

individual contributions of k_E and k_S to the altered ratios.

With increasing bulk of the alkyl substituents there occur shifts in the ratio of the 2- to 1-olefin as well as shifts of the ratio of the *cis*- to *trans*-2-olefins.^{7,8}

Finally, with decreasing rate of substitution, a highly hindered carbonium ion will have an increased opportunity to undergo rearrangement as well as elimination. That is, k_R/k_S should exhibit increasing values with increasing steric requirements of the substituents.

The increasing value of k_R/k_S could result either from a decrease in k_S or from an increase in k_R (or both). The difference in the behavior of the two ions, $\text{Me}_3\text{CCEt}_2^+$ and $\text{Me}_3\text{CCEtMe}^+$, has been attributed primarily to a large change in k_S for the two structures. A considerable difference in the mag-

nitude of k_R for the two ions would not be expected. However, replacement of the three methyl groups on the quaternary carbon atoms by other groups of large steric requirements would be expected to cause increased strain at the branched center and result in an increased value of k_R (steric assistance). Unfortunately, at the present time we are unable to determine the value of k_R alone and must be content with the ratio of k_R/k_S . Nevertheless, it is apparent from the available results that the value of k_R/k_S does indeed increase with increasing branching.

In conclusion the theory of B-strain appears capable of accounting for the data now available on the behavior of highly branched carbonium ions in ionization, substitution, elimination and rearrangement reactions.

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[CONTRIBUTION OF THE SCHOOL OF SCIENCE, BRANDEIS UNIVERSITY]

Phenyl-azo-diphenylmethane and the Decomposition of Azo Compounds¹

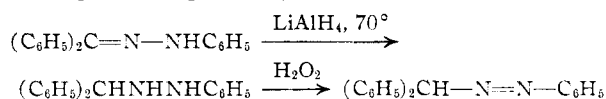
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Phenyl-azo-diphenylmethane, $\text{C}_6\text{H}_5\text{—N=N—CH(C}_6\text{H}_5)_2$ (I), was prepared by reduction of benzophenone phenylhydrazone, followed by oxidation of the hydrazo compound. It decomposed at 124.5 and at 144.5° in decalin with first-order kinetics, $k = 1.66 \times 10^{14} e^{-34,000/RT}$. Comparison with $\text{C}_6\text{H}_5\text{—N=N—C(C}_6\text{H}_5)_3$, and with $(\text{C}_6\text{H}_5)_2\text{CH—N=N—CH(C}_6\text{H}_5)_2$, indicates that substitution of each α -phenyl for α -hydrogen lowers E_A 6–7 kcal., probably largely by affecting the resonance stabilization of the radicals, and that symmetrical azo compounds may decompose by simultaneous rupture of both carbon–nitrogen bonds. The decomposition of I in decalin led to benzene (ca. 70% yield) and to 1,1,2,2-tetraphenylethane (ca. 30% yield). The decomposition of I in diphenylmethane led to benzene (ca. 20% yield), and to 1,1,2,2-tetraphenylethane (ca. 104% yield, based on azo compound).

As part of our study of the effects of structure on the decomposition of azo compounds and on the reactions of the free radicals which are formed, we have prepared and examined the kinetics and products of decomposition of phenyl-azodiphenylmethane, $(\text{C}_6\text{H}_5)_2\text{CH—N=N—C}_6\text{H}_5$ (I). This compound was of interest for comparison with the previously studied phenyl-azo-triphenylmethane,² $(\text{C}_6\text{H}_5)_3\text{C—N=N—C}_6\text{H}_5$ (II) and azo-bis-diphenylmethane,³ $(\text{C}_6\text{H}_5)_2\text{CH—N=N—CH(C}_6\text{H}_5)_2$ (III).

The compound I was prepared from the isomeric benzophenone phenylhydrazone



Attempts to effect the reduction by low pressure catalytic hydrogenation or by treatment with lithium aluminum hydride in ether failed, while the latter reagent at 70° led to the hydrazine in 35% yield, accompanied by a small quantity of 1,1,2,2-tetraphenylethane. Lithium aluminum hydride in our experiments has failed to convert benzalazine and benzophenone azine³ to the corresponding disubstituted hydrazines, and converted the latter, in part, to 1,1,2,2-tetraphenylethane, but did convert the hydrazone³ and phenylhydrazone of benzo-

phenone to the respective hydrazines. The oxidation of N-benzhydrazyl-N'-phenylhydrazine to I by hydrogen peroxide proceeded slowly. Compound I had been isolated in low yield from the autoxidation of benzalphenylhydrazone.⁴

The absorption spectra of phenyl-azo-diphenylmethane, and the isomeric benzophenone phenylhydrazone were determined in ethanol. The azo compound shows a small absorption maximum, $\log \epsilon$ 3.67, at 345 m μ , which is characteristic of aliphatic azo compounds,⁵ conjugation with the phenyl group leading to fairly strong end absorption and yellow color $\log \epsilon$ 2.10 at 450 m μ . However, the phenylhydrazone, unlike aliphatic hydrazone isomers of azo compound,⁵ also showed a strong maximum at 345 m μ , $\log \epsilon$ 4.26, but not accompanied by end absorption and color. The melting points and thermal stabilities of the phenyl-azo compound and the phenylhydrazone were markedly different, the azo compound showing a half-life in solution, as measured by nitrogen evolution of 7 hours at 124.5°, while the hydrazone showed no change in melting point and to this extent no evidence of decomposition when heated in the solid state under these conditions.

The rates of decomposition of phenyl-azo-diphenylmethane in approximately 0.01 molar solution in decalin were determined at 124.5 and at 144.5° by measurement of evolution of nitrogen as a function

(1) Presented at the meeting of the American Chemical Society, New York, September 13, 1954.

(2) S. G. Cohen and C. H. Wang, *THIS JOURNAL*, **75**, 5504 (1953).

(3) S. G. Cohen and C. H. Wang, *ibid.*, **77**, 2457 (1955).

(4) M. Busch and H. Kunder, *Ber.*, **49**, 2345 (1916).

(5) G. Fodor and P. Szarvas, *ibid.*, **76B**, 334 (1943).

of time. Satisfactory duplicate runs were obtained. Typical plots of rate data are given in Figs. 1 and 2. Linear plots of $\ln V_\infty/(V_\infty - V_t)$ against time indicate that the reactions were first order; rate constants were calculated from the plots and are probably accurate to within $\pm 4\%$. The data are summarized in Table I where they may be compared with the corresponding data for phenyl-azotriphenylmethane and azo-bis-diphenylmethane.

TABLE I
DECOMPOSITION OF AZO COMPOUNDS

Compound	T , °C.	K_1 $\times 10^4$, sec. ⁻¹	E_A , kcal. mole ⁻¹	ΔS^\ddagger , cal. mole ⁻¹ degree ⁻¹
I (C ₆ H ₅) ₂ CH—N=N— N—C ₆ H ₅ ^a	124.5	0.344	34.0 \pm 1.3	3.9 \pm 3.1
II (C ₆ H ₅) ₂ C=N=N— C ₆ H ₅ ^b	53.3	2.25	27.0 \pm 1.0	5.2 \pm 3.0
III (C ₆ H ₅) ₂ CH—N=N— N—CH(C ₆ H ₅) ₂ ^b	64.0	3.40	26.6 \pm 1.3	2.2 \pm 3.3

^a In decalin. ^b In toluene.

Phenyl-azo-diphenylmethane (I) decomposes much more slowly than phenylazo-triphenylmethane (II) comparable rates being found at 144 and 53°, respectively, and extrapolation indicating that I decomposes about one twelve thousandth as rapidly as II at 53°. The difference in reactivity is almost entirely due to difference in activation energy, 7 kcal. Since scale models indicate the absence of steric interaction between the aralkyl and phenyl groups in the *trans* forms of these compounds, it seems likely that the difference in activation energies is to be correlated with differences in the resonance stabilization energies of the diphenylmethyl and triphenylmethyl radicals, that of the latter being higher despite the fact that lack of planarity prevents it from having maximum stabilization. Stabilization of the radicals contributes to stabilization of the transition states and thus affects the pertinent bond-dissociation energies and the activation energies. Alternatively, the increased reactivity of II may reflect steric strain in the tetravalent triphenylmethane derivative II which is relieved in the triphenylmethyl radical.

The difference in activation energy resulting from substituting phenyl for hydrogen in these two compounds, 7 kcal., is but little more than half of that (12 kcal.) which results from substituting a pair of phenyls for a pair of hydrogen atoms as observed in the comparison of the symmetrical compounds, azo-

$$\begin{array}{c} \text{CH}_3 \qquad \qquad \text{CH}_3 \\ | \qquad \qquad \quad | \\ \text{bis-}\alpha\text{-phenylethane, } \text{C}_6\text{H}_5\text{CH}-\text{N}=\text{N}-\text{CH}-\text{C}_6\text{H}_5 \\ \text{and azo-bis-diphenylmethane, } (\text{C}_6\text{H}_5)_2\text{CH}-\text{N}=\text{N}- \\ \text{N}-\text{CH}(\text{C}_6\text{H}_5)_2 \text{ with azo-methane } \text{CH}_3-\text{N}=\text{N}- \\ \text{CH}_3 \text{ and azo-bis-2-propane } (\text{CH}_3)_2\text{CH}-\text{N}=\text{N}- \\ \text{N}-\text{CH}(\text{CH}_3)_2. \end{array}$$
 This indicates that in the decomposition of symmetrical azo compounds, substitution in each alkyl group contributes to decreasing the activation energy and that the decomposition of such compounds may proceed not by rupture of one carbon-nitrogen bond leading to two radicals of the type R· and R—N=N·, but by a symmetrical dissociation of both carbon-nitrogen bonds, leading to two alkyl radicals and a molecule of nitrogen, the high heat of formation of the latter contributing importantly to the driving force. The

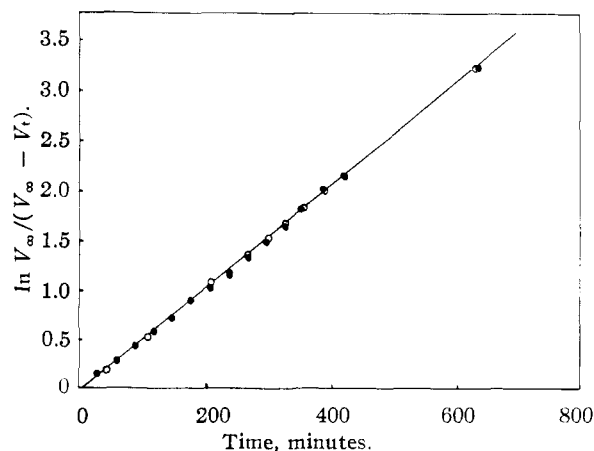


Fig. 1.—Decomposition of phenyl-azo-diphenylmethane in decalin, 124.5°: —○—●— duplicate runs.

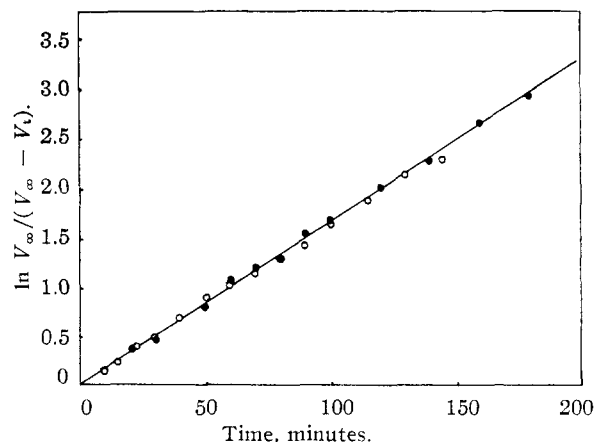


Fig. 2.—Decomposition of phenyl-azo-diphenylmethane in decalin, 144.5°: —○—●— duplicate runs.

rupture of the two carbon-nitrogen bonds of the unsymmetrical azo compounds, I and II, need not be simultaneous. A similar interpretation may be given to comparison of I with azo-bis-diphenylmethane (III), I decomposing much more slowly and III being comparable to phenyl-azo-triphenylmethane (II). Since both I and III have in common the relatively easily broken diphenylmethyl-azo linkage, it seems unlikely that rupture of one bond of this type can be the rate-determining process in both decompositions and the symmetrical rupture of the two carbon-nitrogen bonds in III and in other symmetrical azo compounds is favored. This comparison of I and III is complicated by conjugation of the azo and phenyl groups in I which may so alter the electronic configuration of the molecule as to strengthen the diphenylmethyl nitrogen bond. More direct comparisons would have been available if our attempts to prepare methyl-azo- and benzyl-azo-diphenylmethane had been successful. Oxidation of the corresponding hydrazines led to oily products which appeared to be mixtures of the hydrazones which are isomeric with the desired azo compounds.

It may be noted that attempts to prepare azo-bis-triphenylmethane by oxidation of the hydrazine at -40° have failed, and have led to decomposition

products.⁶ If, as seems reasonable, the decrement in activation energy of 6–7 kcal. which results from substituting phenyl for hydrogen in both the symmetrical arylalkyl-azo compounds and in going from I to II, should persist in going from azo-bis-diphenylmethane (III) to azo-bis-triphenylmethane, the irreversible decomposition of the latter would have an activation energy of about 13 kcal., a value consistent with its apparent thermal instability.

Products of Decomposition.—Synthetic dilute solutions of benzene, 1,1,2,2-tetraphenylethane, triphenylmethane and diphenylmethane in decalin were worked up, leading to recovery of the first three materials in 67, 79 and 88% yields, respectively. The diphenylmethane was recovered in 47% yield as a pure solid, with an additional 45% yield as a solution in decalin as assayed by refractive index. From these results correction factors may be applied to the yields of isolated products of decomposition.

A solution resulting from the decomposition of phenyl-azo-diphenylmethane in 0.025 molar solution in decalin at 130° was distilled and products of decomposition were identified. Benzene was recovered in 49% yield (0.70 g.), corrected, 73%; no evidence of triphenylmethane was found; 1,1,2,2-tetraphenylethane was recovered in 25% yield, corrected, 32%. We were unable to isolate diphenylmethane as a solid of melting point *ca.* 26°, but product boiling in the correct range was found, and calculation of the content of several fractions from refractive index measurements indicated that this product may have been formed in about 60% yield. In another attempt to isolate this possible product of decomposition, solutions resulting from some kinetic runs, corresponding to 1.15 g. of azo compound, were combined and worked up for tetraphenylethane, which was recovered in 10% yield, and for diphenylmethane. Material boiling at 245–255°, which may have been largely diphenylmethane but which did not solidify, was isolated in 54% yield. That this contained diphenylmethane was indicated by oxidation with selenium dioxide and treatment with phenylhydrazine, which led to benzophenone phenylhydrazone in about 10% yield based on the original azo compound. The high yield of benzene and the apparent absence of triphenylmethane parallel the formation of benzene and the low yield of tetraphenylmethane in the decomposition of phenyl-azo-triphenylmethane^{7a,b} and indicate that the major reaction of the phenyl radical is abstraction of hydrogen from the aliphatic solvent. Although this type of reaction may be quite rapid it is not clear that it should take place practically to the exclusion of radical recombination, particularly if the phenyl and diphenylmethyl radicals are formed in close proximity. It may be that the weaker diphenylmethyl–nitrogen bond breaks first, while the phenyl–nitrogen bond, strengthened by conjugation of the phenyl and azo groups, retains partial bond character long enough to allow the phenyl-azo radical, $C_6H_5-N=N\cdot$, to diffuse

away before decomposing. In the case of the trityl compound a steric effect may increase the activation energy of the radical combination reaction and suffice to account for the low yield of tetraphenylmethane.^{7c}

The low (*ca.* 30%) yield of tetraphenylethane and apparent formation of diphenylmethane is in contrast to the results obtained previously in the decomposition of azo-bis-diphenylmethane in decalin at a lower temperature, 60°, in which diphenylmethyl radicals dimerized to form tetraphenylethane in 79% yield (corrected 90%) and thus did not react to a large extent with the solvent. Some phenyl-azo-diphenylmethane was decomposed at 60° in decalin by exposure to ultraviolet light and tetraphenylethane was isolated in only 21% yield, the low yield from this azo compound thus being little dependent on the temperature at which the diphenylmethyl radicals were generated. Dimerization of the radicals may well be favored when they are formed in close proximity in pairs from the symmetrical azo-bis-diphenylmethane and reaction with the solvent may thus become relatively more important in the decomposition of the unsymmetrical compound. However, the high yield of tetraphenylethane from the symmetrical compound cannot be entirely due to a cage effect, since this material is a polymerization initiator,⁸ and a considerable fraction of the product must be formed by dimerization of free diphenylmethyl radicals. Further, the low temperature dependence of the yield of tetraphenylethane from the unsymmetrical compound indicates that it is unlikely to be determined by competition between a dimerization of low activation energy and a hydrogen abstraction of relatively high activation energy. It seems likely that the yield of dimer is decreased by combination or disproportionation reactions between the diphenylmethyl radical and the decalyl radicals which are presumably formed by abstraction of hydrogen from the decalin by phenyl.

In a final experiment the products of decomposition of phenyl-azo-diphenylmethane at 130° in diphenylmethane as solvent were examined. The yield of benzene was low, about 20%, as compared with 49% (corrected 73%), in decalin. Phenyl radical, which can both substitute⁸ into aromatic compounds and abstract hydrogen from aliphatic compounds apparently substitutes into the aromatic nuclei of this solvent more readily than it abstracts hydrogen. The yield of tetraphenylethane was very high, 104% based on phenyl-azo-diphenylmethane, the conversion of some phenyl to benzene by abstraction of hydrogen from the methylene group of solvent diphenylmethane forming diphenylmethyl radical which leads to this extent to additional tetraphenylethane. The diphenylmethyl radicals from the azo compound apparently dimerized to a very large extent.

Experimental⁹

Benzophenone Phenylhydrazone.—Benzophenone (27.6 g., 0.15 mole), m.p. 47–48°, was condensed with phenyl-

(6) L. A. Pinck, *THIS JOURNAL*, **55**, 1711 (1933).

(7) (a) H. Wieland, E. Popper and H. Seefried, *Ber.*, **55**, 1816 (1922); (b) M. Gomberg, *ibid.*, **30**, 2043 (1897); (c) this was pointed out by the referee.

(8) (a) D. H. Hey, *J. Chem. Soc.*, 1966 (1934); (b) H. Wieland, *Ann.*, **514**, 145 (1934).

(9) Melting points are uncorrected. Elementary analyses are by S. M. Nagy, Massachusetts Institute of Technology.

hydrazine (16.2 g., 0.15 mole), in 150 ml. of warm ethanol containing 10 ml. of acetic acid; white needles, 37 g. (90% yield), m.p. 137–138°, reported 137–138°. ¹⁰

N-Benzhydryl-N'-phenylhydrazine.—Lithium aluminum hydride (4.5 g., 0.13 mole) was added to 200 ml. of ether and stirred overnight under nitrogen. A solution of 20 g. (0.074 mole) of benzophenone phenylhydrazone in 600 ml. of *n*-butyl ether and 100 ml. of benzene was added slowly to the lithium aluminum hydride and the mixture was kept at 70° for eight hours. A solution of 60 g. of sodium potassium tartrate in 300 ml. of water was added, the organic layer was separated, dried over magnesium sulfate, concentrated *in vacuo*, and cooled, leading to 0.35 g., 3% yield, of white crystals which sintered at 208°, melted at 212°, melting point not depressed when mixed with 1,1,2,2-tetraphenylethane, and to 7.0 g., 35% yield, of white solid, N-benzhydryl-N'-phenylhydrazine, m.p. 115°, from ethanol. One gram of this was dissolved in ether and converted to the hydrochloride, m.p. 178–180°, from ethanol. *Anal.* Calcd. for C₁₉H₁₉N₂Cl: C, 73.4; H, 6.16. Found: C, 73.6; H, 6.42. The reduction with lithium aluminum hydride failed when attempted to diethyl ether.

Phenyl-azo-diphenylmethane.—Six grams of N-benzhydryl-N'-phenylhydrazine was dissolved in 20 ml. of ethanol and 50 ml. of ether and stirred with 11.4 g. of 30% hydrogen peroxide at room temperature for two days. The ethereal solution was concentrated, leading to the azo compound, yellow crystals from methanol, 3.2 g. (54% yield), m.p. 73–75°, reported⁴ 74.75°. *Anal.* Calcd. for C₁₉H₁₅N₂: C, 83.8; H, 5.94; N, 10.3. Found: C, 83.9; H, 6.30; N, 10.3.

Rates of decomposition were measured as described previously.² The solvent was redistilled (Eastman Kodak Co.) decalin, b.p. 73–74° (15 mm.), *n*_D²⁰ 1.4690.

Isolation of Products. 1. Synthetic Mixtures. (a).—A solution of 1.74 g. of benzene in 10 ml. of decalin was distilled through a 10-inch glass spiral, leading to 1.16 g. of benzene (67% recovery), m.p. 5–6°. (b).—A solution of 0.353 g. of tetraphenylethane, 1.24 g. of triphenylmethane and 2.00 g. of redistilled (Matheson) diphenylmethane, b.p. 133° (8 mm.), m.p. 25–26°, *n*_D²⁰ 1.5781, in 150 ml. of decalin, was examined. Decalin was removed at 73–74° (15 mm.); the lightly colored residue was taken up in 30 ml. of ethanol, filtered and washed with ethanol, leading to 0.240 g. of tetraphenylethane, m.p. 208–210°. The filtrate was distilled and fractions were obtained at (i) 73–118° (5 mm.), 4.16 g., *n*_D²⁰ 1.4968, 22 volume % diphenylmethane by refractive index, corresponding to 0.92 g. (45% yield), and (ii) at 118–120° (5 mm.), 0.93 g., m.p. 25–26°, 47%. The residue was treated with hot alcohol and filtered leading to 0.040 g. of tetraphenylethane m.p. and mixed m.p. 208–210°, combined yield 0.280 g. (79%). Concentration of the filtrate led to triphenylmethane, 1.09 g. (88% recovery), m.p. 89–91°, mixed m.p. 90–92°.

2. Products of Decomposition. (a).—A solution of 5.0 g. (0.0184 mole) of phenyl-azo-diphenylmethane in 750 ml. of decalin was heated at 130 ± 2° under nitrogen for 24 hours. Fifteen ml. of distillate was taken and redistilled through a 10-inch glass spiral, leading to benzene, b.p. 77–79°, m.p. 5–6°, 0.70 g. (49% yield, corrected 73%).

The remainder of the decalin was removed at 63–66° (6 mm.). The dark semisolid residue was taken up in 20 cc. of ethanol and a first fraction of impure tetraphenylethane was collected and washed with 20 ml. of ethanol, 0.960 g., sintering at 170° and melting at 195–205°. The alcohol was removed from the filtrates and distillation was continued leading to a forerun, 67–115° (5 mm.), 6.53 g., and a fraction, 115–120° (5 mm.), 0.45 g., *n*_D²⁰ 1.5320, apparently containing 57%, 0.25 g. of diphenylmethane, and a tarry residue 4.34 g. The residue was taken up in alcohol and concentrated leading in several fractions to a total of 0.104 g. of impure tetraphenylethane. This was combined with the first fraction and crystallized from carbon tetrachloride-

ethanol, leading to 0.78 g. of tetraphenylethane, m.p. and mixed m.p. 208–210°, 25% yield (corrected 32%). No other solid product was isolated. The materials boiling at 67–120° (5 mm.) were combined, rinsed in with decalin and redistilled. Only a forerun fraction was obtained, 7.75 g., *n*_D²⁰ 1.4920, corresponding to 18% or 1.56 g. of diphenylmethane, and a residue, 1.43 g., *n*_D²⁰ 1.5390, corresponding to 63% or 0.284 g. of diphenylmethane, maximum total diphenylmethane, 1.84 g., 60%.

(b).—The solutions resulting from studies of the rates of decomposition in decalin at 124 and 144° were combined, 1.15 g. (0.0042 mole) of the azo compound in 400 ml. of decalin, and the solvent was removed at 68° (8 mm.), leaving 3 g. of residue. The residue was treated with cold ethanol and a solid was recovered and crystallized from ethyl acetate, 1,1,2,2-tetraphenylethane, 0.050 g., m.p. and mixed m.p. 208–209°. The filtrates were concentrated and an oily distillate (i) was collected, 0.70 g., b.p. 105–108° (4 mm.). The residue was again treated with alcohol leading to an additional 0.020 g. of 1,1,2,2-tetraphenylethane, m.p. 205–210°, mixed m.p. 206–210°, total yield 10%. The filtrates were again concentrated and the residue was oxidized with selenium dioxide at 140–150° for 15 minutes, but neither triphenylcarbinol nor benzophenone phenylhydrazone was isolated.

The oily distillate (i) was redistilled at atmospheric pressure leading to a product the boiling range of which included that of diphenylmethane, 0.35 g. (54% crude yield), b.p. 245–255°, *n*_D²⁰ 1.585. This was oxidized with 0.25 g. of selenium dioxide at 205–215° for two hours, extracted with ether, concentrated, dissolved in alcohol and treated with 6 drops of phenylhydrazine and one drop of acetic acid, leading to benzophenone phenylhydrazone, m.p. and mixed m.p. 135–138°, 0.045 g. (8% yield, 4% based on the original azo compound). A control oxidation of 0.20 g. of diphenylmethane with 0.16 g. of selenium dioxide under similar conditions led to benzophenone phenylhydrazone in 38% yield.

(c).—A solution of 0.365 g. of phenyl-azo-diphenylmethane, in 200 ml. of decalin was maintained at 60 ± 3° with stirring under nitrogen for five days while exposed to a Hanovia Serial 26329 Type SH U.V. lamp. The per cent. transmission at 345 mμ was checked periodically in a Beckman DU spectrophotometer. The molecular extinction coefficient of a 1:300 dilution fell from 3780 initially to 104 after two days. The solvent was removed at 55–60° (4 mm.), and the residue was treated with cold ethanol, leading to 0.048 g. (21% yield) of 1,1,2,2-tetraphenylethane, m.p. and mixed m.p. 207–209°. The filtrates were concentrated and treated with selenium dioxide at 140–150° for one-half hour. Neither triphenylcarbinol nor benzophenone phenylhydrazone was isolated.

(d).—A solution of 5.0 g. (0.0184 mole) of phenyl-azo-diphenylmethane in 430 ml. of diphenylmethane was heated at 130 ± 2° under nitrogen for 24 hours. Twenty-five ml. of distillate was taken and redistilled through a 10-inch glass spiral, leading to a forerun boiling 50–75°, apparently a benzene-water mixture, 0.131 g., and benzene, boiling 73–75°, m.p. and mixed m.p. 5–6°, 0.232 g. (16% yield). The diphenylmethane was removed at 124° (5 mm.), and the residue, 6 g., was treated with 25 ml. of ethanol, filtered and washed with 25 ml. of warm ethanol, leading to tetraphenylethane, 3.00 g., m.p. 206–208°, mixed m.p. 207–209°, and, from the filtrates an additional 0.182 g., m.p. 204–206°, total yield 104%, based on azo compound.

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(10) W. Plattner and R. Behrend, *Ann.*, **278**, 369 (1894).