Mechanism of initiation in the thermal polymerization of styrene. Thermal decomposition of *cis*-3,6-diphenyl-3,4,5,6-tetrahydropyridazine^{1,2,3}

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Thermal decomposition of *cis*-3,6-diphenyl-3,4,5,6-tetrahydropyridazine, **1**, $(k = 5.6 \times 10^{-4} \text{ s}^{-1} \text{ at 79.5}^\circ)$ results in the formation of about 60% styrene, 27% *cis*- and 13% *trans*-1,2-diphenylcyclobutane. The relative product yields vary little over the temperature range 64–133°. This indicates that **1** decomposes exclusively to the 1,4-diphenyl-1,4-butadiyl diradical, **2**, and nitrogen. The diradical, **2**, cannot be trapped by styrene and **1** is not an initiator of styrene polymerization. Therefore, **2** is not the radical intermediate responsible for the thermal initiation of styrene polymerization.

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The thermal decomposition of 3,6-diphenyl-3,4,5,6-tetrahydropyridazine, 1, was studied a number of years ago (1). A possible initial decomposition product, the 1,4-diphenyl-1,4-butadiyl diradical, 2, has a structure identical to the classical Flory diradical whose formation by "tail to tail" dimerization of styrene, eq. [1], had been held to be responsible for the initiation of the

thermal polymerization of this monomer (2). The only nitrogen-free decomposition product from 1 which was identified was styrene, as the dibromide, in 7% yield. There was no evidence to indicate whether the diradical, 2, was actually formed as an intermediate in the decomposition of 1 or whether there occurred a concerted decomposition reaction to give styrene and nitrogen directly. It was found that 1 was a poor initiator of styrene polymerization. Previous reports also indicated that diradicals generated by thermal decomposition of cyclic peroxides (3, 4), by photolysis of a cyclic disulfide (5), and by thermal decomposition of a cyclic azo compound (6) are poor polymerization initiators. These experimental results had been anticipated by kinetic considerations (7, 8).

For these and other (9) reasons it had come to be considered unlikely that the thermal polymerization of styrene is initiated by formation of 2. However, the report (9–11) that 1,2-diphenylcyclobutane, among other dimers, could be isolated from the thermal polymerization of styrene in dilute solution or in the presence of inhibitors maintained the question of the formation of 2 from dimerization of styrene.

In the present study the decomposition of 1 has been reinvestigated in order to determine the mode and products of the reaction, and to measure more accurately the efficiency of 1 as an initiator of styrene polymerization.

Results

Preparation and Stereochemistry of 1

Attempted preparation of 1 according to the published procedure (1) resulted in the isolation in low yield of material which did evolve gas upon melting but which always melted over a broad temperature range. This material was shown by ultraviolet (u.v.) and nuclear magnetic resonance (n.m.r.) spectroscopy to consist of 1 contaminated with appreciable amounts of the corresponding hydrazone, 3,6-diphenyl-2,3,4,5-tetrahydropyridazine, 9. In this procedure saponification of cis-1,2-dicarbethoxy-3,6-diphenylhexahydropyridazine, 4, with potassium hydroxide in methanol is followed by dilution of the reaction mixture with water and then ether extraction of the resulting basic solution. Decarboxylation of the dipotassium salt, 5, was assumed to take place after the aqueous dilution. In the present study it was found the decarboxylation was slow and incomplete even in only slightly alkaline solution. The azo compound, 1, could be obtained in a high state of purity in 75% yield, based on 4, if

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decarboxylation of 5 was carried out in acidic solution and all operations involving the hydrazine, cis-3,6-diphenylhexahydropyridazine, 6, and its salts were carried out under nitrogen until 6 was oxidized by atmospheric oxygen in a dried ether solution free of inorganic acid or base (Scheme 1).

When a solution of 4 and potassium hydroxide in ethanol was heated under reflux for several hours, a water-soluble precipitate formed. This was shown to be mainly the half acid salt-half ester, 7, by its conversion to the mono-ester, *cis*-3,6-diphenyl-1-carbethoxyhexahydropyridazine, 8, in 53% overall yield upon addition of acid.

The presence of small amounts of acid resulted in the immediate isomerization of 1 to 9. Attempts to take spectra of 1 even in purified carbon tetrachloride or chloroform resulted only in spectra corresponding to 9. Stable solutions of 1 could be prepared in purified hydrocarbon solvents and in ether. The n.m.r. spectrum of 1 taken in benzene- d_6 confirms its structure and shows a complex multiplet centered at τ 3.2 for the phenyl protons, a multiplet centered at τ 7.2 for the benzylic protons, and a broad multiplet absorption from τ 8.9 to 9.8 for the methylene protons. The shifts given are relative to tetramethylsilane used as external standard. The stereochemistry of 1 cannot be determined with certainty from its n.m.r. spectrum, but can be deduced from the n.m.r. spectra of its precursors, 3 and 4. It is now well established that 3 prepared by treatment of 1,4-diphenylbutadiene with diethyl azodicarboxylate has the *cis* configuration (12–17). Hydrogenation of **3** to **4** would not be expected to be accompanied by isomerization. That it was not, is shown by the n.m.r. spectrum of **4** taken in carbon tetrachloride which shows two broad one proton absorptions centered at τ 4.70 and at τ 5.16 for the benzylic protons. Only one signal would have been expected for these protons if **4** were the *trans* isomer. It is also unlikely that any isomerization occurred during saponification of **4** since **4** could be recovered unchanged after prolonged treatment with sodium ethoxide in boiling ethanol. It thus seems quite certain that **1** also has the *cis* configuration.

A number of attempts were made to prepare the corresponding *trans* azo compound, but these were unsuccessful.

Products from 1

The thermal decomposition of 1 was accompanied by only small amounts of isomerization to 9 if carried out in carefully cleaned apparatus and purified hydrocarbon solvents. In preliminary experiments the yield of nitrogen from the decomposition of 1 at 100° under these conditions was 90-100%. At lower temperatures somewhat less nitrogen was evolved. The presence of the hydrazone, 9, could be detected in these reaction mixtures by u.v. spectroscopy. Control experiments showed that 9 did not rearrange or decompose under the experimental conditions used in this study.

Rates of decomposition of 1 were determined

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TABLE I Decomposition of **1** in ethylbenzene

Temperature, °C	N_2	$k^* \times 10^4$, s ⁻¹
64.7	80	1.0
75.0	100	3.0
79.5	96	5.6

At 79.5°, $\Delta H^ = 26.7$ kcal/mole, $\Delta S^* = 2.4$ eµ.

Product analyses were made on a series of runs carried out with degassed solutions of 1 in benzene- d_6 in sealed n.m.r. tubes. The solutions were heated for 10 half-lives of decomposition and analyzed by n.m.r. spectroscopy and by gas chromatography (g.c.). Styrene and cis- and trans-1,2-diphenylcyclobutane, cis- and trans-10, were the only products detected by both methods. The presence of 10% hydrazone could have been detected in the n.m.r. spectrum. The composition of the products changes but little with temperature over the range 64–133°, Table II. In this range 1 decomposes to give 58-62% styrene, 25-29% cis-10, and 12-14% trans-10. The proportions of styrene and trans-10 formed, increase somewhat with increasing temperature at the expense of cis-10. In each case the n.m.r. spectrum of the solution after decomposition of **1** was essentially superimposable upon that of a benzene- d_6 solution of styrene, *cis*- and *trans*-10 present in the molar ratio 57.5:28.0:14.5 and in a concentration corresponding to 100% decomposition of 1. The

formation of diphenylcyclobutane in low yield from decomposition of 1 has previously been reported but the stereochemistry of the product was not determined (19).

Authentic samples of *cis*- and *trans*-10 were prepared from 1,2-diphenylcyclobutene (20). Hydrogenation of this material gave *cis*-10 which was isomerized to *trans*-10 by potassium *t*butoxide in dimethyl sulfoxide. The syntheses of *cis*- and *trans*-10 by this route have since been reported (21). The properties of these compounds prepared in the present study agree with those reported except for the n.m.r. absorption of the phenyl protons of *cis*-10. These were reported to appear as a singlet whereas we find a multiplet similar to that reported for the absorptions of the phenyl protons of *cis*-1,2-diphenylcyclopropane (22).

A careful search was made for the presence of 1-phenyltetralin, 11, among the products of decomposition of 1 but it could not be detected. Had 11 been formed in 0.1% yield it could have been found.

Attempts to decompose 1 photochemically resulted in the formation of only traces of styrene, *cis*- and *trans*-10. Irradiation of a benzene solution of 1 in Pyrex apparatus at 0° with light from a medium pressure mercury lamp gave the hydrazone, 9, as the major product. Similar photoinduced rearrangements of azo compounds to hydrazones have been observed with 1-phenylazoalkanes (23).

1 as a Polymerization Initiator

The efficiency of 1 as an initiator in the polymerization of styrene was measured by determining the amount of diphenylcyclobutanes formed in the decomposition of 1 in pure styrene and by following the rate of polymerization of styrene containing 1.

The yields of *cis*- and *trans*-10 formed from decomposition of 1 at 98° in styrene and in an

TABLE II Product distribution* from the thermal decomposition of 1 in benzene

				Styrene	cis-10
Temperature, °C	%Styrene	%cis-10	%trans-10	cis- + trans-10	trans-10
64 78 98 133	60.0, 57.9 60.4, 58.0 61.2, 58.9 62.2, 59.7	28.6, 29.4 27.2, 28.7 26.5, 28.0 24.8, 26.3	11.9, 12.8 12.4, 13.2 12.3, 13.1 13.1, 14.0	1,42 1,46 1,50 1,56	2.35 2.19 2.15 1.89

*Relative yields.

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Product yields from decomposition of 1 in benzene and styrene at 98 °C

Solvent	9	%cis-10	%trans-10	Styrene
Benzene	9.8*	24.2† 26.8†	12.9† 14.3†	57.8†
Styrene	20.3*	20.2† 25.4‡	10.5† 13.2‡	

*Percent yield as determined by u.v. analysis. †Percent yield as determined by g.l.c. using chlorobenzene as internal standard. ‡Percent yield based on 1 not isomerized to 9.

TADLE IV		
Rates of polymerization in the presence of 1 and A	n of styrene ABN‡ at 70.0 °C	

TADLE IV

Added compound	Concentration $M \times 10^3$	$k_a^* \underset{s^{-1}}{\times} 10^4$	$R_p imes 10^6 M^{-1} { m s}^{-1}$	Kinetic chain length
None ABN‡ 1	3.79 3.79	45.6§ 1.9¶	4.70† 102† 5.76**	674 8 1.5††

 $*k_d$ = rate constant for decomposition. \uparrow Reference 24. 2,2'-Azobis-(2-methylpropionitrile).SReference 25. ||Molecules of styrene polymerized per molecule of initiator decomposed calculated

using eq. [2]. ¶Calculated from data in Table II. **Average of two determinations: 5.66×10^{-6} and 5.86×10^{-6} . ††Contribution due to 1 only after correction for thermal rate.

additional run in benzene are shown in Table III. Undetectable amounts of cis- and trans-10 were formed when pure styrene was heated at 98° in the absence of 1 for the same length of time. There appears to be an error in the analysis as the total yield of 9, cis-10, trans-10, and styrene formed from decomposition of 1 in benzene in this run is 105.1%. Also, upon correction of the product yields for isomerization of 1 to 9, the yield of styrene seems to be ca. 4% too high by comparison with the results from the runs given in Table II. The corrected yields of *cis*- and *trans*-10 are more in line. It appears that the quantitative g.c. analysis for styrene was in error and that the u.v. analysis for 9 was correct. This means that the corrected yields for cis- and trans-10 given in Table III must be near the actual values, and the amounts of *cis*and *trans*-10 formed in styrene are only slightly smaller than the amounts formed in benzene. Very little, if any, of the diradical, 2, is trapped under these conditions.

The rate of polymerization of styrene at 70° in the presence of **1** was followed by the dilatometric method. The data in Table IV indicate that the rate of polymerization of styrene in the presence of 1 is about 20% greater than the thermal rate, whereas the 2,2'-azobis-(2-methyl-propionitrile), ABN, initiated rate was 22 times faster. The rate of polymerization in the presence of 1 was slower than that in the presence of ABN at the same concentration in spite of the faster rate of decomposition of 1. That 1 is a poor initiator is also seen by a comparison of the apparent kinetic chain lengths in the two cases. These were calculated using the relationship in eq. [2] where R_p is the rate of

kinetic chain length = $R_{\rm p}/R_{\rm i} = R_{\rm p}/k_{\rm d}I$ 21

polymerization, R_i is the rate of initiation, k_d is the rate of decomposition of the initiator, and I is its concentration. The kinetic chain length, 8, determined in this way for polymerization in the presence of 1 must be corrected for the contribution which the thermal rate makes to the overall rate of polymerization. When this is done it is seen that only 1.5 molecules of styrene are polymerized for each molecule of 1 which decomposes. This shows 1 to be about 0.4% as efficient as ABN in initiating the polymerization of styrene. By either

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method of analysis it is seen that $\mathbf{1}$ is indeed a very inefficient initiator. This is in agreement with the earlier work (1) in which it was estimated from the increase in weight of polymer isolated from polymerization of styrene containing $\mathbf{1}$, that about 8 molecules of styrene were polymerized per molecule of $\mathbf{1}$ decomposed at 80°.

Discussion

Decomposition of 1

There is good evidence that the thermal decomposition of symmetrical aliphatic azo compounds leads directly in a one step process to a pair of radicals in acyclic systems (18, 26), and to 1,3diradicals in 5-membered ring systems (27, 28). But it does not follow that the 1,4-diradical, 2, is formed from the thermal decomposition of 1, for 1 has available to it a concerted, thermally allowed route (29) which leads directly to styrene and nitrogen. That 1 does not decompose exclusively by such a process is shown by the isolation of the 1,2-diphenylcyclobutanes, cis- and trans-10, in ca. 40% yield from the decomposition of 1. In fact, although it is difficult to rule it out definitely, the concerted process does not appear to contribute to the thermal decomposition of 1 at all. The concerted route leading directly to styrene and the route leading to 2 would undoubtedly have different stereoelectronic requirements, and, therefore, probably different activation parameters. If both routes were operative this might result in a change in product distribution with temperature. In fact, there is a very small change in product distribution with temperature. This suggests that the products are formed exclusively from a common intermediate, the 1,4-diradical, 2, via paths requiring small activation energies, Scheme 2.

Other 6-membered ring azo compounds also decompose to diradical intermediates, at least to a large extent, rather than by way of concerted processes (30, 31). These examples do not constitute violations of the Woodward-Hoffmann rules. It has already been pointed out (29) that these are not obligatory rules.

Reactions of the 1,4-Diradical, 2

The cyclization of 2, obtained from 1, is stereoselective and results predominantly in the formation of the thermodynamically less stable cis-10 of retained configuration. This cyclization is less stereoselective than are the cyclizations of the diradicals obtained from both the thermal and photochemical decompositions of meso- and dl-3,6-diethyl-3,6-dimethyl-3,4,5,6-tetrahydropyridazine (31). The cyclobutanes obtained from these compounds are formed with virtual complete retention of configuration. Thus, while cyclization of 2 does compete well with internal rotation about the 1,2- and 3,4-carbon-carbon bonds of 2, the competition is much less effective than is the case with either of the other diradicals. On the other hand the ratio of cleavage to cyclization of 2, ca. 60:40, is only slightly greater than it is in the other systems, ca. 53:47. A meaningful evaluation of these differences must await information for the decomposition of the trans isomer of 1.

In order for cyclization of 2 to compete effectively with internal rotation about the carboncarbon bonds of 2 the rate constant for cyclization must be at least 10^{10} s^{-1} (32). This is equivalent to an intermolecular rate constant for the coupling of two monoradicals of at least $2 \times 10^{10} M^{-1} \text{ s}^{-1}$ (8) which corresponds well with the rate constant, 3×10^9 , for the coupling of benzylic radicals (33) considering that the radical ends of 2 probably have no diffusive barrier to overcome. Such a rate is far too great for chain transfer with styrene or addition to styrene [for styrene at 60° , $k_{tr} \sim 10^{-2}$ (34) and $k_p \sim 10^2$ (35)] to compete with cyclization of 2, unless, as has been pointed out (9), 2 is very abnormally reactive compared to a polystyryl radical.

The results obtained from the decomposition of 1 in styrene provide further evidence on this point. Only 1.8 molecules of styrene are consumed for each diradical 2 produced, and little, if any, decrease in yield of cis- and trans-10 is observed compared with yields from decompositions carried out in benzene. This indicates that most of the extra styrene consumed as a result of the presence of 1 is converted to high polymer. Assuming a molecular weight of ca. 10⁶ for polystyrene produced at low conversions and under the conditions used (36), then only one of each 5000 to 10000 of 2 produced will cause the formation of a molecule of high polymer. Approximately 40% of the diradicals produced cyclize. On this basis, if the diradical, 2, were responsible for the initiation in the thermal polymerization of styrene, there should be roughly about 1/4 to 1/2 as much 1,2diphenylcyclobutane formed, by weight, as of polystyrene in the thermal polymerization of pure styrene. This is not observed (9). The weight of dimers produced is only a small fraction of the weight of polymer formed. If some of the small amount of extra polymer formed in the presence of 1 is due to an impurity in 1 then the fraction of 2 diverted to polymer is even smaller than indicated. The present results provide direct experimental evidence for arguments made long ago (9) that 2 cannot be involved in the initiation of the thermal polymerization of styrene.

A recent report describes the study of the dimerization of styrene under a variety of conditions (37). The stereochemistry of the 1,2diphenylcyclobutanes produced, varied considerably depending upon the experimental conditions. Thermal dimerization at 110° resulted in the formation of cis- and trans-10 in a cis/trans ratio of 1/2. Thermal decomposition of 1 gives these materials with a cis/trans ratio of 2. While the ratios are different the results are still compatible with the formulation in both cases that the 1,2diphenylcyclobutanes are formed by way of the 1,4-diradical, 2. Since in 2 cyclization competes with bond rotation, the stereochemistry of the products will be dependent upon the conformation of 2 when it is initially produced. The results suggest that 2 derived from 1 has a very different initial conformation from that of 2 obtained by thermal "tail to tail" dimerization of styrene, and it appears that both of these initial conformations

are different from that of 2 formed by the photosenitized dimerization of styrene (37).

Experimental

Melting points and boiling points are uncorrected. Refractive indices were measured on a Bausch and Lomb Abbe-3L refractometer. Infrared spectra were recorded on a Beckman IR-7 recording spectrophotometer. The n.m.r. spectra were recorded on a Varian analytical spectrometer, Model A-60. Unless otherwise specified ca. 10% solutions in carbon tetrachloride containing tetramethylsilane as internal standard were used. Analyses by g.c. were carried out with an Aerograph-202 gas chromatograph using a 9.5 ft \times 1.4 in. stainless steel column packed with 20% SF-96 on 60/80 Chromosorb P. Ultraviolet spectra were recorded on a Bausch and Lomb Spectronic 600 spectrophotometer. Elemental analyses were performed by Mrs. Darlene Mahlow.

cis-3,6-Diphenyl-1,2-dicarbethoxy-1,2,3,6tetrahydropyridazine (3)

This material was prepared according to the method of Alder and Niklas (38) by the addition of diethyl azodicarboxylate to 1,4-diphenylbutadiene and had a m.p. 132–133°. Reported (38) m.p., 132°.

cis-3,6-Diphenyl-1,2-dicarbethoxyhexahydropyridazine (4)

The Diels-Alder adduct, 3, was hydrogenated in ethanol using platinum oxide at 30 p.s.i. at room temperature. The syrupy liquid remaining after filtering the catalyst and removing the solvent was taken up in the minimum amount of methanol. Water was added until the solution just became turbid. The crystals which were deposited on allowing the solution to stand at 0° overnight were recrystallized in the same manner, m.p. 83-87°. Reported (38) m.p., 87°. Further recrystallization from methanol water did not improve the melting point. The n.m.r. spectrum (CDCl₃) showed absorption at τ 2.45–3.18 (multiplet with a strong, sharp absorption at τ 2.98, 9.96H) for the phenyl protons, at τ 4.60 (broad, 1/2 width = 17 c.p.s., 1.0H) and τ 5.03 (broad, 1/2 width = 10 c.p.s., 1.0H) for the benzylic protons, at τ 5.85 and 6.10 (a pair of overlapping quartets, J = 7.0 c.p.s., 4.0H) for the methylene protons of the carbethoxy groups, at τ 7.8-8.5 (broad multiplet, 4.0H) for the methylene protons of the ring and τ 8.76 (a pair of closely overlapping triplets, J = 7.0 c.p.s., 6.0H) for the protons of the methyl groups.

cis-3,6-Diphenyl-1-carbethoxyhexahydropyridazine (8)

A solution of 10 g (0.0254 mole) of 4 and 11.5 g (0.2 mole) of potassium hydroxide in 100 ml absolute ethanol was boiled under nitrogen for 6 h. A fine white precipitate had formed. The solvent was removed under vacuum and the remaining residue stirred in ether. The precipitate was filtered and dried, yield 11.0 g. The precipitate was taken up in water and the resulting solution acidified with acetic acid. There was effervescence and an oil separated which solidified on standing. The solid was taken up in ether, solution dried over magnesium sulfate, and then pentane was added. On cooling 5.0 g (53%) of crystals were deposited, m.p. 59–60°.

Can. J. Chem. Downloaded from www.nrcresearchpress.com by 115.124.4.34 on 11/09/14 For personal use only. The infrared spectrum (KBr) showed N—H absorption at 3420 cm^{-1} and absorption at 1695 cm^{-1} for the carboethoxy group.

The n.m.r. spectrum showed absorption at $\tau 2.9$ (multiplet, 10.0H) for the phenyl protons, at $\tau 4.65$ (broad, 1.0H) for the benzylic hydrogen at C-6, at $\tau 5.20$ (broad, exchanges with D₂O, 0.95H) for the amine proton, at $\tau 5.85$ (quartet, J = 7 c.p.s., 2.0H) for the methylene protons of the carbethoxy group, at $\tau 6.22$ (broad multiplet, 1.0H) for the benzylic proton at C-3, at $\tau 7.6-8.1$ (broad multiplet, 2.0H) and at $\tau 8.15-8.41$ (broad multiplet $\tau 8.74$ (triplet, J = 7.0 c.p.s., 3.0H) for the protons of the methylene protons of the ring, and $\tau 8.74$ (triplet, J = 7.0 c.p.s., 3.0H) for the protons of the methyl group.

Anal. Calcd. for $C_{19}H_{22}O_2N_2$: C, 73.52; H, 7.14; N, 9.03. Found: C, 73.66; H, 6.88; N, 8.98.

cis-3,6-Diphenyl-3,4,5,6-tetrahydropyridazine (1)

A solution of 3.75 g (0.095 mole) of 4 and 7.5 g (0.13 mole) of potassium hydroxide in 17.5 ml methanol was boiled for 4 h and then cooled. Twenty-five ml of water were added to the reaction mixture and the resulting solution was acidified under nitrogen with acetic acid. There was effervescence and an oil separated. The mixture was stirred for 30 min and was then made alkaline to phenolphthalein with aqueous potassium hydroxide. Potassium carbonate was added to this mixture until the aqueous layer became saturated. The resulting mixture was extracted with ether and the ether layer was dried over potassium carbonate. All these operations were carried out under nitrogen. After drying, the loosely stoppered ether solution was allowed to stand overnight. Long flat crystals were formed. Concentration of the mother liquor yielded further crystals, total yield 1.9 g, m.p. 109-112° with decomposition. Recrystallization from benzene-octane yielded 1.75 g (75%) of plates, m.p. 112-113° with gas evolution. Reported (1) decomp. at 110° with gas evolution.

This material's facile isomerization to the hydrazone, 9, made characterization difficult. It was stable in redistilled hydrocarbon solvents and methanol when the glassware containing its solutions had been carefully neutralized. The n.m.r. spectrum has been given in the text. The u.v. spectrum showed maximum absorption at 285 mµ, log ϵ 2.45 and at 385 mµ, log ϵ 2.56. Reported (1) λ_{max} (cyclohexane) 287 mµ, log ϵ 3.49 and 387 mµ, log ϵ 2.89. Material prepared in this way contained less than 2% of the hydrazone, 9, on the basis of its absorbance at 285 mµ.

3,6-Diphenyl-2,3,4,5-tetrahydropyirdazine (9)

A small quantity of **1** was dissolved in carbon tetrachloride and in a few minutes, fine, needle-shaped crystals formed, m.p. 157–158°, λ_{max} (methanol) 285 mµ, log ε 4.14. Reported (1) m.p. 157–159°, λ_{max} (chloroform) 292 mµ, log ε 4.19. Solutions of this material in ethylbenzene did not evolve any gas upon prolonged heating at 100°, and it could be recovered quantitatively.

cis-1,2-Diphenylcyclobutene (cis-10)

cis-1,2-Diphenylcyclobutene (20) (250 mg), m.p. 53-54°, reported (20) m.p. 53-54°, was hydrogenated at atmospheric pressure in methanol solution with 5% palladium on charcoal. The hydrogenation was inter-

rupted after one mole had been consumed. The catalyst was filtered and the solvent removed to give an oil which solidified at 0°. This was recrystallized twice from methanol at -20° to yield 180 mg (72%) crystals, m.p. 37–38°. Reported (21) m.p. 38–39°. The n.m.r. spectrum showed absorption at τ 2.8–3.3 (multiplet centered at τ 3.10, 10.0H) for the phenyl protons, at τ 6.06 (broad multiplet, 2.02H) for the benzylic protons, and at τ 7.57 (multiplet, 4.0H) for the methylene protons).

trans-1,2-Diphenylcyclobutane (trans-10)

A solution of 45 mg of *cis*-10 and 100 mg potassium *t*-butoxide in 5 ml anhydrous dimethyl sulfoxide was heated on a steam bath for 15 min. The reaction mixture was diluted with water and the resulting mixture extracted with 10 ml carbon tetrachloride. The organic layer was dried and the solvent removed. The residue was distilled in a microdistillation apparatus to give 37 mg of an oil. Analysis by g.c. showed that no starting material (*cis*-10) or 1,4-diphenylbutane were present in the product. The n.m.r. spectrum showed absorption at $\tau 2.90$ (singlet, 10.0H) for the phenyl proton, at $\tau 6.51$ (multiplet, 1.9H) for the methylene protons, in excellent agreement with the reported (21) n.m.r. spectrum.

Product Studies

All operations and reactions involving 1 were carried out using glassware which had been cleaned with a mixture (3:1) of concentrated sulfuric acid and nitric acid, rinsed several times with distilled water, soaked for several hours with dilute ammonium hydroxide solution, and finally dried at 130° .

Benzene- d_6 solutions 0.033 M in 1 were placed in n.m.r. sample tubes and degassed with 3 freeze-thaw cycles to 10⁻³ mm. The tubes were sealed and then heated at the appropriate temperature for 10 half-lives of decomposition. The n.m.r. spectra of the solutions were then taken and were found to be superimposable upon the spectrum of a benzene- d_6 solution of styrene, cis-10 and trans-10 present in the molar ratio 57.5:28.0:14.5 and in a concentration corresponding to 100% decomposition of 1. No absorption attributable to the hydrazone, 9, could be detected. Quantitative relative product yields were determined by analyzing the contents of the tubes by g.l.c. using temperature programming from 100 to 180° at 4°/min and a helium flow rate of 60 ml/min. The only products detected were styrene, cis-10, and trans-10. These were identified by comparison of their relative retention times with authentic samples. No trace of 1-phenyltetralin could be found at the time where authentic material was eluted. The product distributions, corrected using molar response factors, are given in Table II.

Determinations of the absolute product yields from the decomposition of 1 in benzene and in styrene were made on runs carried out as described above. After decomposition was complete a measured amount of chlorobenzene was added to each tube, the contents mixed, and analyzed by g.c. as above. The relative thermal response factors used are chlorobenzene, 100; styrene, 96; *cis*-10, 153; *trans*-10, 163. Solvent was then completely removed from the samples at reduced pressure and the residue was taken up in methanol. The amount of hydrazone, 9, present was estimated by measuring the absorbance of the methanol solutions at 285 mu. The results are presented in Table III.

Kinetics of Decomposition of 1

The rates of nitrogen evolution from solutions of 1, ca. 0.1 M in ethylbenzene, were measured using an apparatus and a procedure similar to that described by Petersen et al. (39). At 64.7° insufficient nitrogen was evolved and plots of log $(V_{\infty} - V_{t})$ showed curvature after one half life. Rate constants were determined from the slopes of plots of log ($V_{\infty} - V_t$) vs. time. For runs at 64.7° initial slopes and the theoretical values for V_{∞} were used. The results are summarized in Table I.

Polymerization of Styrene in the Presence of 1

The rate of polymerization of styrene in the presence of 1 was measured by the dilatometric method described in the accompanying paper (24). The results are given in Table IV.

Control Experiments

A sample of cis-10, together with some diphenylmethane as an internal standard, was heated at 140° in a degassed benzene solution for 18 h. Analysis by g.c. of the solution after heating showed no change had taken place. No trace of styrene or of trans-10 could be detected.

A sample of the hydrazone, 9, was heated in benzene solution at 98° for 39 min. Analysis by g.c. after heating showed the presence of no materials other than the starting compound. Another sample of 9 was heated at 80° in ethylbenzene solution for 24 h in the apparatus used for measuring nitrogen evolution. No nitrogen was evolved.

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