sample of the 5-nitro-1-phenylcyclopentene, m.p. 29–32°, was obtained from the equilibration solution and a mixture melting point with a known sample was not depressed.

(17) Unpublished results of T. A. Whitney and F. G. Bordwell, Northwestern University.

(18) I. M. Kolthoff, T. S. Lee, and M. A. Mairs, *J. Polymer Sci.*, **2**, 199 (1947); G. Braun, "Organic Syntheses," Coll. Vol. I, John Wiley and Sons, Inc., New York, N. Y., 1948, p. 431.