μ; $\mu_{max}^{CH_2Cl_2}$ 238 mμ (log ϵ 4.22), 288 mμ (log ϵ 4.15), 363 mμ (log ϵ 3.23).

Anal. Calcd. for $C_{23}H_{22}N_2O_2$: C, 80.36; H, 5.30; N, 6.69. Found: C, 80.40, 80.40; H, 5.22, 5.35; N, 6.88, 6.77.

The filtrate from the isolation of this product was freed of solvent *in vacuo* to give a viscous, yellow-orange oil. This was triturated with a little ether and the solution filtered from some benzilazine and evaporated. The residual oil was taken up in benzene and chromatographed on alumina (Woelm No. 1 Neutral). Elution with benzene gave a pale yellow, semi-solid product (0.90 g.) which yielded on trituration with a small amount of ether a pale yellow crystalline solid (0.82 g.). This product was recrystallized from ether to give very pale yellow needles, m.p. 124.5–125.5°, $\lambda_{max}^{CH_2Cl_2}$ 5.95 μ; λ_{max}^{EtOH} 254 mμ (log ϵ 4.29), 285 mμ (log ϵ 4.21).

Anal. Calcd. for $C_{22}H_{18}N_2O_2$: C, 77.17; H, 5.30; N, 8.18; 1 OCH_3, 9.06. Found: C, 77.50, 77.14; H, 5.05, 5.02; N, 7.95, 8.35; OCH_3, 9.80.

Evaporation of the ethereal solution from the trituration gave an oil with a sweet odor which showed all the bands of methyl benzoate and of benzonitrile in its infrared spectrum. Later fractions from the chromatogram yielded only a considerable quantity of benzilazine and a small amount of benzamide, identified by mixed melting point and infrared spectral comparison: the total recovery from the chromatogram was low (*ca.* 50%). The basic aqueous layer from the treatment of the original reaction mixture with water yielded benzoic acid (0.54 g.).

When benzilazine was heated under reflux with excess sodium methoxide in methanol overnight no purple color was formed and the azine could be recovered unchanged.

CAMBRIDGE, MASS.

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

Azo Compounds.[1] An Eight-membered Cyclic Azo Compound

BY C. G. OVERBERGER AND I. TASHLICK[2]

RECEIVED JUNE 6, 1958

The eight-membered cyclic azo compound, 3,8-diphenyl-1,2-diaza-1-cycloöctene (II), has been prepared and characterized. The spectral and kinetic properties of II have been investigated. This azo compound exhibited an unexpected thermal stability; its calculated rate of decomposition at 80° was 1/180 of that obtained for 1-azo-bis-1-phenylpropane. The decomposition of II gave 50% of 1,6-diphenyl-1-hexene and 43% of a mixture of *cis-* and *trans*-1,2-diphenylcyclohexane, the products expected from the disproportionation and combination of the 1,6-diphenyl-1,6-hexadiyl diradical.

The study of compounds which would thermally decompose to give moderately active diradicals in solution is being continued. We report here a synthesis of the eight-membered cyclic azo compound, 3,8-diphenyl-1,2-diaza-1-cycloöctene (II), its spectral properties, the kinetics of decomposition and the decomposition products.

Recent syntheses of cyclic azo compounds were reviewed in reference 7, the preparation and properties of the seven-membered analog of II were reported and the available data were interpreted.

A. Preparation of the Azo Compound.—The synthesis of the parent cyclic azine, 1,2-diazo-3,8-diphenyl-2,8-cycloöctadiene (I), has recently been reported.[1b] The preparation of the di-*p*-methoxy derivative has also been described recently.[8] The preparation of the azo compound from the azine was readily accomplished by the procedure employed in the syntheses of the 7-, 20-, 24- and 28-membered ring azo compounds.[7,9] The subsequent hydrogenation and oxidation steps afforded 56% of the cyclic azo compound II.

B. Kinetics of Decomposition.—The rates of decomposition were determined in duplicate in the manner previously described,[10] at four tempera-

TABLE I

SPECTRAL AND KINETIC DATA OF AZO COMPOUNDS, R—N═N—R

R =	Rate constants (sec.$^{-1}$), 80°	Ultraviolet max. mμ	ϵ	E_a, kcal./mole	Ref.
CH_3–	6.9×10^{-16}[a]	340	4.5[3a]	50.2	3b
	2.8×10^{-15}[a]			46.0	3c
$(CH_3)_2CH$–	2.9×10^{-12}[a]	355	18	40.9	4
$Ph\overset{\vert}{C}H(CH_2)_2\overset{\vert}{C}HPh$	6×10^{-4}	387	775	. . .	5
$Ph\overset{\vert}{C}H(CH_2)_3\overset{\vert}{C}HPh$	4.27×10^{-4}	390	127	29.7	7
$Ph\overset{\vert}{C}H(CH_2)_4\overset{\vert}{C}HPh$	3.5×10^{-8}[b]	368	45	36.7	This work
$Ph\overset{\vert}{C}H(C_2H_5)$	1.9×10^{-6}[b]	359	47	32.3	This work, 6

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[1] (a) This is the 25th 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 H. Gainer, THIS JOURNAL, **80**, 4561 (1958). (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 submitted by I. Tashlick in partial fulfillment of the requirements of the degree of Doctor of Philosophy in the Graduate School of the Polytechnic Institute of Brooklyn.

(3) (a) H. C. Ramsperger, THIS JOURNAL, **50**, 123 (1928); (b) O. K. Rice and D. V. Sickman, *J. Chem. Phys.*, **4**, 239, 242, 608 (1936); (c) M. Page, H. O. Pritchard and A. F. Trotman-Ackerman, *J. Chem. Soc.*, 3878 (1953).

(4) H. C. Ramsperger, THIS JOURNAL, **50**, 714 (1928); B. W. Langley, B. Lythgoe and L. S. Rayner, *J. Chem. Soc.*, 4191 (1952).

(5) S. G. Cohen, S. Hsaio, E. Saklad and C. H. Wang, THIS JOURNAL, **79**, 2661, 4400 (1957).

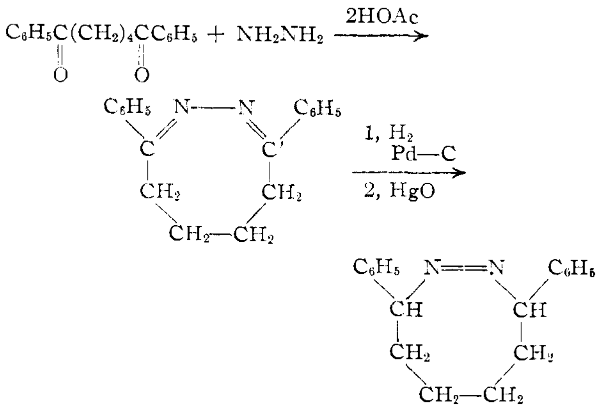
(6) S. G. Cohen, S. J. Groszos and D. B. Sparrow, *ibid.*, **72**, 3947 (1950).

(7) C. G. Overberger and J. G. Lombardino, *ibid.*, **80**, 2317 (1958).

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

(9) C. G. Overberger, I. Tashlick, M. Bernstein and R. G. Hiskey, THIS JOURNAL, **80**, 6556 (1958).

(10) C. G. Overberger and H. Gainer, *ibid.* **80**, 4561 (1958).



tures in tetralin. The quantity of nitrogen collected ranged from 93 to 98% of theory with the smaller volumes collected at the lower temperatures. The rates were found to be unimolecular; the linear plots are shown in Fig. 1, the values found are summarized in Table II. The entropy of activation for the decomposition of II was calculated to be 10.4 ± 1.7 e.u., while the energy of activation was found to be 36.7 ± 0.7 kcal./mole, more than 4 kcal./mole greater than the value reported for 1-azo-bis-1-phenylpropane.[6]

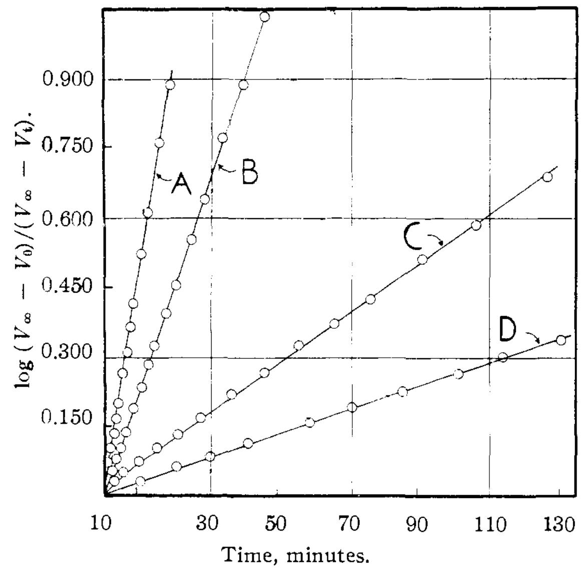


Fig. 1.—The decomposition of 3,8-diphenyl-1,2-diaza-1-cycloöctene in tetralin: A, 173°; B, 165°; C, 151°; D, 143°.

TABLE II

DECOMPOSITION OF II IN TETRALIN SOLUTION

Temp °C.	$k \times 10^{-4}$, sec.$^{-1}$
143	0.952 ± 0.038
151	2.09 ± .06
165	8.77 ± .38
173	18.2 ± .4

C. Discussion.—The ultraviolet spectrum of the 8-membered ring azine I exhibited typical azine absorption, $\lambda_{\max}^{\mathrm{MeOH}}$ 269, log ϵ 4.35. Likewise the infrared spectrum showed strong peaks at 6.27 and 6.41 μ. The former was diminished and the latter almost disappeared upon conversion of I to the corresponding azo compound. The infrared spectra of the azine and azo compounds derived from propiophenone were identical.

The spectral properties of the 8-membered ring azo compound II, however, indicate that it is not comparable with any of the azo types previously reported.[5,7] From the data in Table I, it can be seen readily that the ultraviolet maximum due to the azo link of the 8-membered ring is about half-way between the maxima of the 6- and 7-membered ring compounds and that of 1-azo-bis-1-phenylpropane, while the intensity is that of the linear compound, even though the 6-, 7- and 8-membered rings all probably contain a *cis*-azo linkage.

The examination of the rate data provides a more striking example of the unusual nature of an azo linkage incorporated in an 8-membered ring. At 80° the rate of decomposition of 1-azo-bis-1-phenylpropane is about 180 times greater than II, while the 6- and 7-membered rings have rates more than 10,000 times greater.

The relative instability of the 6- and 7-membered rings as compared to the linear analogs has been attributed to the *cis* configuration of the azo linkage.[5,7] The effect of the *cis* linkage on the stability of an azo compound is not clear—a linear *cis* azo compound is presumably in a higher energy state than a linear *trans* isomer,[11] but the magnitude of the difference and its effect on the rate of thermal decomposition is uncertain. In the 6-, 7- and 8-membered rings, the *cis* isomer would be expected to be in the lower energy state because of steric strain.

The difference of 9 kcal./mole in the heats of hydrogenation of *cis*- and *trans*-cycloöctene is the largest yet obtained for any pair of *cis–trans* isomers,[12] and appears to reflect the steric strain accompanying the incorporation of a *trans* double bond in an 8-membered ring. The 8-membered azo compound is probably the *cis* isomer, since it is unlikely that if the *trans* isomer does exist, it would be isolated in the yield obtained, and it would certainly not be expected to show the degree of stability which was found.

From Table I, it is possible to examine the effect that substitution of a phenyl group for a methyl group in azoisopropane has upon the ultraviolet absorption spectrum, the maximum being shifted to a slightly longer wave length and the intensity increased by two and a half times. The effect on the rate is more pronounced, however, and the change is a million-fold from azoisopropane to 1-azo-bis-1-phenylpropane. This kind of effect can be attributed[13] to resonance stabilization of the incipient radical in the transition state as the carbon–nitrogen bond is breaking. Thus the phenyl group has a slight effect on the ultraviolet spectrum, and a very large effect on the dissociation energy of the carbon–nitrogen bond. This labiliz-

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[11] A. H. Cook, *J. Chem. Soc.*, 877 (1938).

[12] R. B. Turner and W. R. Meador, THIS JOURNAL, **79**, 4133 (1957).

[13] C. G. Overberger, H. Biletch, A. B. Finestone, J. Lilker and J. Herbert, *ibid.*, **75**, 2078 (1953); C. Walling, "Free Radicals in Solution," J. Wiley and Sons, Inc., New York, N. Y., 1957, p. 5.

ing effect operates on all known azo compounds of this type except the 8-membered ring azo compound II. This difference in stability between II and other azo types could be due to either the existence of the 8-membered ring compound at a lower energy level than all the other azo compounds, or the fact its transition state on decomposition is at a higher energy level than the other compounds. It seems unlikely that the cyclic compound could be at a lower energy level than the linear analogs; thus the second alternative appears more probable.

From a consideration of molecular models a rationalization of this phenomenon can be deduced. In all the cases considered, the benzyl group can readily become coplanar with the azo group. In fact, in the cases of the 6- and 7-membered ring, the most probable conformations appear to be those in which both benzyl groups are forced into coplanarity with the azo groups and may provide a reason for their enhanced rate of decomposition. However, in the most probable conformations of the 8-membered ring compound, the benzyl groups are not coplanar with the carbon–nitrogen bonds. This requirement for coplanarity would arise from resonance stabilization of the incipient radical in the transition state and as this occurs the bonding on the benzyl carbon will acquire some planar sp^2-character. As coplanarity becomes more difficult to attain before or during the transition state, the stability of the compound may approach that of an azo compound not containing a benzyl group.

An alternate explanation of the unusual stability of II may lie in the formation of a transannular tautomer. We are currently investigating these possibilities.

D. Decomposition Products of 3,8-Diphenyl-1,2-diaza-1-cyclooöctene.—A comparison of the products of decomposition of II with those obtained from other azo compounds was then initiated. The most closely related compound, the 7-membered ring, 3,7-diphenyl-1,2-diaza-1-cycloheptene, on decomposition at 110° in xylene yielded 65% of a mixture of the *cis*- and *trans*-1,2-diphenylcyclopentanes and 23% of 1,5-diphenyl-1-pentene.[17]

The decomposition of the 8-membered ring azo compound was carried out in tetralin at 165-170°. The amount of olefin found by quantitative hydrogenation was 49%, while a determination by quantitative ultraviolet spectroscopy gave a value of 52%. The olefin was separated from the saturated products in the reaction mixture by conversion to 2,4-dinitrobenzenesulfenyl chloride derivatives followed by elution chromatography of the resulting mixture. The saturated fraction was isolated in 43% yield by this method. The saturated products were subsequently identified by an independent synthesis, mixed melting point determinations and comparison of infrared spectra.

The synthesis of 1,6-diphenyl-1-hexene, which would be expected to result from disproportionation of the 1,6-diphenyl-1,6-hexadiyl diradical, was accomplished by the Clemmensen reduction of 5-benzoylvaleric acid to give 6-phenylhexanoic acid. Treatment of 6-phenylhexanoyl chloride with idphenylcadmium afforded 1,6-diphenyl-1-hexanone, which on reduction to the corresponding carbinol and dehydration yielded the desired olefin.

The olefin was isolated from the azo decomposition mixture by formation of two 2,4-dinitrobenzenesulfenyl chloride derivatives—one was the normal chlorine containing adduct,[14] while the other did not contain chlorine and gave no evidence of unsaturation. This latter compound was not identified rigorously, but we are currently investigating this interesting reaction.

Treatment of authentic 1,6-diphenyl-1-hexene with 2,4-dinitrobenzenesulfenyl chloride gave a 46% yield of the saturated adduct and a 22% yield of the normal chlorine-containing derivative. Since these derivatives were identical in all respects to those obtained from the decomposition products, all the olefin present in the decomposition mixture was undoubtedly 1,6-diphenyl-1-hexene.

The syntheses of the *cis*- and *trans*-1,2-diphenylcyclohexanes have been reported[15,16]; however, their structures do not appear to have been unequivocally established. Parmerter[15] prepared the alleged *cis* isomer by hydrogenation of an olefin assumed to be 1,2-diphenylcyclohexene although the material was later shown by ozonolysis and ultraviolet spectral data to be 2,3-diphenylcyclohexene.[17] The product obtained in this work, m.p. 46–47°, was that reported by Parmerter[15] and will be referred to as the low melting isomer. The higher melting isomer, m.p. 53–54°, was synthesized by the reaction of disodium *trans*-stilbene with 1,4-dichlorobutane.[16]

When the mixture of saturated products isolated from the decomposition of the 8-membered ring azo compound was seeded in turn with the high and low melting isomers, approximately equal quantities of each isomer, amounting to a total of 70% of the mixture, was isolated. A mixture of the two authentic isomers was found to be an oil at room temperature whose infrared spectrum was identical to that of the saturated products isolated from the decomposition.

The results of the product analysis, isolation of 43% a mixture of *cis*- and *trans*-1,2-diphenylcyclohexane and 50% of 1,6-diphenyl-1-hexene, raise the question as to whether the relatively large quantity of olefin formed is due to the high temperature of the decomposition or is due to a property of the 1,6-diradical formed by the elimination of nitrogen. Previous work involving the reactions of benzyl radicals shows that the coupling reaction between the radicals predominates—thus α-alkyl substituted benzyl radicals formed by the thermal decomposition of acetyl peroxide in alkylbenzene solvents were found to give rise almost exclusively to coupled products.[18] Decomposition of 1,1′-azo-bis-(1,3-diphenylpentane) gave 95% of coupled product at 90° and 89% at 144°[19]; while

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[14] N. Kharasch and C. M. Buess, THIS JOURNAL, **71**, 2724 (1949).

[15] S. M. Parmerter, *ibid.*, **71**, 1127 (1949).

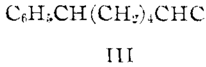
[16] J. W. B. Reesor, J. G. Smith and G. F. Wright, *J. Org. Chem.* **19**, 940 (1954).

[17] G. P. Mueller, J. G. Fleckenstein and W. H. Tallent, THIS JOURNAL, **73**, 2651 (1951).

[18] M. S. Kharasch, H. C. McBay and W. H. Urry, *J. Org. Chem.*, **10**, 401 (1945).

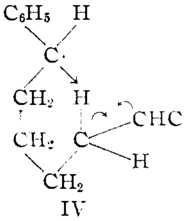
[19] C. G. Overberger and A. B. Finestone, THIS JOURNAL, **78**, 1638 (1956).

the decomposition of α,α'-azotoluene at 185° gave primarily products of combination, although some disproportionation was demonstrated.[20] Thus it seems the effect of temperature on the amount of disproportionation which occurs is relatively small, and the coupling reaction of the 1,6-diradical (III) to form a 6-membered ring occurs to a much smaller extent than might be expected. The disproportionation reaction in the case of this diradical may be aided by a cyclic transition state (IV) of lower energy than that occurring in bimolecular disproportionation. The temperature of decomposition may also be a factor favoring disproportionation in this instance.



$C_6H_5\dot{C}H(CH_2)_4\dot{C}HC_6H_5$

III



IV

Although the cyclic azo compound can exist in *cis* and *trans* configurations, presumably the sharp melting crystalline solid used in this work was pure diastereoisomer, thus it appears the diradical becomes free enough to lose its stereoidentity before it can couple.

Experimental[21]

3,8-Diphenyl-1,2-diaza-2,8-cycloöctadiene.—The procedure which van der Zanden and DeVries[8] employed for the preparation of the dimethoxy derivative of this compound was employed. From the reaction of 47.9 g. (0.18 mole) of 1,6-diphenyl-1,6-hexanedione, 120 g. (1.2 moles) of potassium acetate and 60 g. (0.57 mole) of hydrazine dihydrochloride, 47 g. of crude light yellow azine was obtained. Recrystallization from 500 ml. of ethanol gave 41 g. (87%), m.p. 135–136°. The slightly yellow color could be removed by recrystallization from benzene to give white crystals, m.p. 136–137°. The ultraviolet spectrum showed $\lambda^{\text{MeOH}}_{\text{max}}$ 268, log ϵ 4.43.

Anal. Calcd. for $C_{18}H_{18}N_2$: C, 82.42; H, 6.92; N, 10.68; mol. wt., 262. Found: C, 82.64; H, 6.90; N, 10.43; mol. wt., 281 (ebullioscopic in butanone).

3,8-Diphenyl-1,2-diaza-1-cycloöctene.—A solution of 9.2 g. (0.035 mole) of 3,8-diphenyl-1,2-diaza-2,8-cycloöctadiene in 100 ml. of tetrahydrofuran was hydrogenated at 45 lb. pressure at room temperature with 2 g. of 10% palladium-on-charcoal in a Parr apparatus. The reduction was complete in 3 hours, the catalyst was removed by filtration, and 35 g. (0.16 mole) of mercuric oxide was immediately added. The mixture was stirred for 20 hr., the solid removed by filtration and the tetrahydrofuran was distilled at 40–50° under vacuum. The residual yellow solid was dissolved in 75 ml. of boiling methanol, the solution was decolorized with charcoal and filtered; long white needles were deposited on cooling overnight, 5.2 g. (56%), m.p. 86–87°. An analytical sample, m.p. 88–90°, was obtained after three recrystallizations from methanol. The ultraviolet spectrum gave a $\lambda^{\text{CHCl}_3}_{\text{max}}$ 368, log ϵ 1.65.

Anal. Calcd. for $C_{18}H_{20}N_2$: C, 81.77; H, 7.63; N, 10.60; mol. wt., 264. Found: C, 81.60; H, 7.47; N, 10.73; mol. wt., 297 (ebullioscopic in butanone), 279 (cryoscopic in cyclohexane).

The Decomposition Products from 3,8-Diphenyl-1,2-diaza-1-cycloöctene.—A 100-ml. flask, equipped with a side arm and a magnetic stirrer, containing 43 ml. of tetralin (dried over Drierite and redistilled) was flushed with nitrogen while the system was brought to 165–170°. A sample of 6.80 g. of 3,8-diphenyl-1,2-diaza-1-cycloöctene was introduced, and the solution was vigorously stirred while 97% of the theoretical amount of nitrogen was collected in 90 minutes. The tetralin was removed at 20 mm. to give a residue of a dark brown oil, 6.50 g. This oil was distilled at 5 mm. through a small hollow tube column; a forerun, 0.29 g., b.p. 158–160°, was obtained, and the rest of the distillate was collected at 169–186°, 5.53 g. (90%)—a mixture of olefinic and unsaturated hydrocarbon isomeric products.

Quantitative hydrogenation of this mixture with 10% palladium-on-charcoal in ethanol indicated the presence of 49.3% olefin. A quantitative ultraviolet determination gave a value of 52% olefin content.

A solution of 4.01 g. of this mixture and 2.4 g. of 2,4-dinitrobenzenesulfenyl chloride (recrystallized from Skelly C, m.p. 96–97°) in 18 ml. of glacial acetic acid was heated on the steam-bath for 1 hr. The solution was allowed to stand overnight, then 30 ml. of ether was added and the resulting solution was extracted with two 25-ml. portions of water, 25 ml. of 5% sodium carbonate and 25 ml. of water. The ether layer was dried with magnesium sulfate after removal of solvent, the resulting dark colored residue was dissolved in a solution of 5 ml. of benzene and 5 ml. of *n*-hexane and absorbed on a column of 100 g. of alumina (Woelm, almost neutral, activity 1). The column was eluted with *n*-hexane, 1:1 hexane–benzene, benzene and 10% ether in benzene.

The first fractions were combined to give a clear white hydrocarbon oil 1.73 g. (43%), which gave no evidence of unsaturation by its ultraviolet and infrared spectra or with bromine in carbon tetrachloride.

The remainder of the fractions were very viscous yellow oils, weighing 2.20 g. and 0.52 g. The first yellow oil was recrystallized from ethanol to give 1.41 g., m.p. 97–99°. Recrystallization from ethanol, and then isopropyl alcohol gave an analytical sample, m.p. 100–101°. The analysis indicated it to be an adduct from 1,6-diphenyl-1-hexene and 2,4-dinitrobenzenesulfenyl chloride in which chlorine has been removed. The ultraviolet spectrum gave a $\lambda^{\text{MeOH}}_{\text{max}}$ 340, log ϵ 4.01.

Anal. Calcd. for $C_{24}H_{24}O_4N_2S$: C, 66.03; H, 5.54; N, 6.42; S, 7.34. Found: C, 66.04; H, 5.86, 5.80; N, 6.32, 6.31; S, 7.35.

The second yellow oil was crystallized from ethanol to give 0.4 g., m.p. 127–128°. Another recrystallization from ethanol gave an analytical sample, m.p. 129–130°. The analysis indicated it to be the normal adduct from 1,6-diphenyl-1-hexene and 2,4-dinitrobenzenesulfenyl chloride. The ultraviolet gave a $\lambda^{\text{MeOH}}_{\text{max}}$ 330, log ϵ 4.05.

Anal. Calcd. for $C_{24}H_{23}O_4N_2SCl$: C, 61.20; H, 4.92; N, 5.95. Found: C, 61.28; H, 4.84, N, 5.89.

A solution of 0.5 g. of the saturated hydrocarbon fraction in 4 ml. of methanol was seeded with a tiny crystal of the high melting 1,2-diphenylcyclohexane and kept at −10° for 40 hr. to yield white prisms, 0.18 g., m.p. 35–40°. This was twice recrystallized from methanol to give 0.06 g., m.p. 52–53°. A mixed melting point determination with the authentic high melting isomer, m.p. 53–54°, melted at 51–53°.

The mother liquor was now seeded with a small crystal of the low melting 1,2-diphenylcyclohexane and kept at −10° for 20 hours; the white needles, 0.17 g., m.p. 37–42°, were removed by filtration. Recrystallization from methanol gave 0.08 g., m.p. 46–47°. The infrared spectra of the isomers isolated from the decomposition mixture were identical with those of the authentic isomers.

Preparation of 1,6-Diphenyl-1-hexanone.—6-Phenylhexanoic acid was prepared from 5-benzoylvaleric acid by the Clemmensen reduction as modified by Martin.[22] From 100 g. (0.49 mole) of 5-benzoylvaleric acid, 72 g. (77%) of 6-phenylhexanoic acid was obtained, b.p. 155–160° (0.3 mm.), n^{25}D 1.5198, b.p. 167–169° (1 mm.) (72%).[23]

To 36.9 g. (0.19 mole) of 6-phenylhexanoic acid in 125 ml. of benzene was added 29.8 g. (0.25 mole) of the thionyl chloride, and the resulting solution was warmed on the steam-bath for 3 hr. The benzene was removed under vacuum to give a dark oil. (In another experiment, the

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[20] A. F. Bickel and W. A. Waters, *Rec. trav. chim.*, **69**, 312 (1950).

[21] All melting points are uncorrected. Analyses by the Schwarzkopf Microanalytical Laboratory, New York, N. Y., and the Clark Microanalytical Laboratory, Urbana, Ill.

[22] E. L. Martin, This Journal, **58**, 1438 (1936).

[23] D. Papa, E. Schwenk and H. Hankin, *ibid.*, **69**, 3018 (1947).

crude acid chloride was distilled to give 67%, b.p. 140–145° (5 mm.), of a colorless liquid which turned brown in a few hours, 146–147° (9 mm.).[24])

Phenylmagnesium bromide was prepared from 5.8 g. (0.24 g. atom) of magnesium and 39.3 g. (0.25 mole) of bromobenzene in 125 ml. of ether. The solution was cooled to 10°, 23.8 g. (0.13 mole) of anhydrous cadmium chloride was added and the mixture was refluxed for 45 minutes. The ether was distilled almost to dryness and 170 ml. of benzene was added; 50 ml. was distilled to remove traces of ether. The solution was cooled to 10° and the crude 6-phenylhexanoyl chloride, dissolved in 40 ml. of benzene, was added in 5 minutes with stirring and the reaction mixture was kept at 70–80° for 4 hr. The mixture was decomposed with 20% sulfuric acid and water; the benzene layer was washed with water, 10% sodium hydroxide, water, a saturated salt solution and dried over magnesium sulfate. The residue, 28.8 g. of a dark oil, was distilled to give 10.6 g. (22%), b.p. 169–196° (0.2 mm.), of crude ketone. Redistillation of 5.0 g. gave an analytical sample, 1.9 g., b.p. 160° (0.1 mm.), of a liquid $n^{25}\text{D}$ 1.5601, $d^{25}{}_4$ 1.025. The ultraviolet spectrum showed a $\lambda_{\max}^{\text{MeOH}}$ 242, log ϵ 4.11, indicative of a conjugated carbonyl group.

Anal. Calcd. for $C_{13}H_{20}O$: C, 85.67; H, 7.99. Found: C, 85.82; H, 8.19.

From 0.5 g. of the ketone, 0.85 g. (99%) of a 2,4-dinitrophenylhydrazone derivative, m.p. 130–135°, was obtained. An analytical sample was obtained by successive recrystallizations from isopropyl alcohol and cyclohexane to give red plates, m.p. 131–132°.

Anal. Calcd. for $C_{24}H_{24}O_4N_4$: C, 66.65; H, 5.59; N, 12.96. Found: C, 66.61; H, 5.87; N, 12.68.

From 0.5 g. of the ketone, 0.6 g. (99%) of crude oily semicarbazone, m.p. 126–131°, was obtained. Two recrystallizations from ethanol gave an analytical sample, m.p. 133–135°.

Anal. Calcd. for $C_{19}H_{23}ON_3$: C, 73.75; H, 7.49; N, 13.58. Found: C, 73.51; H, 7.61; N, 13.83.

Preparation of 1,6-Diphenyl-1-hexene and its 2,4-Dinitrobenzenesulfenyl Chloride Derivatives.—The olefin was prepared from the ketone by a procedure essentially the same as that used for the preparation of 1,5-diphenyl-1-pentene.[25]

A solution of 5.6 g. (0.22 mole) of 1,6-diphenyl-1-hexanone in ether was reduced with 1.1 g. (0.03 mole) of lithium aluminum hydride. The crude carbinol was isolated and dehydrated in benzene solution with 2.2 g. (0.015 mole) of phosphorus pentoxide. The dark colored residue, 3.25 g., was distilled to give 1.52 g. (29%) of an oil, b.p. 128–132° (0.15 mm.), $n^{25}\text{D}$ 1.5711, $d^{25}{}_4$ 0.974. The infrared spectrum showed the band at 10.35 μ characteristic of this type of olefin.[7] The ultraviolet spectrum showed a $\lambda_{\max}^{\text{MeOH}}$ 252 mμ, log ϵ 4.22, $\lambda_{\max}^{\text{MeOH}}$ 283, log ϵ 3.09, characteristic of a substituted styrene.[26]

Anal. Calcd. for $C_{18}H_{20}O$: C, 91.47; H, 8.53. Found: C, 91.37; H, 8.65.

A solution of 0.35 g. (0.0015 mole) of the olefin and 0.42 g. (0.0018 mole) of 2,4-dinitrobenzenesulfenyl chloride in 2 ml. glacial acetic acid was heated on the steam-bath for 20 minutes. The solution was treated in the manner above for the mixture of decomposition products and chromatographed on 40 g. of alumina. Two oils were collected, the first, 0.30 g. (46%), gave 0.14 g. of yellow feathery crystals, m.p. 98–99°. Further recrystallization gave m.p. 99–100° and a mixture melting point with the first derivative from the decomposition mixture (the adduct without chlorine), m.p. 99–100°, melted at 99–100°. The second oil, 0.15 g. (22%), gave 0.093 g. of yellow needles, m.p. 128–130°, from ethanol. A mixture melting point with the second derivative from the decomposition mixture (the normal adduct), m.p. 129–130°, melted at 128–130°.

Preparation of the *cis*- and *trans*-1,2-Diphenylcyclohexanes. A. The high melting isomer was prepared by a modification of the procedure of Reesor, Smith and Wright.[16] The *trans*-disodium stilbene was rapidly prepared by stirring with sodium dispersion instead of shaking with sodium chunks and after addition of the 1,4-dichlorobutane at −78° the reaction was allowed to warm to room temperature. From 3.6 g. of *trans*-stilbene (0.02 mole) and 5.6 g. (0.044 mole) of 1,4-dichlorobutane there was obtained 2.3 g. (49%) of 1,2-diphenylcyclohexane, m.p. 51–53°. Recrystallization from methanol gave white prisms, m.p. 53–54° (m.p. 54.5–55.5°, 77%).[16] The ultraviolet spectrum showed a $\lambda_{\max}^{\text{MeOH}}$ 259 mμ, log ϵ 1.60.

B. The low melting isomer was prepared according to the procedure described by Parmerter, m.p. 46–47°.[15] The ultraviolet spectrum showed $\lambda_{\max}^{\text{MeOH}}$ 259 mμ, log ϵ 1.58.

When the high and low melting isomers were mixed together for a mixture melting point, an oil resulted whose infrared spectrum was identical to that of the mixture of saturated products obtained from the decomposition of the 8-membered ring azo compound II.

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BROOKLYN, N. Y.

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[CONTRIBUTION FROM THE DEPARTMENT OF ORGANIC CHEMISTRY, HEBREW UNIVERSITY]

Diels–Alder Reactions with 1-Formylcyclohexene and 1-Formylcyclopentene

BY ERNST D. BERGMANN AND ABRAHAM BECKER

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1-Formylcyclohexene and 1-formylcyclopentene give with butadiene, 2,3-dimethylbutadiene and 1-vinylcyclohexene normal Diels–Alder adducts. The product from 1-formylcyclohexene and 1-vinylcyclohexene, which gives no carbonyl derivatives, does not have the steroid-like structure III, but is IV; this has been shown by an unambiguous synthesis of the acid IX, obtained by the degradation of IV. The analogous product from 1-formylcyclopentene gives normal carbonyl derivatives. *cis*-9-Methyldecahydronaphthalene (XXIV) and *cis*-8-methylhydrindane (XXV) have been prepared from I and XV, respectively.

Diene reactions with 1-formylcyclohexene and 1-formylcyclopentene have more than systematic interest. These diene reactions may lead to polycyclic compounds containing the aldehyde group in an angular position as it occurs in a number of natural products: strophanthidin,[1] antiarigenin,[1] helleborigenin,[2] scilliglucosidin[3] and aldosterone.[4]

Some experiments on the condensation of 1-formylcyclohexene with dienes have been reported previously by Szmuszkowicz and Bergmann.[5]

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