# Azo Compounds. XXXIX. Olefin Formation. The Mercuric Oxide Oxidation of 1-Amino-2-(*p*-methoxyphenyl)-6-phenylpiperidine[1]

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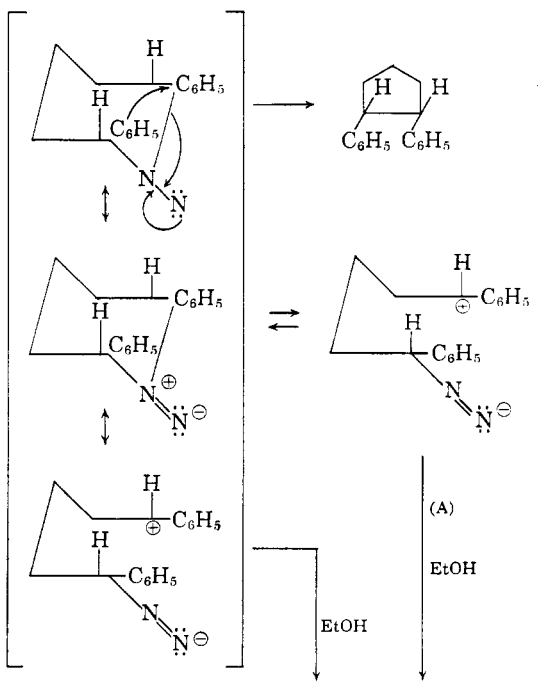
An isomer, tentatively assigned the *cis* configuration, of 1-amino-2-(*p*-methoxyphenyl)-6-phenylpiperidine was synthesized and treated with yellow mercuric oxide in ethanol resulting in evolution of nitrogen and the formation of olefin, consisting of a mixture of 1-(*p*-methoxyphenyl)-5-phenyl-1-pentene and 5-(*p*-methoxyphenyl)-1-phenyl-1-pentene in the ratio of 2 to 1. The mechanism of the reaction is discussed in relation to the ratio of olefinic products.

In an earlier paper[3] we reported the stereoselective oxidation of *cis*-1-amino-2,6-diphenylpiperidine with yellow mercuric oxide to give 65% of *cis*-1,2-diphenylcyclopentane accompanied by 25% of 1,5-diphenyl-1-pentene and of *trans*-1-amino-2,6-diphenylpiperidine to give 59% of *trans*- and 12% of *cis*-1,2-diphenylcyclopentane along with 14% of 1,5-diphenyl-1-pentene. It was then proposed that olefin formation most probably occurred by largely an $E_1$ process involving an intermediate carbonium ion (A) as indicated below. As will be noted later, there is no clear cut evidence for any appreciable concentration of (A).

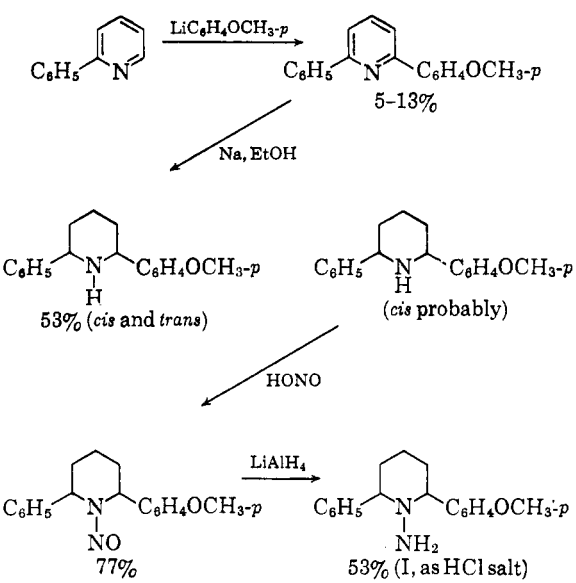



$C_6H_5CH{=}CHCH_2CH_2CH_2C_6H_5 + N_2$

We have now prepared and oxidized an unsymmetrical 1-amino-2,6-diarylpiperidine where one $\alpha$-substituent has a much greater capacity for resonance stabilization of a carbonium ion than the other. The effect of such substitution on the ratio of the two possible olefins formed as well as on the total olefin produced was of interest. It was anticipated that, if olefin were produced by an $E_1$ mechanism, conjugation with the *p*-anisyl group should predominate.

## Results and Discussion

An isomer of 1-amino-2-(*p*-methoxyphenyl)-6-phenylpiperidine (I) was synthesized as follows




Scholtz and Meyer had reported the preparation of 2-(*p*-methoxyphenyl)-6-phenylpyridine by heating the oxime of cinnamal-*p*-methoxyacetophenone.[4] They characterized the compound as a basic, yellow crystalline material, m.p. 119°. However, the compound as prepared in our hands proved to be a white, crystalline solid, m.p. 130–132°. The disubstituted pyridine could be prepared only in poor yield (5–13%) by treating a 50% excess of 2-phenylpyridine in toluene with an

(1) This is the 39th in a series of papers dealing with the preparation and reactions of azo and related compounds. For the previous paper in this series, see C. G. Overberger and L. P. Herin, *J. Org. Chem.*, **27**, 417 (1962).

(2) This paper comprises a portion of the dissertation submitted by Louis P. Herin in partial fulfillment of the requirements for the Ph.D degree at the Polytechnic Institute of Brooklyn.

(3) C. G. Overberger, J. G. Lombardino, and R. G. Hiskey, *J. Am. Chem. Soc.*, **79**, 6430 (1957).

(4) M. Scholtz and W. Meyer, *Ber.*, **43**, 1865 (1910).

ether solution of *p*-anisyllithium. The low yield of disubstituted pyridine is probably due to several factors. Firstly, there is undoubtedly considerable metalation[5] of unchanged *p*-bromoanisole by the *p*-anisyllithium already formed during the preparation of the organometallic ether solution. Secondly, some Fittig-type coupling may occur during the formation of the *p*-anisyllithium. Thirdly, it was observed that with the "low-sodium" grade of lithium metal produces by the Lithium Corp. of America in ingot, ribbon, or wire form, *p*-bromoanisole was completely inert, as were also *p*-chloroanisole, *p*-iodoanisole, and *p*-dimethylaminobromobenzene.[6] However, these halides were quite reactive with the regular grade of lithium metal having 0.05% of sodium (the "low-sodium" grade has 0.002% sodium).[7]

Reduction of 2-(*p*-methoxyphenyl)-6-phenylpyridine with sodium alcohol gave two isomeric piperidines (presumably *cis* and *trans*) which were separated by fractional crystallization and purified as the hydrochlorides, 37% of one isomer of 2-(*p*-methoxyphenyl)-6-phenylpiperidine hydrochloride m.p. 270–271° dec. and 16% of the other isomer, m.p. 198–200° dec. The free bases were generated from these hydrochlorides.

By comparison with the physical properties of *cis*- and *trans*-2,6-diphenylpiperidines[3] it is reasonable to assign tentatively the *cis* configuration to the solid isomer and the *trans* configuration to the liquid isomer.

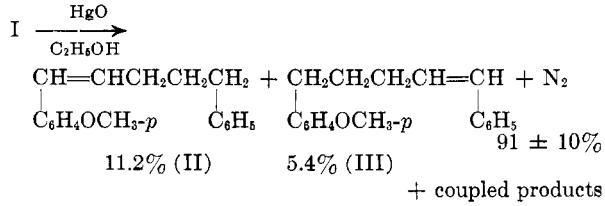
The high-melting isomer of 2-(*p*-methoxyphenyl)-6-phenylpiperidine hydrochloride was nitrosated (77%) in 50% acetic acid using solid sodium nitrite. Reduction with lithium aluminum hydride in ether afforded the corresponding hydrazine (I), isolated as the hydrochloride in 53% yield. The free base was generated and proved to be a solid. The hydrazine was further characterized by the preparation of a benzal derivative.

The low-melting isomer of 2-(*p*-methoxyphenyl)-6-phenylpiperidine hydrochloride was nitrosated under the same conditions as described above (86%).

An ethanol solution of I, maintained at 64°, was decomposed by the addition of solid yellow mercuric oxide. An almost theoretical evolution of nitrogen was obtained and a crude oily product was isolated in 100% yield which analyzed closely to the empirical formula $C_{18}H_{20}O$.

Quantitative semi-micro catalytic hydrogenation of a sample of this crude product with platinum dioxide in ethanol showed the presence of 17.3% olefin.

A quantitative comparison of ultraviolet spectra in methanol indicated the presence of 11.2% of II and 5.4% of III, a total of 18% of conjugated olefin. This determination was carried out in the following way. From the spectrum of authentic II we obtained $\lambda_{max}$ 261 mμ, ε 29,250 and at λ 251 mμ, ε 23,380, while from the spectrum of authentic III, $\lambda_{max}$ 251 mμ, ε 24,750 and at λ 261 mμ, ε 18,480. From the spectrum of a sample of the crude reaction product in methanol we obtained D = 0.616 at λ 251 mμ and D = 0.712 at $\lambda_{max}$ 261 mμ, the concentration being $1.42 \times 10^{-4}$ molar assuming a molecular weight which corresponds to the formula $C_{18}H_{20}O$.




This solution was then subjected to catalytic hydrogenation over platinum dioxide and again the ultraviolet spectrum was examined and found to have the following absorption: λ 251 mμ, D = 0.066 and λ 261 mμ, D = 0.128. Since these latter optical densities can be attributed entirely to absorption by aromatic substituents unconjugated with a double bond, multiplying them by a factor of 0.827 will give the contribution to optical density, at the respective wave lengths by non-olefinic product compounds in the original unreduced solution. The concentrations of II, $c_1$, and the concentration of III, $c_2$, in this solution were determined from the following equations (see R. A. Friedel and M. Orchin, "Ultraviolet Spectra of Aromatic Compounds," John Wiley and Sons, Inc., New York, 1951, p. 29).

$$0.616 - 0.827 \times 0.066 = 23{,}380\ c_1 + 24{,}750\ c_2$$

$$0.712 - 0.827 \times 0.128 = 29{,}250\ c_1 + 18{,}480\ c_2$$

The chalcone, cinnamal-*p*-methoxyacetophenone, was reduced in 75% yield with 10% palladium on-charcoal to give 1-(*p*-methoxyphenyl)-5-phenyl-1-pentanone which gave II in 73% yield on further reduction with lithium aluminum hydride followed by distillative dehydration of the alcohol in the presence of a trace of acid. III was similarly prepared from the chalcone, *p*-methoxycinnamalacetophenone, 5-(*p*-methoxyphenyl)-1-phenyl-1-pentanone being obtained in 69% and III in 55% yield.

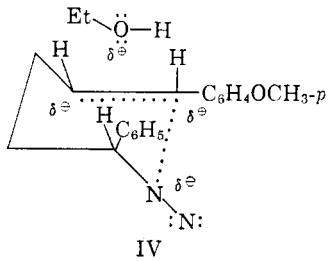
If it is assumed that I is the *cis* isomer of the hydrazine, then the total yield of olefin is found to be comparable to, though somewhat less than, that obtained on oxidation of *cis*-1-amino-2,6-diphenylpiperidine. Analysis of the products have shown that II and III were formed in a ratio of 2 to 1. In the light of the results obtained on oxidation of 1-amino-2-phenylpiperidine,[1] these data are consistent with either an $E_1$ or an $E_2$ mechanism for the formation of olefin. The effect of the *p*-anisyl group in an $E_1$ elimination has already been

(5) H. Gilman, *Org. Reactions*, **VIII**, 294 (1954).

(6) Other authors have reported the similar behavior of deactivated aryl halides with the newer "low-sodium" lithium. J. B. Wright and E. S. Gutsell, *J. Am. Chem. Soc.*, **81**, 5193 (1959). C. W. Kamienski and D. L. Esmay, *J. Org. Chem.*, **25**, 1807 (1960).

(7) J. A. Beel, *et al.*, *ibid.*, **24**, 2036 (1959).

discussed and the formation of a larger amount of olefin conjugated with this group should be anticipated. Moreover, in an $E_2$ elimination the *p*-anisyl group can stabilize the transition state to a greater degree than the phenyl group since a partially positive charge must develop at the $\alpha$-carbon atom as shown in IV, thus tending, though, perhaps not as greatly as in a $E_1$ elimination, to favor the formation of olefin conjugated with the *p*-anisyl group.




IV

It seems clear however, that formation of a discrete ionic intermediate in these oxidations is unlikely since the isomer ratio of olefins was only 2:1 in favor of the *p*-methoxyphenyl. If a true ionic intermediate such as A were present, the ratio should be much higher. We ascribe olefin formation largely as a result of a transition state with some ionic character. This is of course indistinguishable from a radical process for the formation of olefin in a solvent cage. This question has been previously discussed in some detail.[8]

## Experimental[9]

**2-(*p*-Methoxyphenyl)-6-phenylpyridine.**—A solution of 187 g. (1.0 mole) of *p*-bromoanisole in 400 ml. of anhydrous ether was added to a stirred suspension of 16.8 g. (2.4 g.-atoms) of lithium ribbon (regular grade, containing 0.05% of sodium[7] and cut into approximately 0.5 inch squares) in 400 ml. of anhydrous ether under a continuous flow of dry nitrogen, dropwise and at a rate to maintain vigorous spontaneous refluxing. Upon completion of the addition, the reaction was heated at reflux for 0.5 hr., cooled, and a solution of 230 g. (1.5 moles) of 2-phenylpyridine[10] in 400 ml. of anhydrous toluene was added rapidly (this addition proved to be only slightly exothermic).

The dark brown to black reaction mixture was then heated at reflux and solvent removed by means of a Kaye distilling-head until the internal temperature had reached 100°. During this period, an additional 400 ml. of toluene was added dropwise. The reaction was cooled in an ice bath and hydrolyzed with a large excess of water (1000 ml.). The organic layer was separated and dried over potassium hydroxide, filtered, and solvent was removed under vacuum. The residue was distilled through a short section of Vigreux column at reduced pressure, employing a distilling-head suitable for solids. A 74.6-g. fraction of yellow solid, b.p. 170–197° (0.2 mm.), was collected.

Recrystallization from benzene–petroleum ether (b.p. 30–60°) yielded a 32.1-g. (12.5%) crop of white needles, m.p. 129–131°. A second recrystallization afforded an analytical sample, m.p. 131–132.2°.

*Anal.* Calcd. for $C_{18}H_{15}NO$: C, 82.73; H, 5.79; N, 5.36. Found: C, 82.95; H, 6.04; N, 5.07.

A picrate was prepared and recrystallized from ethanol as yellow prisms, m.p. 159–160°.

*Anal.* Calcd. for $C_{24}H_{18}N_4O_8$: C, 58.77; H, 3.70; N, 11.43. Found: C, 58.67; H, 3.93; N, 11.27.

**High- and Low-Melting 2-(*p*-Methoxyphenyl)-6-phenylpiperidine Hydrochlorides.**—A solution of 51.4 g. (0.20 mole) of 2-(*p*-methoxyphenyl)-6-phenylpyridine in 1000 ml. of dry[11] absolute ethanol was heated to reflux with stirring under a continuous flow of dry nitrogen. Approximately 250 g. (11 g.-atoms) of freshly-cut sodium metal were added in small pieces over a period of several hours so as to maintain a very vigorous reflux, care being taken to safely vent the hydrogen formed. An additional 1500 ml. of ethanol was added dropwise during the reaction to prevent any precipitation of sodium ethoxide. On completion of addition of the sodium, the reaction was cooled in an ice bath, hydrolyzed with 1000 ml. of water, and extracted with ether in several portions and the ether extracts treated with hydrogen chloride gas. Some precipitate formed but it was not filtered off. Instead, the mixture was evaporated to dryness under vacuum and the solid residue recrystallized from ethanol giving 22.7 g. (37%) of white solid, m.p. 270–271° dec.

*Anal.* Calcd. for $C_{18}H_{22}NOCl$: C, 71.15; H, 7.30; N, 4.61; neut. equiv., 303.5. Found: C, 71.41; H, 7.47; N, 4.86; neut. equiv., 305.

The mother-liquor from above was concentrated by evaporation on a steam bath and a quantity of ether added. Further crystallization yielded 22.6 g. (37%) crude), m.p. 190–200° dec. This was recrystallized from ethanol–ether to give a first crop of 2.9 g., m.p. 240–260° dec., followed by a second crop of 9.7 g. (16%), m.p. 198–200°.

*Anal.* Calcd. for $C_{18}H_{22}NOCl$: C, 71.15; H, 7.30; N, 4.61; neut. equiv., 303.5. Found: C, 71.25; H, 7.25; N, 4.77; neut. equiv., 305.

**Liquid 2-(*p*-Methoxyphenyl)-6-phenylpiperidine.**—A 5-g. (0.016 mole) sample of low-melting 2-(*p*-methoxyphenyl)-6-phenylpiperidine hydrochloride was treated with 50 ml. of 20% aqueous sodium hydroxide and extracted with ether in several portions. The extracts were dried over anhydrous magnesium sulfate, solvent was removed under vacuum and the oily residue was distilled at reduced pressure. A 2.5-g. (55%) fraction was collected, b.p. 188–191° (0.6 mm.), $n^{25}D$ 1.5818.

*Anal.* Calcd. for $C_{18}H_{21}NO$: C, 80.86; H, 7.92; N, 5.24. Found: C, 80.94; H, 7.92; N, 4.99.

The compound absorbed weakly at 3300 cm.$^{-1}$ in the infrared region.[12]

**Solid 2-(*p*-Methoxyphenyl)-6-phenylpiperidine.**—High-melting 2-(*p*-methoxyphenyl)-6-phenylpiperidine hydrochloride, 10 g. (0.032 mole), was treated with an excess of 10% aqueous sodium hydroxide and extracted with ether in several portions. The combined ether extracts were dried over anhydrous magnesium sulfate, filtered and solvent was removed under vacuum, leaving an oily residue which soon crystallized, 7.9 g. (90%). Recrystallization from petroleum ether (b.p. 30–60°) afforded an analytical sample, m.p. 54.6–56°.

*Anal.* Calcd. for $C_{18}H_{21}NO$: C, 80.86; H, 7.92; N, 5.24. Found: C, 80.74; H, 8.01; N, 4.96.

The infrared spectrum of the solid had a weak absorption band at 3300 cm.$^{-1}$.[12]

**The Nitrosation of High-Melting 2-(*p*-Methoxyphenyl)-6-phenylpiperidine Hydrochloride.**—To a solution of 23.3 g.

(8) C. G. Overberger and N. P. Marullo, *J. Am. Chem. Soc.*, **83**, 1378 (1961).

(9) (a) Melting points are uncorrected. (b) All analyses were carried out by Schwarzkopf Microanalytical Laboratory, Woodside, N. Y.

(10) Prepared essentially by the procedure of J. C. Evans and C. F. H. Allen, *Org. Syntheses*, Coll. Vol. II, p. 517 (1943).

(11) L. F. Fieser, "Experiments in Organic Chemistry," D. C. Heath and Co., Boston, 1957, p. 286.

(12) L. J. Bellamy, "The Infrared Spectra of Complex Molecules," John Wiley and Sons, Inc., New York, N. Y., 1958, p. 248.

(0.077 mole) of high-melting 2-(*p*-methoxyphenyl)-6-phenylpiperidine hydrochloride in 200 ml. of water and 200 ml. of glacial acetic acid, stirred and maintained at 40° by means of an oil-bath, was added at once 6 g. (0.087 mole) of solid sodium nitrite. Stirring and heating were continued for 2 hr., when heating was discontinued and the reaction stirred at room temperature for 24 hr. An amber-colored oil formed. The reaction was extracted with four 100-ml. portions of 1,2-dichloroethane, the combined extracts washed with several 100-ml. portions of water and then dried over anhydrous sodium sulfate. After filtering the solution, solvent was removed under vacuum leaving 17.5 g. (77%) of a very viscous glass-like residue which could not be crystallized, nor could it be distilled without decomposition.

*Anal.* $C_{18}H_{20}N_2O_2$: C, 72.95; H, 6.80; N, 9.45. Found: C, 72.77; H, 7.26; N, 9.10.

The presence of the *N*-nitroso group was indicated by strong absorption bands at 1401 cm.$^{-1}$ and 1350 cm.$^{-1}$ in the infrared region.[13]

**The Nitrosation of Low-Melting 2-(*p*-Methoxyphenyl)-6-phenylpiperidine Hydrochloride.**—In a manner similar to that employed for the nitrosation of high-melting 2-(*p*-methoxyphenyl)-6-phenylpiperidine hydrochloride, 15.3 g. (0.050 mole) of low-melting 2-(*p*-methoxyphenyl)-6-phenylpiperidine hydrochloride was dissolved in 150 ml. of water and 125 ml. of acetic acid and treated with 4 g. (0.058 mole) of solid sodium nitrite. There was isolated 13 g. (88%) of a glass-like residue which, again, could not be crystallized.

*Anal.* Calcd. for $C_{18}H_{20}N_2O_2$: C, 72.95; H, 6.80; N, 9.45. Found: C, 72.90; H, 7.07; N, 9.29.

Absorption bands at 1430 cm.$^{-1}$ (s) and 1380 cm.$^{-1}$ (m) in the infrared region support the presence of the *N*-nitroso group.[13]

**The Lithium Aluminum Hydride Reduction of Nitrosated High-Melting 2-(*p*-Methoxyphenyl)-6-phenylpiperidine.**—A solution of 17.5 g. (0.059 mole) of this isomer of 1-nitroso-2-(*p*-methoxyphenyl)-6-phenylpiperidine in 150 ml. of anhydrous ether was added dropwise and under a continuous flow of dry nitrogen to a slurry of 2.5 g. (0.065 mole) of lithium aluminum hydride in 200 ml. of anhydrous ether. An immediate exothermic reaction was observed, with spontaneous refluxing. Upon completion of the addition, the reaction was maintained at reflux by means of a hot water-bath for 2 hr., then cooled in an ice-bath and hydrolyzed with 100 ml. of water. The reaction mixture was filtered through a mat of glass wool to remove the precipitated aluminates and the precipitate washed with a portion of ether. The ether layer was separated, dried over anhydrous magnesium sulfate and filtered. Treatment of the filtrate with hydrogen chloride gas afforded 15.4 g. (82%) of a voluminous white precipitate, m.p. 242–247° dec., which was recrystallized from ethanol to give 10 g. (53%) of white crystals, m.p. 248–249° dec. The compound reduced yellow mercuric oxide with the evolution of gas.

*Anal.* Calcd. for $C_{18}H_{23}N_2OCl$: C, 67.80; H, 7.27; N, 8.79; neut. equiv., 318.5. Found: C, 68.07; H, 7.43; N, 9.07; neut. equiv., 317.

**1-Amino-2-(*p*-methoxyphenyl)-6-phenylpiperidine (I) (Isomer Derived from High-Melting 2-(*p*-Methoxyphenyl)-6-phenylpiperidine Hydrochloride).**—A sample, 3.9 g. (0.012 mole), of the hydrochloride of X was treated with 50 ml. of 20% aqueous sodium hydroxide and extracted with ether in two 50-ml. portions. The combined extracts were dried over anhydrous magnesium sulfate, filtered and solvent was removed under vacuum to give a residue, m.p. 70–75° dec. Recrystallization from ethanol yielded 2.2 g. (63%) of white crystals, m.p. 77.5–79.5° dec.

*Anal.* Calcd. for $C_{18}H_{22}N_2O$: C, 76.56; H, 7.85; N, 9.92. Found: C, 77.24; H, 8.10; N, 10.15.

The infrared spectrum of the compound had a very weak absorption band at 3330 cm.$^{-1}$ which is indicative of a 1,1-disubstituted hydrazine.[14]

(13) Ref. 12, p. 306.

**The Benzal Derivative of 1-Amino-2-(*p*-methoxyphenyl)-6-phenylpiperidine (X) (Isomer Derived from High-Melting 2-(*p*-Methoxyphenyl)-6-phenylpiperidine Hydrochloride).**—The derivative was prepared by heating 0.5 g. (0.0016 mole) of the hydrochloride of X, 0.8 g. (0.0075 mole) of benzaldehyde and 1 g. of potassium acetate in 20 ml. of absolute ethanol on a steam-bath for 0.25 hr. On cooling, an oil separated which crystallized after standing overnight. Recrystallization from ethanol yielded 0.4 g. (68%) of white needles, m.p. 108.2–109.6°.

*Anal.* Calcd. for $C_{25}H_{26}N_2O$: C, 81.04; H, 7.07; N, 7.56. Found: C, 81.27; H, 7.28; N, 7.37.

An absorption band at 1630 cm.$^{-1}$ in the infrared region indicated the presence of C=N.[15]

In the ultraviolet region, a cyclohexane solution of the compound had the following absorption spectrum: shoulder, $\lambda$ 300 m$\mu$, $\epsilon$ 3600; $\lambda_{max}$ 283 m$\mu$, $\epsilon$ 4400; $\lambda_{max}$ 277 m$\mu$, $\epsilon$ 4300; shoulder, $\lambda$ 243 m$\mu$, $\epsilon$ 7700; and $\lambda_{max}$ 223 m$\mu$, $\epsilon$ 12,800.

**The Mercuric Oxide Decomposition of 1-Amino-2-(*p*-methoxyphenyl)-6-phenylpiperidine (I) (Isomer Derived from High-Melting 2-(*p*-Methoxyphenyl)-6-phenylpiperidine Hydrochloride).**—A solution of 4.5 g. (0.0160 mole) of unrecrystallized I in 50 ml. of absolute ethanol was heated to 64° with stirring under a continuous flow of nitrogen and in a system equipped for the collection of evolved gases. Nitrogen flow was then stopped, the system closed and allowed to come to equilibrium. Yellow mercuric oxide, 4.6 g. (0.022 mole), was added at once from a solids addition funnel. Immediate evolution of gas was observed and in less than 1 hr., 300 ml. of nitrogen (91 ± 10%) were collected over water at 14°.

When gas evolution had ceased, the hot reaction mixture was filtered through Celite and the filtrate evaporated under vacuum leaving a 4.0 g. (100%) residue of crude product.

A sample, 0.482 g. (0.00191 mole), of this crude product, dissolved in 10 ml. of absolute ethanol, was added to 50 mg. of pre-reduced platinum dioxide in 20 ml. of absolute ethanol in an atmospheric pressure semi-micro catalytic hydrogenation apparatus and the mixture stirred for 0.5 hr., until no further hydrogen was absorbed. A total of 8 ml., measured at 24°, was taken up, which represents 17.3% of the theoretical amount for one double bond per mole based on the molecular formula $C_{18}H_{20}O$.

An $1.42 \times 10^{-4}$ molar solution of the crude product in methanol had the following absorption in the ultraviolet region: $\lambda$ 251 m$\mu$, D = 0.616 and $\lambda_{max}$ 261 m$\mu$, D = 0.712. This solution was catalytically hydrogenated over platinum dioxide until no further hydrogen was taken up. An ultraviolet spectrum of the resulting solution had the following absorption: $\lambda$ 251 m$\mu$, D = 0.066 and $\lambda$ 261 m$\mu$, D = 0.128.

A 1.5-g. sample of the crude product was distilled at reduced pressure through a small Vigreux column to give 1.2 g. (80%) of a colorless viscous liquid, b.p. 111–123° (0.01 mm.).

*Anal.* Calcd. for $C_{18}H_{20}O$: C, 85.67; H, 7.99. Found: C, 85.89; H, 8.11.

***p*-Methoxycinnamaldehyde.**—The procedure of Scholtz[16] was followed. From 136 g. (1.0 mole) of anisaldehyde, 44 g. (1.0 mole) of acetaldehyde and 50 ml. of 10% ethanolic potassium hydroxide in 400 ml. of absolute ethanol was obtained 30.1 g. (19%) of crude yellow solid, b.p. 108–119° (0.05 mm.) [b.p. 173–176° (14 mm.)]. Recrystallization from ethanol afforded 20.7 g. (13%) of light-yellow needles, m.p. 54.2–57.2° (m.p. 58°).[16]

A 2,4-dinitrophenylhydrazone was prepared[17] and recrystallized from ethyl acetate, m.p. 263.5–265° dec.

(14) Ref. 12, p. 251.

(15) Ref. 12, p. 267.

(16) M. Scholtz and A. Wiedemann, *Ber.*, **36**, 845 (1903).

(17) R. L. Shriner, R. C. Fuson, and D. Y. Curtin, "The Systematic Identification of Organic Compounds," John Wiley and Sons, Inc., New York, N. Y., 1956, p. 111.

*Anal.* Calcd. for $C_{16}H_{14}N_4O_5$: C, 56.14; H, 4.12; N, 16.37. Found: C, 56.05; H, 3.97; N, 16.47.

**p-Methoxycinnamalacetophenone.**—As in the preceding preparation, the procedure of Scholtz[16] was employed. The reaction of 28 g. (0.17 mole) of *p*-methoxycinnamaldehyde, 20.5 g. (0.17 mole) of acetophenone and 10 ml. of 20% aqueous sodium hydroxide in 300 ml. of ethanol yielded, after recrystallization from ethanol, 24.8 g. (55%) of deep yellow needles, m.p. 115.8–116.8° (m.p. 118°).[16]

A 2,4-dinitrophenylhydrazone was prepared[17] and recrystallized from ethyl acetate, m.p. 212.5–214° dec.

*Anal.* Calcd. for $C_{24}H_{20}N_4O_5$: C, 64.86; H, 4.54; N, 12.61. Found: C, 65.50; H, 5.05; N, 12.67.

**5-(*p*-Methoxyphenyl)-1 phenyl-1-pentanone.**—A mixture of 21.8 g. (0.083 mole) of *p*-methoxycinnamalacetophenone and 2 g. of 10% palladium-on-charcoal in 200 ml. of absolute ethanol was placed in a Parr shaking apparatus and subjected to catalytic hydrogenation at a pressure of 2–3 atmospheres and room temperature for a period of 21 minutes, until the theoretical quantity of hydrogen had been absorbed. Catalyst was then removed by filtration and the colorless solution concentrated by evaporation on a steam bath. On cooling, 15.4 g. (69%) of colorless needles, m.p. 38–39.6° were crystallized.

*Anal.* Calcd. for $C_{18}H_{20}O_2$: C, 80.56; H, 7.51. Found: C, 80.74; H, 7.60.

An infrared spectrum of the solid had a strong absorption band at 1684 cm.$^{-1}$.[18]

A 2,4-dinitrophenylhydrazone[17] was prepared and recrystallized from ethanol, m.p. 135.6–137.4°.

*Anal.* Calcd. for $C_{24}H_{24}N_4O_5$: C, 64.27; H, 5.39; N, 12.49. Found: C, 63.99; H, 5.21; N, 12.68.

**5-(*p*-Methoxyphenyl)-1-phenyl-1-pentene (III).**—A solution of 13.4 g. (0.05 mole) of 5-(*p*-methoxyphenyl)-1-phenyl-1-pentanone in 50 ml. of anhydrous ether was added dropwise, with stirring and under a continuous flow of dry nitrogen, to a suspension of 0.6 g. (0.016 mole) of lithium aluminum hydride in 40 ml. of anhydrous ether, so as to maintain rapid spontaneous refluxing. On completion of the addition, the reaction was heated at reflux for 1.5 hr., then cooled in an ice-bath and hydrolyzed first with 25 ml. of water, then with 50 ml. of 10% sulfuric acid to dissolve the precipiated aluminates.

The ether layer was separated and the aqueous layer extracted with a portion of ether. The combined, still slightly acidic ether layers were dried over anhydrous magnesium sulfate, filtered and solvent was removed under vacuum. The residue was distilled at reduced pressure through a Vigreux column to give 6.9 g. (55%) of a colorless oil, b.p. 157° (0.2 mm.), $n^{25}D$ 1.5797. After standing a few days, this oil crystallized as transparent needles, m.p. 31.6–32.6° after recrystallization from ethanol. The material rapidly absorbed bromine in carbon tetrachloride without the evolution of hydrogen bromide gas and gave a negative ceric nitrate test in dioxane.

*Anal.* Calcd. for $C_{18}H_{20}O$: C, 85.67; H, 7.99. Found: C, 86.02; H, 8.24.

An infrared spectrum had the following absorption bands: 1660 cm.$^{-1}$ (w) and 970 cm.$^{-1}$ (s).[19]

In the ultraviolet region, the compound absorbed at $\lambda_{max}^{CH_3OH}$ 251 mμ, ε 24,750 and $\lambda_{max}^{CH_3OH}$ 261 mμ, ε 18,480.

**Cinnamal-*p*-methoxyacetophenone.**—Following the procedure of Scholtz,[20] from 50 g. (0.38 mole) of cinnamaldehyde, 45 g. (0.30 mole) of *p*-methoxyacetophenone and 20 ml. of 10% aqueous sodium hydroxide in 200 ml. of ethanol were obtained, after recrystallization from ethanol, 43 g. (54%) of deep yellow needles, m.p. 92.8–94.2° (m.p. 93°).[20]

A 2,4-dinitrophenylhydrazone was prepared[17] and recrystallized from ethyl acetate, m.p. 216–217.5°.

*Anal.* Calcd. for $C_{24}H_{20}N_4O_5$: C, 64.86; H, 4.54; N, 12.61. Found: C, 64.58; H, 4.52; N, 12.64.

**1-(*p*-Methoxyphenyl)-5-phenyl-1-pentanone.**—Cinnamal-*p*-methoxyacetophenone was catalytically hydrogenated in a manner similar to that employed for *p*-methoxycinnamalacetophenone. A solution of 66 g. (0.25 mole) of cinnamal-*p*-methoxyacetophenone in 300 ml. of absolute ethanol, with 1 g. of 30% palladium-on-charcoal, absorbed the theoretical amount of hydrogen after approximately 4.5 hr. A crop of 40.6 g. (75%) of transparent blocks, m.p. 41.6–42.6°, was crystallized from the resulting solution. Recrystallization afforded a sample, m.p. 42.6–43.6°.

*Anal.* Calcd. for $C_{18}H_{20}O_2$: C, 80.56; H, 7.51. Found: C, 80.76; H, 7.42.

An infrared spectrum of the solid had a strong absorption band at 1682 cm.$^{-1}$.[18]

A 2,4-dinitrophenylhydrazone was prepared[17] and recrystallized from ethanol, m.p. 142.2–143.8°.

*Anal.* Calcd. for $C_{24}H_{24}N_4O_5$: C, 64.27; H, 5.39; N, 12.49. Found: C, 64.09; H, 5.49; N, 12.64.

**1-(*p*-Methoxyphenyl)-5-phenyl-1-pentene (II).**—Following the procedure employed for the preparation of III, 26.8 g. (0.1 mole) of 1-(*p*-methoxyphenyl)-5-phenyl-1-pentanone in 100 ml. of anhydrous ether reacted with 1.1 g. (0.028 mole) of lithium aluminum hydride in 80 ml. of anhydrous ether to give 18.3 g. (73%) of a colorless oil, b.p. 135° (0.05 mm.), $n^{25}D$ 1.5833.

*Anal.* Calcd. for $C_{18}H_{20}O$: C, 85.67; H, 7.99. Found: C, 85.72; H, 8.09.

An infrared spectrum had the following bands: 1660 cm.$^{-1}$ and 968 cm.$^{-1}$.[19]

The compound absorbed in the ultraviolet region: $\lambda_{max}^{CH_3OH}$ 261 mμ, ε 29,250 and $\lambda_{max}^{CH_3OH}$, 251 mμ, ε 23,380.

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(18) L. J. Bellamy, "The Infra-Red Spectra of Complex Molecules," John Wiley and Sons, Inc., New York, N. Y., 1958, p. 137.

(19) Ref. 18, p. 45.

(20) M. Scholtz, *Ber.*, **28**, 1730 (1895).