1,4-Diphenyl-1,4-butadiyl Diradicals from Thermolysis of *cis*- and *trans*-3,6-Diphenyl-3,4,5,6-tetrahydropyridazine^{1,2}

KARL R. KOPECKY AND JOSÉ SOLER

Department of Chemistry, University of Alberta, Edmonton, Alberta T6G 2G2 Received January 10, 1974

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Reduction of 3,6-diphenyl-2,3,4,5-tetrahydropyridazine with sodium amalgam in ethylene glycol at 130° produces a 1:2 mixture of *cis*- and *trans*-3,6-diphenylpiperidazine (*cis*- and *trans*-4) from which *trans*-4 was obtained by fractional crystallization. Oxidation of *cis*- and *trans*-4 with oxygen gave *cis*- and *trans*-3,6-diphenyl-3,4,5,6-tetrahydropyridazine (*cis*- and *trans*-1). For thermolysis of *trans*-1 at 62.5° $E_a = 25.3 \pm 1.1$ kcal/mol and $\Delta S^{\pm} = 0.4 \pm 3$ e.u. At 63° the relative yields of styrene, *cis*- and *trans*-1,2-diphenylcyclobutane (*cis*- and *trans*-7) formed from *cis*-1 are 55.3, 30.1, and 18.6% and those formed from *trans*-1 are 59.1, 1.7, and 39.2%, respectively. For the 1,4-diphenyl-1,4-butadiyl diradical from thermolysis of *cis*-1 $k_{cleav}/k_{rot} = 1.1$ and $k_{cyc}/k_{rot} = 1.5$ whereas for that of *trans*-1 $k_{cleav}/k_{rot} = 10$ and $k_{cyc}/k_{rot} = 14$. At 205° *cis*-7 decomposes to yield a 4.8:1 ratio of styrene: *trans*-7. This is near the ratio expected if the initial geometries of the diradicals produced from *cis*-1 and *cis*-7 are similar.

KARL R. KOPECKY et JOSÉ SOLER. Can. J. Chem. 52, 2111 (1974).

La réduction da la diphényl-3,6-tétrahydro-2,3,4,5-pyridazine avec l'amalgame de sodium dans l'éthylène glycol à 130° donne un mélange de *cis*- et *trans*-diphényl-3,6-piperidazine (le *cis*- et *trans*-4) dans le rapport 1:2. A partir de ce mélange le *trans*-4 a été obtenu par crystallization fractionnée. L'oxidation du *cis*- et *trans*-4 par l'oxygène donne le *cis*- et *trans*-diphényl-3,6-tétrahydro-3,4,5,6-pyridazine (le *cis*- et *trans*-1). Pour la thermolyse du *trans*-1 à 62.5° on a trouvé $E_a = 25.3 \pm 1.1$ kcal/mol et $\Delta S^{\pm} = 0.4 \pm 3$ cal/mol. A 63° les rendements relatifs de styrène, de *cis*- et *trans*-diphényl-1,2-cyclobutane (le *cis*- et *trans*-7) formés à partir du *cis*-1 sont 55.3, 30.1 et 18.6% et ceux, formés à partir du *trans*-1, sont 59.1, 1.7 et 39.2% respectivement. Pour le diradical diphényl-1,4-butadiyl-1,4 provenant de la thermolyse du *cis*-1 on a obtenu $k_{rupturc}/k_{rotation} = 1.1$ et $k_{cyclization}/k_{rotation} = 1.5$ et pour le diradical provenant du *trans*-1 les valeurs sont $k_{rupture}/k_{rotation} = 10$ et $k_{cyclization}/k_{rotation} = 14$. A 205° le *cis*-7 se décompose en donnant un mélange de styrène:*trans*-7 dans le rapport 4.8:1. Ceci est presque le rapport attendu si les géométries initiales des diradicaux produit à partir du *cis*-1 et du *cis*-7 sont voisines.

Recently, *cis*-3,6-diphenyl-3,4,56-tetrahydropyridazine, *cis*-1, was prepared and thermolized in connection with a study of the mechanism of the thermal initiation of styrene polymerization (1). Because of interest in the stereochemistry of azoalkane decompositions (2) and in reactions of 1,4-diradicals (3) *trans*-1 has been prepared and thermolyzed. The relative rates of rotation, cyclization, and decomposition to styrene of the 1,4-diphenyl-1,4-butadiyl diradicals derived from *cis*- and *trans*-1 can be determined now.

Results

The preparations of *trans*-1 and of related compounds are outlined in Scheme 1. Of the

several methods which were used to reduce 3,6diphenyl-2,3,4,5-tetrahydropyridazine 3 the one which gave the most useful yields of trans-3,6diphenylpiperazine, trans-4, was treatment of 3 with sodium amalgam in ethylene glycol at 130°. A mixture containing cis- and trans-4 in a $\sim 1:2$ ratio together with unreacted 3 was formed. This mixture could be separated readily by chromatography of the monocarbomethoxy derivatives, cis- and trans-1-carbomethoxy-3,6-diphenylpiperidazine, cis- and trans-5, and 2-carbomethoxy-3,6-diphenyl-2,3,4,5-tetrahydropyridazine 6 which were formed by treatment of the crude reaction mixture with methyl chloroformate. Saponification of cis- and trans-5 followed by decarboxylation afforded the pure hydrazines. These were oxidized readily by oxygen to the azo compounds. Pure trans-4 could be obtained also from the reduction of 3 by fractional crystallization.

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Scheme 1

Examination by t.l.c. of the crude monocarbomethoxy derivatives *cis*- and *trans*-5 obtained by treatment of the hydrazines *cis*- and *trans*-4 separately with methyl chloroformate showed that each isomer, and, therefore, the corresponding azo compound, was contaminated with undetectable amounts (<0.5%) of the other.

The assignment of stereochemistry to *cis*- and *trans*-1 is based on the assumption that the Diels-Alder adduct 2 of *trans*,*trans*-1,4-diphenyl-1,3-butadiene and diethyl azodicarboxylate, in which the phenyl groups are *cis* (4), is converted without isomerization to *cis*-1. Therefore, the isomeric azo compound, which is obtained from the major product of the reduction of 3, must

be *trans*-1. In support of this conclusion the n.m.r. spectrum of *trans*-1 has a much more simple pattern than does that of *cis*-1 as would be expected from the higher symmetry of *trans*-1. The spectrum of *trans*-1 has a sharp singlet for the phenyl protons at τ 2.7 and one set of signals for the methylene protons centered at τ 8.1, whereas that of *cis*-1 has two broad multiplets for the phenyl protons between τ 2.4 and 2.9 and two sets of multiplets for the methylene protons centered at τ 7.9 and 8.7.

The rates and activation parameters of thermolysis of *cis*- and *trans*-1 given in Table 1 indicate that *trans*-1 thermolyzes about 5-6times as rapidly as does *cis*-1. The difference in the rates of decomposition of *cis*- and *trans*-1 is

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TABLE 1. Kinetic data for the	ermolysis ^a of <i>cis</i> - a	and <i>trans</i> -1 in eth	vlbenzene
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Compound	Temperature (°C)	$\frac{k_{\rm obs} \times 10^4}{({\rm s}^{-1})}$	% N2	% 30	$\frac{k_{\text{corr}} \times 10^{4^{\circ}}}{(\text{s}^{-1})}$
trans-1 ⁴	62.4 62.6 44.8 44.8 80.0	5.53 5.30 0.730 0.633	95 95 92 94	1 2 5.5 5.5	5.48 5.20 0.690 0.600 34.9 ^e
cis-1	64.7 79.5				1.0 ^r 5.6 ^r

^aFor cis-1 at 79.5° $\Delta H^{\neq} = 26.7 \pm 1.2 \text{ kcal/mol}, \Delta S^{\neq} = 2.4 \pm 4 \text{ e.u.}$ (1). For trans-1 at 62.5° $\Delta H^{\neq} = 24.6 \pm 1.1 \text{ kcal/mol}, \Delta S^{\neq} = -0.4 \pm 3 \text{ e.u.}$ ^bDetermined from the u.v. spectrum of the solution after thermolysis. ^ck_{corr} = k_{obs} × 0.01 %-hydrocarbon. ^dSolvent contained 2% ethyldiisopropylamine. ^eExtrapolated. ^fFrom ref. 1.

TABLE 2. Product distribution in the thermolysis of cis- and trans-1 in benzene

		Relative yields (mol %)"		
Compound	Temperature (°C)	Styrene	cis-7	trans-7
cis-1	280°	66.8	21.3	11.9
	133	61.3	24.9	13.7
	63	55.3	30.1	14.6
trans-1	280 ^b	66,5	2.0	31.4
	133	61.7	1.9	36.4
	63	59.1	1.7	39.2

^aThe values are averages of at least two separate runs, each analyzed in triplicate. Errors are estimated to be $\pm 0.5\%$. ^bTemperature of the injection port of the gas chromatograph into which solutions of *cis*- and *trans*-1 were injected.

greater than has been observed with diastereomeric pairs of acyclic azo compounds (5). The enthalpies of activation for the thermolysis of cis- and trans-1 and that (27.5 kcal/mol) of trans-3,5-diphenyl-1-pyrazoline (6) are considerably lower than that (32 kcal/mol) of the acyclic analogue 1,1'-diphenylazoethane (7). It may be that the factors which cause acyclic cis azo compounds to thermolize much more rapidly than their trans isomers (8) also affect the thermolysis of these cyclic azo compounds.

The product distributions obtained on thermolysis of *cis*- and *trans*-1 are given in Table 2. That of cis-1 agrees well with values obtained previously (1, 9). Styrene and cis- and trans-1,2diphenylcyclobutane, cis- and trans-7, account for >98% of the starting materials in each case. A small amount, <0.5%, of another product, reported to be 1-phenyltetralin (9), was detected from both isomers but not identified. In addition, $\sim 1\%$ of hydrazone was formed in

 $C_6H_5CH = CH_2 +$ cis- or trans-1 \rightarrow



those reactions which were carried out in solution at 133 and 63°.

The thermolysis of cis-7 produces styrene and trans-7 (10). These experiments were not made under conditions suitable for comparison with the results of the thermolysis of *cis*- and *trans*-1 so that the thermolysis of cis-7 was reexamined. At 205° in benzene the decomposition of 0.1 Mcis-7 is 45% complete after 1 h. The ratio of styrene to trans-7 is 4.8 and falls slowly to 4.7 after 9.5 h when 2% of cis-7 remain. This ratio of styrene to trans-7 is somewhat higher than the reported ratio of $\sim 4:1$ obtained at 165° (10c). 2114

The rate of disappearance of cis-7 at 205° is $\sim 1 \times 10^{-4} \text{ s}^{-1}$ which compares well with a value of $1.1 \times 10^{-4} \text{ s}^{-1}$ calculated from the reported activation parameters (10c). Control experiments showed that after 1 h at 205° negligible amounts of *trans*-7 would have decomposed to styrene and that negligible amounts of styrene would have polymerized or dimerized to *trans*-7.

Discussion

Thermolysis of cis- and trans-1

Although the styrene produced from thermolysis of cis- and trans-1 might be formed by a concerted, thermally allowed route (11) cis- and trans-7 definitely are not formed in the same way. There is only a small effect of temperature on the ratio of cleavage to cyclization products in the thermolysis of both azo compounds. This would be unlikely if the styrene were formed by a concerted route directly from the azo compounds while cis- and trans-7 were formed by another pathway. Such different modes of decomposition would very likely have quite different activation parameters. Thus the azo compounds appear to decompose by only one path. Recent evidence for one bond cleavage in certain azo compounds (8b and c, 12) makes it necessary to consider such a process here. There is evidence from the effect of pressure on the rate of thermolysis of cis-1 that both C-N bonds are breaking simultaneously (9). Also, the relative amounts of *cis*and trans-7 formed from the two azo compounds indicate that these materials are not formed by intramolecular radical displacement of N_2 (13) in a species, such as 8, in which only one C-N

 $H \xrightarrow{CHC_6H_5} H \xrightarrow{CHC_6H_5} H \xrightarrow{H} \xrightarrow{C} H \xrightarrow{C} H$

bond is broken. Otherwise, one might expect more *trans*-7 to be formed from *cis*-1 than is observed since this would require fewer overall rotations than would the formation of *trans*-7 from *trans*-1 by such an internal displacement. The results from the thermolysis of *cis*-7 indicate that the diradical produced from this material, which cannot contain nitrogen, must have

properties very similar to the material formed initially from *cis*-1. If the same initial diradical were produced from thermolysis of both *cis*-1 and *cis*-7 one can predict from the data in Table 2 that the ratio styrene: *trans*-7 formed from *cis*-7 at 205° should be ~5.1. This is quite close to the actual value of 4.8. Thus, it is quite likely that all the products of thermolysis of *cis*- and *trans*-1 are formed by way of 1,4-diphenyl-1,4butadiyl diradicals. The calculations below assume that these are formed directly by simultaneous cleavage of both C—N bonds.

Reactions of the Diradicals

The diradicals formed by simultaneous cleavage of both C-N bonds will have initial conformations at least approximating those given in Scheme 2. That formed from thermolysis of *cis*-7 will have the initial conformation as shown for *cis*-DR. It is most probable that the ratio of conformers of trans-DR formed by interconversion of cis-DR is different from that formed directly from trans-1 and that these two conformers undergo the several reactions indicated with somewhat different rate constants. The relative rates of interconversion, cleavage, and cyclization given in Table 3 were calculated (14) with the assumption that both conformers of trans-DR undergo these reactions with the same rates. This may distort the values of the relative rates a bit but there seems to be no other way of handling the data. However, this should still allow a good comparison of the relative rates of reaction of *cis*- and *trans*-DR to be made.

The rate constants k_1 and k_2 are the rate constants for the interconversion of one diradical into the other. Since rotation about either the C_1 — C_2 or the C_3 — C_4 bond will interconvert the diradicals the actual rate constants for rotation about one of these bonds are $\frac{1}{2}k_1$ and $\frac{1}{2}k_2$. Thus, for each diradical the rate of cyclization to the cyclobutane is faster than the rate of rotation about the C_1 — C_2 or C_3 — C_4 bonds by factors of ~14 for trans-DR and ~1.5 in cis-DR at 63°. The ratio of the rate of cleavage to the rate of rotation is $k_4/\frac{1}{2}k_2 \sim 10$ for *trans*-DR but that for *cis*-DR is only $k_5/\frac{1}{2}k_1 \sim 1$. Certainly the suggestion (15) that barriers to rotation might be greater than barriers to cleavage in singlet 1,4-diradicals is not generally applicable.

For both of the diradicals the rate of rotation of the radical center is much smaller relative to the rate of cyclization (coupling) than it is for

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C₆H₅ Н Н ЪH C₆H₅ and/or trans-1 cis-1 - H н́ Ċ₆H₅ Ċ₆H₅ cis-DR trans-DR cis-7 Styrene trans-7

TABLE 3. Relative rates^a of interconversion, cyclization, and cleavage of the 1,4-diphenyl-1,4butadiyl diradicals derived from cis- and trans-1^b

SCHEME 2

					k_{1}/k_{6}
Temperature (°C)	k_5/k_6	k_4/k_3	k_2/k_3	k1/k6	k_2/k_3
63	0.56 ± 0.01	0.73 ± 0.03	0.15 ± 0.01	1.27 ± 0.04	8.8 ± 0.6
133	0.78 ± 0.01	0.81 ± 0.02	0.21±0.01	1.57 ± 0.02	7.4 ± 0.4
280°	1.02 ± 0.04	1.00 ± 0.03	0.31 ± 0.02	1.85 ± 0.04	6.0 ± 0.5

^eRate constants are those depicted in Scheme 2. ^bErrors determined from estimated experimental errors in Table 2. Only values of product distributions from present work were used.

caged radical pairs formed from thermolysis of acyclic azo compounds whose structures are otherwise closely analogous to those of cis- and trans-1 (2b and c). It has been suggested that diradicals from cyclic azo compounds cyclize faster than caged radical pairs from acyclic azo compounds couple because the latter are born with an intervening nitrogen molecule, which must diffuse away before coupling can occur, while the former are not (2b). Superimposed on this could be the slower rate of rotation about the C_1 -- C_2 and C_3 -- C_4 bonds which may be intrinsic to singlet diradicals (15).

Another way of analyzing the relative rates of rotation and cyclization in cis- and trans-DR is by means of the retention ratios p, trans-7/cis-7 from trans-1; q, cis-7/trans-7 from cis-1; and their product, pq (16). Selectivity is lost as temperature increases: pq = 48 at 63°, 36 at 133°, and 28 at 280°. The product pq derived from the present system is much higher than those derived from diradicals produced by alkene dimerization (3a, 17) but not as high as that obtained on thermolysis of meso- and dl-3,6-diethyl-3,6-dimethyl-3,4,5,6-tetrahydropyrazoline 9 (3b) where pq > 1800 at 145°. Steric hindrance to cyclization of the diradicals formed from *meso*- and *dl*-9 must be as great or greater



than that of cis- and trans-DR, especially of trans-DR, so that it is necessary to look elsewhere for the large difference in the pq's. Two possible factors come to mind, both of which result from the stabilization of the benzylic diradicals by delocalization of the odd electrons into the benzene rings. First, such diradicals would be less reactive and might couple more slowly than unstabilized diradicals. Second, this delocalization could cause the alkenic contributing structure (15), for example, 10, of the diradicals to be less important in cis- and trans-DR than it is in the aliphatic diradicals thus decreasing the barrier to rotation about the C_1 — C_2 and C_3 — C_4 bonds in the former relative to the latter diradicals.

The 1,4-diphenyl-1,4-butadiyl diradical can be produced in yet a third way, as well as from cis- and trans-1 and cis-7. Pure styrene dimerizes slowly to form cis- and trans-7 in a ratio of $\sim 1:2$ at 110° (18) by a reaction which is inde-

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TABLE 4. Nuclear magnetic resonance spectra^{*a*} of some 3,6-diphenylpyridazine derivatives

	Protons					
Compounds	Aromatic	Benzylic	Methylene	Other		
cis-1 ^b	2.4–2.85(m)	$6.0(m, w_{1/2} = 20)$	7.8-8.1(m,2H) 8.5-8.9(m,2H)			
trans-1 ^b	2.7(s)	$5.4(m, w_{1/2} = 18)$	7.8-8.3(m)			
cis-4	2.5-2.8(m)	$5.95(m, w_{1/2} = 8)$	7.9-8.1(m)	NH: 6.7(s)		
trans-4	2.65(s)	$6.2(m, w_{1/2} = 15)$	7.7-8.2(m)	NH:6.6(s)		
3	2.2-2.4(m), 2.6-2.8(m)	5.9(d of d), J = 5.5 and 8.5	7.2–7.5(m,2H) 7.7–7.8(m,2H)	NH:4.4(b)		
cis- 5	2.6-2.8(m)	4.5(t, J=4, 1H), 6.1(t, J=6, 1H)	7.5–7.9(m,2H) 8.0–8.3(m,2H)	NH:5.5(s) CH ₃ :6.2(s)		
trans-5	2.5-2.8	4.75(t, J = 5, 1H) 5.90(t, J = 5, 1H)	7.8-8.0(m)	NH:5.7(s) CH₃:6.35(s)		
6	2.15–2.35(m) 2.6–2.9(m)	$4.4(m,w_{1/2}=8)$	7.7-7.9(m)	CH ₃ :6.2(s)		

^aIn deuteriochloroform; chemical shifts in τ values, J and half-widths in Hz; s = singlet, d = doublet, t = triplet, m = multiplet, b = broad. ^bIn carbon tetrachloride containing some ethyldiisopropylamine.

pendent of the process which leads to the thermal polymerization of styrene (10c, 19). It is very doubtful that this dimerization can be a concerted reaction (20). It has been noted (1) that the initial conformation of the diradical produced from styrene must be different from that formed from *cis*-1. The present results show that it is different from that from trans-1 as well. It thus appears that an extended (21) form of the diradical is produced initially. If this then converted to cis- and trans-DR with equal probability cis- and trans-7 would be formed in a 1:2 ratio which is the same as would be obtained from the thermolysis of equal amounts of cisand trans-1.

It should be mentioned that theoretical calculations indicate that there is no energy minimum for the simple 1,4-butadiyl diradical between cyclobutane and two molecules of ethylene (22). If such a situation were generally true for 1,4-diradicals calculation of the relative rates of reaction for such species would be meaningless (23). However, there is such a large body of data on reactions which involve 1,4diradicals which can be analyzed in a reasonable and self-consistent manner by assuming that the diradicals behave as true intermediates that we feel justified in continuing this practice for cisand trans-DR as well.

Experimental

Melting points were taken with a Reichert hot-stage melting point apparatus and are uncorrected. Nuclear

magnetic resonance spectra were recorded on Varian analytical spectrometers, Models A-60 and A-56/60, and are listed in Table 4. Ultraviolet spectra were recorded on a Bausch and Lomb Spectronic 600 spectrophotometer which was calibrated with holmium oxide. Analyses by gas chromatography were carried out with an Aerograph 202 gas chromatograph using a 9.5 ft $\times \frac{1}{4}$ in. stainless steel column packed with 20% SF-96 on 60-80 Chromosorb P. Elemental analyses were performed by Mrs. Darlene Mahlow and Mrs. Andrea Dunn.

3,6-Diphenyl-2,3,4,5-tetrahydropyridazine (3)

A solution of 32 g (0.57 mol) of potassium hydroxide in 100 ml methanol was added to 15 g (0.04 mol) cis-3,6diphenyl-1,2-dicarboethoxy-1,2,3,6-tetrahydropyridazine 2 (24) dissolved in 175 ml boiling methanol. The resulting mixture was heated under reflux under nitrogen for 24 h and cooled. The white precipitate which formed was collected on a filter and then dissolved in 150 ml water. The stirred solution was acidified with acetic acid and stirred at 20° for 1/2 h. The mixture was then made alkaline to phenolphthalein with a solution of potassium hydroxide. After a short while the mixture was decolorized with a few drops of ammonium chloride solution. The precipitate was filtered, washed with water, and dried to give 7.6 g of 3, m.p. 160-161° (lit. (25) m.p. 157-159°).

Evaporation of the methanolic filtrate and treatment of the resulting solid as above gave another 1.4 g of 3, m.p. 155-159°. Total yield 95%.

trans-3,6-DiphenyIpiperidazine (trans-4)

A solution of 20 g (0.085 mol) of 3 in 1 l of ethylene glycol at 130° was stirred vigorously while three portions of 50 g (0.26 g-atom) each of 4% sodium amalgam were added at 20 min intervals. Stirring was continued for 30 min after the last addition and the clear yellow solution was decanted from the mercury and cooled to 0° under nitrogen. After 3 h the precipitate was filtered and dried to give 5.2 g of material which was mainly unreacted 3 together with some trans-4. The filtrate was diluted with

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700 ml of concentrated ammonium chloride solution and the resulting mixture extracted twice with 1 l ether. The extracts were combined, concentrated, and the concentrate cooled to 0° under nitrogen. The crystals of the hydrazine were filtered. The filtrate was successively concentrated, cooled, and freed from precipitate several more times in this way until hydrazone 3 began to precipitate. A total of 5.6 g, 28%, hydrazine was collected which was recrystallized from 1:1 ether-pentane to give cotton-like crystals, m.p. 134–135°. A sample of this material was converted to the monocarbomethoxy derivative *trans*-5 with methyl chloroformate. The crude product was shown by t.l.c. to be free of *cis*-5. Control experiments showed that 0.5% *cis*-5 could have been detected clearly.

Evaporation of the mother liquor yielded 5.3 g of a mixture of hydrazone 3, *trans*-4. and oily *cis*-4. Total recovery of material was 85%.

Hydrazine *trans*-4 is stable as a solid if kept at -10° but in solution is oxidized rapidly by air. Samples of *trans*-4 can also be separated from hydrazone and *cis*-4 by column chromatography on silica gel using ether as eluent.

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

A solution of 650 mg *trans*-4 in 200 ml benzene was stirred in the dark under oxygen in a neutralized 500-ml erlenmeyer flask for 2 h. The solution was concentrated to 125 ml and 300 ml heptane was added to the concentrate. The resulting solution was concentrated to about 200 ml and cooled to 0° to give 285 mg yellow crystals of *trans*-1, sinter 80-85°, m.p. 94-95° with gas evolution; λ_{max} (cyclohexane) 382 nm, ϵ 166. The absorption peak is broader, half width 40 nm, than that of *cis*-1 and an absorption tail extends to the visible, ϵ_{400} 0.56.

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Solid *trans*-1 can be stored at -10° for several weeks without change. In solution it is reasonably stable in hydrocarbon solvents if neutralized glassware is used. It isomerizes slowly to the hydrazone 3 in methanol but does so within a minute in carbon tetrachloride or chloroform. Addition of small amounts of ethyldiisopropylamine to the latter solvents stops the isomerization for at least a day.

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

This material was prepared as described previously (1). Its properties were identical to those reported except for the u.v. spectrum which was now found to be λ_{max} (cyclohexane) 377 nm, ε 178, half-width 30 nm, (lit. (1) λ_{max} (cyclohexane) 385 nm, ε 363). Recently reported values of the u.v. spectrum of *cis*-1 also appear to be in error (26). As reported previously this material is also very readily isomerized to the hydrazone 3. As in the case of *trans*-1 addition of ethyldiisopropylamine to solutions of the azo compound drastically reduces the rate of isomerization.

cis-1-Carbomethoxy-3,6-diphenylpiperidazine (cis-5) and trans-1-Carbomethoxy-3,6-diphenylpiperidazine (trans-5)

The hydrazone 3 (4.5 g) in 250 ml ethylene glycol was treated with 55 g 4% sodium amalgam as described above. The cooled reaction mixture was poured into 250 ml concentrated ammonium chloride solution and the resulting mixture extracted with 500 ml ether. The ether layer was washed with 2×100 ml ammonium chloride solution, dried (MgSO₄), and filtered. The filtrate was cooled to 0° under nitrogen, 35 ml pyridine was added followed by dropwise addition with stirring of 30 ml methyl chloroformate in 25 ml ether. This mixture was

allowed to warm to 20°, stirred for 1 h, and filtered. The filtrates were washed with 3×100 ml saturated sodium chloride solution, dried, and concentrated. The residue was taken up in 50 ml benzene and the resulting solution concentrated. This was repeated until the pyridine was removed. Finally, the oily residue was chromatographed on 400 g silica gel using 1:1 ether-hexane as eluent. First eluted after 3 was *cis*-5 which was crystallized from ether to give 0.8 g, 15%, of product, m.p. 61-63°.

Anal. Calcd. for $C_{18}H_{20}N_2O_2$: C, 72.95; H, 6.80; N, 9.45. Found: C, 72.69; H, 6.85; N, 9.57.

A solution of 510 mg cis-5 and 1.0 g potassiumhydroxide in 5 ml ethanol was heated to reflux for 4 h under nitrogen, cooled, and diluted with 20 ml water. The resulting solution was treated with 1.5 ml acetic acid, stirred for $\frac{1}{2}$ h, and made alkaline with potassium hydroxide solution, and then extracted with 100 ml ether. The dried (MgSO₄) ether solution was concentrated to give 347 mg (88%) cis-4 as an oil that could not be induced to crystallize. A portion of this oil was dissolved in a small amount of ether and the resulting solution was allowed to stand overnight. The precipitate which formed was collected, washed with cold ether and shown to be pure cis-1 (m.p. mixture m.p., n.m.r. spectrum).

Further elution of the chromatography column removed *trans*-5 and 6 together which were separated by fractional crystallization from ether (*trans*-5 crystallizes rapidly, 6 more slowly) to give 1.1 g (18%) of *trans*-5, m.p. 121–122°, and 0.95 g (17%) of 6.

Anal. Calcd. for $C_{18}H_{20}N_2O_2$ (*trans-5*): C, 72.95; H, 6.80; N, 9.45. Found: C, 73.22; H, 6.79; N, 9.53.

Using the same procedure as used for the preparation of *cis*-5, 380 mg *trans*-5 was saponified using potassium hydroxide and the resulting salt decarboxylated with acetic acid. The reaction mixture was made alkaline with potassium hydroxide and the resulting precipitate filtered, washed with water, and dried under vacuum to give 280 mg (90%) of *trans*-4, identical (m.p., mixture m.p., n.m.r. spectrum) with material prepared as described above. A portion of the material was dissolved in ether and the solution allowed to stand overnight. This solution was shaken with water, dried and concentrated. The resulting crystals were shown to pure *trans*-1 (m.p., mixture m.p., and n.m.r. spectrum).

2-Carbomethoxy-3,6-diphenyl-2,3,4,5-tetrahydropyridazine (6)

A solution of 0.5 g 3 in a solution of 10 ml ether and 10 ml pyridine was treated with 2 ml methyl chloroformate in 5 ml ether as described above for the preparation of *cis*- and *trans*-5. The product, 0.12 g (20%) was isolated as described above and recrystallized from ether, m.p. 112-113.5°.

Anal. Calcd. for C₁₈H₁₈N₂O₂: C, 73.44; H, 6.16; N, 9.52. Found: C, 73.32; H, 6.27; N. 9.52.

Product and Rate Studies

Decompositions of *cis*- and *trans*-1 and the analysis of the decomposition products were carried out as described (1). Samples of *cis*- and *trans*-1 were decomposed and analyzed in parallel. The results are listed in Table 2.

The rate of decomposition of *trans*-1 was measured in the same way as described (1) for *cis*-1 except that the solvent, ethylbenzene, contained 2% ethyldiisopropylamine which greatly decreased the amount of isomerizaTABLE 5. Product distribution from thermolysis of cis-1,2-diphenylcyclobutane, cis-7, in benzene at 205°

	Product Distribution (relative mol %)				
Гime (h)	cis-7	trans-7	Styrene		
0.17	94.7	Trace	5.3		
1	55.4	7.7	36.8		
2	34.2	11.1	54.6		
4	17.8	14.4	67.7		
9.5	1.9	17.3	80.7		
21		17.8	82.2		

tion of *trans*-1 to the hydrazone 3. The amount of hydrazone formed was determined by u.v. spectroscopy.

Thermolysis of cis-1,2-Diphenylcyclobutane (cis-7)

Benzene solutions 0.1 *M* in *cis*-7 and in chlorobenzene as internal standard were placed in several heavy-walled 1-mm i.d. tubes and degassed to 10^{-3} mm. The tubes were sealed and placed in a bath of boiling benzyl alcohol (205.5 ± 0.5°). Tubes were removed after appropriate intervals and the contents were analyzed by gas chromatography. Results are presented in Table 5.

Control experiments showed that after 17 h at 205° a benzene solution initially 0.2 *M* in styrene contained 67% of the initial styrene, 1.5% *trans*-7, and no *cis*-7. Another experiment indicated that after the same treatment a solution initially 0.1 *M* in *trans*-7 now contained 70% of the initial amount of *trans*-7 and 17% styrene.

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