triazole in 300 ml. of concd. hydrochloric acid and 150 ml. of concd. nitric acid was heated for one week under reflux. The solution was cooled and the crystalline product collected on a filter, washed and dried to give 1.2 g. (62%) of crude product. Recrystallization from nitromethane gave the pure product, m.p. 256–260°. On admixture this material does not depress the m.p. of an authentic sample of 4,5,6,7-tetrachlorobenzotriazole.

2-Methyl-4,5,6,7-tetrachlorobenzotriazole from 2,5-Dimethylbenzotriazole.—A solution of 1.5 g. (0.01 mole) of 2,5-dimethylbenzotriazole in 80 ml. of concd. hydrochloric acid and 80 ml. of concd. nitric acid was heated under reflux for 10 hr. The solution was cooled and the crystalline product collected on a filter, washed and dried. Three recrystallizations of this solid from methanol gave the pure product, m.p. 181–183°. On admixture this product does not depress the m.p. of an authentic sample of 2-methyl-4,5,6,7-tetrachlorobenzotriazole.

2,5-Dimethylbenzotriazole.—A solution of diazomethane in ether was added slowly to 13.3 g. (0.1 mole) of 5-methylbenzotriazole dissolved in ether until a slight yellow color persisted. The resulting solution was refluxed until the slight excess of diazomethane was removed and dried over anhydrous sodium sulfate. Dry hydrogen chloride was then bubbled through the ethereal solution. The precipitated hydrochlorides were removed by filtration. Evaporation of the ethereal solution gave 8.8 g. (60%) of crude product. Fractionation gave an analytical sample, b.p. 117° (12 mm.); λ_{max}, 276(s)(4.12), 284(4.14), 288(4.11).

Anal. Calcd. for $C_8H_9N_3$: N, 28.55. Found: N, 28.72.

β-1′-(Benzotriazolyl)-butyramide.—To 1.0 g. (0.005 mole) of β-1′-(benzotriazolyl)-butyric acid was added 4.0 ml. of thionyl chloride. After solution was complete, the mixture was added dropwise with stirring to 15 ml. of cold concd. ammonium hydroxide. The product was collected on a filter, washed with water and dried to give 0.3 g. which was 30% of the theoretical amount. Several recrystallizations from water gave an analytical sample, m.p. 104–105°; λ_{max}, 256(3.80), 262(3.80), 280(3.61).

Anal. Calcd. for $C_{10}H_{12}N_4O$: N, 27.44. Found: N, 27.42.

Ultraviolet Absorption Data.—Ultraviolet absorption measurements were made with a Beckman DU photoelectric spectrophotometer with 1.00-cm. silica cells and a hydrogen discharge lamp as the light source. The measurements were made in methanol solution. The data are recorded in the preceding Experimental sections as wave lengths at which maxima or shoulders(s) occur with the corresponding log ε in parentheses.

LOUISVILLE, KENTUCKY

[CONTRIBUTION OF THE SCHOOL OF SCIENCE, BRANDEIS UNIVERSITY]

Preparation and Decomposition of a Cyclic Azo Compound. 3,6-Diphenyl-3,4,5,6-Tetrahydropyridazine

BY SAUL G. COHEN, SHU-HSI HSIAO,[1a] EUGENE SAKLAD AND CHI HUA WANG[1b]

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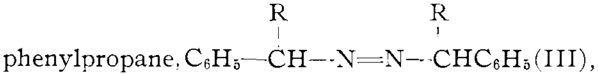
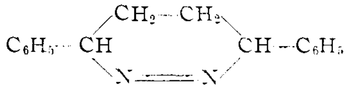
The azo compound I was prepared by addition of diethyl azodicarboxylate to 1,4-diphenylbutadiene-1,3, hydrogenation, hydrolysis, decarboxylation and autoxidation; λ_{max} 387 mμ, log ε 2.89, displaced from 345 mμ of *trans*-aliphatic azo compounds. Compound I decomposes in hydrocarbon solvents, including solutions containing styrene, with essentially quantitative yield of nitrogen, and about 100 times as fast at 80° as acyclic analogs. Solid I, heated at about 125°, led in part to styrene and in part to rearrangement to the hydrazone tautomer. Attempts to obtain products of addition of the biradical 1,4-diphenyl-1,4-butadiyl to stilbene and quinone failed. The mode of decomposition of I and its possible activity as a polymerization initiator are discussed.

As part of our study of the chemistry of azo compounds[2] we undertook to prepare 3,6-diphenyl-3,4,5,6-tetrahydropyridazine (I) and by its decomposition, the biradical 1,4-diphenyl-1,4-butadiyl (II), $C_6H_5\dot{C}HCH_2CH_2\dot{C}HC_6H_5$. Compound I, because of its cyclohexene type structure would be a *cis*-azo compound, while acyclic aliphatic azo compound are normally *trans*, and it seemed of interest to compare its physical properties, its ease of decomposition and its products of decomposition with those of the closely related *trans*-acyclic compounds,[3] 1-azo-bis-1-phenylethane or 1-azo-bis-1-phenylpropane,  $C_6H_5-\overset{R}{\overset{|}{C}H}-N{=}N-\overset{R}{\overset{|}{C}}HC_6H_5$ (III), R = CH_3 or C_2H_5. The 1,4-biradical II, which might be formed, would be of interest both for a study of its chemistry as such and because it is identical with the product of "tail-to-tail" reaction of two molecules of styrene which had once been proposed as the active intermediate in the initiation of the thermal polymerization of styrene,[4] but which is no longer supported.[5]



I

Preparation of Compound I.—The preparation of the azo compound I has been reported[6] by (1) condensation of two molecules of α-chloroacetophenone semicarbazone to a compound which appears to be 2-carbamyl-3,4,5-trihydro-3,6-diphenylpyridazine (a) followed by (2) treatment with sodium ethoxide at 160°. The product was converted to 3,6-diphenylpyridazine by treatment with bromine water and was assigned structure I. We repeated this preparation and found that the compound had an absorption maximum at 292 mμ, log ε 4.19, which has been characteristic of the hydrazones tautomeric with the acyclic azo compounds in this work,[2a,7] and end absorption in the near ultraviolet but no maximum in the range of 300–400 mμ which would be characteristic of the azo compound.[3] This, coupled with the strongly

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[1] (a) This paper is derived in part from a thesis submitted by Shu-hsi Hsiao in partial fulfillment of the degree of Master of Arts in Chemistry, Brandeis University. (b) For preliminary report see C. H. Wang, S. Hsiao, E. Saklad and S. G. Cohen, THIS JOURNAL, **79**, 2661 (1957).

[2] (a) S. G. Cohen and C. H. Wang, *ibid.*, **77**, 2457 (1955); (b) **77**, 3628 (1955).

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

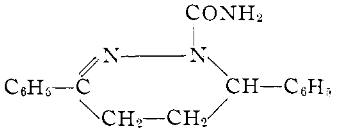
[4] F. R. Mayo, *ibid.*, **65**, 2324 (1943).

[5] F. R. Mayo, *ibid.*, **75**, 6133 (1953).

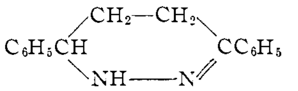
[6] A. P. J. Hoogeveen and C. V. van Hoogstraten, *Rec. trav. chim.*, **52**, 378 (1933).

[7] G. Fodor and P. Szarvas, *Ber.*, **76B**, 334 (1943).

ionizing conditions of preparation, which would favor tautomerism, and the high thermal stability of the material, lead us to assign to it the tautomeric structure IV, m.p. 157–159°.



(a)

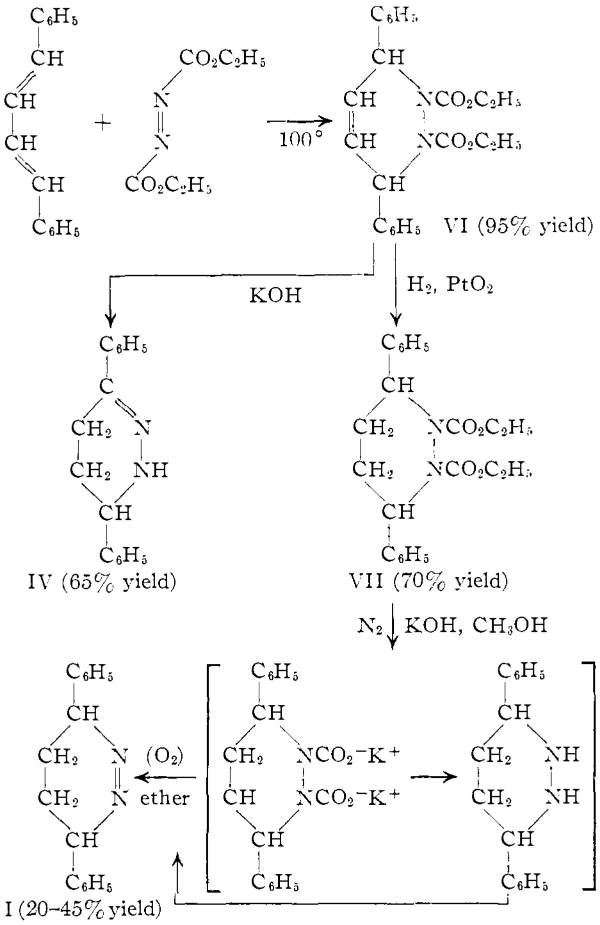


IV

Compounds of type III have been prepared by conversion of the relevant ketone C_6H_5COR to the azine, hydrogenation to the hydrazine and oxidation to the azo compound.[3] However, the reactions of γ-diketones necessary for the formation of cyclic azo compounds related to I do not proceed this simply. The reactions of 1,2-dibenzoylethane[8] and acetonylacetone[9,10] with hydrazine do not lead to isolation of the pure azine, *i.e.*, the 4,5-dihydropyridazine, but to a mixture from which the disproportionation products, the pyridazine and the tetrahydropyridazine, each substituted at the 3- and 6-positions, may be obtained. Again the conditions of formation of the tetrahydro compound would indicate that the one from dibenzoylethane is probably the more stable tautomer IV. In our work treatment of 1,2-dibenzoylethane with hydrazine led to a mixture V which was apparently not readily separated into its components. Attempted hydrogenation to the hexahydropyridazine over platinum oxide in ethanol containing hydrogen chloride led to the hydrazone IV in about 50% yield, while when the reaction was attempted in acetic acid, 3,6-diphenylpyridazine was obtained, also in about 50% yield. While we cannot rule out that these products were formed by disproportionation of the dihydro compound in the presence of the hydrogenation catalyst, they may well have comprised the crude reaction product V. Attempted reduction of the hydrazone IV or the mixture V with lithium aluminum hydride was not successful, although some of the azo compound I may have been present in the product from V. It seemed likely that more vigorous reduction, as with zinc and hydrochloric acid, would lead to cleavage of the nitrogen–nitrogen bond.[11]

The azo compound I was prepared by: (a) Diels–Alder addition of diethyl azo-dicarboxylate to 1,4-diphenylbutadiene, forming the adduct[12] VI, (b) hydrogenation[12] of the carbon–carbon double bond in VI, leading to VII, followed by (c) saponification of the hydrogenated adduct, decarboxylation and, apparently, autoxidation in ether solution to form I (Chart 1). Saponification of the adduct VI in methanol led, as reported,[12] to the tautomeric product IV instead of to the $\Delta^{4,5}$-compound. While hydrogenation of VI did not, in our experiment, lead to a product of quite as sharp a melting point as reported, elementary analysis was satisfactory. Attempted acid hydrolysis of both the adduct VI and the hydrogenated adduct VII led to recovery of the respective starting materials. Alkaline hydrolysis of the hydrogenated adduct, compound VII, in glycol in the presence of air was reported[12] to lead to the tautomeric product of oxidation IV, while saponification in the absence of air led to impure hexahydrodiphenylpyridazine.[12]

CHART 1



In our work, alkaline hydrolysis of VII in glycol under nitrogen followed by attempted precipitation of the hydrochloride of the hexahydro compound from the ether extract of the saponification product led to the hydrazone IV. Observation of some crystals, which decomposed at 110° with gas evolution, in a portion of the product which had not been treated with hydrogen chloride led to successful synthesis of I. The hydrolysis of VII was carried out by treatment with potassium hydroxide in refluxing methanol under nitrogen, decarboxylation apparently occurring concomitantly. The solution was diluted with water and extracted with ether, either with or without prior neutralization with hydrochloric acid. Concentration of the dried ether solution led to the azo compound I, autoxidation of the hydrazo compound apparently taking place at this stage, since autoxidation during

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(8) C. Paal and E. Dencks, This Journal, **36**, 491 (1903).

(9) E. E. Blaise, *Compt. rend.*, **170**, 1324 (1920).

(10) C. G. Overberger, N. R. Byrd and R. R. Mesrobian, This Journal, **78**, 1961 (1956).

(11) O. Diels and K. Alder, *Ann.*, **450**, 237 (1926).

(12) K. Alder and H. Niklas, *ibid.*, **585**, 81 (1954).

the hydrolysis would lead to the hydrazone tautomer.[12] The compound melted with gas evolution when placed in a bath at 110–120°; when heated slowly as in a normal melting point determination it sintered at 120°, discolored and melted at 147–154°, apparently tautomerizing to IV. The facile rearrangement makes isolation and characterization of I difficult. Preparation of a solution of I in acetic acid, followed immediately by concentration in vacuum, led to isomerization to IV. Preparation of a solution of I in benzene, followed by concentration in vacuum, did not lead to rearrangement, I being recovered, dec. 120°. The ultraviolet absorption spectrum of I in cyclohexane showed maxima at 287 mμ, log ϵ 3.49, and at 387 mμ, log ϵ 2.89, the latter apparently to be attributed to the azo linkage and being displaced from $\lambda_{\max}$ 345 mμ, characteristic of the aliphatic azo linkage, because of its *cis* character.

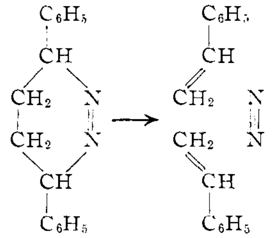
Decomposition of I.—Because of the relatively slow rate of decomposition of the acylic analogs of I (compound III, R = CH_3, half-life, 1.25 hr., 110°), and the ready isomerization of I to IV, it seemed advisable at first to examine the nitrogen evolution from decomposition of I at 135°, wetted with a small amount of redistilled decalin. A high (*ca.* 90%) yield of nitrogen, obtained rapidly, indicated that thermal decomposition could be attained essentially completely without serious interference from rearrangement. The yield of nitrogen appeared somewhat less (*ca.* 80%) when the decomposition was repeated at 90°. It was then found that the decomposition could take place cleanly, in dilute solution (< 1%) in hydrocarbon solvents. Decomposition in decalin at 135° and at 100° led to about 95% yield of nitrogen. Decomposition in ethylbenzene that had not been freshly distilled led to low, non-reproducible yields, rearrangement presumably taking place; distillation of the ethylbenzene led to high yields of nitrogen at 100°.

Since we would wish to examine compound I as an initiator of polymerization and as a source of the biradical II, a possible intermediate in the thermal polymerization of styrene, the decomposition of compound I in 3.46 moles/l. styrene in ethylbenzene was examined briefly. Nitrogen evolution was rapid and essentially quantitative both at 100 and at 80°. The data on evolution of nitrogen are summarized in Table I.

Observations made during the measurements of the evolution of nitrogen indicate that decomposition was essentially complete in about 20 minutes at 100° and that the half-life at 80° was about 20 minutes. In contrast, the half-life for decomposition of the acyclic analog $C_6H_5CH(CH_3)N{=}NCH(CH_3)C_6H_5$ (III) is about 4 hr.[3] at 100°. It may be estimated that the first-order rate constant for decomposition of I at 80° is about 6×10^{-4} sec.$^{-1}$, while that for III is about two orders of magnitude less, 4.5×10^{-6}. Apparently the *cis*-azo structure of I (possibly aided by another factor to be discussed below) leads to increased ease of decomposition, in addition to the shift in absorption maximum noted above. It will be of interest to examine the kinetics of decomposition of cyclic azo compounds of this type. Extreme instability had been reported[13] for a seven-membered cyclic azo compound, but subsequent work[14] assigned a different structure to the material. The six-membered cyclic analog of azo-bis-isobutyronitrile was apparently too unstable to be isolated.[10] A 24-membered[15] cyclic azo compound analogous to I decomposed at the same rate as the acyclic analog III (R = C_2H_5), and had an absorption maximum at 355 mμ, characteristic of the acyclic compounds; the large ring presumably allowed the azo linkages to assume their normally preferred *trans* configurations.

It was of course desirable to ascertain, if possible, the nature of the hydrocarbon products of decomposition. A sample of the azo compound I (0.053 g.) was decomposed in the solid state under nitrogen, and the residue was worked up. The rearranged product IV was obtained in 30% yield, and it appears likely and not unreasonable that the isomerization occurs to a greater extent under these conditions than in dilute solution in hydrocarbon solvents. The odor of styrene was detected readily immediately after the decomposition, and treatment of the filtrate, after removal of IV, with bromine in acetic acid led to styrene dibromide in 7% yield (based on non-rearranged I). Since this product was isolated in only 17% yield in a control experiment carried out under similar conditions, it may be that half of the azo compound which decomposes is converted to styrene. The styrene may be formed (a) in a second reaction from the biradical II or (b) directly from decomposition of the azo compound into three fragments

$$C_6H_5\dot{C}HCH_2CH_2\dot{C}HC_6H_5 \longrightarrow 2C_6H_5CH{=}CH_2 \quad \text{(a)}$$



(b)

The latter course, leading directly to three molecules and no radicals, might well contribute to the observed enhanced ease of decomposition of I. The rupture of the three bonds in process b need not be completely symmetrical, the two carbon–nitrogen bonds being more completely broken in the transition state than the carbon–carbon bond and the transition state possibly having characteristics of the transition state of both processes a and b. This would contribute to increased ease of decomposition and allow both styrene and products of the biradical to be observed.

Attempts were made to find evidence for the formation of the biradical II by carrying out the decomposition of I in the presence of unsaturated material that might react with II. In the presence of stilbene we failed to isolate the possible six-membered cyclic adduct, recovering part of the

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[13] C. G. Overberger, P. T. Huang and T. B. Gibb, THIS JOURNAL, **75**, 2082 (1953).

[14] C. G. Overberger and B. S. Marks, *ibid.*, **77**, 4097 (1955).

[15] C. G. Overberger and M. Lapkin, *ibid.*, **77**, 4651 (1955).

TABLE I

THERMAL DECOMPOSITION OF COMPOUND I
EVOLUTION OF NITROGEN

Expt.	Cmpd. I, g.	Solvent, g.	T, °C.	Ml.	N_2 Yield, %
1	0.0331	0.050[a]	135	3.10	90
2	.0422	.060[a]	136	4.32	99
10	.0194	.050[a]	110	1.80	90
11	.0203	.040[a]	90	1.60	80
12	.0228	2.78[a]	135	2.60	108
15	.0170	2.37[a]	135	1.70	95
16	.0199	2.16[a]	100	2.00	96
17	.0165	1.90[a]	100	1.70	96
20	.0148	1.74[b]	100	1.29	82
21	.0298	2.76[b]	100	0.50	16
22	.0173	1.65[c]	100	1.60	89
27	.0264	2.52[c]	100	2.85	103
33	.0215	2.09[c]	100	2.20	99
23	.0140	1.57[d]	100	1.40	96
24	.0210	2.21[d]	100	2.13	97
29	.0253	1.97[d]	100	2.58	98
31	.0211	2.07[d]	100	2.20	100
34	.0207	2.23[d]	80	2.22	103
36	.0223	2.12[d]	80	2.25	97

[a] Decalin. [b] Ethylbenzene (not distilled). [c] Ethylbenzene (distilled). [d] 3.46 moles/l. styrene in ethylbenzene.

TABLE II

THERMAL DECOMPOSITION OF COMPOUND 1 IN 3.46 M./L.
STYRENE IN ETHYLBENZENE. POLYMER CONTENT

Exp. no.	Cmpd. I, m./l.	T, °C.	Time, min.	Sample, g.	Polymer g.	Polymer %	Mole polymd. per mole cmpd. I
23[a]	0.033	100	30	1.461	0.0351	5.8	4.3
24[a]	.035	100	30	2.112	.0427	4.9	3.1
25[a]	...	100	30	2.658	.0199	1.8	
26[a]	...	100	30	2.089	.0145	1.7	
34[b]	.034	80	150	2.128	.0842	8.7[c]	8.6
36[b]	.039	80	150	2.015	.0897	9.7[c]	8.5
35[b]	...	80	150	2.115	.0026	0.3	
37[b]	...	80	150	1.952	.0011	0.1	

[a] Sample was diluted with methanol and insoluble portion was weighed. [b] Sample was evaporated to constant weight in vacuum, room temperature. [c] Correction applied, assuming half the hydrocarbon part of the azo compound remains in the residue.

stilbene. In the presence of quinone the possible derivative of naphthohydroquinone was not found. In addition to recovered quinone and quinhydrone, a small amount of the rearrangement product IV and a considerable quantity (47% yield) of the product of dehydrogenation of I or IV, 3,6-diphenylpyridazine, were obtained.

In order to obtain preliminary information about the efficacy of this potential biradical source as a polymerization initiator, the styrene–ethylbenzene solutions in which the azo compound had been decomposed in the nitrogen evolution experiments were examined for polymer contents and compared with blank solutions treated in the same way in the absence of compound I. The data are summarized in Table II. In experiments carried out at 100° (expts. 23, 24, 25, 26), the polymer was precipitated in methanol; an undesirably high yield of polymer was found in the blank run in the absence of azo compound I. After correction for this, it appeared that about 4 molecules of styrene had been polymerized per molecule of I originally present. In experiments carried out at 80° (expts. 34, 35, 36, 37), the volatile components were removed in vacuum until the residue was brought to constant weight; satisfactory low yields were obtained in the absence of I and the small corrections were made. It appeared that about 8 molecules of styrene were rendered non-volatile per molecule of I originally present. Such a number has significance for comparison with other initiators only if (a) the rate of decomposition of the azo compound and (b) the fraction which is converted to radicals (as distinguished from styrene molecules) are known. Using the approximate rate constant, given before, and making the necessary corrections for concentration and temperature, we estimate[16] that benzoyl peroxide would polymerize about 70 molecules of styrene per molecule of peroxide under similar conditions. It is not clear, however, whether this larger number is due to the peroxide leading to long chains, while the azo compound through its biradical leads to smaller cyclic products,[5,17,18] or arises from a comparatively low yield of effective biradical from the azo compound, the larger part of it decomposing to styrene—the reverse of a possible initiating step in the thermal polymerization. Study of the kinetics of decomposition of I and of the properties of the polymer that may be formed in low yield are required to give indication as to whether the biradical II may lead to high polymer and be involved in the thermal polymerization of styrene.

Experimental[19]

3,6-Diphenyl-2,3,4,5-tetrahydropyridazine (IV). **A.**—α-Chloroacetophenone, 15.5 g. (0.1 mole), in 125 ml. of ethanol was treated with 11 g. (0.1 mole) of semicarbazide hydrochloride in 12.5 ml. of water at 40° with gradual addition of 8.5 g. (0.1 mole) of sodium bicarbonate. The mixture was boiled and cooled, and the product was collected, washed with ethanol and dried; α-chloroacetophenone semicarbazone 12.5 g. (0.059 mole), 59% yield, m.p. 151–152°, reported[20] 156°. The semicarbazone, 12.5 g., was heated under reflux for 1.2 hr. with 11 g. (0.13 mole) of sodium bicarbonate in 200 ml. of 1:1 ethanol–water. The product was collected and dried; 7.3 g. (0.026 mole), 44% yield, m.p. 213–216°, 218.5–220° after two crystallizations from benzene, reported[6] 221°. *Anal.* Calcd. for $C_{17}H_{17}ON_3$: C, 73.10; H, 6.13; N, 15.04. Found: C, 72.87; H, 5.85; N, 14.78. The product above, 2 g. (0.0072 mole), was heated for 6 hr. at 160° in a solution of 6 g. of sodium in 120 ml. of ethylene glycol and cooled. The product IV was collected and crystallized from ethanol, 1.6 g. (0.0068 mole), 94% yield, m.p. 157–159°, reported[6] 159°. No gas was evolved when it was heated to 300°. The absorption spectrum was determined in chloroform in a Beckman DU spectrophotometer and showed a small minimum at 245 mμ, log ε 3.68, a maximum at 292 mμ, log ε 4.19, which fell off rapidly to log ε 1.20 at 365 mμ and more slowly to log ε 0.45 at 400 mμ.

B.—Succinyl chloride, 20 g. (0.13 mole), in 56 ml. of thiophene-free benzene was added at room temperature over a period of 2 hr. with stirring to 25 g. (0.19 mole) of aluminum chloride in 200 ml. of benzene. The mixture was treated with ice and 20 ml. of concentrated hydrochloric

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[16] S. G. Cohen, THIS JOURNAL, **67**, 17 (1945).

[17] D. H. Johnson and A. V. Tobolsky, *ibid.*, **74**, 938 (1952); K. E. Russell and A. V. Tobolsky, *ibid.*, **75**, 5052 (1953).

[18] B. H. Zimm and J. K. Bragg, *J. Polymer Sci.*, **9**, 476 (1952).

[19] Melting points are uncorrected. Elementary microanalyses were performed by Dr. S. M. Nagy, Massachusetts Institute of Technology.

[20] G. Knopfer, *Monatsh.*, **31**, 108 (1910).

acid. The benzene solution was concentrated and the precipitate was washed and crystallized from ethanol, 1,2-dibenzoylethane, 5.0 g. (0.021 mole), 16% yield, m.p. 144–145°, reported[21] 144–145°. 1,2-Dibenzoylethane, 5 g. (0.021 mole), was dissolved in 30 ml. of ethanol and treated with 2 g. of hydrazine hydrate. A white solid V was obtained, 4.8 g., 96% yield, m.p. 140–210°. Attempted crystallization from ethanol did not lead to pure compounds.

A solution of 3 g. of the mixture V in 200 ml. of ethanol was treated with 5 ml. of ethanol saturated with hydrogen chloride, then with hydrogen over platinum oxide at 50° for 2.5 hr., filtered and cooled. Compound IV crystallized out, 0.650 g., m.p. 144–152°, 155–157°, after recrystallization from alcohol, alone and when mixed with the product from procedure A, above. The original filtrate was made alkaline, leading to an additional 1.1 g. of crude IV, m.p. 140–155°, 155–157° after several recrystallizations. The ultraviolet absorption spectrum was identical with that described in A, above.

C.—The adduct of diethyl azo-dicarboxylate and 1,4-diphenylbutadiene, compound VI below, 1 g. (0.0026 mole), was boiled in 3 ml. of 40% potassium hydroxide in methanol for 1 hr. under nitrogen. The solution was cooled, diluted with 2 ml. of water and acidified with concentrated hydrochloric acid. A solid separated, was collected, washed with water and crystallized from methanol; 0.4 g., 64% yield, m.p. 156–158°, mixed m.p. with IV, 157–159°.

3,6-Diphenylpyridazine. A.—A solution of 1.0 g. of mixture V in 10 ml. of acetic acid was treated with hydrogen over platinum oxide at 30 p.s.i. for 2 hr., filtered and concentrated in vacuum, leading to 3,6-diphenylpyridazine, 0.50 g., 50% yield, m.p. 207–219°, crystallized from ethanol, m.p. 219–220°, reported[12] m.p. 222°.

B.—A solution of IV, 0.384 g. (1.62 mmoles), in 30 ml. of acetone was treated with 6 drops of 30% hydrogen peroxide at room temperature for 16 hr. and concentrated. The residue was crystallized from ethanol, leading to 3,6-diphenylpyridazine, 0.155 g., 40% yield, m.p. and mixed m.p. 218–220°.

Attempted Reductions with Lithium Aluminum Hydride.—A: Treatment of the mixture V, 2 g., with 1.1 g. of $LiAlH_4$ in 50 ml. of ether under reflux for 6 hr. led to material melting 155–180°, 1.6 g. B: Treatment of 4.8 g. of mixture V with 1 g. of $LiAlH_4$ in di-*n*-butyl ether at 80° for 13 hr. led to 2.5 g. of material melting at 95–110°, 116–120° dec. after crystallization from methanol–water in Dry Ice. C: Treatment of the hydrazone IV, 0.5 g., with 0.1 g. of $LiAlH_4$ in 50 ml. of di-*n*-butyl ether at 80° for 13 hr. led to recovered IV, 0.3 g. D: Treatment of the hydrazone IV, 0.350 g., with 0.150 g. of $LiAlH_4$ in 30 ml. of di-*n*-butyl ether under reflux for 5 hr. led to recovered IV, 0.120 g.

1,2-Dicarboethoxy-3,6-diphenyl-1,2,3,6-tetrahydropyridazine (VI).—A: 1,4-Diphenylbutadiene[22] was prepared by condensation of phenylacetic acid (150 g., 1.10 moles) and cinnamaldehyde (169 g., 1.28 moles) in acetic anhydride (155 ml.) in the presence of lead oxide (122 g.) at 145°; 50 g., 22% yield, m.p. 152–153°, from benzene–ethanol, reported[22] 152.5–153.5°. B: Diethyl 1,2-hydrazinedicarboxylate[23] was prepared from reaction of hydrazine hydrate (78.2 g.) with ethyl chlorocarbonate (108 g., 1.00 mole) in ethanol at 0°; 47.5 g. (0.27 mole), 54% yield, m.p. 132–133° from water, reported[23] 130°. C: Diethyl azo-dicarboxylate[24] was prepared by treatment of a solution of 20 g. (0.11 mole) of diethyl 1,2-hydrazinedicarboxylate in 24 ml. of concentrated nitric acid with 4.8 ml. of fuming nitric acid at 0° for 1.5 hr. The mixture was poured into ice-water, extracted with ether, washed with sodium bicarbonate, dried and distilled; 8.3 g. (0.048 mole), 42% yield, b.p. 106–108° (13 mm.), reported[24] 106° (13 mm.). D: 1,2-Dicarboethoxy-3,6-diphenyl-1,2,3,6-tetrahydropyridazine (VI) was prepared by reaction of 9.0 g. (0.05 mole) of diethyl azodicarboxylate with 9 g. (0.044 mole) of 1,4-diphenylbutadiene in 10 ml. of toluene on the steam-bath for 3 hr. The toluene was removed in vacuum and the adduct VI was crystallized from ethyl acetate; 15.8 g., 95% yield, m.p. 134–136°, reported[12] 132°. *Anal.* Calcd. for $C_{22}H_{24}N_2O_4$: C, 69.44; H, 6.36. Found: C, 69.13; H, 6.42.

3,4,5,6-Tetrahydro-3,6-diphenylpyridazine (I). **A.**—The adduct VI, 5 g. (0.013 mole), was hydrogenated in 300 ml. of acetic acid over platinum oxide at 30 p.s.i. The solution was filtered and concentrated and the residue was crystallized from ethanol, 3.5 g., 70% yield, m.p. 85–87°, solid persisting to 95°, reported[12] 87°. Recrystallization from ethanol did not affect the melting range. *Anal.* Calcd. for $C_{22}H_{26}N_2O_4$: C, 69.06; H, 6.85. Found: C, 69.22; H, 6.96. Treatment of the hydrogenated adduct VII above with concentrated hydrochloric acid in methanol under reflux for 1 hr. led to recovery of VII. The adduct VI was also unaffected under these conditions.

B (1): A solution of 1.0 g. (2.6 mmoles) of VII and 1.5 g. of potassium hydroxide in 5 ml. of ethylene glycol was boiled under nitrogen for 2 hr., cooled, diluted with 25 ml. of water and extracted with peroxide-free ether. The solution was dried over magnesium sulfate and treated with dry hydrogen chloride. An oil precipitated, at first white, then turning orange, crystallization of which from ethanol and water and from ethyl acetate led to the hydrazone IV, m.p. 156–158°. Some crystals were observed in the magnesium sulfate; the latter was dissolved in water, the crystals were collected and dried, dec. 110° with gas evolution when heated rapidly, sintered 98°, melting over a range to 145° when heated slowly. (2). A second saponification was carried out in the same way. The dried ether extract was concentrated and cooled leading to long flat crystals, 0.284 g. (1.25 mmoles), 48% yield, decomposing with gas evolution at 110°. (3): Saponification of 1.0 g. of VII by 2 g. of potassium hydroxide in 5 ml. of boiling methanol was carried out similarly. The dried ether extract was concentrated and crystals were obtained and dried in a desiccator; 0.15 g. (0.64 mmole), 25% yield, dec. 110°. (4): The hydrogenated adduct VII, 1.0 g. (2.6 mmoles), was boiled for 1 hr. under nitrogen in a solution of 2.0 g. of potassium hydroxide in 5 ml. of methanol, cooled in ice, diluted with 10 ml. of water, brought to *p*H 8 with 6 *N* hydrochloric acid and extracted with ether. The ether solution was dried over magnesium sulfate, concentrated and refrigerated. Elongated plate-like crystals formed, 0.135 g., 22% yield, decomposing with gas evolution when placed in a bath at 120°. *Anal.* Calcd. for $C_{16}H_{16}N_2$: C, 81.30; H, 6.82; N, 11.85. Found: C, 81.48; H, 6.92; N, 11.75. In other runs yields varied from 20 to 45%. The ultraviolet absorption spectrum in cyclohexane showed maxima at 287 mμ, log ϵ 3.49, and at 387 mμ, log ϵ 2.89.

Rearrangement of I.—A small quantity of the azo compound I was dissolved in acetic acid and the solution was immediately evaporated to dryness in vacuum at room temperature, leading to the hydrazone IV, m.p. and mixed m.p. 155–158°.

Decomposition of I. A. Nitrogen Evolution.—The azo compound I was dissolved in a small quantity of redistilled solvent in a test-tube connected to a thermostated gas buret, the system (including the solution) was swept with oxygen-free nitrogen and leveled, the test-tube was heated at 135° or 110° for 0.5 hr. or at 100 or 90° for 1 hr. or at 80° for 2.5 hr. and brought back to the thermostat temperature (30°) and the evolved gas was measured. The interim readings were observed at the reaction temperature. The volumes measured were small and the accuracy was probably about ±5%. The data are summarized in Table I.

B. **Products of Decomposition.**—(1): Compound I, 0.053 g. (0.225 mmole), in a tared centrifuge-tube under nitrogen, was heated at 110° for a few minutes, then placed in an oil-bath at 125° for 5 minutes, strong nitrogen evolution ensuing and droplets condensing on the walls of the tube. The tube was opened and the odor of styrene was detected; the tube was swept again with nitrogen, stoppered and reweighed, loss of 0.008 g. being observed. The residue (solidified) was treated with 3 ml. of 95% ethanol, leading to compound IV, 0.016 g., 30% yield, m.p. 156–158°, mixed m.p. 157–158°. The filtrate was treated with 4% bromine in acetic acid until a pale yellow color persisted, diluted with 1 ml. of water and cooled, leading to styrene dibromide, m.p. and mixed m.p. 68–70°, 0.006 g. (0.023 mmole), 7% yield. Styrene, 0.100 g. (1 mmole), was dissolved in 3 ml. of ethanol and brominated as described above, leading to styrene dibromide, m.p. 68–70°, 0.044

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(21) S. Kapf and C. Paal, *Ber.*, **21**, 3056 (1888).

(22) B. B. Corson, "Organic Syntheses," Coll. Vol. II, John Wiley and Sons, Inc., New York, N. Y., 1948, pp. 229–230.

(23) U. Sachsse, *Ber.*, **27**, 773 (1894).

(24) O. Diels and P. Fritzsche, *ibid.*, **44**, 3018 (1911).

g. (0.17 mmole), 17% yield, reported[25] 72–73°. The infrared spectra of the two samples were identical, showing a strong carbon–bromine bond at 695 cm.$^{-1}$.

(2) A solution of compound I, 0.050 g. (0.212 mmole), and stilbene, 0.036 g. (0.212 mmole), in 1 ml. of ethylbenzene (b.p. 134–134.5°) was heated in vacuum at 100° for 50 minutes, concentrated to dryness in vacuum and treated with methanol. Stilbene was recovered; 0.014 g., 39% yield, m.p. and mixed m.p. 123–125°. The residue was an oil.

(3) A solution of I, 0.061 g. (0.26 mmole), and freshly sublimed quinone, m.p. 114–115°, 0.221 g. (2.0 mmoles), in 6 ml. of benzene was heated under nitrogen at 90° (bath temperature) for 42 hr. The solution was concentrated and sublimed in vacuum leading to recovery of quinone and separation of some black solid, 0.020 g. melting unsharply above 160°, presumably quinhydrone. The black residue, 0.145 g., was heated with a little ethanol, leading to compound IV, 0.003 g., 5% yield, m.p. and mixed m.p. 155–157°. The residue was chromatographed on alumina, leading to 3,6-diphenylpyridazine, 0.028 g., 47% yield, m.p. and mixed m.p. 219–220°

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WALTHAM, MASS.

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[25] R. Fittig and E. Erdmann, *Ann.*, **216**, 194 (1883).

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Quinazolinediones from Aromatic Amines and Carbon Dioxide

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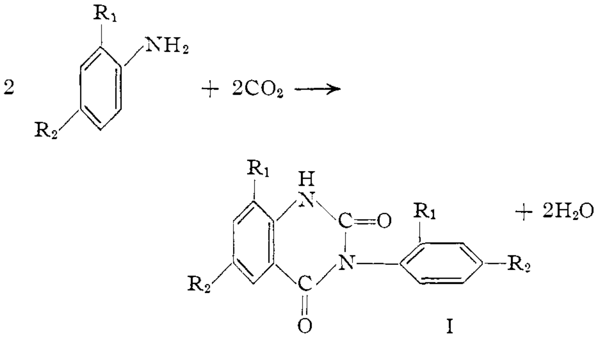
The reaction of carbon dioxide with certain primary aromatic amines at 8500 atm. and 200–250° has given high conversions to 3-aryl-2,4(1H,3H)-quinazolinediones (I). A sharp pressure threshold for the reaction was found at about 3300 atm.; the quinazolinediones were not formed at lower pressures, while conversions increased to 65–70% at the highest temperatures and pressures investigated.

Previous communications[1] from this Laboratory have described investigations of the effects of pressures of 6000 to 8500 atm. on chemical reactions. This paper reports a new reaction, the high pressure synthesis of 3-aryl-2,4(1H,3H)-quinazolinediones (I) from certain primary aromatic amines and carbon dioxide according to the equation[2]



I

This unusual transformation has been examined in terms of the effects of temperature, pressure, solvents, catalysts and substituents. Conversions of aniline to 3-phenyl-2,4(1H,3H)-quinazolinedione (I, $R_1 = R_2 = H$) as high as 70% were obtained at temperatures above 200° at 8500 atm., but the conversion fell to zero at 150°. A sharp pressure threshold for the reaction was found at about 3300 atm. The quinazolinedione was not formed at lower pressures, and the conversion increased rapidly with increased pressures above the threshold value. The reaction occurred in the presence of either alkaline or acidic catalysts, but with acidic catalysts the yield of quinazolinedione was decreased by formation of unidentified by-products. In the uncatalyzed reaction, formation of the corresponding *sym*-diarylurea was the chief competing reaction.

Quinazolinediones were also obtained from *o*-toluidine (15% conversion, $R_1 = CH_3$, $R_2 = H$) and from *p*-toluidine (50% conversion, $R_1 = H$, $R_2 = CH_3$). Quinazolinediones were not identified among the reaction products when the aromatic amine contained nitro, halogen or hydroxyl substituents or when the amine was α- or β-naphthylamine.

Primary aromatic diamines have given complex intractable products with carbon dioxide under these conditions. These products may have been low molecular weight polymeric quinazolinediones or polymeric ureas.

Experimental

Aniline and CO_2.—Aniline (4.08 g.) and carbon dioxide (2.39 g.) were charged into a stainless steel cylinder fitted with a movable piston.[3] In some runs a small quantity of nitrogen (*ca.* 0.3 g.) was used to ensure return of the piston to its original position when the external pressure on it was released at the end of the experiment. The cylinder was placed in a Bridgman-type pressure apparatus,[4] and its contents were subjected to an initial pressure of 8500 atm. at room temperature. The entire high-pressure system was then heated to 200°. After 14 hr. the apparatus was cooled to room temperature. The final pressure was about 7900 atm. The pressure was released and the cylinder removed and vented. The reaction product was washed from the vessel with ether and collected on a filter to give 3.37 g. of crude solid, m.p. 267–268°. It was purified by recrystallization from a mixture of ethanol and benzene or by sublimation under reduced pressure to give white crystals, m.p. 275–280°.

Anal. Calcd. for $C_{14}H_{10}N_2O_2$: C, 70.57; H, 4.23; N, 11.76. Found: C, 70.76; H, 4.43; N, 11.60, 11.65.

The product was identified as 3-phenyl-2,4-(1H,3H)-quinazolinedione by hydrolysis to aniline and anthranilic

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[1] (a) T. L. Cairns, G. L. Evans, A. W. Larchar and B. C. McKusick, THIS JOURNAL, **74**, 3982 (1952); (b) T. L. Cairns, A. W. Larchar and B. C. McKusick, *ibid.*, **74**, 5633 (1952); (c) *J. Org. Chem.*, **17**, 1497 (1952); (d) **18**, 748 (1953); (e) T. L. Cairns, D. D. Coffman, Richard Cramer, A. W. Larchar and B. C. McKusick, THIS JOURNAL, **76**, 3024 (1954).

[2] W. W. Gilbert, U. S. Patent 2,680,741, June 8, 1954.

[3] *Cf.* reference 1a, p. 3986; 1d, p. 749.

[4] P. W. Bridgman, "The Physics of High Pressure," G. Bell and Sons, London, 1949, pp. 30–59.