rapidly 14.8 g. (0.10 mole) of piperidinium nitrate, made by the method of Chute.[4] The resulting solution was maintained two hours at 25°, concentrated to approximately half-volume by distillation at reduced pressure, poured onto 100 g. of ice and then made basic (*p*H 9) with 10 *N* sodium hydroxide. This solution contained no water-insoluble N-nitropiperidine. Its continuous ether extraction (5 hours), followed by drying the ethereal solution over magnesium sulfate and saturating with dry hydrogen chloride, gave 7.31 g. (60.5%) of piperidinium hydrochloride, m.p. 238–240° (literature value[20] m.p. 237°).

B. With Chloride Catalysis.—The following reagents were mixed in the manner described in A above and allowed to react for one hour at 20° and one hour at 35° (reflux): 0.068 mole of piperidinium nitrate, 0.196 mole of trifluoroacetic anhydride, 0.034 mole of absolute nitric acid and 0.0034 mole of anhydrous zinc chloride. No water-insoluble N-nitropiperidine was formed; unreacted piperidine was not isolated in this experiment.

C. With Preliminary Formylation.—To 69 cc. (0.50 mole) of trifluoroacetic anhydride at 0° was added 5.66 cc. (0.15 mole) of 98% formic acid and then, at −50°, 8.4 g. (0.10 mole) of freshly distiled piperidine. The latter addition was very exothermic. When completed (20 minutes), the solution was warmed to −20° and 6.3 cc. (0.15 mole) of absolute nitric acid was added dropwise, causing a vigorous evolution of colorless gas. After one hour at −20°, the reaction mixture was concentrated to approximately half volume by distillation at −10° and 20 mm., then poured onto 100 g. of ice. After making basic (*p*H 9), no water-insoluble product was found, indicating N-nitropiperidine to be absent.

Acknowledgment.—Determination of the X-ray data by Donald Moore is acknowledged gratefully.

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[20] A. Ladenburg, *Ber.*, **18**, 2959 (1885).

[CONTRIBUTION FROM THE SCHOOL OF SCIENCE, BRANDEIS UNIVERSITY]

Azo-bis-diphenylmethane and the Decomposition of Aliphatic Azo Compounds. The Diphenylmethyl Radical[1]

BY SAUL G. COHEN AND CHI HUA WANG

RECEIVED OCTOBER 21, 1954

Azo-bis-diphenylmethane, $(C_6H_5)_2CH{-}N{=}N{-}CH(C_6H_5)_2$ (I), has been prepared and compared with the isomeric benzophenone benzhydrylhydrazone. The reduction of benzophenone hydrazone to benzhydrylhydrazine by lithium aluminum hydride is described. The azo compound I decomposed in toluene with first-order kinetics, $E_A = 26.6$ kcal. mole^{-1}, $\Delta S^{\pm} = 2.2$ cal. mole^{-1} degree^{-1}. Comparison of azomethane, azo-bis-2-propane, 1-azo-bis-1-phenylethane and I indicates that symmetrical substitution of a pair of methyls for hydrogen lowers E_A 5 kcal., substitution of a pair of phenyls for hydrogen lowers E_A 12 kcal. The results are discussed in terms of resonance stabilization of the radicals. The decomposition of I leads to diphenylmethyl radicals which dimerize, forming 1,1,2,2-tetraphenylethane, quantitatively in the absence of solvent and in somewhat lower yield in several hydrocarbon solvents. The diphenylmethyl radical initiates the polymerization of styrene. Comparison with benzoyl peroxide indicates that the initiation step is slow and that the diphenylmethyl radical also terminates chains.

As part of our study of the decomposition of azo compounds and of the reactions of the free radicals which may thereby be produced, it was of interest to us to prepare and decompose azo-bis-diphenylmethane, $(C_3H_5)_2CH{-}N{=}N{-}CH(C_6H_5)_2$ (I), and to examine the chemistry of the diphenylmethyl radical. The preparation of this azo compound, the kinetics of its decomposition, the yield of 1,1,2,2-tetraphenylethane formed by its decomposition in several hydrocarbon solvents and its effectiveness as an initiator of the polymerization of styrene are described in this paper. The kinetics of decomposition and the initiation of polymerization are compared with those of some other relevant sources of free radicals.

Preparation of Azo-bis-diphenylmethane.—The azo compound I was prepared from benzophenone and hydrazine by the following series of reactions which are similar in general and differ in some details from the reactions used to convert other ketones to the respective secondary azo-bis-alkanes.[2,3]

$$(C_6H_5)_2C{=}O + H_2NNH_2 \longrightarrow$$

$$(C_6H_5)_2C{=}NNH_2 \xrightarrow{H^+ \text{ or } OH^-}$$

$$(C_6H_5)_2C{=}NN{=}C(C_6H_5)_2 \xrightarrow{2H_2,Pt}$$

$$(C_6H_5)_2CHNHNHCH(C_6H_5)_2 \xrightarrow{H_2O_2 \text{ or } HgO}$$

$$(C_6H_5)_2CH{-}N{=}N{-}CH(C_6H_5)_2$$

The conversion of benzophenone to the azine *via* the hydrazone is convenient and makes unnecessary the use of a sealed tube.[4] The reduction of benzophenone azine to N,N′-bis-benzhydrylhydrazine and benzhydrylamine by sodium amalgam in ethanol had been described previously.[5] When our first attempts to carry out this hydrogenation catalytically failed, the reduction by lithium aluminum hydride was examined. Reaction in ether led to an unstable white compound which decomposed on standing to a yellow viscous mixture from which the original azine was recovered. Treatment of the azine with this reagent at 90–100° led to rupture of the molecule and isolation of 1,1,2,2-tetraphenylethane, and apparently, diphenylmethane. Conditions for satisfactory hydrogenation over platinum oxide at slightly elevated temperature to form N,N′-bis-benzhydrylhydrazine were then worked out. The oxidation of this hydrazine with mercuric oxide had been reported[5] to lead not to the azo compound I, but to the decomposition products 1,1,2,2-tetraphenylethane and nitrogen. The oxidation had been carried out at too high a temperature. Despite occasional difficulties in this preparation, oxidation of the hydrazine with either hydrogen peroxide or

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[1] Presented at the Meeting of the American Chemical Society, New York, September 13, 1954.

[2] H. L. Lochte, W. A. Noyes and J. R. Bailey, THIS JOURNAL, **44**, 2556 (1922).

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

[4] E. R. Blout, V. Eager and R. M. Gofstein, *ibid.*, **68**, 1983 (1946).

[5] A. Darapsky, *J. prakt. Chem.*, **67**, 112, 164 (1903).

mercuric oxide at about 10° followed by rapid recrystallization at low temperature leads to this azo compound in high yield and purity. In connection with the difficulty of preparing azo-bis-diphenylmethane it may be noted that reported attempts to prepare azo-bis-triphenylmethane, $(C_6H_5)_3C—N═N—C(C_6H_5)_3$,[6a] have failed even when the oxidation of the corresponding hydrazine was carried out at −40°.[6b] The azo compound I melted at 114–115° with rapid evolution of nitrogen and resolidified to form 1,1,2,2-tetraphenylethane, melting at 205–210° alone and when mixed with an authentic sample (m.p. 208–210°). The absorption spectrum of I in ethanol shows a minimum at 310 mμ and a maximum at 345 mμ, log ε 3.38, which is characteristic of the aliphatic azo linkage.[7]

Benzophenone benzhydrylhydrazone is reported[5] to be unstable and melt at 91°. In our preparation benzophenone hydrazone was reduced with lithium aluminum hydride to benzhydrylhydrazine and this was condensed with benzophenone leading to a slightly colored solid which melted over a range to about 120° with slow gas evolution and did not resolidify to form 1,1,2,2-tetraphenylethane, and which, when mixed, altered the melting point behavior of the azo compound. The absorption spectrum of this compound in ethanol shows a minimum at 250 mμ and a maximum at 290 mμ, log ε 4.18, and resembles that of benzophenone hydrazone, minimum at 255 mμ and maximum at 275 mμ, log ε 4.18. The spectra of the isomeric azo-bis-diphenylmethane and benzophenone benzhydrylhydrazone are similar to those of the 1-azo-bis-1-phenylalkanes and their hydrazone tautomers.[7]

Kinetics of Decomposition.—The rates of decomposition of azo-bis-diphenylmethane in approximately 0.01 *M* solution in toluene were determined at 54.0° and 64.0° by measurement of the rate of evolution of nitrogen.[8] Typical plots of rate data are given in Fig. 1. Linear plots of ln $V_\infty / V_\infty - V_t$ *vs.* time indicate that the reactions were first order. Rate constants were calculated from the slopes of the plots and are accurate to within ±3%. Similar rate constants were found both when pure samples of the azo compound were decomposed, leading to nearly quantitative yields of nitrogen, and when impure samples were used, leading to 70–80% yields of nitrogen. The compound decomposes quite rapidly, the specific rate at 54°, 1.01×10^{-4} sec.$^{-1}$, being about half as great as that of phenyl-azo-triphenylmethane, 2.25×10^{-4} sec.$^{-1}$,[9] but almost two orders of magnitude greater than that of benzoyl peroxide at this temperature, 1.8×10^{-6} sec.$^{-1}$ [10] and than that calculated from published data[8] for azo-bis-isobutyronitrile, 3.5×10^{-6} sec.$^{-1}$.

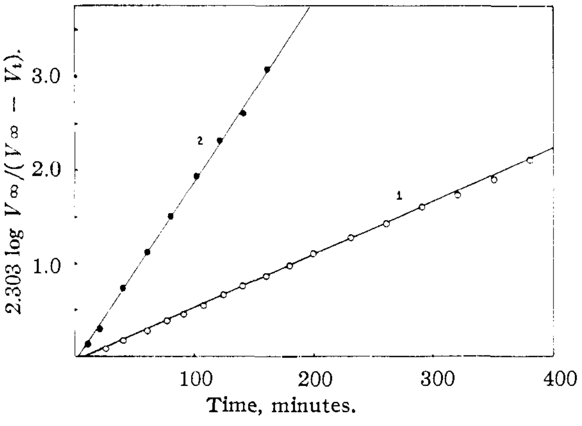

Fig. 1.—Decomposition of 0.01 *M* azo-bis-diphenylmethane in toluene: curve 1, 54°; curve 2, 64°.

The results are summarized in Table I and compared with those of the closely related 1-azo-bis-1-phenylethane (II)[3] and those reported for the vapor phase decompositions of azo-methane[11] IV and azo-bis-2-propane (III).[12] Comparison of the reactions of the azo-bis-arylalkanes in solution with those of the gaseous decomposition of the azo-alkanes is difficult because of this difference in phase and it may be that the activation energies observed for the latter would be somewhat less if obtained in the liquid phase, solvation of the transition state and the radicals probably facilitating the dissociation.

TABLE I

DECOMPOSITION OF AZO COMPOUNDS, R,R'CH—N═N—CHR,R'

	R	R'	*T*, °C.	$10^4 k_1$, sec.$^{-1}$	E_A kcal. mole^{-1}	$\Delta S^{\ddagger}$, cal. mole^{-1} deg.$^{-1}$
I	C_6H_5	C_6H_5	54.0	1.01	26.6 ± 1	2
			64.0	3.40		
II	C_6H_5	CH_3	110.3	1.69	32.6	7
III	CH_3	CH_3	250	4.8	40.9	1
IV	H	H	300	5.6	50.2	11

Substitution of hydrogen by methyl and of methyl by phenyl in these azo compounds leads to increased ease of decomposition. The compounds I, II, III and IV have roughly comparable rates of decomposition at about 65, 120, 250 and 300°, the increased reactivity resulting largely from decreases in activation energy. The effects of these symmetrical substitutions appear to be approximately additive, a pair of methyls lowering E_A about 5 kcal., and a pair of phenyls lowering E_A about 12 kcal. Scale models indicate the absence of steric interaction between the two alkyl or arylalkyl groups in the *trans* forms of these compounds and it seems likely that the differences in activation energy are correlated with differences in the resonance stabilization energies of the radicals.[13] High stabilization energies may lead to lower dissociation energies[14] of the relevant carbon–nitrogen bonds by contributing to resonance stabilization of the transition states, and thus to lower activation energies. The stabilization of the benzhydryl and α-phenylethyl radicals may be described in terms of

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(6) (a) H. Wieland, *Ber.*, **42**, 3020 (1909); (b) L. A. Pinck, THIS JOURNAL, **55**, 1711 (1933).

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

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

(9) S. G. Cohen and C. H. Wang, *ibid.*, **75**, 5504 (1953).

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(11) O. K. Rice and D. V. Sickman, *J. Chem. Phys.*, **4**, 242, 239, 608 (1936).

(12) H. C. Ramsperger, THIS JOURNAL, **50**, 714 (1928).

(13) L. Pauling and G. W. Wheland, *J. Chem. Phys.*, **1**, 362 (1933).

(14) M. G. Evans and E. Warhurst, *Trans. Faraday Soc.*, **39**, 19 (1943).

the familiar benzyl-type resonance, that of the former being greater.[18] The isopropyl radical may have 12 kcal. stabilization as compared with methyl,[14,15] the delocalization being described by formulas of the type[16] $CH_3—\dot{C}H—CH_3 \leftrightarrow H\cdot CH_2{=}CH—CH_3$, this being less effective than that afforded by benzyl-type resonance. The less favorable entropies of activation of I and III may result because greater planarity and restriction of configuration in the transition states is required in these cases to assure maximum resonance stabilization while the more favorable entropy of activation in azo-methane IV may result from decreased geometrical restriction of the transition state where stabilizing contributions from resonance of neither type are available.

The Diphenylmethyl Radical.—The decomposition of azo-bis-diphenylmethane at its melting point, 114°, leads to 1,1,2,2-tetraphenylethane in practically quantitative yield, while the decomposition in approximately 0.01 *M* solution in hydrocarbon solvents at about 60° leads to this product in somewhat lower yield. Table II includes the yields of isolated material and yields corrected for losses in manipulation as indicated by isolation of the product from the stated solvent under similar conditions in blank runs; these losses parallel the boiling points of the solvents.

TABLE II

FORMATION OF 1,1,2,2-TETRAPHENYLETHANE FROM AZO-BIS-DIPHENYLMETHANE

Solvent	Yield, % Isolated	Corrected
Toluene	77	81
Decalin	79	90
Diphenylmethane	79	94
None	94	99

Since the polymerization of styrene is initiated by this decomposition, free radicals are formed in the decomposition and part of the tetraphenylethane is formed by combination of free diphenylmethyl radicals. It is highly probable that a considerable part of the tetraphenylethane is formed by combination of pairs of diphenylmethyl radicals before they have been able to diffuse apart. The corrected yields indicate that diminished formation of tetraphenylethane may result from reaction of diphenylmethyl with the solvent, probably largely extraction of hydrogen and conversion of the radical to diphenylmethane, which was not isolated in these experiments. The loss was greatest in toluene in which the benzyl–hydrogen bond is weakened,[17] less in decalin, and least in diphenylmethane, where hydrogen extraction may be easiest, reflecting the lowest carbon–hydrogen bond dissociation energy,[17] but regenerates diphenylmethyl for subsequent dimerization.

A few experiments on the polymerization of 3.46 m./l. of styrene in benzene by approximately 0.01 m./l. azo-bis-diphenylmethane at 54.0° have been completed. If, as seems reasonable, we assume that the rate of decomposition of the azo compound is not affected appreciably by the change in solvent[8] and the rate found in toluene is used, then an average rate of decomposition of 8.1×10^{-7} m./l./sec. led, after one hour, to 2.55% of methanol-insoluble polystyrene, $[\eta] = 0.10$, and an average rate of 6.9×10^{-7} m./l./sec. led, after two hours, to 4.80% of polymer or to 2.40% per hour, $[\eta] = 0.12$. We have reported previously[10] that, at the same monomer concentration and temperature, a rate of decomposition of benzoyl peroxide of 4.25×10^{-7} m./l./sec. led, in one hour, to 3.97% of polystyrene, $[\eta] = 0.15$. With the approximation that the rate of polymerization of styrene is proportional and the molecular weight inversely proportional to the square root of the rate of decomposition of benzoyl peroxide[18] the corresponding values may be calculated for polymerization initiated by benzoyl peroxide decomposing at the rates now being reported for azo-bis-diphenylmethane. They are for 8.1×10^{-7} m./l./sec., 5.50% polystyrene, $[\eta] = 0.11$, and for 6.9×10^{-7} m./l./sec., 5.06% polystyrene, $[\eta] = 0.12$. Azo-bis-diphenylmethane leads to less than half the rate of polymerization that benzoyl peroxide does, and to a polymer of almost the same molecular weight.

Since the specific rates of chain propagation are the same in the two systems, the differences must result from effects in the initiation and/or termination steps. If the initiation process and the polymerization were slow solely because the decomposition of the azo compound led to fewer free radicals—as would be the case if a simultaneous ejection of nitrogen and formation of 1,1,2,2-tetraphenylethane or if a dimerization of diphenylmethyl radicals in a solvent cage before diffusion were of major importance—then the slow rate of polymerization would be accompanied by high molecular weight of product. This is not the case and it seems that the initiation rate is low not only because of low yield of free diphenylmethyl radicals but also because the initiation reaction requires the comparatively slow addition of the more stabilized diphenylmethyl radical to styrene, forming the less stabilized α-phenylmethyl radical, and that some diphenylmethyl radicals survive long enough to terminate polymer chains, the combined effects leading to both low rates of polymerization and to low molecular weights.

Experimental[19]

Benzophenone Hydrazone.—When equimolar quantities of hydrazine hydrate (64% in water, Eastman Kodak Co.) and benzophenone (m.p. 47–48°) were heated in absolute alcohol under reflux for five hours, yellow crystals, were obtained, 90% crude, m.p. 91°, crystallized from ethyl alcohol, m.p. 97–98°, reported 97–98°.[5]

Benzophenone Azine.—(a) Thirty grams (0.153 mole) of benzophenone hydrazone (m.p. 91°) was dissolved in 350 ml. of hot 95% ethanol, and 9 ml. of concentrated sulfuric acid was added. The solution was boiled for one hour and cooled, and the azine was collected and recrystallized from ethanol; 24 g. (0.066 mole), 87% yield, m.p. 164° reported 164°.[4] (b) In an attempted methylation of benzophenone hydrazone, this material (20 g., 0.1 mole), methyl iodide (14.2 g., 0.1 mole) and 11 g. of potassium hydroxide in 350 ml. of

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(15) E. C. Baughan, M. G. Evans and M. Polanyi, *Trans. Faraday Soc.*, **37**, 377 (1941).

(16) G. W. Wheland, *J. Chem. Phys.*, **2**, 479 (1937).

(17) M. Szwarc, *Disc. Faraday Soc.*, **10**, 336 (1951).

(18) G. V. Schulz and E. Husemann, *Z. physik. Chem.*, **B39**, 246 (1938).

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

95% ethanol were boiled for three hours. The product was cooled, leading to benzophenone azine, m.p. 160° alone and when mixed with an authentic sample, 12.5 g., 68% yield.

N,N′-Bis-benzhydrylhydrazine.—Hydrogenation of benzophenone azine in acetic acid or in ethanol at 20 p.s.i. and at room temperature was unsuccessful.

Treatment of the azine (12 g., 0.033 mole) with lithium aluminum hydride (3 g. in 400 ml. of ether) at 35° for 36 hours led to a white solid, 8.5 g., m.p. 90°, which slowly turned to a yellow viscous mass from which the azine was recovered and identified by mixed melting point. Treatment of the azine (8 g.) with lithium aluminum hydride (4 g. in 100 ml. of benzene) and 200 ml. of dibutyl ether at 90–100° for five hours led to 1,1,2,2-tetraphenylethane, 1 g., 14% yield, m.p. and m.p. of mixture with an authentic sample 206–208°, and crude diphenylmethane 1.5 g., 20% yield, b.p. 255–260°, melting 20–25°, reported[20] 26–27°; n^{20}_{D} 1.5692, reported,[21] 1.5712.

Five grams of benzophenone azine in 250 ml. of glacial acetic acid was hydrogenated for three hours at 40 p.s.i. and 60–70° over platinum oxide. The solution was filtered and concentrated in vacuum, leading to the hydrazine, 1.8 g., 36% yield, melting 110–130°, reported 120–133°.[5] A portion was converted to the hydrochloride, m.p. 205°, reported 205°.[5]

Azo-bis-diphenylmethane was prepared by oxidation of the crude hydrazine (1.3 g., m.p. 114–130°) in 40 ml. of acetone and 50 ml. of ethanol with 1.25 g. of 30% hydrogen peroxide at 10–15° for eight hours. The solvent was evaporated and the residue was crystallized from ethanol, 1 g., 76% yield, m.p. 115° dec. The melt solidified and melted again at 205–210°; the melting point of a mixture of this with an authentic sample of 1,1,2,2-tetraphenylethane (m.p. 208–210°) was 205–210°. *Anal.* Calcd. for $C_{26}H_{22}N_2$: C, 86.1; H, 6.13. Found: C, 85.7; H, 6.10.

Oxidation of N,N′-bis-benzhydrylhydrazine (0.5 g.) with 4.2 g. of mercuric oxide in benzene suspension at 10–15° for three hours led to the same azo compound, 0.45 g., 90% yield, m.p. 114° dec., solidified and melted again at 200–205°.

1,1,2,2-Tetraphenylethane.—Benzhydrol was converted to benzhydryl chloride,[22] and an ether solution of this was treated with magnesium, leading to 1,1,2,2-tetraphenylethane, 10% yield, m.p. 208–210°, reported 209–211°.[23]

Benzhydrylhydrazine.—Benzophenone hydrazone, 20 g., m.p. 96–97°, in 400 ml. of ether was added slowly to a solution of lithium aluminum hydride (5 g., in 400 ml. of ether) and boiled with stirring for eight hours under nitrogen. The mixture was hydrolyzed with water, the solid was dissolved by addition of 10% sodium hydroxide and the ether solution was separated and dried over sodium hydroxide pellets. The ether was evaporated and the residue slowly solidified, 8.8 g., 43% yield, sinter 50°, melting 55–60°, reported,[5] sinter 50°, m.p. 58–59°.

Benzophenone Benzhydrylhydrazone.—Benzhydrylhydrazine (15 g., 0.076 mole) and benzophenone (14 g., 0.077 mole) were boiled under reflux for 4 hours in 220 ml. of absolute ethanol and 10 ml. of acetic acid. The product was cooled, leading to white needles, 8 g., sinter 105°, melting 110–120°, with slow decomposition on further heating, reported m.p. 91°,[5] melting range of a mixture with azo-bis-diphenylmethane, 97° to 160° (1,1,2,2-tetraphenylethane apparently being formed from the azo compound). *Anal.* Calcd. for $C_{26}H_{22}N_2$: C, 86.1; H, 6.13. Found: C, 85.9; H, 5.82.

Kinetics.—Rates of decomposition were measured as described previously.[3,8]

Isolation of 1,1,2,2-Tetraphenylethane.—(a) Solutions from some kinetic runs at 54 and 64° were combined, corresponding to 1.19 g. of the azo compound in 400 ml. of toluene, and the solvent was removed at 55° (115 mm.), leaving 3 g. of residue. This was triturated with cold ethanol, leading to tetraphenylethane, m.p. 208–210°, alone and when mixed with an authentic sample, 0.85 g., 77% yield. A solution of 0.500 g. of 1,1,2,2-tetraphenylethane in 260 ml. of toluene was warmed at 60° for 48 hours and worked up in the same way; 0.474 g., 95% yield, m.p. 208–210°.

(b) Solutions from some kinetic studies in decalin at 54° were combined (0.260 g. of azo compound in 200 ml.) and the decalin was removed at 66° (8 mm.). The residue was treated as above leading to tetraphenylethane in 79% yield, m.p. and mixed m.p. 208–210°. A solution of 0.430 g. of tetraphenylethane in 200 ml. of decalin was warmed at 65° for 20 hours and concentrated at 67° (8 mm.), and the residue was washed with 10 ml. of ethanol, 0.378 g., 88% recovery, m.p. and mixed m.p. 208–210°.

(c) A solution of 0.206 g. of the azo compound in 80 ml. of freshly distilled diphenylmethane was heated at 60° for 32 hours and concentrated at 133° (8 mm.) and the residue was washed with ethanol, 0.150 g., 79%, m.p. and mixed m.p. 207–209°. A solution of 0.206 g. of tetraphenylethane in 80 ml. of diphenylmethane was treated in the same way, leading to recovery of 0.180 g., 84%, m.p. 208–210°.

(d) The azo compound I, 0.0406 g., was heated in a test-tube to 114°. A violent decomposition occurred and a white solid formed. This was washed with 3 ml. of ethanol and dried; tetraphenylethane, 0.0351 g., 94% yield, m.p. and mixed m.p. 207–209°. Tetraphenylethane (0.0400 g.) was suspended in 3 ml. of ethanol and manipulated in the same way, leading to recovery of 0.0380 g., 95%.

Polymerization.—A solution of 0.185 g. of azo-bis-diphenylmethane (93.5% assay by evolution of nitrogen at 54°) in 20 ml. of styrene was diluted to 50 ml. with thiophene-free benzene. Aliquots were sealed in vacuum and heated at 54.0° for one hour and for two hours. The tubes were cooled, the contents were transferred to weighed flasks, and weighed, and the polystyrene was precipitated by cold methanol, dried to constant weight in vacuum and weighed. The average of several samples was taken, 8.70 g. of solution leading to 0.0905 g. of polystyrene after one hour, and 8.73 g. of solution leading to 0.171 g. of polystyrene after two hours.

Intrinsic viscosities were measured in benzene in an Ostwald viscosimeter at 30.0°.

Acknowledgment.—We are pleased to acknowledge generous support of this work by the National Science Foundation, Frederick Gardner Cottrell Grants of Research Corporation, and the Committee on Research Grants of Brandeis University.

WALTHAM, MASSACHUSETTS

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[23] H. Biltz, *Ann.*, **296**, 220 (1897).