3.3 (s, 3 H). These data suggest the structure of the substance to be α-methoxythioanisole. The ir spectrum of the third peak gave major bands at 3050, 1745, 1580, 1480, 1360, 1310, 1210, 1010, 980, 820, and 740 cm^{-1}; nmr: δ 7.2 (aromatic complex), 5.3 (s, CH_2), and 2.0 (s, CH_3). These data suggest the structure to be α-acetoxythioanisole. The relative areas of the peaks on the vpc were 12.1:1.0:1.6.

General Procedure for Treatment of Sulfoxides with Acetic Anhydride. To a solution of the sulfoxide in benzene was added 1 equiv of acetic anhydride. After refluxing *ca.* 4 hr, the solvent and acetic acid were distilled off at atmospheric pressure. The α-acyloxy sulfide was purified by distillation or vapor phase chromatography. In each case the vpc of the crude product showed only one peak (see Table I).

General Procedure for Treatment of Dimethylmethoxysulfonium Fluoroborate with Sodium Carboxylates. The alkoxysulfonium salt was added to a saturated solution of the sodium carboxylate in DMSO. After stirring for about 1 hr, a liberal amount of water was added followed by extraction of the resulting mixture with pentane. Evaporation of the pentane gave the crude product which was purified by distillation or recrystallization (see Table II).

Treatment of Isopropylmethylmethoxysulfonium Fluoroborate with Sodium Acetate in DMSO. The same procedure as that for dimethylmethoxysulfonium fluoroborate was employed. Vapor phase chromatography (silicone gum rubber, 0.25 in. × 6 ft, 100°) indicated four compounds were present. The first had the same retention time as isopropyl methyl sulfide. The second was not identified. The third was collected and its mass spectrum was determined. The molecular ion was found to be *m/e* 120 (calcd for $C_5H_{12}OS$: 120). Other major peaks were 28, 39, 41, 43, 45, 78, and 88; ir (selected bands): 3050, 1475, 1380, 1360, 1300, 1250, 1200, 1175, 1090, 940, and 900 cm^{-1}. These data are consistent with methoxymethyl isopropyl sulfide. The fourth peak was also collected and found to be acetoxymethyl isopropyl sulfide; ir (selected bands): 3000, 1735, 1480, 1420, 1360, 1310, 1220, 1170, 1025, 970, 135, and 810 cm^{-1}; nrm: see Table I. The relative areas of the peaks in the chromatogram (in order of elution) were 1.0:1.0:3.5:12.0.

When this salt was treated with sodium methoxide in methyl alcohol, only isopropyl methyl sulfide was formed as evidenced by vpc analysis under the same conditions as stated above.

The Synthesis of *cis*- and *trans*-N-Amino- and N-Nitroso-2,5-diphenylpyrrolidines. Their Abnormal Oxidation and Reduction with Mercuric Oxide and Sodium Hydrosulfite[1]

C. G. Overberger,[2] M. Valentine, and J.-P. Anselme

Contribution from the Department of Chemistry,
Polytechnic Institute of Brooklyn, Brooklyn, New York 11201.
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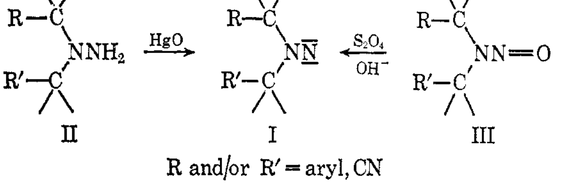
Abstract: The synthesis of *cis*- and *trans*-2,5-diphenylpyrrolidines as well as that of their N-nitroso and N-amino derivatives is reported. The assignment of the structures of each isomer pair is also described. The "abnormal" oxidation of the hydrazines and the "abnormal" reduction of the N-nitrosamines give 1,2-diphenylcyclobutane of retained configuration in fair to high yield; styrene is a by-product in these reactions in an apparently fixed yield. The possible mechanisms of these reactions are discussed.

N-Nitrene intermediates (I) have been used as a convenient rallying point for a number of reactions.[3] Experimental support for this type of intermediate came from the work of McBride and Kruse[4] and Urry, *et al.*,[5] and the recent successful trapping of α-carbonyl N-nitrenes.[6]

Although the evidence for the intermediacy of N-nitrenes is still tenuous, the mechanism by which these presumed intermediates are converted to the observed products is a subject of deep controversy and wide speculation. Our previous contributions dealt mainly with the fragmentation of α-cyano- and of α-aryl-substituted N-nitrenes, which were presumably generated by the mercuric oxide oxidation of the corresponding 1,1-hydrazines (II) or the reduction of the N-nitrosamines (III) with sodium hydrosulfite in basic solution.



R and/or R' = aryl, CN

In principle, N-nitrenes (I) are valence tautomers of the corresponding azo compounds (IV). The decomposition, with loss of nitrogen, of suitably substituted N-nitrenes results in the formation of products which very often are similar to those obtained from the decomposition of azo compounds. The study of the two series of compounds, particularly those with α-aryl substituents and those where the N–N systems are incorporated in a

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[1] This is the 45th in a series of papers concerned with the preparation and decomposition of azo compounds. For the previous paper in this series, see C. G. Overberger and S. Altscher, *J. Org. Chem.*, **31**, 1728 (1966).

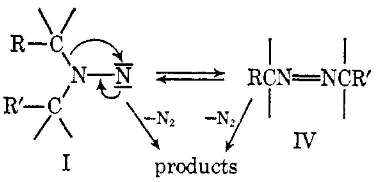
[2] Author to whom inquiries should be addressed at the Department of Chemistry, The University of Michigan, Ann Arbor, Mich. 48104.

[3] C. G. Overberger, J.-P. Anselme, and J. G. Lombardino, "Organic Compounds with Nitrogen–Nitrogen Bonds," The Ronald Press Co., New York, N. Y., 1966, p 89 ff; see also D. M. Lemal and T. W. Rave, *J. Amer. Chem. Soc.*, **87**, 393 (1965).

[4] Reference 3, p 91.

[5] W. H. Urry, P. Szecsi, C. Ikoku, and D. W. Moore, *J. Amer. Chem. Soc.*, **86**, 2224 (1964).

[6] R. S. Atkinson and C. W. Rees, *Chem. Commun.*, 1238 (1967).



cycle, has been under investigation in our laboratories. The present paper deals with the synthesis of *cis*- and *trans*-N-amino- and N-nitroso-2,5-diphenylpyrrolidines) (VII and VIII, respectively). The oxidation of the N-amino isomers with mercuric oxide and the alkaline reduction with sodium hydrosulfite of the corresponding N-nitroso compounds are also reported and discussed.

Synthesis

Previous studies of the "abnormal" oxidation of simple monocyclic 1,1-disubstituted hydrazines (and the "abnormal" reduction of the corresponding N-nitrosamines) had been confined largely to the piperidine system. The extension of this study to other ring sizes such as homopiperidines, azetidines, and pyrrolidines was expected to bring out new features of the reactions.

Three schemes were investigated for the preparation of N-amino- and N-nitroso-2,5-diphenylpyrrolidines (VII and VIII). The starting point in each route was 1,2-dibenzoylethane, which was obtained in 81% by the hydrosulfite reduction of *trans*-1,2-dibenzoylethylene.[7] The attempted ring closure of the diamine prepared by the reduction of the corresponding dioxime failed to give the expected pyrrolidine. The reaction of the 1,2-dibromo-1,2-diphenylethane with hydrazine gave what presumably was the N-amino-2,5-diphenylpyrrolidine, (VII) (vigorous reaction with mercuric oxide) but this route was abandoned owing to the excessive difficulties in the separation of the isomers.

The reduction of 2,5-diphenylpyrrole was then investigated. Several methods of reduction were attempted.[8] For example, catalytic hydrogenation over rhodium on alumina, zinc and acetic acid, sodium in ethanol as well as in *n*-amyl alcohol[9] all failed to effect reduction. However, there had been previous reports of reduction of pyrroles to pyrrolines[10] by zinc in hydrochloric acid. By the use of very pure zinc dust and a high initial concentration of acid, the reduction of 2,5-diphenylpyrrole (V) gave mainly the pyrrolidine VI mixed with small variable amounts of pyrroline. The quantity of pyrroline formed was indicated by the subsequent catalytic reduction of the crude reduction product. This second reduction was performed routinely to reduce any pyrroline to the pyrrolidine. The separation of isomers was not attempted at this point; instead, the *cis* and *trans* isomers were obtained from denitrosation of the respective nitrosamine. Although quite variable, the yield of pyrrolidine from the pyrrole reduction was found to run as high as 87% of theory.

Nitrosation of 2,5-diphenylpyrrolidine was accomplished by addition of sodium nitrite to an ice-cooled solution of the pyrrolidine in an ethanol–hydrochloric acid mixture. Fractional crystallization of the crude product using acetone–water mixtures gave two yellow solids; these were the *trans* isomer (VIIIb) (51%, mp 139.5–142.5°) and the *cis* isomer (VIIIa) (20%, mp 96.0–98.0°) of N-nitroso-2,5-diphenylpyrrolidine. Infrared spectra and elemental analyses confirmed the identity of the products while nmr studies permitted the assignment of configuration (see below). Nitrosation of the pyrrolidine in acetic acid solution gave 40% *trans* and 16% *cis* product.

Passage of hydrogen chloride gas through an ethereal suspension of *trans*-N-nitroso-2,5-diphenylpyrrolidine (VIIIb) gave a pyrrolidine hydrochloride salt melting at 196.5–198.0° while similar treatment of the *cis* isomer (VIIIa) gave a hydrochloride salt melting at 224.7–225.5°. Both salts analyzed correctly as hydrochlorides of VI. On treatment with cold base the low-melting hydrochloride yielded *trans*-2,5-diphenylpyrrolidine (VIb) and the high-melting hydrochloride *cis*-2,5-diphenylpyrrolidine (VIa).

Reduction of the nitrosamine isomers to the respective N-aminopyrrolidines proved to be a severe problem. In contrast to the N-nitrosopiperidines,[11] VIII gave only trace amounts of the corresponding hydrazine with lithium aluminum hydride in ether or tetrahydrofuran. Instead, the hydride reductions were attended by gas evolution, a striking green-to-blue coloration of the reaction mixture, and the formation of hydrocarbon products. Among the hydrocarbon products were styrene and polystyrene, the former identified through its dibromide. In one instance, chromatography of the products obtained from hydride reduction of VIIIb gave a trace amount of a solid hydrocarbon, mp 39.2–39.9°, whose infrared, ultraviolet, and nmr spectra and elemental analysis identified it as *cis*-1,2-diphenylcyclobutane. Low yields of hydrazine accompanied by relatively high yields of hydrocarbon products were also observed for the reduction of VIIIb with sodium in ethanol and with zinc in acetic acid, although the latter system gave appreciably higher yields of hydrazine than either the hydride or the sodium-in-alcohol methods.

These results suggested that abnormal reduction of the nitrosamines was taking place. As in the hydrosulfite reduction of the N-nitroso-2,6-diphenylpiperidines[12] formation of an N-hydroxylamine intermediate IX could be followed by proton abstraction with concurrent or subsequent elimination of hydroxide ion to give the diazene X. The diazene could then decompose to nitrogen gas and hydrocarbons. In the above formulation, B^- would be AlH_4^-, $C_2H_5O^-$, or $CH_3CO_2^-$, that is, the conjugate bases present in the reducing systems described above. The low basicity of the acetate ion probably accounts for the higher yield of hydrazine obtained by the zinc and acetic acid reduction. The following results provided further evidence for abnormal reduction.

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[7] J. B. Conant and H. B. Cutter, *J. Amer. Chem. Soc.*, **44**, 2651 (1922).

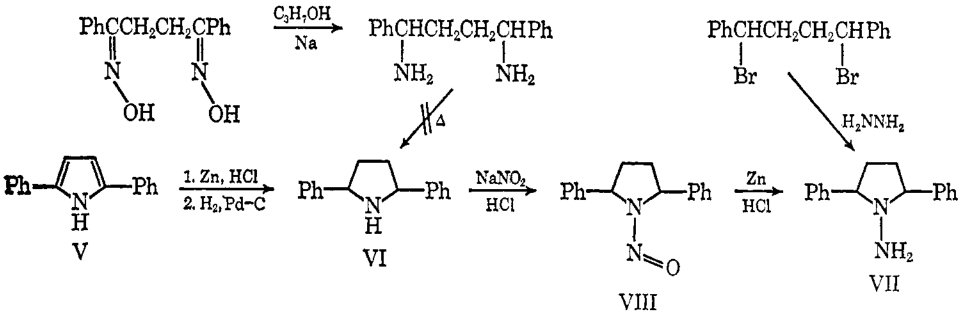
[8] L. P. Herin, Ph.D. Thesis, Polytechnic Institute of Brooklyn, 1962, p 32.

[9] M. Valentine, unpublished results.

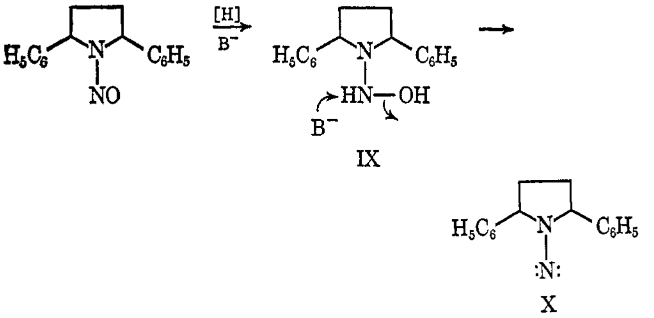
[10] (a) L. Knorr and P. Rabe, *Ber.*, **34**, 3492 (1901); (b) J. P. Wibaut and J. Dhont, *Rec. Trav. Chim.*, **62**, 272 (1943).

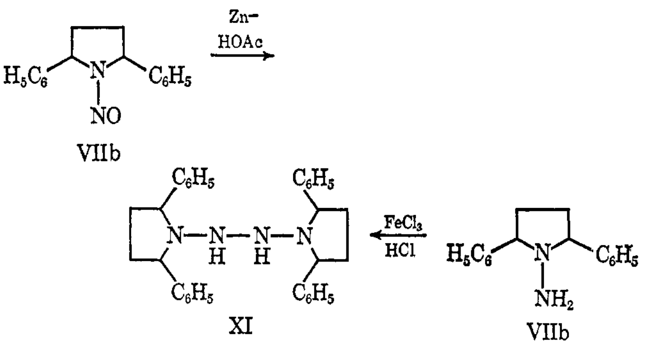
[11] C. G. Overberger, L. Palmer, B. Marks, and N. Byrd, *J. Amer. Chem. Soc.*, 77, 4100 (1955); C. G. Overberger, J. G. Lombardino, and R. G. Hiskey, *ibid.*, **79**, 6430 (1957); C. G. Overberger and L. P. Herin, *J. Org. Chem.*, 27, 417, 2423 (1962).

[12] C. G. Overberger, J. G. Lombardino, and R. G. Hiskey, *ibid.*, **22**, 858 (1957).



First, reduction of the *trans*-nitrosamine VIIIb with zinc and acetic acid gave a very small amount of a colorless solid, mp 157.0–158.8°, possessing N–H groups and a decidedly basic character. Since this material matched the solid (mp 157.2–158.7°) obtained by oxidation of *trans*-N-amino-2,5-diphenylpyrrolidine (VIIb) with ferric chloride in hydrochloric acid, it was probably the tetrazane XI. Tetrazane formation could have occurred by insertion of the diazene intermediate into the N–H bond of the hydrazine, and, therefore, would have required the presence of both a hydrazine and a somewhat stabilized diazene. Inasmuch as acid media can stabilize a diazene by formation of a diazenium ion, the zinc and acetic acid reduction of the nitrosamine fulfilled the conditions of tetrazane production.





Secondly, catalytic hydrogenation of the nitrosamines did not yield hydrocarbons. Presumably, the lack of hydrocarbon products was due to the absence of a basic species which could extract a proton from IX. Unfortunately, catalytic reduction also produced little or no hydrazine. As in the case of the pyrrole, either no hydrogen uptake occurred (platinum in tetrahydrofuran at 45°), or it proceeded only to give hydrogenolysis products (10% Pd–C in ethanol at 45–50°).

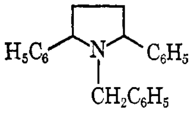
The reduction of the nitrosamines with zinc and hydrochloric acid gave much higher yields of hydrazine. The success of this reducing system was apparently due to the absence of a conjugate base which could aid in diazene formation. The *trans* isomer VIIIb gave a solid in 30% yield while the *cis*-nitrosamine VIIIa yielded 39% of a liquid, presumably the *trans* and *cis* isomers of N-amino-2,5-diphenylpyrrolidine (VII), respectively. In both cases the reduction gave some of the parent pyrrolidine (VI); denitrosation of the starting nitrosamine or deamination of the product hydrazine was likely. The hydrochloride salts of isomeric hydrazines gave correct elemental analyses as did their N-benzoyl derivatives. The infrared spectrum of each hydrazine isomer, as well as the elemental analysis of the free *trans* isomer, confirmed their identities. Vapor phase chromatography could not be used to check isomeric purity because the requisite column conditions proved severe enough to cause isomerization.

Assignment of configuration in the 2,5-diphenylpyrrolidine series was made in the following way. The sequential relation of products was

low-melting pyrrolidine hydrochloride ⇄ high-melting nitrosamine → solid hydrazine

high-melting pyrrolidine hydrochloride ⇄ low-melting nitrosamine → liquid hydrazine

Benzyl bromide reacted with the pyrrolidine derived from the high-melting hydrochloride to give a compound analyzing correctly as the N-benzyl derivative XII. The pyrrolidine from the low-melting hydrochloride salt would not react with benzyl bromide.



XII

HCl salt: mp 215.5–217.5°

The nmr spectrum of XII showed a singlet absorption at τ 6.59 (benzylic protons). According to Hill and Chan,[13] singlet peaks in the benzylic region of α,α'-disubstituted pyrrolidines or piperidines is evidence for *cis* configuration; *trans* disubstitution gives rise to quartets. Both XII and its pyrrolidine precursor are, therefore, assigned a *cis* configuration.

The pyrrolidine from the low-melting hydrochloride salt must, therefore, be the *trans* isomer. The steric hindrance in such a configuration could explain the

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(13) R. K. Hill and T. Chan, *Tetrahedron*, **21**, 2015 (1965).

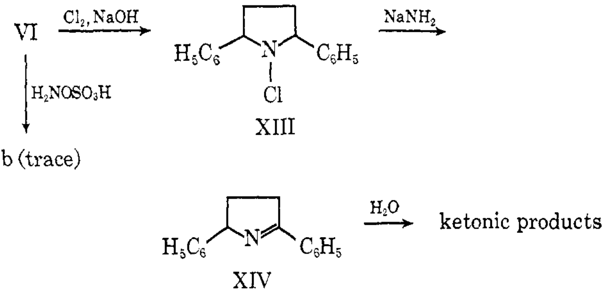
lack of reactivity of the pyrrolidine toward benzyl bromide. Furthermore, the solid hydrazine derived from this pyrrolidine gave optically active components upon fractional recrystallization of its D-camphorsulfonic acid salt. Only *trans* disubstitution allows optical isomers in this system, so that the hydrazine, and quite reasonably the parent nitrosamine and pyrrolidine, have *trans* configurations.

The nmr spectra of the isomeric nitrosamines and hydrazines each show three absorptions assigned to the aromatic, benzylic, and methylenic protons (Table I). Neither the chemical shifts nor the proton spin couplings could be unequivocally related to the configuration.

Table I. τ Values (ppm) for Isomers of N-Amino- and N-Nitroso-2,5-diphenylpyrrolidine

	Aromatic protons		Benzylic protons		Methylene protons	
	cis	*trans*	*cis*	*trans*	*cis*	*trans*
Hydrazine						
in CCl_4	2.89	2.78	6.62	6.07	8.03	7.83
in $CDCl_3$	2.69				8.06	
Nitrosamine						
in CCl_4	2.88		4.55		7.79	
In $CDCl_3$	2.76	2.81	4.25	4.24	7.76	7.82

Attempts to relate the hydrazine isomers directly to their pyrrolidine precursors by N-amination of the latter isomers failed. Treatment of N-chloro-2,5-diphenylpyrrolidine (XIII) with sodamide in liquid ammonia gave largely the 1-pyrroline XIV, as indicated by the ketonic products formed during aqueous work-up of the reaction products. Prolonged treatment of VI with hydroxylamino-O-sulfonic acid in triethylamine gave only traces of the hydrazine.



The "Abnormal" Oxidation and Reduction

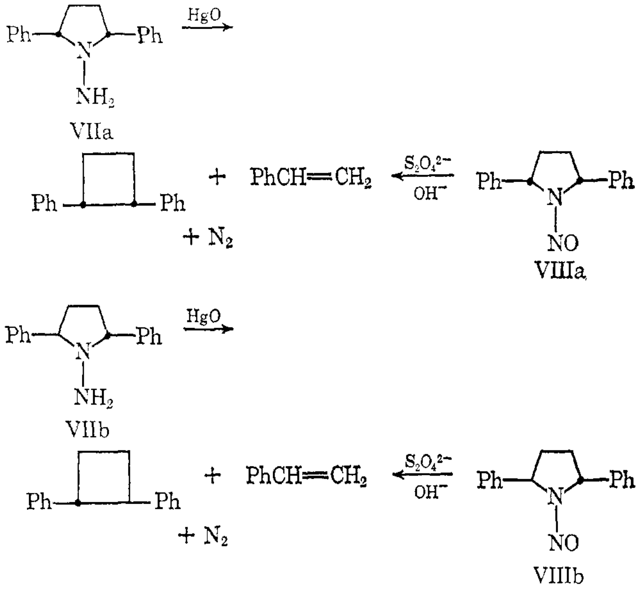
The oxidation of *cis*- and *trans*-N-amino-2,5-diphenylpyrrolidine was carried out by adding an ethanolic solution of the hydrazine to a stirred slurry of yellow mercuric oxide in ethanol. The oxidation was allowed to proceed overnight at room temperature, provision being made to collect the evolved nitrogen. The oxidation solution was then filtered and the filtrate subjected to vacuum evaporation at room temperature, the vapor being recondensed in a series of Dry Ice traps. Both the residue and the condensate from the evaporation process were assayed by a combination of elemental analysis, comparative vapor phase chromatography, and ultraviolet spectrophotometry.

The abnormal reduction of the isomeric nitrosamines VIII was accomplished by adding the nitrosamine all at once to a stirred slurry of sodium hydrosulfite in an alkaline ethanol–water mixture. The reductions were run overnight at 60–70° in the same apparatus used in the abnormal oxidations. Work-up and analysis of the product mixture were similar to that used in the oxidations.

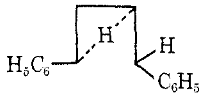
From the product analyses of these reactions (Table II), three observations can be made. (1) Styrene, *not* 1,4-diphenyl-1-butene, is the olefinic product in these reactions, and it is formed in a relatively constant yield throughout the series. (2) A high degree of stereoretention is observed in the formation of cyclic product. (3) Side products are formed in the abnormal reductions of the nitrosamines which are largely lost on work-up. Each of these observations will be considered in turn.

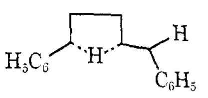
Table II. Product Analysis of Oxidation and Reduction of *cis*- and *trans*-Amino- and N-Nitroso-2,5-diphenylpyrrolidines

		Hydrocarbons, %			
		1,2-Diphenylcyclobutane			
Reactants	Nitrogen, %	*cis*	*trans*	Styrene	Butene
VIIa (*cis*)	79	66.0	6.5	12.6	0
VIIIb (*trans*)	95	0	85.0	12.4	0
VIIIa (*cis*)	96	69.0	8.5	8.5	0
VIIIb (*trans*)	98	56.0	16.4	12.9	0



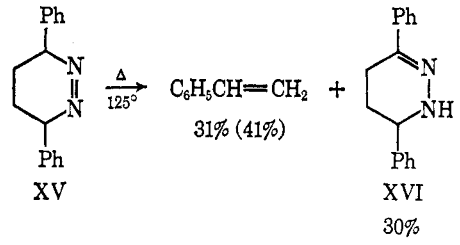
The lack of 1,4-diphenyl-1-butene in the product mixture indicates a prohibitively high transition-state barrier to butene formation, for otherwise the butene (and also the cyclobutane) would be expected to be thermodynamically favored over styrene. This transition state is probably a four-membered one of relatively high strain, so that the breakdown of the diazene leads to cyclization or carbon–carbon bond cleavage,





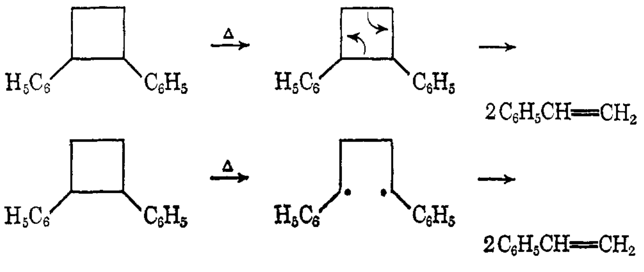
not hydrogen transfer. In the piperidine system, a five-membered transition state is possible for hydrogen transfer, and the lower energy of this transition state makes it competitive with the cyclization process.

Styrene was not an unexpected product; it had been observed previously in the attempted reduction of the nitrosamines to hydrazines. It had also been identified[14] as a pyrolysis product of 3,6-diphenyl-1,2-diaza-1-cyclohexene (XV). However, since 59% of the starting material could not be accounted for, the comparison of the two sets of results is difficult and it is possible that the cyclobutane may have escaped detection.



The abnormal oxidation of VIIb (*trans* isomer) in styrene solution gave some polystyrene of molecular weight of about 11,000. When this oxidation was reported in the presence of hydroquinone, quinone but not polystyrene was obtained. Suitable control runs showed that the polymerization was not being initiated thermally or by inorganic radicals. Carbon radicals were probably responsible for the polymerization and were being generated by the oxidation process. The passage of pure *cis*- or *trans*-1,2-diphenylcyclobutane over a heated silicone-packed chromatography column resulted in the partial decomposition of the cyclobutane to styrene. Not only did the *cis* isomer give more styrene at 238° than the *trans* isomer at 260° (for the same retention time), but some of the *cis* isomer also isomerized to the *trans* isomer. At 180° neither isomer decomposed or isomerized to any detectable degree.

The thermal decomposition of 1,2-diphenylcyclobutane to styrene may be viewed either as a concerted process or as a stepwise process involving a diradical. However, the thermal isomerization is almost certainly a radical process. It is interesting that no 1,4-diphenyl-1-butene was detected; the butene is stable under the conditions employed. Destabilization by steric interaction of the *cis*-phenyl groups could account for the greater ease of decomposition and the isomerization observed for the *cis*-cyclobutane.



The high yield of *cis*-1,2-diphenylcyclobutane in the abnormal reduction of VIIIb (*trans* isomer) was due to prior *trans*-to-*cis* isomerization. In a separate experiment, VIIIb was subjected to the conditions of the abnormal reduction without the hydrosulfite. The recovered nitrosamine consisted of 40% *trans* and 21% *cis* isomer, the remainder being a eutectic mixture difficult to resolve.

The assignment of configuration to the 1,2-diphenylcyclobutanes provided by the abnormal oxidations and reductions was made by comparison to authentic material by nmr spectroscopy. The solid cyclobutane (mp 39.5–40.5°) was identical in all respects with the *cis*-cyclobutane prepared independently.[15] As shown in Table III, the the τ values for the phenyl hydrogens and the α-hydrogens of the cyclobutanes fit into the pattern observed for other isomer pairs of 1,2-diphenylcycloalkanes.[16] In the cyclobutanes, the aromatic protons appeared as a clean singlet for the *trans* isomer but slightly split (J = 2.4 cps) for the *cis* isomer. For the benzylic protons, the *cis* isomer showed a triplet (J = 4.8 cps) resplit into a septet (secondary splittings, J = 2.4 cps); the *trans* isomer was poorly resolved and less symmetrically split, but it appeared to be at least a septet. Not shown in Table III were the methylene proton resonances, whose τ values were 7.88 (*trans*) and 7.59 (*cis*). The *cis* isomer produced a triplet (J = 3.8 cps) with the central peak showing incipient splitting. The *trans* isomer gave basically a triplet undergoing complex resplitting; the primary splitting had a coupling constant of 4.4 cps.

Table III. τ Values for the Aromatic and Benzylic Proton Magnetic Resonances in *cis* and *trans* Isomers of 1,2-Diphenylcycloalkanes[a]

Ring size	Aromatic protons		Benzylic protons		Ref
	trans	*cis*	*trans*	*cis*	
3[b]	2.87	3.04	7.87	7.55	16a
4	3.00	3.24	6.54	6.11	
5	3.01	3.22	7.00	6.68	16a
6	3.06	3.21	7.38	6.92	16b

[a] Given in τ values; carbon tetrachloride solution with TMS as an internal standard, 60 Mc. [b] Relative to water, 40 Mc.

The oxidation of N-amino-2,5-diphenylpyrrolidine with mercuric oxide and the reduction of N-nitroso-2,5-diphenylpyrrolidine with sodium hydrosulfite each proceeded in the abnormal manner to give nitrogen gas and hydrocarbon products. As in the piperidine series, the abnormal reactions give largely the cyclic product, in this case 1,2-diphenylcyclobutane. In contrast to the piperidine series, however, the abnormal reactions in the pyrrolidine series yield a cleavage product, styrene, and not a hydrogen-transfer product, 1,4-diphenyl-1-butene. A high degree of stereoretention is observed in the formation of the cyclobutanes.

In these reactions, the cyclobutanes and the styrene are probably generated by different modes of fragmentation of the intermediate N-nitrenes (I). The high degree of stereoretention observed in the cyclo-

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[14] (a) S. G. Cohen, S. Hisiao, E. Saklad, and C. H. Wang, *J. Amer. Chem. Soc.*, **79**, 4400 (1957). (b) The percentages given in the equation are "corrected" from the experimental data given in ref 14a. The value of 41% given in parentheses for styrene is the percentage when the fraction of undecomposed azo compound (as the hydrazone) is taken into consideration.

[15] R. M. Dodson and A. G. Zielske, *J. Org. Chem.*, **32**, 28 (1967).

[16] (a) D. Y. Curtin, H. Gruen, Y. G. Henrickson, and H. E. Knipmeyer, *J. Amer. Chem. Soc.*, **83**, 4838 (1961); **84**, 863 (1962); (b) C. G. Overberger and J.-P. Anselme, *Chem. Ind.* (London), 280 (1964).

butane products suggests a three-center mechanism. The formation of styrene may occur either *via* the formation of the 1,4-diphenylbutadiyl radical or by a concerted process similar to that suggested by Lemal, Rave, and McGregor for the fragmentation of XVII to ethylene and nitrogen.[17]

XVII

Experimental Section[18]

1,2-Dibenzoylethane. An extensive modification of the procedure of Conant and Cutter[7] was used. Into a 4-l. beaker equipped with a large-blade stirrer was placed 120 g (0.689 mol) of sodium hydrosulfite, and 700 ml of boiling water was added with moderate stirring. After about 10 sec, the stirring was made increasingly vigorous as a solution of 100 g (0.424 mol) of *trans*-1,2-dibenzoylethylene in 1400 ml of boiling 95% ethanol was quickly added. The mixture was stirred for 30 min and then diluted to a volume of 4 l. by addition of cold water. The resulting precipitate was collected, washed thoroughly with water, and suction dried. Recrystallization from 5:1 acetone–carbon tetrachloride gave 81.2 g (81%) of 1,2-dibenzoylethane which was obtained as long, white needles, mp 145.7–147.0°.

2,5-Diphenylpyrrole. A modification of the method of Kapf and Paal[19] was used. Into a 3-l. round-bottomed flask equipped with a mechanical stirrer, a reflux condenser, and a gas inlet tube were placed 106 g (0.445 mol) of 1,2-dibenzoylethane, 200 g (2.59 mol) of ammonium acetate, and 1200 ml of glacial acetic acid. The stirred mixture was gently refluxed for 3 days under nitrogen gas. The cooled mixture was slowly poured into a stirred suspension of 1000 g of crushed ice in 2 l. of concentrated aqueous ammonia. Filtration followed by washing with water gave a quantitative yield of the crude 2,5-diphenylpyrrole as an off-white powder. This material could be used without further purification in the next step.

Recrystallization of the pyrrole from methanol–aqueous ammonia gave shiny flakes, mp 139–141°.

2,5-Diphenylpyrrolidine. The initial stages of this reaction follow the procedure of Wibaut and Dhont.[10b] Into a 5-l., three-necked, round-bottomed flask equipped with a mechanical stirrer and two reflux condensers (one with a straight central bore) was placed 200 g (0.913 mol) of crude 2,5-diphenylpyrrole, 1600 ml of 95% ethanol, and 400 ml of concentrated hydrochloric acid. The stirred mixture was brought to reflux, the stirring then made very vigorous, and 205 g (3.14 g-atoms) of reagent grade zinc dust added in 10-g portions over a 1.5-hr period in alternation with 20 20-ml portions of concentrated hydrochloric acid. The zinc dust was admitted through the straight bore condenser, with an occasional small portion of ethanol to wash it in. Reflux and rapid stirring were continued overnight. If at the end of this period the mixture showed a red color, more zinc dust and acid were added until the color was discharged and the reaction mixture showed no tendency to redden after 2–3 hr of additional stirring. The mixture was then cooled and filtered, and the bulk of the ethanol removed from the filtrate by vacuum distillation with gentle warming. The aqueous residue was then slowly poured into a stirred suspension of 1000 g of crushed ice in 1500 ml of concentrated aqueous ammonia. The resulting two-phase mixture was divided into three portions and each portion extracted with three portions (200, 100, and 100 ml) of ether. The combined ether extracts were dried over magnesium sulfate, filtered, and evaporated to an oily residue. This material could be used in the nitrosation step without further purification; however, the best yields were obtained when the crude pyrrolidine was subjected to mild catalytic hydrogenation to reduce any intermediary pyrroline in the product.

The oily residue was subjected to vacuum to remove any ether or ammonia, weighed by difference during transfer to a Paar hydrogenation bottle, and dissolved in 100 ml of added ethanol. One equivalent weight of concentrated hydrochloric acid plus 10% excess was slowly added to the ethanolic solution, the Paar bottle flushed with nitrogen gas, and 1 g of 10% palladium on carbon added. The mixture was hydrogenated at 2 atm pressure and room temperature until uptake ceased or became very slow (usually at about 10–20% of the total crude pyrrolidine taken). The hydrogenate was filtered under a nitrogen flow, the bulk of the alcohol removed from the filtrate under vacuum, and the residue worked up as in the previous chemical reduction. Vacuum distillation afforded 178.5 g (88%) of a colorless liquid, bp 130–145° (0.15–0.20 mm), collected in four fractions having a refractive index range 1.5875–1.5915 at 25°. Chemically and isomerically pure pyrrolidines were obtained by nitrosation, isomer separation, and denitrosation, as described below.

N-Nitroso-2,5-diphenylpyrrolidine. Separation of the *cis* and *trans* Isomers. A solution of 138.4 g (0.621 mol) of 2,5-diphenylpyrrolidine in 210 ml of ethanol and 100 ml of concentrated hydrochloric acid was prepared in 1-l., three-necked, round-bottomed flask equipped with stirrer, addition funnel, and gas outlet. With good stirring and ice-bath cooling, a solution of 61.5 g (0.891 mol) of sodium nitrite in 100 ml of water was added dropwise over a 2-hr period, and the mixture then allowed to stir overnight while coming to room temperature. At the end of this time, the mixture was poured into 1 l. of water and the precipitate filtered and thoroughly washed with water. The crude product, 160 g, was fractionally recrystallized from acetone to give 79.9 g (51%) of the high-melting isomer, mp 139.5–142.5°, and 31.7 g (20%) of the low-melting isomer, mp 96.0–98.0°.

Anal. Calcd for $C_{16}H_{16}N_2O$: C, 76.16; H, 6.39; N, 11.18. Found for high-melting isomer (mp 140.0–140.9°): C, 76.20; H, 6.38; N, 11.18. Found for low-melting isomer (mp 97.0–98.0°): C, 76.13; H, 6.41; N, 10.60.

The infrared spectrum of low-melting nitroso isomer (KBr) showed a strong $-N{=}O$ peak at 1416 cm^{-1} and a weak one at 1359 cm^{-1}; the high-melting isomer had strong peaks at 1420 and 1344 cm^{-1}. The most notable differences were the weak splittings of the 1453-cm^{-1} (CH_2 deformation) and the 697-cm^{-1} (phenyl) peaks of the low-melting isomer, which were single in the high-melting isomer, and the differences in the relative intensities and positions of the three peaks in the 1053–1000-cm^{-1} (possibly ring vibrations or hydrogen deformations) region.

Denitrosation of *cis*- and *trans*-N-Nitroso-2,5-diphenylpyrrolidines. In a 500-ml erlenmeyer flask equipped with a gas inlet tube having a fritted glass dispersion tip was stirred a suspension of 6.31 g (0.025 mol) of the high-melting nitroso isomer in 300 ml of anhydrous ether. The mouth of the flask was loosely plugged with glass wool while hydrogen chloride gas was slowly bubbled through the suspension for 2 hr. During this time, the nitroso compound slowly dissolved to give an orange-red solution. After standing overnight, the colored solution was extracted with three 100-ml portions of water (violent exotherm during addition of first portion), the aqueous extracts were subjected to vacuum to remove any ether, and NaOH was added to the residue until it was distinctly alkaline (pH 9–10). The free pyrrolidine was then extracted with three 50-ml portions of ether which was dried over magnesium sulfate before evaporation. The pyrrolidine was distilled to give 2.5 g (45%) of a colorless liquid, bp 136° (0.30 mm), $n^{25}D$ 1.5866. A hydrochloride, precipitated from ether, melted at 196.5–198.0°.

Infrared spectra of the free base (neat) showed a weak peak at 3330 cm^{-1} for N–H stretch and three peaks in the 1110–1025-cm^{-1} region, at least one of which is skeletal C–N vibration, although assignment is uncertain. Most pyrrolidines examined had strong absorption at about 1100 cm^{-1}.

A stirred slurry of 15.0 g (0.594 mol) of the low-melting isomer in 200 ml of ether was treated with hydrogen chloride for 5 hr, and on standing overnight 14.1 g (91%) of the pyrrolidine hydrochloride precipitated as a white powder, mp 224.7–225.5°. The free base was isolated as in the previous case, using 10.0 g of the hydrochloride, and on vacuum distillation gave 3.14 g (32%) of colorless liquid, bp 121.8–123.4° (0.20 mm), $n^{25}D$ 1.5850.

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(17) D. M. Lemal, T. W. Rave, and S. D. McGregor, *J. Amer. Chem. Soc.*, **85**, 1944 (1963).

(18) All melting points and boiling points are uncorrected. The infrared spectra were recorded on a Perkin-Elmer Model 521 infrared spectrophotometer. Ultraviolet spectra were obtained on the Perkin-Elmer Model 350 spectrophotometer. Analytical vapor phase chromatography was performed on a Perkin-Elmer Model 154D vapor fractometer. Preparative chromatography was carried out on the Aerograph Model A-700 Autoprep (Wilkens Corp.). Nuclear magnetic resonance spectra were obtained on a Varian Model HR60 nmr spectrometer. Elemental analyses were provided by the Schwarzkopf Microanalytical Laboratory, Woodside, N. Y.

(19) S. Kapf and C. Paal, *Ber.*, **21**, 3053 (1888).

Anal. Calcd for $C_{16}H_{17}N$: C, 86.05; H, 7.67; N, 6.27. Found: C, 86.19; H, 7.56; N, 6.50.

Reduction of *trans*-N-Nitroso-2,5-diphenylpyrrolidine to *trans*-N-Amino-2,5-diphenylpyrrolidine. In a flask provided with a mechanical stirrer was placed 61.5 g (0.244 mol) of the *trans*-N-nitroso-2,5-diphenylpyrrolidine, 63 g (0.965 g-atom) of zinc dust, and 450 ml of 95% ethanol. Under nitrogen flow and with good stirring and ice-bath cooling was added dropwise overnight 168 ml of concentrated hydrochloric acid. The unreacted zinc was filtered and the filtrate stripped of most of its alcohol *in vacuo*. The aqueous residue was slowly poured into 500 ml of concentrated ammonia with cooling and the resulting two-phase mixture extracted with four 200-ml portions of ether. The combined ether extracts were dried over magnesium sulfate prior to evaporation. The crude hydrazine was vacuum distilled, a single fraction being taken boiling at 114–124° (0.24 mm). Recrystallization of the partially solidified distillate from hexane gave 17.3 g (30%) of white solid hydrazine, mp 63.7–65.7°. An analytical sample melted at 66.0–67.0°; the hydrochloride (ether) melted at 204.0–206.5°.

Anal. Calcd for $C_{16}H_{18}N_2$: C, 80.63; H, 7.61; N, 11.75. Found: C, 80.70; H, 7.85; N, 11.65.

An N-benzoyl derivative was prepared by warming the hydrazine with excess benzoyl chloride in ether–pyridine. A purified sample melted at 162.6–164.1°; its infrared spectrum (KBr) showed two peaks (N–H stretch) at 3510 and 3247 cm^{-1}, the latter being much sharper and stronger; a C=O stretch band at 1642 cm^{-1}, very strong; and an N–H deformation (?) at 1302 cm^{-1}.

Anal. Calcd for $C_{23}H_{22}N_2O$: C, 80.67; H, 6.47; N, 8.18. Found: C, 80.83; H, 6.86; N, 7.88.

Reduction of *cis*-N-Nitroso-2,5-diphenylpyrrolidine to *cis*-N-Amino-2,5-diphenylpyrrolidine. In the reduction of 17.6 g (0.69 mol) of *cis*-nitroso compound 18.0 g (0.276 g-atom) of zinc dust, 130 ml of ethanol, and 48 ml of concentrated hydrochloric acid were used. The reaction was carried out as in the case of the high-melting isomer. The product work-up was essentially the same, except that four 100-ml portions of ether were used to extract the free hydrazine. A preliminary vacuum distillation of the hydrazine gave a major fraction (out of two) of colorless liquid, bp 112–122° (0.15 mm), which was redistilled and gave 6.44 g (39%) of liquid hydrazine as the major (third) fraction, bp 120.0–124.0° (0.15 mm), $n^{25}\text{D}$ 1.5879.

Anal. Calcd for $C_{16}H_{18}N_2$: C, 80.63; H, 7.61; N, 11.75. Found: C, 80.45; H, 7.57; N, 11.72.

Vapor phase chromatography on the Perkin-Elmer Fractometer (PE "O" column, 2 m, 228°, helium flow *ca.* 24 cc/min) indicated the presence of a contaminant which either was introduced with the original sample or was formed on the column by oxidation or thermal rearrangement. Two observations point to thermal rearrangement: first, formation of the hydrochloride (ether), mp 181–184° after two recrystallizations from methanol–ether, followed by release of the free base, gave a sample of the hydrazine with $n^{25}\text{D}$ 1.5864, which showed the same vpc pattern; second, the pyrrolidine derived from *trans*-N-nitroso-2,5-diphenylpyrrolidine, after release from its purified hydrochloride salt (mp 196.2–198.0°), gave a similar contaminated-sample chromatogram. In all cases, there appeared to be two peaks joined by an elevated base-line plot. However, actual contamination cannot be ruled out.

The purified hydrochloride salt (185–188°) gave the following analysis.

Anal. Calcd for $C_{16}H_{19}N_2Cl$: C, 69.93; H, 6.96; N, 10.19; Cl, 12.90. Found: C, 69.83; H, 7.16; N, 10.18; Cl, 12.83.

An N-benzoyl derivative, prepared as previously from another sample of the liquid hydrazine, melted at 159.1–160.0°.

Anal. Calcd for $C_{23}H_{22}N_2O$: C, 80.67; H, 6.47; N, 8.18. Found: C, 80.47; H, 6.45; N, 8.21.

Abnormal Oxidation of N-Amino-2,5-diphenylpyrrolidine. Mercuric Oxide Oxidation of *trans*-N-Amino-2,5-diphenylpyrrolidine. Into a two-necked, 200-ml, round-bottomed flask was placed 31.5 g (0.145 mol) of yellow mercuric oxide, 30 ml of ethanol, and a magnetic stirring bar. One neck of the flask was then fitted with a 100-ml addition funnel containing 11.53 g (0.0484 mol) of *trans*-N-amino-2,5-diphenylpyrrolidine in 50 ml of ethanol, while the other neck was attached to a gas outlet tube leading into a graduated buret inverted over water. After the system had been flushed with nitrogen, the buret filled with water, and the system sealed and allowed to come to equilibrium, the hydrazine solution was added dropwise overnight to the stirred mercuric oxide slurry. Nitrogen gas (95% of the theoretical amount) was collected in the buret, and the reaction mixture was carefully filtered through Supercell with thorough ethanol washing of the residue. The filtrate was evaporated under full pump vacuum, the vapor being caught in a series of Dry Ice–acetone-cooled receivers. This evaporation was continued overnight; the condensate was then allowed to warm to room temperature for dilution in absolute ethanol to 500-ml volume in a volumetric flask. An aliquot of this solution was rediluted 1000-fold and its ultraviolet spectrum in the 200–300-mμ region taken on the Perkin-Elmer spectrometer 350; $\lambda_{\max}^{\text{EtOH}}$ 246.3 mμ, $A = 0.457$. Using a measured value of the extinction coefficient (ε 15,497), the total condensate was found to contain 1.23 g of styrene. This assay checked closely with the value of 1.28 g obtained by scanning an aliquot diluted 100-fold at 282.5 ($A = 0.422$) and 291.0 mμ ($A = 0.325$) (ε 1649 and 1266) from the standard. Careful distillation of the condensate through a 2-ft column packed with metal beads left *ca.* 20 ml of residue whose vapor phase chromatogram indicated that only ethanol and styrene had distilled over during the overnight evaporation of the reaction filtrate. Addition of bromine to this residue gave styrene dibromide, mp 72.5–73.5° after two recrystallizations from ethanol. No melting point depression occurred on mixing with an authentic sample.

The chromatogram (PE "O" column, 181°, helium flow ~28 cc/min) of the oxidation residue (9.45 g, 86.7%) from the overnight evaporation exhibited one peak, and comparison of column retention times of appropriate mixtures showed that this material was not *cis*- or *trans*-1,4-diphenyl-1-butene nor 1,4-diphenylbutane. Its infrared and ultraviolet spectra exhibited only phenyl group unsaturation. A portion of this material (6.860 g), presumably the *trans*-1,2-diphenylcyclobutane, was taken for vacuum distillation, giving 6.075 g of clear, colorless liquid, bp 85–101° (0.030–0.035 mm), $n^{25}\text{D}$ 1.5804–1.5806, in three fractions. An analytical sample boiled at 87.0–88.8° (0.03 mm), $n^{25}\text{D}$ 1.5805.

Anal. Calcd for $C_{16}H_{16}$: C, 92.64; H, 7.36. Found: C, 92.35; H, 7.77.

A mixture consisting of 0.79 g of the cyclobutane, 10 g of potassium permanganate, and 75 ml of acetone was refluxed overnight. Filtration and evaporation of the acetone, addition of 150 ml of water to the residue, extraction with two 50-ml portions of carbon tetrachloride, drying, filtration, and evaporation of the carbon tetrachloride left a residue which upon recrystallization from ethanol melted at 143.7–145.2° and showed strong carbonyl and phenyl absorption in the infrared. Authentic 1,2-dibenzoylethane, mp 143–146°, had an identical spectrum; a mixture melting point showed no depression (143–146°).

On passage through the PE "O" column at 260° (helium flow 24 cc/min), the cyclobutane decomposed extensively and exclusively to styrene.

Mercuric Oxide Oxidation of *cis*-N-Amino-2,5-diphenylpyrrolidine. Using an assembly similar to that of the previous oxidation (but of smaller over-all volume), 2.0 g (9.23 mmol) of mercuric oxide was added all at once to 0.509 g (2.13 mmol) of *cis*-N-amino-2,5-diphenylpyrrolidine in 7 ml of ethanol. Nitrogen (79% of the theoretical) was collected, and the reaction was worked up as in the previous case. Ultraviolet analysis of the ethanolic condensate indicated that 0.0570 g (12.6%) of styrene had been formed in the oxidation, with no other products present in the ethanol. Vapor phase chromatography of the residue (PE "O" column, 184°, helium flow 28 cc/min) showed two peaks, both cyclobutanes, in the ratio of 10.2:1. When 0.09556 g of the residue (out of a total of 0.39615 g) was mixed with 0.12525 g of pure *trans*-1,2-diphenylcyclobutane, the second of the two peaks was enlarged and the ratio fell to 0.5460:1. From these data it was calculated that the residue contained 0.299 g of *cis*- and 0.029 g of *trans*-1,2-diphenylcyclobutane, the remaining 0.058 g being unknown. Part of the residue was sent for analysis.

Anal. Found: C, 91.09; H, 7.78; N, 0.11.

The low nitrogen analysis and the absence of any noncyclobutane peaks in the vapor phase chromatogram of the residue suggest that the less than theoretical nitrogen evolution during the oxidation was due to a leak in the system.

Abnormal Oxidation in Styrene. Into each of three 50-ml, round-bottomed flasks, each equipped with a magnetic stirrer, addition funnel, and gas outlet tube leading to a gas bubbler, was placed 6.0 g (0.0277 mol) of yellow mercuric oxide and 10 ml of freshly distilled styrene. Into flask 2 was placed 1 g of hydroquinone. The addition funnels of flasks 1 and 2 each received 10 ml of a solution prepared by dissolving 5.77 g (0.0242 mol) of solid *trans*-N-amino-2,5-diphenylpyrrolidine in 28 ml of freshly distilled styrene; the remaining addition funnel received 10 ml of pure styrene. After each assembly had been thoroughly flushed with nitrogen gas and allowed to come to equilibrium, the contents of the addition funnels were allowed to drip into the flasks over a 1.5-hr period. The mixture in each flask was allowed to stir overnight at room temperature.

Gas evolution was observed from the reactions of flasks 1 and 2; 25 ml of methanol was added to each flask and the contents filtered through Supercell, the residue being washed with two 25-ml portions of chloroform. The filtrates were separately evaporated down under vacuum with very gentle warming.

The evaporation residue from flask 1 was treated first with 25 ml of boiling hexane and then with 25 ml of boiling methanol. A solid residue of polystyrene remained, weighing 1.17 g after vacuum drying. This material was dissolved in about 5 ml of chloroform (hot) and reprecipitated from 600 ml of methanol. Filtration and vacuum drying gave an amorphous polymer, of which 0.5052 g was taken and dissolved in benzene to give 50.0 ml of solution. The intrinsic viscosity at 25° was 0.257, indicating a molecular weight of 11,710.

Evaporation residue from flask 2 dissolved almost completely in 25 ml of boiling methanol, leaving a negligible amount of dark material behind. During the previous evaporation of the methanol–chloroform, a considerable amount of quinone had sublimed over as bright yellow crystals.

The evaporation residue (oil) from flask 3 was quite negligible and was not treated further.

Abnormal Reduction of N-Nitroso-2,5-diphenylpyrrolidine. Sodium Hydrosulfite Reduction of *trans*-N-Nitroso-2,5-diphenylpyrrolidine. Into a 500-ml, two-necked flask (one neck for a thermometer) was placed 8.802 g (0.0349 mol) of high-melting N-nitroso-2,5-diphenylpyrrolidine, 62.5 ml of 32% aqueous potassium hydroxide, 150 ml of ethanol, and a magnetic stirring egg. The flask was then fitted with a heating mantle and a reflux condenser, with a tube leading from the condenser to a graduated buret inverted over water. The system was flushed with nitrogen and the flask warmed to 67° while the contents were being stirred. After equilibrium had been reached, the buret was filled with water and 18 g (0.103 mol) of sodium hydrosulfite was added all at once to the flask, the system being resealed immediately. Vigorous reaction ensued, the temperature rising to 70°. The reaction temperature was maintained at 67–70° for 4 hr, during which time the bulk of the nitrogen was evolved; thereafter, the stirred reaction mixture was kept at 60° overnight. Nitrogen (98% of the theoretical amount) was collected. The cooled reaction mixture was then filtered and evaporated in the manner described in the oxidation of the *trans*-hydrazine.

Ultraviolet analysis of the ethanol–water condensate from the evaporation revealed 0.717 g (12.9%) of styrene, which vapor phase chromatography disclosed as the only hydrocarbon product.

The residue (4.858 g, 87.3%) from the evaporation was treated with 100 ml of boiling ether for 4 hr. Upon cooling, 50 ml of water was added to the ethereal residue and the ether layer removed after shaking. The water layer was then extracted further with four 30-ml portions of ether, and all the ether layers were combined and dried over Mg_2SO_4 prior to evaporation. The residue from the ether was vacuum distilled to give the following fractions: (1) 0.187 g of colorless liquid, bp 85–90° (0.10 mm); (2) 2.348 g of semisolid material, bp 87.0–89 0° (0.06–0.08 mm), n^{25}D 1.5795; and (3) 1.866 g of semisolid material, bp 89–92° (0.06 mm), n^{25}D 1.5798.

Fraction 1 had a strong odor of acetophenone and displayed a strong carbonyl absorption at 5.97 μ in the infrared. Vapor phase chromatography (PE "O" column, 207°, helium flow 26 cc/min) showed a major peak (out of three) which was enhanced by admixture with authentic acetophenone. Finally, fraction 1 yielded a 2,4-dinitrophenylhydrazone derivative, mp 238.8–240.0° (ethanol–water), which gave a mixture melting point of 242–243° with an authentic sample.

Fractions 2 and 3 were combined and examined by vapor phase chromatography (PE "O" column, 183°, helium flow 28 cc/min). Two large peaks were observed, the peak area ratio of the first to the second being 3.407. When 0.05382 g of the combined cuts was mixed with 0.06395 g of pure *trans*-1,2-diphenylcyclobutane, the second peak was enhanced and the peak area ratio fell to 0.526. Since neither *cis*- nor *trans*-1,4-diphenyl-1-butene nor 1,4-diphenylbutane enlarged either of the above peaks, the conclusion was that the first product peak was *cis*-1,2-diphenylcyclobutane. From the change in peak area ratios the combined cuts were estimated to contain 3.12 g of *cis*- and 0.916 g of *trans*-1,2-diphenylcyclobutane, leaving about 0.17–0.18 g of material unaccounted for (although a rather small third peak was observed in the chromatograms).

The vacuum distillation left 0.457 g of residue whose infrared spectrum suggested that it was largely hydrocarbon in nature.

Sodium Hydrosulfite Reduction of *cis*-N-Nitroso-2,5-diphenylpyrrolidine. In the apparatus described in the previous reduction, 20 g (0.115 mol) of sodium hydrosulfite was added all at once to a stirred suspension of 9.40 g (0.0372 mol) of *cis*-N-nitroso-2,5-diphenylpyrrolidine in 62.5 ml of 32% aqueous potassium hydroxide and 150 ml of ethanol, maintained at 50°. Initial reaction was sluggish, so that the temperature was slowly raised and held to 64° overnight. Nitrogen (96% of the theoretical amount) was evolved. The work-up of the reaction mixture was almost identical with that of the previous reduction.

Analysis of the ethanol–water condensate by ultraviolet spectrometry and vapor phase chromatography showed styrene to be the only hydrocarbon present, in 0.914 g (14.8%) yield.

The residue (5.259 g, 85.3%) from evaporation of the ethanol–water solvent mixture was taken up in 50 ml of water and extracted with four 40-ml portions of ether. The ether layers were combined, dried over magnesium sulfate, and evaporated. The residue was distilled *in vacuo* to give the following fractions: (1) 3.851 g of colorless liquid, bp *ca.* 96.5° (2.3 mm), n^{25}D 1.5798; (2) 0.256 g of colorless liquid, bp 96.5° (2.2 mm), n^{25}D 1.5782; and (3) 0.8417 g of colorless liquid, bp 92° (0.25 mm), n^{25}D 1.5810. There remained 0.308 g of distillation residue.

These fractions were individually examined by vapor phase chromatography (PE "O" column, 183°, helium flow 28 cc/min). Each fraction showed the same two major peaks and little else; chromatography of suitable mixtures indicated that neither peak was due to a 1,4-diphenyl-1-butene or 1,4-diphenylbutane. By measurement of the peak area ratios before and after admixture with pure *trans*-1,2-diphenylcyclobutane, the amount of each cyclobutane isomer in each fraction was determined. The data reveal 4.25 g of *cis*- and 0.52 g of *trans*-1,2-diphenylcyclobutane, leaving 0.18 g of unknown material.

When a portion of fraction 1 was dissolved in a small amount of hexane and cooled overnight in the refrigerator, white crystals were obtained, mp 39.2–39.9°.

Anal. Calcd for $C_{16}H_{16}$: C, 92.26; H, 7.74. Found: C, 92.09; H, 7.95.

This material did not absorb bromine in carbon tetrachloride. Its vapor phase chromatogram displayed one peak with a retention time that identified it as the first *cis*-1,2-diphenylcyclobutane observed in the products of the oxidation–reduction reactions.

Isomerization of *trans*-N-Nitroso-2,5-diphenylpyrrolidine. In an apparatus similar to that used in the abnormal reductions, 7.1956 g (0.0285 mol) of *trans*-N-nitroso-2,5-diphenylpyrrolidine, 52.5 ml of 30.5% aqueous potassium hydroxide solution, and 150 ml of ethanol were stirred together overnight at 68.5°. During this time the nitroso compound dissolved, and about 20 cc of gas collected in the buret. The slight amount of gas in the buret was due to thermal expansion of the nitrogen used to flush out the system; the system had been equilibrated at 60° and then allowed to warm to 68.5°. The mixture was cooled in ice, and the solid which separated was filtered and washed with water. The total filtrate (about 500 ml) was made slightly acid and further precipitated solid filtered and water washed. The final filtrate (now about 700 ml) was concentrated to *ca.* 500-ml volume (cloudiness) and extracted with four 20-ml portions of chloroform. Drying and vacuum evaporation of the chloroform left 0.26 g of viscous, dark, liquid residue, unrecrystallizable from acetone.

The combined filtration residues, 6.66 g, were fractionally recrystallized from acetone to give 2.92 g (40%) of material melting at 138.0–141.5° and 1.59 g (21%) of material melting at 99–99°. A total of 1.28 g (18%) (including chloroform extract) remained as an unresolved residue.

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