in the crystallization of 16 g. (71.5%) of 1-*p*-toluyl-2-benzylhydrazine (XI), m.p. 127°.

Anal. Calcd. for $C_{15}H_{16}N_2O$: C, 74.97; H, 6.71; N, 11.66. Found: C, 75.04; H, 6.66; N, 11.92.

N-Acetyl-p-tolualdehyde hydrazone. To 14.8 g. (0.2 mole) of acetic acid hydrazide in ethanol was added 24 g. of *p*-tolualdehyde and the mixture was warmed on a steam bath for 1 hr. On cooling 16 g. of *N*-acetyl-*p*-tolualdehyde hydrazone, m.p. 132°, crystallized.

Anal. Calcd. for $C_{10}H_{12}N_2O$: C, 68.16; H, 6.86; N, 15.90. Found: C, 68.21; H, 7.06; N, 16.09.

1-Acetyl-2-(α-p-xylyl)hydrazine. To 17.6 g. (0.10 mole) of *N*-acetyl-*p*-tolualdehyde hydrazone in ethanol was added 0.05 g. of 10% palladium-on-charcoal catalyst. The mixture was allowed to take up one molar equivalent of hydrogen on a Paar apparatus. After removal of the catalyst by filtration the solution was cooled and 12.8 g. (72%) of 1-acetyl-2-(α-*p*-xylyl)hydrazine, m.p. 120° was obtained.

Anal. Calcd. for $C_{10}H_{18}N_2O$: C, 67.39; H, 7.92; N, 15.72. Found: C, 67.52; H, 8.03; N, 15.90.

Benzaldehyde α-p-xylylhydrazone. To 26.7 g. (0.15 mole) of 1-acetyl-2-(α-*p*-xylyl)hydrazine in aqueous ethanol was added 50 g. of potassium hydroxide and the mixture refluxed for 18 hr. The mixture was then cooled and extracted with ether and the ether phase separated and dried over anhydrous sodium sulfate. After filtration the ether was removed on a steam bath to leave 11 g. (54%) of crude hydrazine. This was placed in 50 ml. of 50% ethanol and 11 g. (0.092 mole) of benzaldehyde was added. A total of 12 g. of crystalline benzaldehyde α-*p*-xylylhydrazone was obtained. A recrystallization of this material from ethanol resulted in a solid, m.p. 85–86°. The benzoyl derivative was prepared because of the known instability of benzyl hydrazones.

To a solution of 3.5 g. (0.025 mole) of benzoyl chloride in pyridine was added 4.4 g. (0.02 mole) of benzaldehyde α-*p*-xylylhydrazone and the resulting mixture was stirred for 30 min. The mixture was poured into water and extracted with ether. The ether phase was washed with dilute hydrochloric acid and several aqueous bicarbonate rinses. The ether solution was dried over anhydrous sodium sulfate. After filtration the solution was vacuum concentrated and the residue recrystallized from ethanol to yield 5.4 g. (81%) of *N*-benzoylbenzaldehyde α-*p*-xylylhydrazone, m.p. 92–93°.

Anal. Calcd. for $C_{22}H_{20}N_2O$: C, 79.92; H, 6.71; N, 8.48. Found: C, 79.94; H, 6.57; N, 8.25.

The peracetic acid oxidation of benzaldehyde α-p-xylylhydrazone. To 11.2 g. (0.05 mole) of benzaldehyde α-*p*-xylylhydrazone in ether was slowly added with stirring at 0°, 10 g. of a 40% peracetic acid solution in ether. After the addition was complete the solution was stirred for 3 hr. and then allowed to warm to room temperature. The solution was washed twice with water and sufficient times with sodium bicarbonate to remove all acid. The ether solution was dried over sodium sulfate, filtered, and then concentrated to half volume. A total of 2.8 g. (23%) of α-(benzyl-*NNO*-azoxy)-*p*-xylene (X), m.p. 210–211° was isolated.

Anal. Calcd. for $C_{15}H_{16}N_2O$: C, 74.97; H, 6.71; N, 11.66. Found: C, 74.86; H, 6.60; N, 11.69.

The mother liquor from above was cooled and yielded 6.0 g. (50%) of 1-*p*-toluyl-2-benzylhydrazine (XI), m.p. 127°. A mixed melting point of this material with an authentic sample of XI showed no depression.

Acknowledgment. The authors wish to acknowledge funds toward the purchase of a Perkin-Elmer Infracord I. R. spectrophotometer used in this work from the National Science Foundation. They also thank Becco Chemical Division, Buffalo, N. Y., for generous supplies of 40% peracetic acid.

PITTSBURGH 19, PA.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, POLYTECHNIC INSTITUTE OF BROOKLYN]

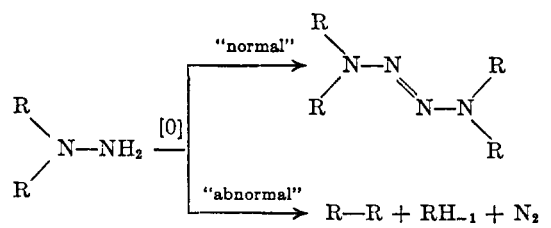
Azo Compounds. XXXVIII. The Mercuric Oxide Oxidation of 1-Amino-2-phenylpiperidine[1]

C. G. OVERBERGER AND LOUIS P. HERIN[2]

Received June 29, 1961

1-Amino-2-phenylpiperidine was synthesized and treated with yellow mercuric oxide to give, depending on the experimental procedure, partial evolution of nitrogen and varying yields of phenylcyclopentane, 1-phenylpentene-1,5-phenylpentene-1, and a tetrazene. These experimental data provide further evidence for the previously proposed mechanism of the reaction.

The so-called "abnormal" oxidation reaction of certain 1,1-disubstituted hydrazines proceeds to give evolution of nitrogen with the formation of coupled, and in some cases also olefinic, hydrocarbon products rather than the "normal" oxidation product, tetrazene.



In earlier papers[4] we have reported the preparation and oxidation of a number of such hydrazines: 1-amino-2,6-dicyano-2,6-dimethylpiperidine; *cis*- and *trans*-1-amino-2,6-diphenylpiperidine; 1-amino-2,6-dicyano-2,4,6-trimethylpiperidine; and *D,D-N*-amino-α,α′-dimethyldibenzylamine. Hinman and

(1) This is the thirty-seventh 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 J. R. Hall, *J. Org. Chem.*, 26, 4359 (1961).

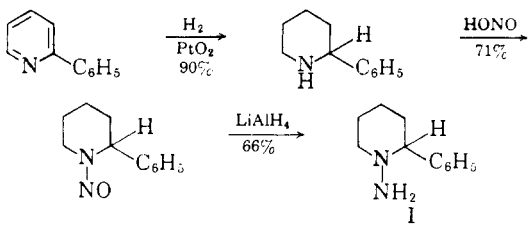
(2) This paper comprises a portion of the Dissertation submitted by Louis P. Herin in partial fulfillment of the requirements for the degree of Doctor of Philosophy at the Polytechnic Institute of Brooklyn.

Hamm[5] have described the oxidation of several unsymmetrical 1,1-dibenzylhydrazines. However, until quite recently,[6] only those 1,1-disubstituted hydrazines which have at both α-carbon atoms substituents such as nitrile or aryl were known to undergo nitrogen elimination on oxidation. It has been suggested[4b] that such groups, by resonance interaction in the transition state, decrease the activation energy for nitrogen-carbon bond cleavage, so that nitrogen elimination is favored rather than tetrazene formation.

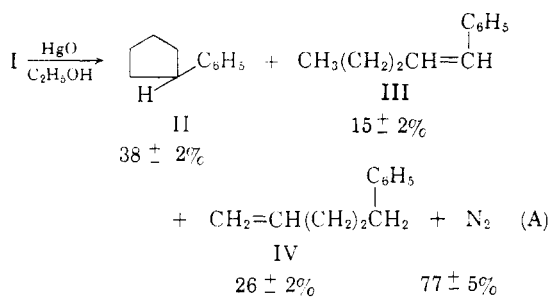
We have now prepared and oxidized a cyclic 1,1-disubstituted hydrazine having such a substituent at only one α-carbon atom and have carried out a complete product analysis.

RESULTS AND DISCUSSION

1-Amino-2-phenylpiperidine (I) was prepared by the following sequence of reactions.



Oxidation of I with yellow mercuric oxide in ethanol at 60–65° gave varying results. Dropwise addition (A) of a solution of the hydrazine to a slurry of mercuric oxide gave a large but less than the theoretical evolution of nitrogen and a 79% yield of a hydrocarbon mixture consisting of phenylcyclopentane (II), 1-phenylpentene-1 (III), and 5-phenylpentene-1 (IV).

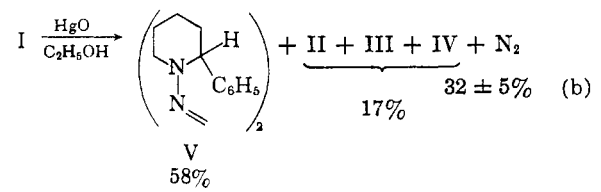


The hydrocarbon mixture was separated from the crude reaction product by distillation and there remained a residue of higher boiling material (17%) which was not identified. A sample of hydrocarbon product mixture gave the correct analysis for the empirical formula $C_{11}H_{14}$. The total olefin content (51 ± 2%) of the mixture was determined by semimicro quantitative hydrogenation and the percentage (19%) of conjugated olefin by a quantitative comparison of the ultraviolet spectra. The presence of terminal olefin was indicated by a strong absorption band at 910 cm.$^{-1}$ in the infrared region.

The identity of the olefin components was confirmed by ozonization of samples of the mixture and reduction of the ozonides with metallic zinc and water to give four aldehydes: benzaldehyde, butyraldehyde, formaldehyde, and 4-phenylbutyraldehyde. These were isolated and identified as the respective 2,4-dinitrophenylhydrazones. The infrared spectrum of an authentic mixture of five parts of II, two parts of III, and three parts of IV was found to be identical to that for a sample of the hydrocarbon product mixture except for very minor differences in absorption intensities. The index of refraction for the known mixture (n_D^{25} 1.5196) agreed closely with that for the product mixture (n_D^{25} 1.5189).

Compounds II, III, and IV were prepared independently. (See Experimental.)

On the other hand, rapid addition of a solution of I to a slurry of mercuric oxide or rapid addition of the solid oxidant to a solution of the hydrazine gave the tetrazene, V, as a major product (B). Nitrogen evolution was considerably diminished, with correspondingly low yields of the $C_{11}H_{14}$ hydrocarbon mixture. The equation below describes a typical example:



V was isolated by crystallization from the ethanolic reaction mixture. Analysis of a sample agreed with the empirical formula $C_{11}H_{14}N_2$ and an ebullioscopic molecular weight determination in carbon tetrachloride gave a value consistent with the molecular formula $C_{22}H_{28}N_4$. In the ultraviolet region, a cyclohexane solution of V absorbed at λ_{max} 284 mμ, ϵ 9640 and λ_{max} 264 mμ, ϵ 9060. A low yield of the hydrocarbon mixture of II, III, and IV was isolated by distillation from the residue remaining after crystallization of V and, again, there remained higher boiling material (15%) which was not identified.

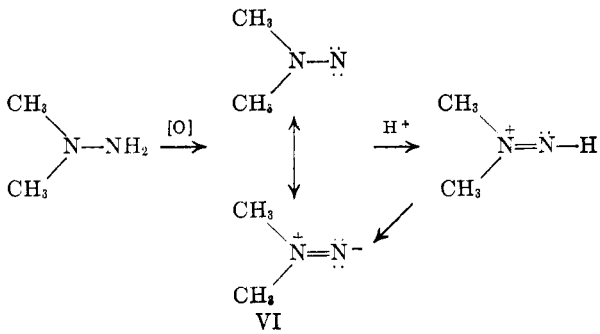
(4) (a) C. G. Overberger *et al.*, *J. Am. Chem. Soc.*, **74**, 3290 (1952); **75**, 2082 (1953); **77**, 4097 (1955); **77**, 4100 (1955); **77**, 4104 (1955). (b) C. G. Overberger, J. G. Lombardino, and R. G. Hiskey, *J. Am. Chem. Soc.*, **79**, 6430 (1957). (c) C. G. Overberger, G. Kesslin, and P. Huang, *J. Am. Chem. Soc.*, **81**, 3779 (1959). (d) C. G. Overberger, N. P. Marullo, and R. G. Hiskey, *J. Am. Chem. Soc.*, **83**, 1374 (1961).

(5) R. L. Hinman and K. L. Hamm, *J. Am. Chem. Soc.*, **81**, 3294 (1959).

(6) While the work described in this paper was being completed, Carpino reported the mercuric oxide decomposition of two 1,1-disubstituted hydrazines having an activating substituent at only one α-carbon atom. Oxidation of 1-*t*-butyl-1-benzylhydrazine gave a 24% yield of 1-phenyl-2,2-dimethylpropane accompanied by 47% of crude dibenzylmercury and oxidation of 1-*n*-butyl-1-benzylhydrazine gave 20% of *n*-amylbenzene. L. A. Carpino, A. A. Santilli, and R. W. Murray, *J. Am. Chem. Soc.*, **82**, 2728 (1960).

1-Nitroso-2-phenylpiperidine did not give "abnormal" reduction on treatment with sodium hydrosulfite.[7] No gas evolution was observed in a 33% yield of I was obtained as the hydrochloride. This would imply that this latter elimination process needs more driving force than the mercuric oxide oxidation.

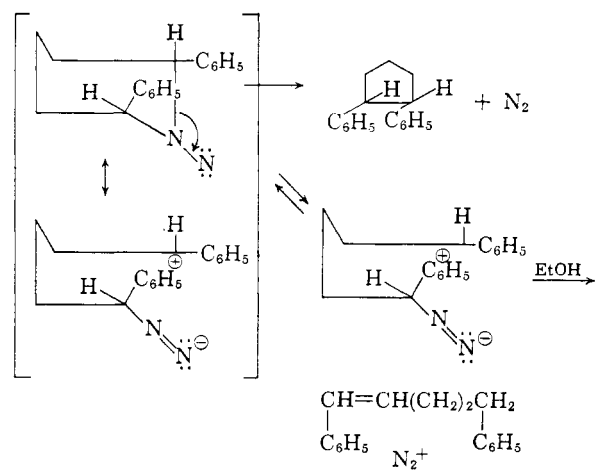
Several authors[4a,8,9] have proposed a diazo-like species having an electron deficient nitrogen atom as an intermediate in the oxidation of 1,1-disubstituted hydrazines. There is no direct experimental evidence to support the existence of such an intermediate except the spectral data obtained by McBride and Kruse,[9] which indicates the presence of the conjugate acid of VI in strong acid solution.



VI

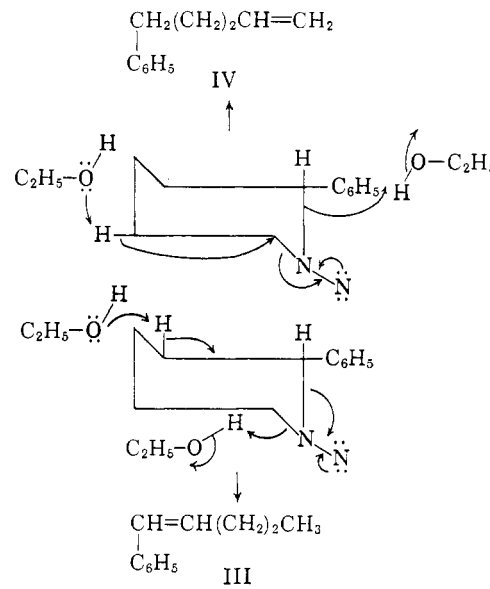
This species has also been postulated as an intermediate in other related reactions, which include the "abnormal" reduction[7] of certain nitrosamines by sodium hydrosulfite and the reaction of certain 1,1-disubstituted sulfonhydrazides[10] with base, both to eliminate nitrogen and give hydrocarbon products.

In a previous paper[4b] where we reported the stereospecific oxidation of *cis*- and *trans*-1-amino-2,6-diphenylpiperidine to give mostly *cis*- and *trans*-1,2-diphenylcyclopentane, respectively, accompanied by smaller amounts of 1,5-diphenylpentene-1, the following mechanism was proposed to account for the observed products. The retention of configuration in the coupled product was explained by suggesting a concerted shift of bonds on collapse of the intermediate and the formation of olefin, by an E_1 process.



The results obtained in the oxidation of 1-amino-2-phenylpiperidine have shown that nitrogen elimination *can* occur on oxidation of a 1,1-disubstituted hydrazine having an activating substituent at only one α-carbon atom and have raised some question about the mechanism previously suggested for olefin formation.

One would expect ionization (E_1) to occur largely at the carbon atom bearing the α-phenyl substituent, the benzyl carbonium ion forming much more readily, and the consequent production of only conjugated olefin. However, the occurrence of almost twice as much unconjugated as conjugated olefin mitigates against a simple E_1 process. We now suggest that olefin is formed probably by a combination of both an E_1 and E_2 process.



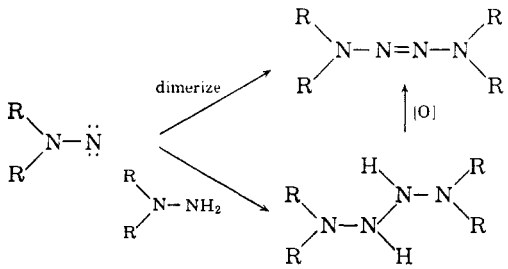
III

Attack by a solvent molecule on the equatorial hydrogen atom at C-5 should be more favored than attack on the equatorial hydrogen atom at C-3 because of steric interaction by the large equatorial phenyl group at C-2. Contribution from an E_1 process, if any, to the olefin forming part of the reaction may be of secondary importance. We have recently proposed[4c] an E_2 mechanism for the abnormal oxidation of 1-amino-2,6-dicyano-2,6-dimethylpiperidine with bromine.

The occurrence of tetrazene as the major product when the hydrazine concentration is high as compared to nitrogen elimination when the hydrazine concentration is low during the course of oxidation supports the role of the diazo-like intermediate in the formation of tetrazene. These results indicate

(7) C. G. Overberger, J. G. Lombardino, and R. G. Hiskey, *J. Am. Chem. Soc.*, **80**, 3009 (1958).
(8) J. Kenner and E. C. Knight, *Ber.*, **69**, 341 (1936).
(9) W. R. McBride and H. W. Kruse, *J. Am. Chem. Soc.*, **79**, 572 (1957).
(10) L. A. Carpino, *J. Am. Chem. Soc.*, **79**, 4427 (1957).

that tetrazene might be formed either by dimerization of the intermediate or by its reaction with a molecule of hydrazine to give a tetrazane which is subsequently oxidized to tetrazene.



As nitrogen elimination is quantitative when an activating group is present at both α-carbon atoms, as in the case of 1-amino-2,6-diphenylpiperidine, even if oxidation is carried out at a high concentration of hydrazine, the activation energy for nitrogen-carbon bond cleavage should be considerably lower than for tetrazene formation. However when such a substituent is present at only one α-carbon atom, as in the case of 1-amino-2-phenylpiperidine, the activation energy for nitrogen-carbon bond cleavage is probably increased so that the two reaction paths, tetrazene formation and nitrogen elimination, become competitive.

EXPERIMENTAL[11]

2-Phenylpiperidine. A mixture of 79.7 g. (0.51 mole) of 2-phenylpyridine,[12,13] 44 ml. of concd. hydrochloric acid dissolved in 300 ml. of 95% ethanol, and 5 g. of platinum dioxide was placed in a Parr shaking apparatus and subjected to catalytic hydrogenation at a pressure of 2 to 3 atm. and room temperature for 44 hr., until the theoretical quantity of hydrogen was absorbed. After removal of the catalyst by filtration, the solution was evaporated to dryness under vacuum. The solid residue of crude 2-phenylpiperidine hydrochloride was treated with 200 ml. of 10% aqueous sodium hydroxide and the free base extracted with ether in several portions. The ether extracts were combined, dried over anhydrous magnesium sulfate, filtered, and solvent was removed under vacuum. Distillation of the residue at reduced pressure through a Widmer column gave 73.3 g. (89.5%) of a colorless oil, b.p. 52° (0.2 mm.), n_D^{25} 1.5350 (b.p. 240°, yield 81%).[14]

Anal. Calcd. for $C_{11}H_{15}N$: C, 81.93; H, 9.37; N, 8.69. Found: C, 82.08; H, 9.47; N, 8.94.

The infrared spectrum of the liquid had a weak absorption band at 3300 cm.$^{-1}$, characteristic of a secondary amine.

Recrystallization of a sample of the hydrochloric acid salt from ethanol-ether gave white needles, m.p. 196.6–198.2° (m.p. 196–197°).[15]

On exposure to moisture, the free base formed a solid hydrate, m.p. 61–62° (m.p. 60–61°).[15]

1-Nitroso-2-phenylpiperidine. 2-Phenylpiperidine was nitrosated essentially by the general procedure of Hatt[16] for the preparation of nitrosamines. From a solution of 73.3 g. (0.46 mole) of 2-phenylpiperidine in 240 ml. of 2*N* hydrochloric acid and 90 ml. of ethanol and a solution of 42 g. (0.6 mole) of sodium nitrite in 180 ml. of water, there was obtained an amber colored oil. This was dissolved in petroleum ether (b.p. 30–60°) and a solid crystallized with much difficulty, careful seeding and cooling being required to prevent "oiling-out." A further recrystallization from petroleum ether (b.p. 30–60°) gave 61.7 g. (71%) of light yellow, transparent blocks, m.p. 46.5–48°.

The solid gave a positive Liebermann nitroso test[17] and an infrared spectrum indicated the presence of the *N*-nitroso group by strong absorption bands at 1420, 1350, and 1290 cm.$^{-1}$[18]

Anal. Calcd. for $C_{11}H_{14}N_2O$: C, 69.47; H, 7.42; N, 14.73. Found: C, 69.71; H, 7.55; N, 14.70.

1-Amino-2-phenylpiperidine (I). From 38 g. (0.2 mole) of 1-nitroso-2-phenylpiperidine and 16 g. (0.4 mole) of lithium aluminum hydride in 750 ml. of anhydrous ether, under a continuous flow of dry nitrogen there was obtained, after the usual work-up a dry ether solution. This was then treated with anhydrous hydrogen chloride, while cooling in an ice bath, until the formation of precipitate ceased. The precipitate was filtered and recrystallized from ethanol-water giving 32 g. (75%) of white solid, m.p. 203–204.5°.

Anal. Calcd. for $C_{11}H_{17}N_2Cl$: C, 62.10; H, 8.06; N, 13.17; neut. equiv., 212.5. Found: C, 62.28; H, 8.18; N, 13.09; neut. equiv., 211.

A solution of 202.2 g. (0.95 mole) of 1-amino-2-phenylpiperidine hydrochloride in 200 ml. of water was treated with 40 g. (1.0 mole) of sodium hydroxide and, when cooled, extracted with ether in several portions. The combined extracts were dried over anhydrous magnesium sulfate, filtered, and the solvent was removed under vacuum. Distillation of the oily residue at reduced pressure through a Vigreux column gave 164.4 g. (88%) of a colorless solid, b.p. 76–77° (0.4 mm.), m.p. 51–53°. The product was stored under nitrogen and in the refrigerator freezer compartment.

Anal. Calcd. for $C_{11}H_{16}N_2$: C, 74.95; H, 9.15; N, 15.90. Found: C, 75.22; H, 9.17; N, 16.05.

N-(p-Chlorobenzal)-1-amino-2-phenylpiperidine. To a solution of 1 g. (0.0047 mole) of 1-amino-2-phenylpiperdine hydrochloride in 50 ml. of absolute ethanol were added 1 g. (0.0071 mole) of *p*-chlorobenzaldehyde and 0.5 g. of potassium acetate. The mixture was heated on a steam bath for 0.25 hr., allowed to cool and diluted with water. An oil separated which crystallized on standing overnight to give 1 g. (71%) of crude solid, m.p. 73–77°. After two recrystallizations from ethanol, pale yellow needles were obtained, m.p. 76.6–78.4°, $\lambda_{max}^{cyclohexane}$ 303 mμ, ϵ 23,400. An infrared spectrum exhibited weak absorbance at 1550 cm.$^{-1}$, which may, with some uncertainty, be assigned to C=N stretching.[19]

Anal. Calcd. for $C_{18}H_{19}N_2Cl$: C, 72.35; H, 6.41; N, 9.38. Found: C, 72.16; H, 6.54; N, 9.12.

Mercuric oxide decomposition of I. *Procedure A.* A stirred suspension of 133 g. (0.61 mole) of yellow mercuric oxide in 300 ml. of absolute ethanol, in a system equipped for gas collection, was heated under a continuous flow of nitrogen to 63° in an oil bath. Nitrogen flow was then stopped and the system closed. When the system had come to equilibrium, a solution of 53.9 g. (0.31 mole) of I in 200 ml. of absolute ethanol was added dropwise from a side-arm addition funnel

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

(12) J. C. Evans and C. F. H. Allen, *Org. Syntheses*, Coll. Vol. II, 517 (1943).

(13) K. Ziegler and H. Zeiser, *Ber.*, 63, 1847 (1930).

(14) J. Overhoff and J. P. Wibaut, *Rec. trav. chim.*, 50, 957 (1931).

(15) S. Gabriel, *Ber.*, 41, 2010 (1908).

(16) H. H. Hatt, *Org. Syntheses*, Coll. Vol. II, 211 (1943).

(17) A. I. Vogel, *A Textbook of Practical Organic Chemistry*, Longmans, Green and Co., London, 1951, p. 621.

(18) L. J. Bellamy, *The Infrared Spectra of Complex Molecules*, Wiley, New York, 1958, p. 306.

(19) L. J. Bellamy, *The Infrared Spectra of Complex Molecules*, J. Wiley and Sons, New York, 1958, p. 267.

over a period of 0.5 hr. Immediate gas evolution was observed. Upon completion of addition of the hydrazine solution, stirring and heating were continued for 0.5 hr., until no further gas was evolved. A volume of 5470 ml. of nitrogen (77 ±5%) was collected over water at 17° and 755 mm.

The cooled reaction mixture was filtered through "Celite" to ensure retention of finely divided mercury particles. The filtrate was fractionally distilled at atmospheric pressure through a helices-packed column to remove all ethanol. The oily residue was then distilled at reduced pressure through a Vigreux column giving 35.1 g. (79%) of a mixture of hydrocarbons, b.p. 85–110° (11 mm.), n_D^{25} 1.5189 and 9 g. (17%) of higher boiling residue which was not distilled.

A sample of the hydrocarbon mixture had a correct analysis for $C_{11}H_{14}$.

Anal. Calcd. for $C_{11}H_{14}$: C, 90.35; H, 9.78. Found: C, 90.19; H, 9.78

A suspension of 50 mg. of platinum dioxide in 20 ml. of absolute ethanol was prereduced in a semimicro atmospheric pressure catalytic hydrogenation apparatus. A solution of 0.416 g. (0.00285 mole) of the $C_{11}H_{14}$ hydrocarbon mixture was then introduced and the reaction stirred at room temperature. The volume of hydrogen absorbed, after uptake had ceased, was 35.5 ml. at 24.5° which corresponds to 51% of the theoretical amount for one double bond per mole.

A solution of 0.00220 mg./ml. (0.000150 mole/l.) of the hydrocarbon product mixture was prepared in spectro-grade cyclohexane. The ultraviolet spectrum[20] had a λ_{max} 250 mμ and was identical to that for the known sample (III) except that the absorbance, D = 0.482 was 19% of the value calculated for a 0.000150 molar solution of pure III in cyclohexane.

The infrared spectrum of the $C_{11}H_{14}$ hydrocarbon mixture had the following absorption bands: 1640 cm.$^{-1}$ (m); 990 cm.$^{-1}$, (m); 964 cm.$^{-1}$ (s); and 910 cm.$^{-1}$ (s). The infrared spectrum of an authentic hydrocarbon mixture prepared from five parts of II, two parts of III and three parts of IV was identical in every absorption band with that for the product mixture except for very small differences in absorption intensities.

Two fractions of the $C_{11}H_{14}$ hydrocarbon product mixture, one containing 9% of III and 66% of IV and the other 30% of III and 0% of IV (as determined by quantitative catalytic hydrogenation and comparison of ultraviolet spectra), were ozonized[21] as follows. Oxygen gas containing 3–5% ozone by volume was bubbled through a solution of approximately 1 g. of sample in 50 ml. of absolute ethanol, maintained at −70° by means of a Dry Ice–acetone bath. The exhaust gas was passed through a solution of 5% potassium iodide in 50% acetic acid, which, on turning reddish brown, indicated no further absorption of ozone by the hydrocarbon. The solution of ozonides was then added to a suspension of 2 g. of powdered zinc in 100 ml. of water, the mixture stirred for 0.5 hr. and filtered. The filtrate was treated in either of two ways: (a) 2,4-dinitrophenylhydrazine reagent[22] was added directly until precipitation was complete; then the 2,4-dinitrophenylhydrazones were filtered, dried and separated by alumina chromatography;[23] or (b) the filtrate was steam distilled and successive distillate fractions treated with 2,4-dinitrophenylhydrazine reagent and the precipitated 2,4-dinitrophenylhydrazones recrystallized from ethanol. Table I lists the 2,4-dinitrophenylhydrazones isolated and identified. The 2,4-dinitrophenylhydrazone of 4-phenylbutyraldehyde is not known and an authentic sample was not prepared; however the 2,4-dinitrophenylhydrazone isolated had an analysis corresponding to that of 4-phenylbutyraldehyde.

TABLE I

Aldehyde	M.P. of 2,4-Dinitrophenylhydrazone Isolated	M.P. of Authentic 2,4-Dinitrophenylhydrazone	Mixture M.P.
Formaldehyde	159.0–160.6	162.2–163.2[a]	161.0–162.8
Butyraldehyde	107.0–108.4	107.0–108.4[b]	105.6–107.8
Benzaldehyde	234.5–235.0	234.0–235.0[c]	234.0–235.0
4-Phenylbutyraldehyde	110.5–112.0	—	—

[a] M.p. 166° [N. R. Campbell, *Analyst*, 61, 392 (1936)]. [b] M.p. 122° [O. L. Brady and G. V. Elsmie, *Analyst*, 51, 78 (1926)]. [c] M.p. 234° [J. Meisenheimer and W. Schmidt, *Ann.*, 475, 182 (1929)].

Anal. Calcd. for $C_{16}H_{16}N_4O_4$: C, 58.53; H, 4.91; N, 17.07. Found: C, 58.55; H, 4.95; N, 17.23.

Procedure B. In a manner similar to the above, a solution of 44.1 g. (0.25 mole) of 1-amino-2-phenylpiperidine in 150 ml. of absolute ethanol was added at once to a slurry of 100 g. (0.46 mole) of yellow mercuric oxide in 400 ml. of absolute ethanol. The reaction temperature was maintained at 65°. Immediate gas evolution was observed. A volume of 1850 ml. of nitrogen (32 ± 5%) was collected over water at 20° and heating and stirring were continued for 0.5 hr. after gas evolution had ceased.

The hot reaction mixture was filtered through "Celite" and the filter-cake washed with several portions of hot ethanol. The combined filtrates were concentrated by evaporation under vacuum and on cooling yielded 25.3 g. (58%) of white crystals melting and decomposing with gas evolution at 130–140°. Recrystallization afforded a sample of the tetrazene, m.p. 135–141° dec.

Anal. Calcd. for $C_{22}H_{28}N_4$: C, 75.82; H, 8.10; N, 16.08; mol. wt., 348. Found: C, 75.68; H, 7.84; N, 16.43; mol. wt., 310 (ebullioscopic in carbon tetrachloride.)

The ultraviolet spectrum of a sample dissolved in spectrograde cyclohexane exhibited two absorption maxima, λ_{max} 284 mμ, ε 9640 and λ_{max} 264 mμ, ε 9060.

The mother liquor from the above was evaporated under vacuum to remove all solvent and the residue was distilled through a Vigreux column at reduced pressure to give 6.1 g. (17%) of a liquid, b.p. 30–40° (0.05 mm.). There remained approximately 6 g. (14%) of higher boiling residue which was not distilled.

An infrared spectrum of the distillate was identical to that for the $C_{11}H_{14}$ hydrocarbon product mixture obtained in Procedure A except for some differences in the relative intensities of absorption.

Phenylcyclopentane (II). The general method of Cagniant[24] for the preparation of arylcyclopentanes was employed. From 100 g. (1.5 moles) of cyclopentene, 470 ml. of benzene, and 14 g. of aluminum chloride was obtained 93.8 g. (43%) of phenylcyclopentane, b.p. 38° (0.05 mm.), n_D^{25} 1.5256 (lit. b.p. 116–117° (37 mm.), n_D^{20} 1.5309).[25]

1-Phenylpentene-1 (III). A solution of *n*-butylmagnesium bromide was prepared in the usual manner by treating 68.5 g. (0.5 mole) of *n*-butyl bromide and 12.2 g. (0.5-g.-atom) of magnesium turnings in 400 ml. of ether. To this was then added 64 g. (0.6 mole) of benzaldehyde in 100 ml. of ether.

(20) A Beckman Model DU spectrophotometer was employed in the determination of all ultraviolet spectra.

(21) The ozonization apparatus employed in these experiments was similar to that described by A. L. Henne and W. L. Perilstein, *J. Am. Chem. Soc.*, 65, 2183 (1943).

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Upon completion of the addition the reaction was heated at reflux for 0.5 hr., cooled and hydrolyzed first with 100 ml. of water, then with 300 ml. of 6*N* sulfuric acid. The organic layer was separated, dried over anhydrous magnesium sulfate, filtered, and the solvent was removed under vacuum. The residue was refluxed with 1 g. of *p*-toluenesulfonic acid at reduced pressure for 2 hr., cooled, redissolved in 200 ml. of ether, and the solution washed first with several 100-ml. portions of 10% aqueous sodium hydroxide, then with several 100-ml. portions of water. After drying the organic layer over anhydrous calcium chloride and removal of the solvent under vacuum, the residue was distilled at reduced pressure to give 39.7 g. (52%) of a colorless liquid, b.p. 84° (7 mm.), n_D^{25} 1.5310 (lit. b.p. 99–100° (15 mm.), n_D^{20} 1.5300, prepared by dehydration of the alcohol over alumina).[26]

A sample of the liquid rapidly absorbed bromine in carbon tetrachloride without evolution of hydrogen bromide gas.

The following absorption bands were observed in the infrared region: 1660 cm.$^{-1}$ (w) and 964 cm.$^{-1}$ (s) which are characteristic of internal olefin. The compound absorbed in the ultraviolet region: $\lambda_{max}^{cyclohexane}$ 250 mμ, ε 16,900.

5-Phenylpentene-1 (IV). The procedure of von Braun[27] was followed. From 5.0 g. (0.2 g.-atom) of magnesium turnings, 40.0 g. (0.22 mole) of β-bromoethylbenzene in 200 ml. of ether and 24.2 g. (0.2 mole) of redistilled allyl bromide was obtained 15.7 g. (53%) of 5-phenylpentene-1, b.p. 70° (6 mm.), n_D^{25} 1.5021 (lit. b.p. 77–78° (10 mm.), n_D^{20} 1.5065).[27]

A sample of the liquid rapidly absorbed bromine in carbon tetrachloride without the evolution of hydrogen bromide gas.

In the infrared region the compound exhibited absorbance which is characteristic of a vinyl olefin: 1645 cm.$^{-1}$ (m), 912 cm.$^{-1}$ (s) and 992 cm.$^{-1}$ (m).

Reduction of 1-nitroso-2-phenylpiperidine with sodium hydrosulfite. In a system equipped for the collection of any evolved gases, a stirred solution of 68.5 g. (0.36 mole) of 1-nitroso-2-phenylpiperidine in 1800 ml. of ethanol and 1500 ml. of 20% aqueous sodium hydroxide was heated under a continuous flow of nitrogen at 60° in an oil bath. In a solids-addition funnel was placed 188 g. (1.1 moles) of powdered sodium hydrosulfite, and the system was closed and allowed to come to equilibrium. The solid sodium hydrosulfite was then added uniformly over a 0.5-hr. period and the reaction stirred at 60° for 10 hr. No gas evolution was observed.

The cooled reaction mixture, containing suspended solid, was extracted with ether in several portions. The combined extracts were dried over anhydrous magnesium sulfate, filtered, and solvent was removed under vacuum. The residue was redissolved in anhydrous ether and treated with hydrogen chloride gas. The resulting voluminous, white precipitate was filtered and recrystallized twice from ethanol giving 25.0 g. (33%) of white solid, m.p. 203–204.5°. A mixture melting point of this material and 1-amino-2-phenylpiperidine hydrochloride obtained by the lithium aluminum hydride reduction of 1-nitroso-2-phenylpiperidine was not depressed.

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Free Radical Chlorination of Cyclobutanecarboxylic Acids

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Cyclobutanecarboxylic acid, 1,1-cyclobutanedicarboxylic acid, and their respective acid chlorides have been chlorinated with sulfuryl chloride in the presence of benzoyl peroxide. Predominantly *trans* chlorination results with major attack at the 3-position. No product was isolated indicating attack at the tertiary hydrogen present in the monoacid and its acid chloride. A chromatographic technique has been developed which separates the five geometric isomers of monochlorocyclobutanecarboxylic acid.

Most data suggest that free radical chlorination of alipahtic compounds attacks C—H bonds in the order primary < secondary < tertiary.[5] Sulfuryl chloride has shown particular selectivity for tertiary hydrogens in aliphatic systems.[6] However, Brown and Ash[7,8] have shown that with substituted aliphatic chains two factors were most important in the liquid phase free radical chlorination: the inductive effect of a substituent and the stability of the organic free radical intermediate. Moreover, they have shown the action of such inductive groups to be additive. In an attempt to extend these generalizations to alicyclic systems we have investigated the free radical chlorination of cyclobutanecar-

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