and 12.5 g. (0.122 mole) of acetic anhydride. The reaction mixture was sealed and heated to 100° in the constant temperature flask with refluxing distilled water for 72 hours. The mixture was processed in the same manner as was the solvolysis mixture; final distillation through the Oldershaw column yielded fraction 1, b. p. 39–130°, 3 ml.; fraction 2, b. p. 130–135°, 1.5 ml.; and fraction 3, b. p. 135–140°, 13.0 ml. The infrared spectra showed the presence of butyl acetate in all three fractions. The fractions were combined and a weighed sample was diluted with a weighed sample of spectro grade carbon tetrachloride. The infrared spectrum was taken in a 0.121-mm. cell using a 0.118-mm. cell containing pure carbon tetrachloride as the reference. Authentic mixtures of dibutyl ether and butyl acetate were prepared, brought to the same dilution with carbon tetrachloride and the infrared spectra were taken in the same cells. In this manner, it was estimated that approximately 2.3 ml. (2.0 g.) of butyl acetate was formed. No alcohol band was apparent.

Isotopic Dilution Experiment for Determination of Excess *n*-Butyl Acetate Produced in the Solvolysis.—In a constant temperature flask, 220 ml. of dibutyl ether was added to 20.0 g. (0.0771 mole) of I dissolved in 180 ml. of dry acetic acid. A neoprene stopper was wired on and the solvolysis was carried out under conditions identical to the previous solvolysis of I-*d*. Before processing the reaction mixture, however, 4.0835 g. of 1-butyl-1,1-d_2 acetate was added. The same procedure was used as before checking carefully for purity of the product with infrared techniques.

The butyl acetate fraction was analyzed for deuterium in the infrared using the analytical curve technique with standard mixtures. Since the ester contained 22.0 ±0.8% of 1-butyl-1,1-d_2 acetate, 14.5 ± 0.7 g. of butyl acetate was produced in the solvolysis. The theoretical yield is 8.96 g.; hence the yield is 162 ±8%.

Test for Solvolytic Cleavage of Diethyl Ether.—In 450 ml. of a mixture of 55% (by volume) of anhydrous diethyl ether and 45% of acetic acid was dissolved 23.5 g. (0.091 mole) of I to give an approximately 0.2 *M* solution. The reaction mixture was heated to 100° for 72 hours in a constant temperature flask using refluxing distilled water as the heating bath. After cooling and basification with aqueous sodium hydroxide in the usual manner, the aqueous layers were extracted with ether. The ether extracts were dried and distilled. A series of fractions were obtained which were shown to consist of ethanol, ethyl acetate, 1-butanol, *n*-butyl acetate and very probably *n*-butyl ethyl ether. The analysis was carried out by infrared spectroscopic comparison with authentic mixtures and by gas phase chromatographic analysis of the products and of authentic mixtures using a K and M Scientific Glassware Co. model 17A gas phase chromatograph. The column was packed with a 25% liquid partition of Dow–Corning Silicone grease on Celite (35/80 mesh, Johns–Manville Chromasorb). The chromatography was conducted at room temperature using helium flow rates of about 50 ml./min. and a filament current of 400 ma. A Varian Recorder, model G10, was used in conjunction with the instrument.

Control Run to Test for Cleavage of Diethyl Ether by *p*-Nitrobenzenesulfonic Acid.—Enough acetic anhydride was added to a 0.2 *M* solution of *p*-nitrobenzenesulfonic acid hydrate in 55% (by volume) anhydrous diethyl ether, 45% acetic acid to take up the calculated amount of water in the sulfonic acid. The reaction was conducted under the same conditions as the previous experiment and was processed in the same manner. Ethyl acetate was identified by comparison of its infrared spectrum with that of an authentic sample. Distillation yielded approximately 5 cc. which was contaminated with ethanol. A pure cut was obtained for the infrared comparison. From the residues, crystalline ethyl *p*-nitrobenzenesulfonate was isolated, m.p. 91.5–92.5° (lit.[14] m. p. 92–92.5°).

Anal.[12] Calcd. for $C_8H_9O_5NS$: C, 41.55; H, 3.92; N, 6.06. Found: C, 41.85; H, 3.96; N, 6.14.

Treatment of *n*-Butyl *p*-Nitrobenzenesulfonate with Tetrahydrofuran at 100°.—Commercial tetrahydrofuran was purified by refluxing 10 liters for 6 hours with 1.5 lb. of phosphorus pentoxide. The mixture was distilled and 7 liters (b. p. 65–66°) was collected. The distillate was distilled from sodium ribbon before use.

A solution of 10 g. of I in 130 ml. of tetrahydrofuran was maintained at 100° for 13 days in a constant temperature flask. After cooling, the reaction mixture was found to be acidic. The mixture was brought to about *p*H 7 by the addition of dilute sodium hydroxide solution. After removal of most of the tetrahydrofuran by distillation, 200 ml. of salt water was added and the aqueous solution was extracted 3 times with 100-ml. portions of ether. The combined ether extracts were dried with anhydrous sodium sulfate and the ether was evaporated. Only a black viscous liquid and carbonaceous material remained. Most of this residue was dissolved in hot benzene, but fractional additions of hexane caused only the separation of black tars. No tractable products could be obtained.

BERKELEY, CALIF.

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[14] R. E. Robertson, *Can. J. Chem.*, **31**, 589 (1953).

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

Azo Compounds.[1] Decomposition of Large Ring Azo Compounds

BY C. G. OVERBERGER, I. TASHLICK,[2a] M. BERNSTEIN[2b] AND R. G. HISKEY

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The rates of decomposition of the cyclic azo compounds (II, n = 6, 8, 10) have been determined at three temperatures. All three compounds were found to have activation energies for the decomposition and spectral properties similar to a linear analog, 1-azo-bis-1-phenylpropane. The decomposition of II, n = 8, in *cis*-stilbene yielded only a trace of adduct, while *cis*-stilbene scavenged 16% of the radicals from 1-azo-bis-1-phenylpropane, demonstrating a cage effect operating in the case of the diradicals produced.

In a continuation[3] of a study concerned with the preparation and properties of moderately active diradicals in solution[3] (A discussion of organic diradicals and their role in polymerization appears in reference 3), the results obtained with the 24-membered ring azo compound (II, n = 8), previously reported,[3] are compared with several other large ring azo compounds. This paper describes the preparation of 20-, 24- and 28-membered ring azo compounds (II, n = 6, 8, 10), the spectral properties of the corresponding azines and azo compounds, the determination of the rates of decomposition of the azo compounds at three temperatures and the decomposition of the 2,4-mem-

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[1] This is the 26th 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 I. Tashlick, THIS JOURNAL, in press.

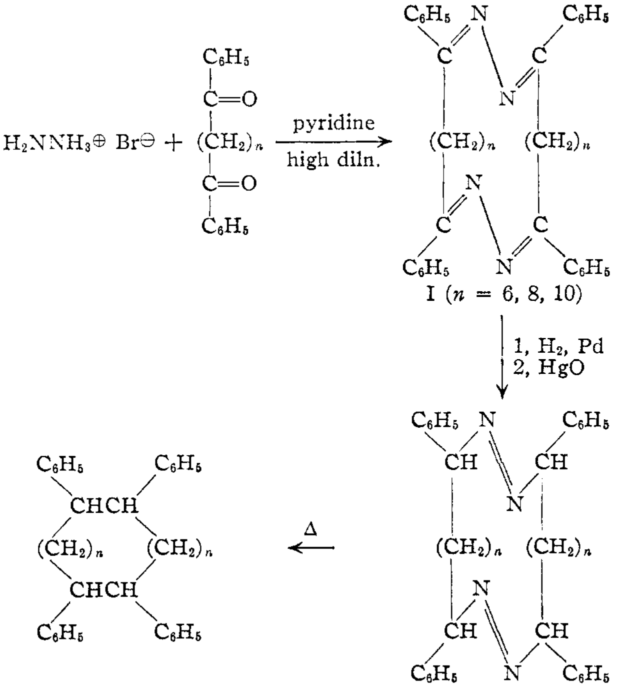
[2] (a) This paper comprises a portion of a thesis presented by Mr. I. Tashlick in partial fulfillment of the requirements for the degree of Doctor of Philosophy in the Graduate School of the Polytechnic Institute of Brooklyn. (b) This paper comprises a portion of a thesis presented by Mr. M. Bernstein in partial fulfillment of the requirements for the Bachelor of Science degree in the Polytechnic Institute of Brooklyn.

[3] C. G. Overberger and M. Lapkin, THIS JOURNAL, **77**, 4651 (1955).

bered ring azo compound (II, $n = 8$) in the presence of radical scavengers.

I. Synthesis of the Large Ring Cyclic Azo Compounds

A. Discussion.—The 24- and 28-membered ring azines used in this work were previously prepared[3] by the reaction of hydrazine hydrobromide with the corresponding ketones under conditions of high dilution. The ketones used were prepared by the Friedel–Crafts reaction of the diacyl chloride and benzene as described in reference 4 for 1,6-diphenyl-1,6-octanedione. In addition, the combined residues from several preparations of the 28-membered ring azine (I, $n = 10$), yielded a trace of yellow solid which analyzed correctly for a 14-membered ring azine.



I (n = 6, 8, 10)

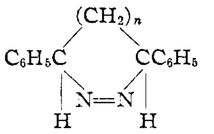
III (n = 6, 8, 10)

II (n = 6, 8, 10)

In developing a synthesis for the 24-membered ring azine (I, $n = 8$), Lapkin[5] had reported a study of the yields of product in the reaction of hydrazine salts with 1,10-diphenyl-1,10-decanedione under varying conditions. In the present work, additional modifications for the cyclization reaction were tried; thus 1,10-diphenyl-1,10-decanedihydrazone was prepared, and several unsuccessful attempts were made to cyclize this dihydrazone either by reaction with additional 1,10-diphenyl-1,10-decanedione or by intramolecular cyclization.

In the preparation of the azo compounds from the azine *via* the intermediate hydrazine, it was found that the product isolated from the hydrogenation was not always a pure azo compound and that oxidation of the intermediate hydrazine on "work up" was often incomplete. Decomposition of material melting at 128-130° led to yields of nitrogen ranging from 25 to 55% of the theoretical amount. Melting point proved to be an inadequate criterion of purity in this instance, since lower melting samples often were found to give higher yields of nitrogen than higher melting ones. This may be due to the fact that the melting points are actually decomposition temperatures, and the samples containing more azo compound would decompose faster.

In order to resolve this difficulty, the ultraviolet spectrum of freshly hydrogenated 24-membered ring azine was examined, and a marked change in absorption with time was noted. The optical density at 360 mμ (λ_{max} for the azo compound), initially 26% of the value for the pure azo compound, rises in 24 hours to a maximum, and then falls. These data are interpreted to mean that air is oxidizing the intermediate hydrazine to the azo compound, which in turn is isomerizing to a hydrazone. The hydrazone was not isolated but would be expected to absorb strongly at 290 mμ.[6] This would account for the large increase in absorption, at wave lengths shorter than 350 mμ, with time. Even after 24 hours, the time of maximum concentration of azo compound, some hydrazone was present as shown by the absence of the characteristic minimum at 302 mμ. When a dilute chloroform solution of pure 24-membered ring azo compound (II $n = 8$) was allowed to stand for 200 hr., the ultraviolet absorption indicated that isomerization to a hydrazone occurred at a slower rate. The 6-and 7-membered ring azo compounds (IV, n = 2, 3) have also been found to be readily tautomerized,[6,7] and their corresponding hydrazines were capable of autoxidation to the azo compounds. Hinman[8] found that attempts to isolate some 1-benzyl-2-alkyl hydrazines gave only the corresponding hydrazones, and other similar examples were cited. In view of the results with the cyclic azo compounds, it would seem reasonable that the azo conpounds are intermediates in the oxidation of these hydrazines to hydrazones.



IV, n = 2, 3, 4

The difficulties involved in the reduction of the large ring azines were previously discussed,[3] and it was found that the procedure previously employed gave insignificant yields with the 20-membered ring azine (I, $n = 6$). It was subsequently found that the use of palladium-on-charcoal in tetrahydrofuran easily reduced the entire series of cyclic azo compounds. The necessity for rapid oxidation of the intermediate hydrazine was met by immediate oxidation with mercuric oxide of the solution from the hydrogenation.

The ultraviolet spectral data of the 20-, 24- and 28-membered ring compounds are summarized in Table I.

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(4) H. Gilman and A. H. Blatt, "Organic Syntheses," Coll. Vol. II, John Wiley and Sons, Inc., New York, N. Y., 1943, p. 169.

(5) M. Lapkin, Ph.D. Thesis, Polytechnic Institute of Brooklyn, 1955.

(6) S. G. Cohen, S. Hsiao, E. Saklad and C. H. Wang, THIS JOURNAL, **79**, 4400 (1957).

(7) C. G. Overberger and J. G. Lombardino, *ibid.*, **80**, 3009 (1958).

(8) R. L. Hinman, *ibid.*, **79**, 414 (1957).

TABLE I

ULTRAVIOLET ABSORPTION MAXIMA OF THE LARGE RING CYCLIC AZO COMPOUNDS

	Azine (in methanol)		Azo (in chloroform)	
Ring size	λ_{max}, mμ	log ε	λ_{max}, mμ	log ε
20	270	4.53	359	2.02
24	270	4.57	360	2.06
28	271	4.56	360	2.05
Propiophenone derivatives	269	4.35	359	1.67

The ε-values in the range of 34,000 to 37,000 are in agreement with the value obtained and shown in the table for the linear analog, propiophenone azine ($\lambda_{max}^{95\%\ EtOH}$, ε 22,500).[9] In the comparison of data with the linear analogs the ε-values should be divided in half since the cyclic compounds contain two azine groups.

An independent value (found in this work) for the absorption of 1-azo-bis-1-phenylpropane[10] correlates with the cyclic compounds and the other linear homologs. Thus the cyclic azo compounds have the same maxima and very similar intensities of absorption, per azo group, as the linear analogs. Although the C=N absorption, in the infrared, of acetoneazine occurs at 6.04 μ and furfuralazine at 6.15 μ,[11] the 24- and 28-membered ring azines (I, $n = 8, 10$) have strong peaks at 6.25 and 6.38 μ. The same peaks are present in the 20-membered ring azine (I, $n = 6$) at 6.23 and 6.35 μ. In each case conversion to the azo compound causes the peak at 6.23 μ to diminish considerably in intensity while the one at 6.35 μ almost disappears. The infrared spectra of the 8-membered ring azines and azo compounds (IV, $n = 4$) and the azine and azo compounds derived from propiophenone show identical behavior. It would appear that these two bands are associated with the azine link in these particular compounds.

B. **Experimental.**[12] **1,10-Decanedicarboxylic Acid.**—The acid was prepared according to the procedure of Jones.[13] The benzoyl peroxide-catalyzed addition of hydrogen bromide to 443 g. (2.4 moles) of 10-undecenoic acid gave 380 g. (60%) of 11-bromoundecanoic acid, m.p. 50–51° (m.p. 49–50°, 66–70%).[13]

From 245.0 g. (0.92 mole) of 11-bromoundecanoic acid, there was obtained by nitrile substitution and subsequent hydrolysis 190 g. (90%) of 1,10-decanedicarboxylic acid, m.p. 127–128° (m.p. 121–124.5, 50%),[3] (m.p. 126°, 93%).[13]

Preparation of the α,ω-Dibenzoyl Alkanes.—All the diketones were prepared according to the procedure in reference 4 for 1,6-diphenyl-1,6-hexanedione.

(A) **1,8-Diphenyl-1,8-octanedione.**—From 75 g. of suberic acid (0.43 mole) there was obtained 107 g. (88%) of 1,8-diphenyl-1,8-octanedione, m.p. 90–91° (m.p. 91°, no yield reported[14]).

(B) **1,10-Diphenyl-1,10-decanedione.**—From 200 g. (0.84 mole) of sebacyl chloride there was obtained 235 g. (91%) of 1,10-diphenyl-1,10-decanedione, m.p. 94–95° (m.p. 94–96°, 75%).[3]

(C) **1,12-Diphenyl-1,12-dodecanedione.**—From 189 g. (0.82 mole) of 1,10-decanedicarboxylic acid there was obtained 200 g. (70%) of 1,12-diphenyl-1,12-dodecanedione, m.p. 97–98° (m.p. 98–99°, 68%).[3]

Preparation of the Large Ring Cyclic Azines.—These compounds were obtained by a slight modification of the procedure previously described[3] for the 24-membered ring azine (I, $n = 8$). A solenoid valve was used to control the addition every 30 seconds for a period of 5 days and instead of precipitating the crude azine with water and removing the resulting sticky solid by filtration with filter-aid, it was extracted with benzene and washed with water and dilute acid several times, and subsequently recovered from the benzene layer.

A. **3,10,13,20-Tetraphenyl-1,2,11,12-tetraaza-2,10,12,-20-cycloeicosatetraene (I, $n = 6$).**—From 20.34 g. (0.18 mole) of hydrazine monohydrobromide and 53.0 g. (0.18 mole) of 1,8-diphenyl-1,8-octanedione there was obtained 13 g. (25%) of yellow crystals, m.p. 169–170°, from acetone.

Anal. Calcd. for $C_{40}H_{44}N_4$: C, 82.71; H, 7.64; N, 9.65; mol. wt., 580. Found: C, 82.54; H, 7.44; N, 9.77; mol. wt., 582, 621 (ebullioscopic in acetone).

B. **3,12,15,24-Tetraphenyl-1,2,13,14-tetraaza-2,12,14,-24-cyclotetracosatetraene (I, $n = 8$).**—From 20.34 g. (0.18 mole) of hydrazine monohydrobromide and 58.0 g. (0.18 mole) of 1,10-diphenyl-1,10-decanedione there was obtained 11.4 g. (20%), m.p. 145–146°, yellow crystals (m.p. 146–147°, 22%).[3]

C. **3,14,17,28-Tetraphenyl-1,2,15,16-tetraaza-2,14,16,-28-cycloöctacosatetraene (I, $n = 10$).**—From 20.34 g. (0.18 mole) of hydrazine monohydrobromide and 63.1 g. (0.18 mole) of 1,12-diphenyl-1,12-dodecanedione there was obtained 9.3 g. (15%), m.p. 111–112° (m.p. 108–109.5°, 26% crude[3]). An elementary analysis and Rast molecular weight was reported in reference 3.

Anal. Calcd. for $C_{48}H_{60}N_4$: mol. wt., 693. Found: mol. wt., 741 (ebullioscopic in butanone).

D. **Isolation of 3,14-Diphenyl-1,2-diaza-2,14-cyclotetradecadiene.**—A 30-g. portion of the residual yellow oil remaining from the isolation of the 28-membered ring azine (I, $n = 10$) was washed with 80 ml. of boiling methanol. The methanol was decanted and the oily residue was extracted with 100 ml. of boiling petroleum ether (b.p. 39–50°). The sticky yellow residue from the petroleum ether solution was decolorized with carbon and recrystallized from petroleum ether to give 75 mg. of long yellow needles, m.p. 90–95°. After three recrystallizations from petroleum ether (b.p. 39–50°), there was obtained 47 mg., m.p. 96–98°; a mixed melting point determination with 28-membered ring azine m.p. 111–112°, melted at 92–94°.

Anal. Calcd. for $C_{24}H_{30}N_2$: C, 88.22; H, 8.73; N, 8.09; mol. wt., 346. Found: C, 83.53, 83.35; H, 8.62, 8.76, N, 7.73; mol. wt., 297 (Rast), 359 (ebullioscopic in butanone).

The infrared spectrum was different from that of the 28-membered ring azine (I, $n = 10$) but showed strong peaks at 6.24 and 6.34 μ.

Preparation of 1,10-Diphenyl-1,10-decanedihydrazone.—A solution of 38.9 g. (0.12 mole) of 1,10-diphenyl-1,10-decanedione and 14.5 g. (0.246 mole) of 85% hydrazine hydrate were dissolved in 250 ml. of ethanol and refluxed for 7 hours. The solution was cooled overnight and 27 g. (64%) of yellow crystals, m.p. 104–105°, was collected. An analytical sample was obtained by recrystallizing twice from methanol and twice from carbon tetrachloride; yellow needles, m.p. 106–108°.

Anal. Calcd. for $C_{22}H_{30}N_4$: C, 75.39; H, 8.63; N, 15.98. Found: C, 75.67; H, 8.32; N, 15.80, 16.07.

Preparation of the Large Ring Azo Compounds from the Azines. A. 3,10,13,20-Tetraphenyl-1,2,11,12-tetraaza-1,-11-cycloeicosadiene (II, $n = 6$).—To a solution of 9.0 g. (0.015 mole) of the 20-membered ring azine (I, $n = 6$) in 140 ml. of tetrahydrofuran, 1.8 g. of 10% palladium-on-charcoal was added. The solution was hydrogenated at an initial pressure of 43 p.s.i. at room temperature for 14 hours and the theoretical amount of hydrogen was absorbed. It was found advantageous to cover the neoprene stopper of the Parr apparatus with a polyethylene cap to prevent excessive softening of the rubber. The catalyst was removed by filtration, 30 g. (0.14 mole) of mercuric oxide was added, and the resulting slurry was magnetically stirred for 9 hours.

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(9) L. N. Ferguson and T. C. Goodwin, THIS JOURNAL, **71**, 633 (1949).

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

(11) L. Bellamy, "The Infrared Spectra of Complex Molecules," John Wiley and Sons, Inc., New York, N. Y., 1954, p. 227.

(12) All melting points are uncorrected. Analyses by Schwarzkopf Microanalytical Laboratory, Woodside, N. Y., and Clark Microanalytical Laboratory, Urbana, Ill.

(13) R. G. Jones, THIS JOURNAL, **69**, 2350 (1947).

(14) L. A. Wiles and E. C. Baughan, *J. Chem. Soc.*, 933 (1953).

The solid was removed by filtration, and the tetrahydrofuran was removed under vacuum at 20°. The residue, a yellow-orange oil, was dissolved in 20 ml. of benzene and 80 ml. of ethanol, the hot solution was decolorized with charcoal, filtered and cooled to give white crystals, 3.2 g., m.p. 118–121° dec. Recrystallization from 20% benzene in ethanol gave 1.5 g. (17%), m.p. 150–151° dec. An analytical sample was obtained by recrystallization from 12.5% benzene in ethanol, m.p. 150–151° dec.

Anal. Calcd. for $C_{40}H_{48}N_4$: C, 82.15; H, 8.27; N, 9.58; mol. wt., 585. Found: C, 82.25; H, 8.15; N, 9.61, 9.63; mol. wt., 562 (ebullioscopic in butanone).

B. 3,12,15,24-Tetraphenyl-1,2,13,14-tetraaza-1,13-cyclotetracosadiene (II, *n* = 8).—From 21.0 g. (0.033 mole) of 24-membered ring azine (I, *n* = 8) was obtained 10.4 g. (49%) white crystals, m.p. 120–123° dec. Recrystallization from ethanol gave 8.0 g. (38%), m.p. 124–125° dec. (m.p. 130–131° dec. 80% crude, λ_{max} 355 mμ log ϵ 2.1).

C. 3,14,17,28-Tetraphenyl-1,2,15,16-tetraaza-1,15-cyclooctacosadiene.—From 5.0 g. (0.0072 mole) of 28-membered ring azine (I, *n* = 10) was obtained 1.5 g. (30%), m.p. 126–128° dec., of the 28-membered ring azo compound (II, *n* = 10) (m.p. 129–131° dec., 25% crude).[3] An element analysis is reported for this compound in reference 3.

Anal. Calcd. for $C_{48}H_{64}N_4$: mol. wt., 697. Found: mol. wt., 631 (ebullioscopic in benzene).

Preparation of Propiophenone Azine and 1-Azo-bis-1-phenylpropane.—These compounds were prepared according to the method of Cohen, *et al.*[10]

II. The Decomposition of the Large Ring Azo Compounds

A. Experimental.[12] Decomposition Product from the 28-Membered Ring Azo Compound (II, *n* = 10).—A glass tube was filled with a solution of 1.5 g. (0.00215 mole) of 28-membered ring azo compound in 25 ml. of xylene, flushed several times with nitrogen, evacuated and sealed. The tube was kept at 111° for 35 hours, opened and rinsed with chloroform. The solvents were removed under vacuum to give a yellow opaque oil which was dissolved in 30 ml. of chloroform, treated with decolorizing charcoal and filtered. Removal of solvent gave 1.4 g. of a viscous light yellow liquid. The distillation of 0.77 g. of this liquid in a Craig column at 10^{-5} mm. and a bath temperature of 310° afforded 0.65 g. (84%) of a white glass which did not decolorize potassium permanganate solution. The glass analyzed correctly for the 24-membered ring cyclic hydrocarbon, 1,2,13,14-tetraphenylcyclotetracosane (III, *n* = 10). The infrared spectrum was identical to the hydrocarbon obtained from the 24-membered ring azo compound (II, *n* = 8).[3,5]

Anal. Calcd. for $C_{48}H_{64}$: C, 89.94; H, 10.06; mol. wt., 641. Found: C, 89.96, 90.10; H, 9.89, 9.94; mol. wt., 608 (ebullioscopic in benzene).

Decomposition Product from the 20-Membered Ring Azo Compound (II, *n* = 6).—The xylene solutions from six rate determinations in which a total of 1.30 g. (0.0022 mole) of 20-membered ring azo compound (II, *n* = 6) was decomposed were combined and the solvent was removed. The residue was washed into the tared tube of a sublimation apparatus with petroleum ether (b.p. 39–50°), the solvent was evaporated and the residue was dried in a vacuum oven for 5 hours at 110°. The residue weighed 1.11 g. (86%) and was distilled molecularly in the sublimation apparatus at 190–200° (0.1 mm.) for 60 hours to yield 0.85 g. (66%) of a white wax. For an analytical sample, 0.2 g. was redistilled molecularly at 190° (0.1 mm.) for 12 hours, and a colorless glass, which did not decolorize potassium permanganate solution, was collected. The compound analyzed correctly for the cyclic hydrocarbon, 1,2,9,10-tetraphenylcyclohexadecane (III, *n* = 6). The infrared spectrum of this compound differed mainly in the fingerprint region, when compared to the spectra of the hydrocarbons from the 24- and 28-membered ring azo compounds.

Anal. Calcd. for $C_{40}H_{48}$: C, 90.85; H, 9.15; mol. wt., 529. Found: C, 91.18; H, 8.89; mol. wt., 540 (ebullioscopic in butanone).

Decomposition of the 24-Membered Ring Azo Compound (II, *n* = 8) in Maleic Anhydride.—A glass tube was filled with 1.6 g. (0.0025 mole) of 24-membered ring azo compound (II, *n* = 8) and 9.8 g. (0.1 mole) of maleic anhydride, flushed with nitrogen, evacuated and sealed. The tube was heated at 110° for 14 hours to give a clear amber solution. The contents of the tube were boiled with water for a half-hour, and then extracted with 100 ml. of ether. The residue from the ether solution was a yellow oil which was dissolved in 60 ml. of 5% potassium hydroxide, stirred with decolorizing carbon and filtered. Acidification of the solution with dilute hydrochloric acid gave 1.5 g. of a tan precipitate, m.p. 120–132°. Reprecipitation from basic solution with hydrochloric acid gave a tan solid, m.p. 122–140° (*Anal.;* C, 70.21; H, 6.87). The composition of the crude adduct corresponds approximately to 3.7 units of maleic anhydride for every two diradical residues.

Attempts at purification by recrystallization, elution chromatography and ion exchange chromatography failed to yield a homogeneous product.

Decomposition of the 24-Membered Ring Azo Compound (II, *n* = 8) in *cis*-Stilbene.—In a 50-ml. flask, equipped with a top-entering magnetic stirrer and a side arm through which the nitrogen to be evolved was collected, was placed 35 g. (0.19 mole) of *cis*-stilbene.[15] The system was flushed with nitrogen and the flask kept at 120°. After the addition of 2.53 g. (0.0039 mole) of 24-membered ring azo compound (II, *n* = 8), 99% of the theoretical quantity of nitrogen was collected in 5.5 hours.

The stilbene was removed by vacuum distillation and the residue was washed into the tared tube of a sublimation apparatus with ether; after removal of solvent the residue was dried in a vacuum oven 4.5 hours at 120°. The sublimation apparatus was assembled and heated at 90–100° (0.1 mm.) for 30 hours, and 0.3 g. of *trans*-stilbene, m.p. 124–125°, was collected. A mixture melting point with authentic *trans*-stilbene, m.p. 124–125°, was not depressed. The temperature was raised to 165–175° (0.1 mm.), and a white glass, 1.37 g., was collected on the cold finger in 12 hours. This glass was dissolved in petroleum ether (b.p. 39–50°) and cooled to 15°, to give a white sticky wax, which was recrystallized from petroleum ether to give 0.09 g. of white solid, m.p. 94–100°. The white glass, 1.28 g. (55%), was redistilled molecularly to give an analytical sample which analyzed correctly for the 20-membered ring hydrocarbon, 1,2,11,12-tetraphenylcycloeicosane (III, *n* = 8) previously reported.[3] The infrared spectrum was identical with the previous spectrum of that compound.[5]

Anal. Calcd. for $C_{44}H_{56}$: C, 90.35, H, 9.65, mol. wt., 585. Found: C, 90.23, H, 9.83; mol. wt., 628 (ebullioscopic in butanone).

The temperature of the sublimation apparatus was then raised to 170–190° (0.1 mm.) and 0.16 g. of a white wax was collected. This was combined with the white solid already isolated to give 0.25 g. (11%) and recrystallized from *n*-hexane gave 0.08 g., m.p. 110–112°. The infrared spectrum showed a strong peak at 10.38 μ indicative of unsaturation.[7] The ultraviolet spectrum exhibited a cyclohexane λ_{max} 249, log ϵ 4.26, and a shoulder at 285 mμ, log ϵ 3.21. The compound slowly decolorized bromine in carbon tetrachloride and analyzed correctly for a product consisting of two diradical residues.

Anal. Calcd. for: $C_{44}H_{56}$: C, 90.35; H, 9.65; mol. wt., 585. Found: C, 90.26, 90.57; H, 9.76, 9.66; mol. wt., 518, 537 (Rast).

The dark residue left in the sublimation apparatus weighed 0.67 g. (29%). The dark residue 0.63 g. from a similar experiment could be eluted from a 22-g. column of alumina (Woelm, activity 1, almost neutral) with *n*-hexane to give 0.46 g. of white glass and 0.008 g. of dark yellow oil. The glass was dried at 175° (0.1 mm.) for 25 hours to give an analytical sample whose analysis agreed with that of the compound isolated by molecular distillation above. Found: C, 90.69, H, 9.58; mol. wt., 668 (ebullioscopic in benzene). The infrared spectrum was also identical with that of the previously isolated 20-membered cyclic hydrocarbon, 1,2,11,12-tetraphenylcycloeicosane.[5]

In another experiment, 2.4 g. (0.0037 mole) of the 24-membered ring azo compound was decomposed in 27 g. (0.15 mole) of *cis*-stilbene in a sealed tube at 120° for 6 hours. The *cis*-stilbene was removed by vacuum distillation and the residue was eluted from 25 g. of alumina with petroleum ether (b.p. 39–50°), and 1.03 g. of a white semi-solid and 0.55 g. of a white glass was isolated. The semi-solid was recrystallized from petroleum ether (b.p. 39–50°) at 20° to give 0.51 g. of white sticky solid. A 0.45-g. portion of this solid was recrystallized twice with 6-ml. portions of petro-

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[15] R. E. Buckles and N. G. Wheeler, *Org. Syntheses*, **33**, 88 (1953).

TABLE II

THE DECOMPOSITION OF THE LARGE RING CYCLIC AZO COMPOUNDS IN XYLENE

Compound	$k \times 10^{-4}$ sec.$^{-1}$ 110°	120°	130°	E, kcal./mole	S(120°), e.u.
II, $n = 6$	0.720 ± 0.035	2.30 ± 0.09	6.90 ± 0.15	34.8 ± 0.4	13.1 ± 1.2
II, $n = 8$	.763 ± .038	2.46 ± .12	7.12 ± .22	34.4 ± .3	12.0 ± 1.3
II, $n = 10$	.919 ± .001	2.99 ± .02	8.15 ± .08	33.7 ± .1	10.4 ± 0.5
1-Azo-bis-1-phenylpropane[10]	.72	2.1 (calcd.)		32.2	

leum ether (b.p. 30–60°) to give 0.046 g., m.p. 98.5–100°. The infrared spectrum showed a strong band at 10.41 μ indicative of unsaturation[7] and differed considerably from that of the unsaturated hydrocarbon isolated above. The material analyzed correctly for a hydrocarbon consisting of two diradical residues and one stilbene molecule.

Anal. Calcd. for $C_{56}H_{68}$: C, 91.04; H, 8.96; mol. wt., 765. Found: C, 91.17, 91.14; H, 8.83, 9.22; mol. wt., 703 (ebullioscopic in benzene).

Attempted Initiation of the Copolymerization of Styrene and Maleic Anhydride with II, $n = 8$.—A solution containing 6.120 g. of maleic anhydride and 6.579 g. of styrene (carefully distilled through a packed column) diluted to 100 ml. with cyclohexanone was prepared and a 25-ml. aliquot was added to each of three tubes; one contained 0.0898 g. (3.37 × 10^{-4} mole) of 1-azo-bis-1-phenylpropane, another contained 0.1150 g. (1.79 × 10^{-4} mole) of 24-membered ring azo compound (II, $n = 8$) and the third had no catalyst. The tubes were degassed at 10^{-5} mm., sealed and kept at 100° for one hour. The polymers formed were precipitated with benzene and reprecipitated from acetone solution with benzene. The tube with 1-azo-bis-1-phenylpropane contained 10.624 g. of polymer (83.7% conversion), the tube with the cyclic azo compound contained 1.346 g. of polymer (10.6% conversion) and the control tube contained 0.740 g. of polymer (5.8% conversion).

Decomposition of 1-Azo-bis-1-phenylpropane in *cis*-Stilbene.—A solution of 5.00 g. (0.019 mole) of 1-azo-bis-1-phenylpropane in 60 g. (0.33 mole) of *cis*-stilbene was kept at 120–122° for 6.5 hours in the manner described above and 101% of the theoretical quantity of nitrogen was collected. The stilbene was distilled through a helices packed column b.p. 148–152° (17 mm.), until the volume of the residue was approximately 10 ml. The stilbene fraction was preceded by a small forerun 0.54 g. (12%), b.p. 60–82° (17 mm.), whose ultraviolet spectrum showed a peak at 248 mμ and a shoulder at 283 mμ.

The 10-ml. residue was distilled through a small Vigreux column, and a mixture of liquid and solid, 3.9 g., b.p. 157–169° (22 mm.), was collected. Recrystallization from *n*-hexane–methanol mixture gave 0.8 g., m.p. 116–120°. Another recrystallization from methanol gave crystals, m.p. 124–125°. A mixed melting point with authentic *trans*-stilbene, m.p. 124–125°, melted at 123–124°.

Another fraction, 5.43 g., m.p. 62–112°, b.p. 170–175° (22 mm.), gave pure *trans*-stilbene. The *n*-hexane "mother liquor" from the above crystallization was eluted from a 100-g. column of alumina (Woelm, almost neutral, activity 1) to give 1.72 g. (38%) of waxy solid, m.p. 48–65°. The remainder of the fractions obtained were white solids, m.p. 120–122°, which were shown to be *trans*-stilbene by recrystallization and mixed melting point determinations. The 1.72 g. of solid was recrystallized from acetone–methanol to give 0.58 g., m.p. 85–87°. Recrystallization from methanol gave white crystals, 0.43 g., m.p. 88–89°. The literature reports melting points 83–84°,[16a] 88–89°[16b] and 91–92°[16c] for *meso*-3,4-diphenylhexane.

Anal. Calcd. for $C_{18}H_{22}$: C, 90.70; H, 9.30. Found: C, 90.81; H, 9.30.

The mother liquors from the recrystallizations gave an oily residue, 0.79 g., which was eluted from a 30-g. column of the same type of alumina, with petroleum ether (b.p. 39–50°) to give 0.19 g. of white solid, m.p. 32–40°, which on recrystallization from methanol gave 0.03 g., m.p. 90–91°. A mixed melting point determination with the *meso*-3,4-diphenylhexane previously isolated melted at 89–90°. An oil, 0.35 g., n^{25}D 1.5440, was eluted next, most probably *dl*-3,4-diphenylhexane (n^{20}D 1.5462).[17] A solution of 0.22 g. of this oil in 2 ml. of acetic acid was treated with 1.0 g. of bromine, and heated on the steam-bath one hour. On cooling six days, 0.08 g. of white crystals, m.p. 213–214°, was deposited (reported[16c] for hexabromodiphenylhexane, m.p. 213–215°).

A yellow oil, 1.25 g. (16%), remained from the distillation of the 10-ml. residue through the small Vigreux column. This was dissolved in 5 ml. of boiling *n*-hexane and a few drops of methanol was added; cooling gave 0.072 g. of white crystals, m.p. 180–190°. Recrystallization from methanol gave 0.06 g., m.p. 192–194°, of white crystals whose analysis corresponded to that of a hydrocarbon containing two α-phenylpropyl radicals and one stilbene molecule.

Anal. Calcd. for $C_{32}H_{34}$: C, 91.82; H, 8.18. Found: C, 91.69; H, 8.43.

The residue of the mother liquors from the recrystallizations were distilled molecularly in a sublimation apparatus at 130–140° (0.5–1.0 mm.). The entire residue except for a minute quantity of black tar was collected as a colorless gum on the cold finger of the sublimation apparatus. A portion submitted for analysis was also found to analyze correctly for a hydrocarbon containing two α-phenylpropyl radicals and one stilbene molecule.

Anal. Calcd. for $C_{32}H_{34}$: C, 91.82; H, 8.18; mol. wt., 419. Found: C, 91.59, 91.99; H, 8.19, 8.11; mol. wt., 384, 397 (ebullioscopic in butanone).

B. **Kinetic Measurements.**—The rates of decomposition for each compound were determined in duplicate at three temperatures by the method previously described[18] in xylene solvent. The data obtained are summarized in Table II. All the rates were found to be unimolecular and without an induction period. The plots of log $((V\alpha - V_0)/(V\alpha - Vt))$ *versus* time for the 28-membered ring azo compound (II, $n = 10$) at three temperatures are shown in Fig. 1 as an example.

The rate of decomposition of the 24-membered ring azo compound at 119.8° was reported[3] as 2.2 × 10^{-4} sec.$^{-1}$ and the activation energy was 30.2 kcal./mole. These values are in qualitative agreement with those found in this work. A consideration of molecular models indicated a strain-free molecule with both azo groups *trans* and this is presumably the more stable thermodynamic state.[3] As can be seen in Table II, the rates of decomposition and the activation energies for the decomposition of the large ring cyclic azo compounds are very similar to those reported for the linear analog 1-azo-bis-1-phenylpropane. Thus both the spectral data and the kinetic behavior of the 20-, 24- and 28-membered rings show that the cyclic compounds and their linear analogs are closely related.

C. Discussion.—The main product resulting from the decomposition of the 24-membered ring azo compound (II, $n = 8$) was the 20-membered cyclic hydrocarbon (III, $n = 8$) isolated in 72% yield.[3] The 20- and 28-membered ring cyclic azo compound (II, $n = 6$, 10) were found to give the 16-and 24-membered ring cyclic hydrocarbons (III, $n = 6$, 10) in 84 and 66% yield, respectively. A high yield of coupled products would be expected from the formation of benzyl radicals.[21]

Lapkin[5] decomposed the 24-membered ring azo compound in the presence of several radical scaven-

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(16) (a) G. Brownlee, F. C. Copp, W. M. Duffin and I. M. Tonkin, *Biochem. J.*, **37**, 572 (1943); (b) Ng. Ph. Buu-Hoi and Ng. Hoang, *J. Org. Chem.*, **14**, 1023 (1949); (c) A. G. Brook, H. L. Cohen and G. F. Wright, *ibid.*, **18**, 447 (1953).

(17) A. Lepin and W. Reich, *J. Russ Phys. Soc.*, **47**, 154, 158 (1915); Beilstein, "Handbuch der Organischen Chemie," First Supplement, 4th edition, Vol. V, J. Springer, Berlin, 1930, p. 295.

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

gers, but the results were inconclusive. In this work the azo compound seemed to react with some of the scavengers used but no significant quantities of a pure product could be isolated. For example, from the irradiation of a benzene solution of the azo compound and nitric oxide with ultraviolet light, and from the thermal decomposition of the azo compound in carbon tetrabromide only black tars could be isolated. When maleic anhydride was used as a solvent-scavenger, good yields of a heterogeneous product, which contained approximately 3.7 maleic anhydride residues for every two diradical fragments, were isolated; however, this product could not be purified.

The decomposition products of the 24-membered ring azo compound (II, $n = 8$), in *cis*-stilbene were investigated in detail. Of the four fractions separated in the analysis of the products, two fractions (84%) were the cyclic hydrocarbon (III, $n = 8$), and a third product (11%) was an unsaturated solid whose ultraviolet absorption showed it was a substituted styrene.[19] The molecular weight indicated it to be a disproportionated product containing two diradical fragments. A fourth fraction, separated in trace quantities by elution chromatography, analyzed correctly for two diradicals plus one stilbene molecule and showed a peak in the infrared at 10.4 μ which is indicative of unsaturation.[7] This compound was probably a true adduct of stilbene and a diradical, and it was concluded that the diradical produced reacted with *cis*-stilbene to a very small extent.

It is interesting to compare the behavior of the cyclic azo compound in *cis*-stilbene solvent and that of phthaloyl peroxide (a possible diradical source) in a 1.1% solution of *cis*-stilbene in carbon tetrachloride.[20] In the latter case the yields of adducts are almost quantitative. Although the diradicals which would be produced in these two cases are different, it seems unlikely that if both processes were occurring *via* a diradical intermediate that one intermediate would react quantitatively at low concentrations of scavenger while the other would hardly react at all in the presence of pure scavenger. Therefore it is possible that the peroxide reaction may be proceeding by the alternative path involving attack by the peroxide on the olefin and not formation of a diradical.

In order to obtain some measure of the reactivity of a benzyl monoradical with *cis*-stilbene, the linear compound 1-azo-bis-1-phenylpropane was decomposed in *cis*-stilbene. About 12% of the radicals was accounted for by a mixture of the disproportionated products of the benzyl radicals, and the *dl*- and *meso*-3,4-diphenylhexanes accounted for another 38% of the radicals. A mixture of the isomers of V was found to contain 16% of the radicals produced. The results are in agreement with the expected tendency of benzyl radicals to couple.[21] Although the product analysis only accounted for 66% of the radicals formed, the smallest loss would be expected to occur in the isolation of V since this compound was the non-volatile residue. The yield of adduct obtained shows that 16% is the minimum extent to which the benzyl radicals were scavenged by *cis*-stilbene, and in the light of this evidence the results with the 24-membered ring azo compound (II, $n = 8$) are of particular interest. It is clear that the radicals derived from the linear azo compound are less inclined to recombine in a primary cage than the diradical from the cyclic azo compound. *This may be due to the molecular restrictions imposed on the diradical obtained from the cyclic compound.*

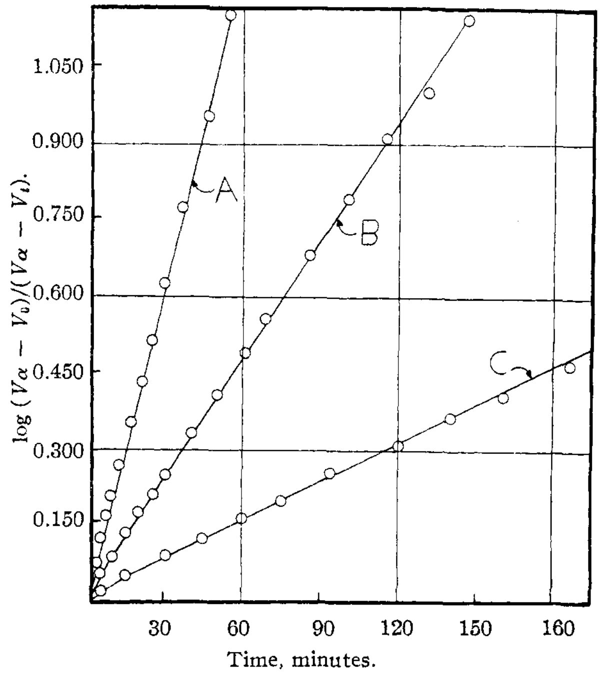
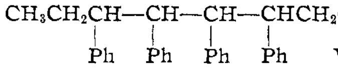


Fig. 1.—Decomposition of the 28-membered ring azo compounds in xylene: A, 130°; B, 120°; C, 110°.



$$\underset{\textstyle}{CH_3CH_2}\underset{Ph}{CH}-\underset{Ph}{CH}-\underset{Ph}{CH}-\underset{Ph}{CH}CH_2CH_3$$

V

It has been shown[3] that the 24-membered ring azo compound (II, $n = 8$) was an extremely inefficient initiator for the polymerization of styrene. It was thought possible that the cyclic azo compound might initiate the copolymerization of styrene and maleic anhydride more efficiently since the maleic anhydride radical reacts over a hundred times faster with styrene than does a styrene radical, while the styrene radical reacts over twenty times faster with maleic anhydride than styrene monomer.[22] Thus the initiation step should be more efficient, and the propagation of copolymer should be faster and able to compete better with termination by cyclization of the diradical.

The results show that these factors were not important since the conversions of 5.8, 10.6 and 83.7% for no initiator, cyclic azo initiator and 1-azo-bis-1-phenylpropane initiator, respectively were in much the same ratio as those found for styrene.[3]

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[20] F. D. Green, *ibid.*, **78**, 2246, 2250 (1956).

[21] M. S. Kharasch, H. C. McBay and W. H. Urry, *J. Org. Chem.*, **10**, 401 (1945); C. G. Overberger and A. B. Finestone, THIS JOURNAL, **78**, 1638 (1956).

[22] P. J. Flory, "Principles of Polymer Chemistry," Cornell University Press, Ithaca, N. Y., 1953, p. 188.