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

Azo Compounds.[1] A Seven-membered Cyclic Azo Compound

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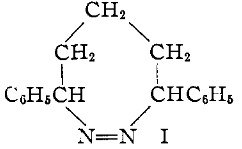
The seven-membered cyclic azo compound 3,7-diphenyl-1,2-diaza-1-cycloheptene (I) has been prepared. Spectral and kinetic properties of I support the postulated *cis* nature of the azo link in a seven-membered ring. The decomposition of I gave mixtures of *cis*- and *trans*-1,2-diphenylcyclopentane and 1,5-diphenyl-1-pentene, the products expected from non-stereospecific combination or disproportionation of the 1,5-diphenyl-1,5-pentadiyl biradical. At lower decomposition temperatures, isomerization of I to the cyclic hydrazone, 3,7-diphenyl-1,2-diaza-2-cycloheptene (IV), was found to compete with normal thermal decomposition. A reason for previous[3] unsuccessful attempts to prepare I is offered.

As part of a continuing program to synthesize cyclic azo compounds which would thermally decompose to give moderately active biradicals in solution, we have synthesized the seven-membered cyclic azo compound 3,7-diphenyl-1,2-diaza-1-cycloheptene (I).



I

The small ring size of I forces a *cis* configuration on the azo link and enables a comparison of the spectral and kinetic data of I with linear, *trans*-azo compounds of similar structure. It was also of interest to study the decomposition products of such a cyclic azo compound in order to compare the relative amounts of coupled and disproportionated products from biradicals of this type with those of monoradicals in solution.

The chemistry of large, cyclic, bis-azo compounds previously has been studied by Overberger and Lapkin.[4] These large (24, 28) membered bis-azo compounds can exist with a *trans*-azo configuration and comparison of spectral and kinetic data support a *trans*-azo link. For example, the 24-membered cyclic bis-azo compound, 3,12,15,24-tetraphenyl - 1,2,13,14 - tetraaza - 1,13 - cyclotetracosadiene[4] exhibits an azo absorption at 360 mμ, log ϵ 2.06 and decomposes at 110.8° with a rate constant of 7.6×10^{-5} sec.$^{-1}$. Similarly the *trans*, acyclic azo compound azo-1-phenylethane exhibits[5] an absorption maximum at 355 mμ, log ϵ 1.77 and decomposes at 110.3° with a rate constant of 16.9×10^{-5} sec.$^{-1}$. A smaller cyclic azo compound (6-, 7- or 8-membered) should require a *cis* configuration for the azo link. Recently, a six-membered cyclic compound of type I has been prepared by Cohen, *et al.*,[6] by a Diels–Alder reaction between 1,4-diphenyl-1,3-butadiene and azo-dicarboxylic ester followed by hydrogenation and saponification. The product, a six-membered cyclic azo compound, 3,6-diphenyl-3,4,5,6-tetrahydropyridazine, exhibited an abnormal azo absorption, λ_{max} 387 mμ, log ϵ 2.89, which is attributed to the *cis* configuration forced on the azo bond.

A compound of type I with only one phenyl group also has been prepared recently by a similar method.[7] A five-membered cyclic azo compound prepared by a Diels–Alder reaction of cyclopentadiene with azo-dicarboxylic ester has been described[8]; however, no spectral or kinetic data on this interesting bicyclic azo compound were reported.[8] Two eight-membered cyclic azo compounds[1b,9] also have been reported. The eight-membered cyclic azo analog of I exhibits[1b] λ_{max} 368 mμ, log ϵ 1.65; the interpretation of these values is under investigation. The absorption for the eight-membered[1b] analog of I (at 368 mμ) lies almost midway between a *trans*, acyclic azo absorption (355 mμ)[5] and the absorption of a *cis*-azo link in the six- and seven-membered rings (387 and 389 mμ). These data would indicate that an eight-membered cyclic azo compound is the smallest ring which will permit the azo link to relieve some of the strain associated with a *cis*-azo configuration. Larger rings (24,28-membered)[4] have azo bonds which assume the more stable *trans* configuration.

This paper will report the synthesis, kinetic and spectral properties and decomposition products of the seven-membered cyclic azo compound (I).

A. Preparation of the Azo Compound.—Previous unsuccessful attempts to synthesize I provided a starting point. Thus, Overberger and Monagle[3] reported the synthesis of the precursor hydrazine, 3,7-diphenyl-1,2-diazacycloheptane (III); however, its apparently anomalous oxidation behavior suggested that III was of unusual stability or that I was of high instability. These workers employed the following sequence of reactions in an attempt to synthesize I.

Compound III was reported[3] as a liquid whose infrared spectrum exhibited an N–H stretching frequency. Analysis of III supported a hydrazine structure, but when a variety of methods were employed[3] in an effort to oxidize III to the azo compound I, none was successful. Only bromine in aqueous acid gave a reaction, yielding the unex-

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(1) (a) This is the 21st 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, J. G. Lombardino and R. G. Hiskey, THIS JOURNAL, **79**, 6430 (1957). (b) For a preliminary report of this work, see C. G. Overberger, J. G. Lombardino, I. Tashlick and R. G. Hiskey, *ibid.*, **79**, 2662 (1957).

(2) This paper comprises a portion of a dissertation presented by Joseph G. Lombardino in partial fulfillment of the requirements for the degree of Doctor of Philosophy in the Graduate School of the Polytechnic Institute of Brooklyn.

(3) C. G. Overberger and J. J. Monagle, THIS JOURNAL, **78**, 4470 (1956).

(4) C. G. Overberger and M. Lapkin, *ibid.*, **77**, 4651 (1955).

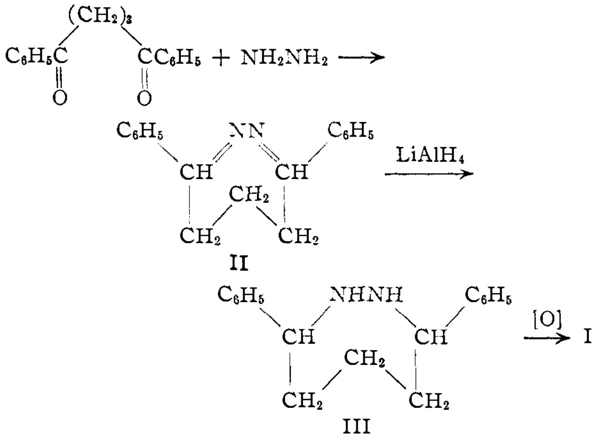
(5) S. G. Cohen, S. J. Groszos and D. R. Sparrow, *ibid.*, **72**, 3947 (1950).

(6) S. G. Cohen, S. Hsiao, E. Saklad and C. H. Wang, *ibid.*, **79**, 2661 (1957); **79**, 4400 (1957).

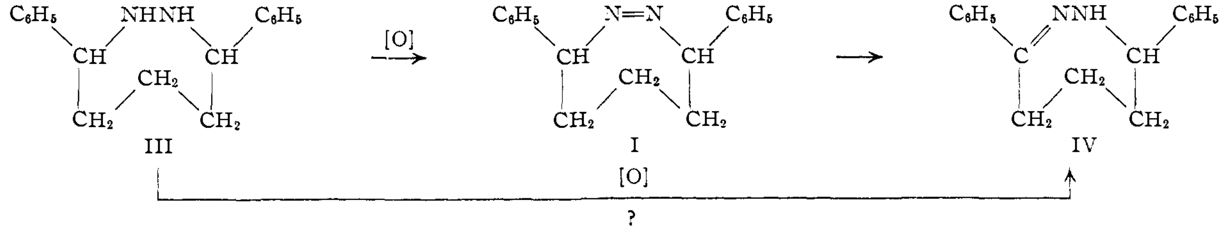
(7) R. J. Levin, M. Kuznin and U. Shabarov, *Moscow Univ. Bull.*, **1**, 170 (1957).

(8) R. Criegee and A. Rimmelin, *Ber.*, **90**, 414 (1957).

(9) J. M. Zanden and G. DeVries, *Rec. trav. chim.*, **75**, 1159 (1956).

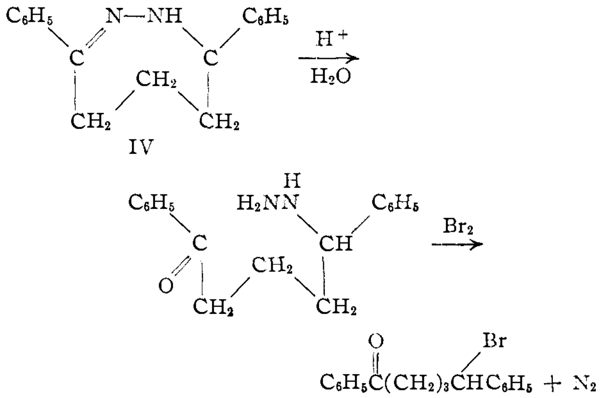


pected δ-bromo-δ-phenylvalerophenone.[3] On repeating the experimental procedure to prepare III, a liquid was obtained which gave an infrared spectrum identical to that reported by Monagle.[10] This liquid resisted oxidation with mercuric oxide in ethanolic solution at 60° for 29 hours. However, this same sample exhibited an ultraviolet spectrum characteristic[6,11] of a hydrazone; λ_{max}^{EtOH} 238 mμ, log ϵ 3.99; λ_{max} 290 mμ, log ϵ 3.73. To demonstrate an unsaturated structure, the liquid was catalytically reduced and then immediately oxidized with mercuric oxide to give the azo compound I. The liquid reacted slowly with a methanolic hydrochloric acid solution of 2,4-dinitrophenylhydrazine to give a high melting orange derivative, confirming the presence of a hydrazone or a ketonic hydrolysis product.



The cyclic azine, 3,7-diphenyl-1,2-diaza-2,8-cycloheptadiene (II), was reduced catalytically using a palladium-on-carbon catalyst. Reduction with one mole of hydrogen gave the cyclic hydrazone, 3,7-diphenyl-1,2-diaza-2-cycloheptene (IV) (λ_{max}^{EtOH} 238 mμ, log ϵ 3.94; λ_{max} 290 mμ, log ϵ 3.71) which reacted slowly with an acid solution of 2,4-dinitrophenylhydrazine to give a high melting orange derivative. Reduction of the cyclic azine II with two moles of hydrogen gave a liquid hydrazine III which was oxidized immediately with mercuric oxide at room temperature to yield the desired cyclic azo compound I. Any attempts to distil or derivatize III, even under a nitrogen atmosphere, gave the cyclic hydrazone IV, indicating that III is sensitive to air oxidation. In one experiment where the cyclic hydrazine III was deliberately exposed to the air, small amounts of the cyclic azo compound I were isolated, these results being consistent with those of Overberger and Lapkin[4] and Cohen and co-workers[5] who report the air oxidation of cyclic 1,2-hydrazines to give cyclic azo compounds. The isomerization of the cyclic azo compound I to the conjugated cyclic hydrazone IV in ethanolic solution has been shown to occur at room temperature (Fig. 2) suggesting that the cyclic hydrazine III is air oxidized to the azo compound I which then isomerizes.

It would appear, then, that the hydrazone III is extremely sensitive to air oxidation and the sample previously reported[3] as III was only hydrazine when freshly distilled under nitrogen, and may have contained some hydrazone IV. If allowed to remain exposed to air for any length of time, the mixture probably was converted to almost pure hydrazone IV which then resisted any further chemical oxidation. The reported[3] bromine oxidation of supposedly pure III gave only δ-bromo-δ-phenylvalerophenone when carried out in strongly acid aqueous solution. If this reported oxidation was carried out on a sample which actually contained large amounts of the hydrazone IV, then acid hydrolysis of IV should give a ketohydrazine which on bromine oxidation would give the observed bromoketone. The latter reaction is well known for phenylhydrazines; its value for replacement of a benzylhydrazine with bromine is currently under investigation.



Confirming the observations of the facile air oxidation of the cyclic 1,2-hydrazine III to a conjugated cyclic hydrazone are the results of Hinman[11] who attempted the synthesis of various 1,2-disubstituted hydrazines. Attempts to distil several 1-benzyl-2-alkylhydrazines yielded only alkyl hydrazones of benzaldehyde. Ultraviolet spectra of freshly distilled "hydrazines" indicated the presence of hydrazone (λ_{max} 289 mμ) with the absorption increasing with time.

Cohen[6] also has reported the facile formation of the cyclic hydrazone 3,6-diphenyl-4,5,6,7-tetrahydropyridazine in one attempted synthesis of

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(10) J. J. Monagle, Ph.D. Dissertation, Polytechnic Institute of Brooklyn, 1955.

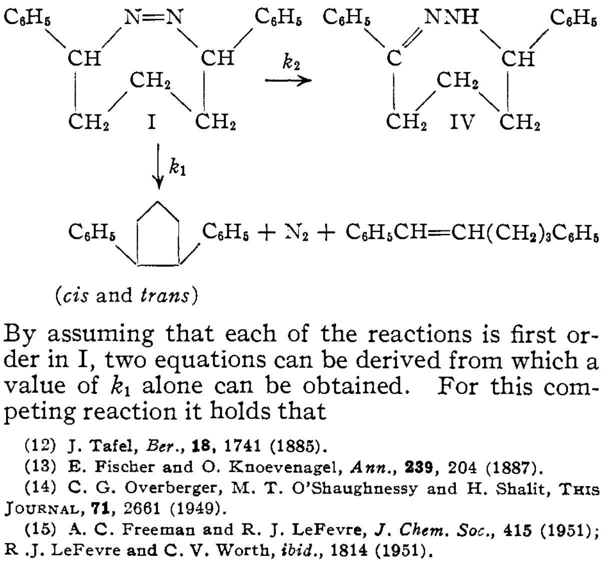
(11) R. L. Hinman, This Journal, 79, 414 (1957).

3,6-diphenyl-3,4,5,6-tetrahydropyridazine, the six-membered analog of the cyclic azo compound I. The six-membered cyclic hydrazone exhibited[6] a λ_{max} 292 mμ, log ϵ 4.19. Previous workers[12,13] have found that mercuric oxide oxidation of 1-benzyl-2-phenylhydrazine yields only the phenylhydrazone of benzaldehyde, again illustrating the greater stability of a conjugated hydrazone over the isomeric azo compounds. The normal azo absorption found in acyclic azo compounds at approximately 355 mμ[5] has been displaced in I to 389 mμ, presumably due to the *cis* configuration of the azo link in I. Cohen, *et al.*,[6] have reported a shift in the azo absorption in a six-membered cyclic azo compound to λ_{max} 387 mμ, log ϵ 2.89; again the shift of the maximum to longer wave lengths is probably due to the *cis* configuration of the azo link. These workers have shown that thermal decomposition of the six-membered cyclic azo compound 3,6-diphenyl-3,4,5,6-tetrahydropyridazine, at 125° yields 30% of the cyclic hydrazone 3,6-diphenyl-4,5,6,7-tetrahydropyridazine and 7% of styrene.[6]

B. Thermal Decomposition of the Azo Compound. I. Procedure.—The general procedure for measuring rates of decomposition has been described previously.[14]

II. Results.—The rate of decomposition of the cyclic azo compound I in xylene at 100.2° (4.04×10^{-3} sec.$^{-1}$) is approximately 100-fold faster than that found for the linear, *trans*-azo-1-phenylethane[15] (5.45×10^{-5} sec.$^{-1}$) (100°).[5] The energy of activation as calculated from decompositions of I carried out at five different temperatures was 29.7 ± 0.2 kcal. per mole, smaller by almost 3 kcal. per mole than that reported for azo-1-phenylethane.[4] Apparently the *cis* configuration of the azo link in I makes this azo compound considerably less stable than a structurally similar linear, *trans*-azo compound.

(a) **Kinetics.**—The thermal decompositions of I at temperatures below 100° were complicated by a competing reaction, that is, isomerization of I to the cyclic hydrazone, 3,7-diphenyl-1,2-diaza-2-cycloheptene (IV).



(*cis* and *trans*)

By assuming that each of the reactions is first order in I, two equations can be derived from which a value of k_1 alone can be obtained. For this competing reaction it holds that

$$-\mathrm{d}I/\mathrm{d}t = (k_1 + k_2)I$$

on integration and substitution of volumes of nitrogen

$$\ln \frac{V_\infty}{V_\infty - V_t} = (k_1 + k_2)t \qquad (1)$$

In this equation V_∞ represents the final experimentally observed volume of nitrogen. For these competing reactions it further follows that

$$B/C = k_1/k_2$$

where B is moles of nitrogen evolved and C is the moles of hydrazone IV at any time t. At the completion of the reaction

$$B_\infty/C_\infty = k_1/k_2 \qquad (2)$$

From equation 1, a plot of ln $V_\infty/V_\infty - V_t$ *versus* time gives a line whose slope is $(k_1 + k_2)$. From equation 2, using the observed final volume of nitrogen for B_∞ and determining C_∞ by difference, a value for the ratio k_1 to k_2 can be derived. Thus, using equations 1 and 2 enables one to determine a value for k_1 alone. Table I summarizes these values for k_1 at the various decomposition temperatures. Linear plots of equation 1 at the various temperatures are shown in Fig. 1.

TABLE I

DECOMPOSITION OF I IN XYLENE SOLUTION

Temp., °C.	Nitrogen evolved, %	k_1,[a] sec.$^{-1}$	Half-life, min.
61.0	68.5	3.80×10^{-5}	305
70.0	88	1.34×10^{-4}	76
80.0	71.5	4.27×10^{-4}	27
89.3	87	1.59×10^{-3}	7.3
100.2	94	4.04×10^{-3}	2.8

[a] The maximum average deviation in these rate constants amounts to no more than ±5% as determined from duplicate experiments.

(b) **Products.**—The products of the thermal decomposition of I were those expected from the intermediate biradical V

$$C_6H_5\underset{\cdot}{C}H(CH_2)_3\underset{\cdot}{C}HC_6H_5$$

V

Intramolecular coupling of V should give 1,2-diphenylcyclopentane while disproportionation of V should give 1,5-diphenyl-1-pentene. Accordingly, quantitative mixtures of authentic 1,5-diphenyl-1-pentene and 1,2-diphenylcyclopentane were prepared and their infrared spectra compared with the spectra of the mixtures of decomposition products of I. For the decompositions carried out at higher temperatures, where essentially quantitative nitrogen had been evolved, the spectra of the mixtures of products and of authentic materials were identical. An absorption assigned to 1,5-diphenyl-1-pentene at 10.35 mμ was shown[1a] to give a semi-quantitative estimate of this olefin (23–27%).

In the decomposition experiments carried out at lower temperatures, where less than the theoretical nitrogen was evolved (Table I), evidence for the formation of the cyclic hydrazone IV was obtained. The products reacted slowly with an acid solution of 2,4-dinitrophenylhydrazine and the products slowly developed carbonyl absorptions in the infrared, giving support for the presence of the hydrazone or its ketonic hydrolysis product. An ultra-

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[12] J. Tafel, *Ber.*, **18**, 1741 (1885).

[13] E. Fischer and O. Knoevenagel, *Ann.*, **239**, 204 (1887).

[14] C. G. Overberger, M. T. O'Shaughnessy and H. Shalit, THIS JOURNAL, **71**, 2661 (1949).

[15] A. C. Freeman and R. J. LeFevre, *J. Chem. Soc.*, 415 (1951); R. J. LeFevre and C. V. Worth, *ibid.*, 1814 (1951).

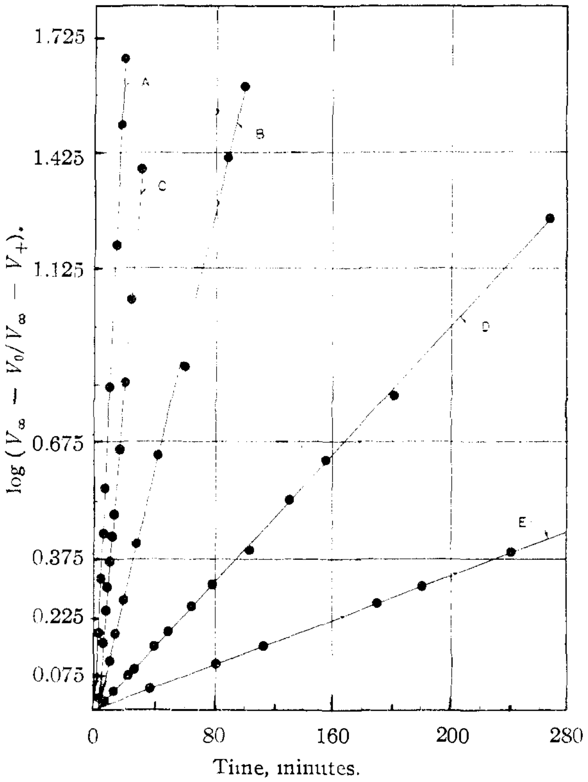

Fig. 1.—Decomposition of 3,7-diphenyl-1,2-diaza-1-cycloheptene (I): A, 100.2; B, 80°; C, 89.3°; D, 79°; E, 61°.

violet spectrum taken immediately on the products of decomposition at 80° showed a characteristic[6,11] ultraviolet absorption for a hydrazone with an absorption at 290 mμ sufficient to account for all of the azo compound I which had isomerized to the hydrazone IV.

In another experiment the mixture of products was chromatographed on alumina, the first few fractions yielding 65% of a mixture of *cis*- and *trans*-1,2-diphenylcyclopentane. An infrared spectrum of this mixture was identical with the spectrum of an authentic mixture of these compounds. The mixture of 1,2-diphenylcyclopentanes (*cis* and *trans*) gives added support for a biradical intermediate which would be expected to combine in a nonstereospecific manner. The white solid azo compound I decomposed in this work represented one of two possible diastereomers. One might favor a *cis* assignment for the phenyl groups in I since reduction of the precursor azine by catalytic means could fix a *cis* configuration on these large groups, although this should be regarded as a tentative suggestion.

A suggested mechanism[16] for the "abnormal" oxidation of 1,1-dibenzyl type hydrazines involves rearrangement of the oxidized hydrazine to the isomeric azo compound which then decomposes to give nitrogen and the reported hydrocarbon products.[16,17] For the oxidation of 1-amino-2,6-diphenylpiperidine,[1a,17] the azo intermediate could be the cyclic azo compound (I).[1a] However, since the oxidations of the hydrazine were rapid at 60°[1a] and I has now been shown to have a half-life of 305 minutes at 61°, this would rule out I as an intermediate. Furthermore, the cyclic products of the oxidation of *cis*- and *trans*-1-amino-2,6-diphenylpiperidine were formed stereospecifically,[1a] whereas decomposition of I gives mixtures of *cis*- and *trans*-1,2-diphenylcyclopentane.

Experimental[18]

Dibenzoylpropane azine (II) was prepared from dibenzoylpropane by the method of Overberger and Monagle,[3] m.p. 160–161.5° (m.p. 162.8–164.2°).[3] Four days under high vacuum were required to completely dry the material.

Reduction of Dibenzoylpropane Azine. (A) Lithium Aluminum Hydride.—The method of Overberger and Monagle[3] was employed, namely, lithium aluminum hydride in tetrahydrofuran and a viscous yellow-green liquid, b.p. 190° (1.0 mm.), $n^{24.2}$ 1.6218 was obtained (yellow-green liquid, b.p. 200° (2.0 mm.), $n^{21.5}$ 1.6189).[3] An infrared spectrum of this material was identical to that of the material prepared by Monagle[10]; an ultraviolet spectrum, however, would favor the assignment[6,11] of a cyclic hydrazone structure IV for this material; λ_{max}^{EtOH} 238 mμ, ε 9770; λ_{max} 290 mμ, ε 5420. This liquid resisted oxidation by mercuric oxide at 60° in ethanol for 29 hours. Treating the liquid with a methanolic hydrochloric acid solution of 2,4-dinitrophenylhydrazine yielded an orange derivative, m.p. 245–252° dec. Attempts to purify this derivative were unsuccessful.

The liquid was reduced for four hours with hydrogen over 10% palladium-on-carbon in tetrahydrofuran solution. After removal of the catalyst, the solution was immediately stirred with 3.5 g. of mercuric oxide for 12 hours. Filtration and removal of solvent yielded the solid azo compound I, m.p. 114° dec. gas evolution.

(B) **Catalytic Reduction.**—Catalytic reductions of the cyclic azine were successful only under the following conditions. To 6.75 g. (0.0272 mole) of recrystallized dibenzoylpropane azine dissolved in 150 ml. of dry, redistilled tetrahydrofuran was added 2.0 g. of 10% palladium-on-carbon (Baker and Co.) and the reaction mixture hydrogenated at 27 lb. for 26 hours in a Parr apparatus. At the end of this time two moles of hydrogen had been absorbed. The reaction was filtered and the filtrate used immediately in the oxidation (see below). In another experiment, the reduction product was evaporated to dryness under a nitrogen atmosphere and the residual liquid scanned in the ultraviolet region (approximately one hour elapsed from the time the dried liquid was weighed until the material was scanned in the ultraviolet), λ_{max}^{EtOH} 290, ε 1160. This absorption would suggest some hydrazone impurity even after this short exposure to air. The reduced material was shown to be susceptible to air oxidation by exposing it to the air for 24 hours and isolating some cyclic azo compound I, m.p. 114–115° dec., gas evolution. In another experiment, dibenzoylpropane azine was reduced using 10% palladium-on-carbon and one mole of hydrogen. The resulting liquid could not be distilled without decomposition. An ultraviolet spectrum was obtained on the crude product: λ_{max}^{EtOH} 290 mμ, ε 5100; λ_{max} 238 mμ, ε 8800, indicating that the material contained mostly cyclic hydrazone IV. This liquid reacted slowly with 2,4-dinitrophenylhydrazine in methanolic hydrochloric acid solution to give an orange solid, m.p. 233–243°. Attempts to purify this derivative were unsuccessful.

Oxidation of 3,7-Diphenyl-1,2-diazacycloheptane (V).—The filtrate of the catalytically reduced dibenzoylpropane azine (0.0272 mole), was immediately oxidized in a nitrogen atmosphere using 47.5 g. (0.22 mole) of mercuric oxide in an erlenmeyer flask stirred magnetically for 18 hours at room temperature. The green reaction mixture was then filtered through filter-aid (Celite) and the filtrate evaporated at 45° under vacuum in a nitrogen atmosphere. To the residual material was added 35 ml. of ethanol and the solution cooled in the freezer to yield 1.40 g. (21%) of a solid, m.p. 115° dec., gas evolution. An analytical sample, prepared by recrystallization from warm ethanol, was analyzed immediately.

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(16) C. G. Overberger and B. Marks, This Journal, **77**, 4104 (1955).

(17) C. G. Overberger, J. G. Lombardino and R. G. Hiskey, *ibid.*, **79**, 1510 (1957).

(18) All melting points are uncorrected. Analyses by Schwarzkopf Laboratories, New York, N. Y.

Anal.[18] Calcd. for $C_{17}H_{18}N_2$: C, 81.56; H, 7.25; N, 11.19. Found: C, 81.51; H, 7.01; N, 11.23.

This compound must be stored in the cold and in a dry state; $\lambda_{max}^{CHCl_3}$ 389 mμ, ε 127, λ_{max} 290 mμ, ε 166. As expected, the infrared spectrum did not show any strong characteristic absorptions for the azo group. The azo compound I was found to isomerize at room temperature in ethanolic solution to the hydrazone IV. Figure 2 shows the decrease in azo absorption (389 mμ) and increase in hydrazone absorption (290 mμ) with time when compound I is allowed to stand at room temperature in ethanolic solution.

Decomposition of 3,7-Diphenyl-1,2-diaza-1-cycloheptene (I).—The thermal decompositions of the cyclic azo compound I at various temperatures were carried out by the same procedure. As an example, the decomposition at 80.0° is described.

In a flask immersed in a constant temperature (±0.10°) oil-bath was placed 35 ml. of xylene and a stream of nitrogen gas was passed through the system for 30 minutes to deoxygenate the solvent. Then, 0.224 g. (0.000894 mole) of I was dropped into the flask by means of a glass "boat," the system was immediately sealed and stirring begun. Timing was begun with the first introduction of the azo compound. Evolved nitrogen was measured by displacing water from a calibrated buret. Nitrogen evolution ceased after 71.5% of the calculated amount had been evolved—this final volume was taken as V_∞. When no further nitrogen evolution was observed, the xylene was removed under vacuum and an ultraviolet spectrum determined on the residual liquid, λ_{max}^{EtOH} 290 mμ, ε 4010 (calculated by assuming that 28.5% of the products consist of the hydrazone 3,7-diphenyl-1,2-diaza-2-cycloheptene (IV) arising from isomerization of the azo compound I). An ether solution of the mixture of products was dried over magnesium sulfate. After removal of solvent, the residual liquid exhibited an infrared spectrum almost identical with a spectrum of an authentic mixture of *cis*- and *trans*-1,2-diphenylcyclopentane[19] and 1,5-diphenyl-1-pentene.[3] The intensity of the absorption at 10.35 μ indicated that 23% of the mixture[20] was 1,5-diphenyl-1-pentene.[1a]

In another decomposition, carried out at 61°, only 68.5% of the theoretical nitrogen was evolved. An infrared spectrum of the mixture of products indicated the presence of a carbonyl group (5.73 μ), probably arising from hydrolysis of the cyclic hydrazone IV. The mixture of products reacted with 2,4-dinitrophenylhydrazine to give a high melting (225–250°) orange derivative which could not be purified by recrystallization.

In another decomposition, carried out on a 0.80-g. (0.0032 mole) sample of I at 110°, approximately 100% of the theoretical nitrogen was evolved. The products were treated with 2,4-dinitrobenzenesulfenyl chloride in acetic acid solution,[1a] the solvent removed and the residual liquid extracted several times with dry Skellysolve B, b.p. 60–70°. The extracts were chromatographed through neutral alumina (Woelm, activity one). The first few fractions, on removal of solvent, yielded 0.46 g. (65%) of a mixture of *cis*- and *trans*-1,2-diphenylcyclopentane, m.p. 37–53°. An infrared spectrum of this mixture was identical to that of a mixture of authentic *cis*-1,2-diphenylcyclopentane, m.p. 47°, prepared according to Japp and Lander,[21] and authentic[19] *trans*-1,2-diphenylcyclopentane, m.p. 65°, obtained from mercuric oxide oxidation of *trans*-1-amino-2,6-diphenylpiperidine.[1a] Attempts to fractionally crystallize the mixture from ethanol–water yielded some *trans*-1,2-diphenylcyclopentane, m.p. 62–64° (65°)[19]; however, further crops were soft solids at room temperature.

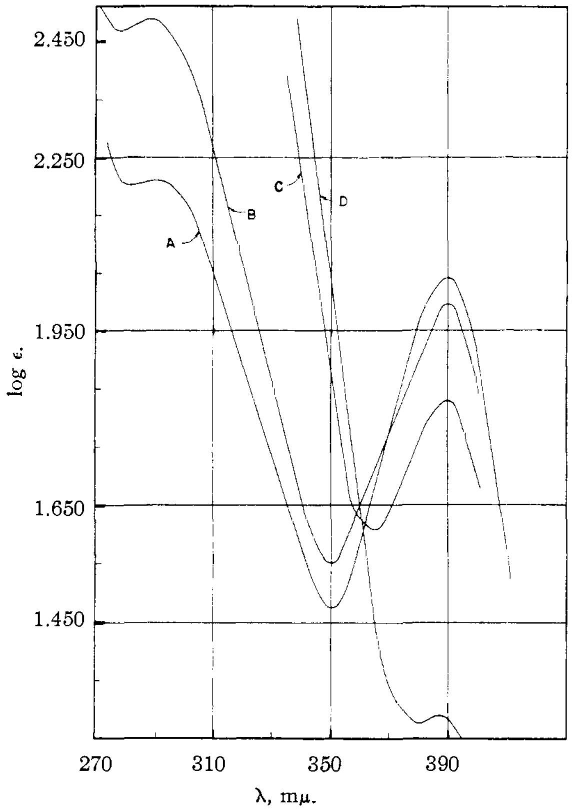

Fig. 2.—Isomerization of 3,7-diphenyl-1,2-diaza-1-cycloheptene (I) to the hydrazone IV: A, hydrazone IV; B, spectrum after 48 hours; C, spectrum after 194 hours; D, spectrum after 697 hours.

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[19] H. Wiedlich, *Ber.*, **71B**, 1601 (1938).

[20] The separation of similar mixtures has been described in reference 1a.

[21] F. Japp and G. Lander, *J. Chem. Soc.*, **71**, 131 (1897).