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

Azo Compounds. XVI. The Termination Reaction for a Model Polystyrene Radical[1,2]

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The termination reaction for a model polystyrene radical has been studied in some detail. 1,1′-Azo-bis-(1,3-diphenylpentane) has been synthesized and characterized. Its decomposition has been carried out in bromobenzene at 89.7 and 144.25°. At both of these temperatures 90% or more of the products indicated termination by coupling rather than by disproportionation.

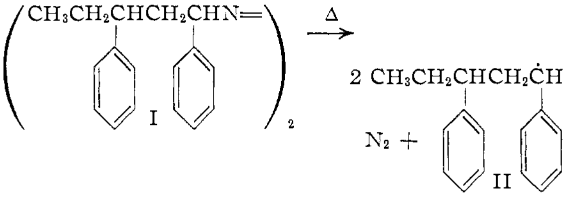
A reaction of considerable importance in any free radical vinyl polymerization involves the mutual bimolecular termination of two growing polymer chains. Most of the conclusions as to whether coupling or disproportionation predominate have required an assumption or calculation of the mechanism of termination from the efficiency of the initiator used in the polymerization. This method has not always provided an unequivocal answer to the problem.

To date the use of radioactive initiators and model compounds have produced the most reliable results as to whether disproportionation or coupling predominate in the termination step of a radical-catalyzed polymerization. Bevington, Melville and Taylor[3] have studied the termination reaction of styrene at 25 and 60° and methyl methacrylate at 0, 25 and 60° with radioactive 2,2′-azo-bis-isobutyronitrile as initiator. The results obtained with styrene at both temperatures showed quite clearly that disproportionation was a negligible reaction.

Bickel and Kooyman[4] reported that the decomposition of 1-azo-bis-1-phenylethane in inert solvents at 125° gave almost exclusively *meso*- and racemic 2,3-diphenylbutane coupled products. The radical formed on decomposition from the latter compound approximates the structure of a growing polystyrene radical. Kharasch, McBay and Urry[5] studied the decomposition of diacetyl peroxide in ethylbenzene, isopropylbenzene and *p*-methoxy-*n*-propylbenzene as solvents and reported that coupling of the benzyl radicals, produced as a secondary process, predominated. All of these results strongly indicate that benzyl radicals of the type $(C_6H_5\dot{C}H\text{–}CH_3)$ couple easily.

It was of interest to study the decomposition of a model azo compound which would produce a radical more closely approximating the steric and polar properties of a growing polystyrene radical than those previously available in order to subject the previously mentioned results and conclusions to a rigorous test. Accordingly, the azo compound derived from β-phenylvalerophenone (I) was prepared and decomposed at two temperatures.

The azo compound 1,1′-azo-bis-(1,3-diphenylpentane) (I) was synthesized according to the general procedure of Cohen, Groszos and Sparrow.[6] The azine was first formed from β-phenylvalerophenone, then reduced to the 1,2-disubstituted hydrazine over platinum in glacial acetic acid and oxidized to the azo compound (I) with hydrogen peroxide. For comparison purposes 1,3-diphenyl-1-pentene and 1,3-diphenylpentane, products which would arise from disproportionation, were synthesized independently from β-phenylvalerophenone. 1,3-Diphenyl-1-pentene was prepared by reduction of β-phenylvalerophenone with lithium aluminum hydride followed by dehydration. This latter compound was then hydrogenated over a Raney nickel catalyst to give 1,3-diphenylpentane.



The procedure for the decomposition of the azo compound was essentially that described previously for measuring the rates of decomposition[7,13] except that the volume of solvent was increased from 45 to 300 ml. in the isolation experiments. The rate of decomposition was determined at 118.8° ($k = 5.6 \times 10^{-4}$ sec.$^{-1}$) in xylene and at 89.7° in bromobenzene, ($k = 1.5 \times 10^{-5}$ sec.$^{-1}$). Since our primary purpose in this work was not a kinetic analysis, only one kinetic decomposition was carried out at these temperatures for comparative purposes. Errors which are applicable to those experiments are discussed in references 7 and 13.

These decomposition rates correspond to those reported by reference 6 for the decomposition of 1-azo-bis-1-phenylethane at 110.3°, $k = 1.69 \times 10^{-4}$ sec.$^{-1}$. Using an activation energy of 32.6 kcal./mole,[6] the rate of decomposition for 1-azo-bis-1-phenylethane at 118.8° is 5.9×10^{-4} sec.$^{-1}$, a very similar value to that reported here. The rate of decomposition of 2,2′-azo-bis-isobutyronitrile was determined in bromobenzene to demonstrate that the solvent did not affect the order or rate of decomposition, $k = 1.84 \times 10^{-4}$/sec. at 80.4° ($k = 1.60$–1.72×10^{-4}/sec. at 80.0°).[13]

The decomposition of the azo compound at 89.7° evolved 72.7% of the theoretical nitrogen. At this temperature the rate of decomposition is very slow

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[1] This is the 16th in a series of papers concerned with the preparation and decomposition of azo compounds. For the 15th paper in this series, see C. G. Overberger and M. Lapkin, THIS JOURNAL, **77**, 4651 (1955).

[2] This paper comprises a portion of a thesis presented by Arnold B. Finestone in partial fulfillment of the requirements for the degree of Doctor of Philosophy in the Graduate School of the Polytechnic Institute of Brooklyn.

[3] (a) J. C. Bevington, M. M. Melville and R. P. Taylor, *J. Polymer Sci.*, **12**, 449 (1954); (b) **14**, 463 (1954).

[4] A. F. Bickel and E. C. Kooyman, *Nature*, **170**, 211 (1952).

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

[6] S. G. Cohen, S. J. Groszos and D. B. Sparrow, THIS JOURNAL, **72**, 3947 (1950).

[7] C. G. Overberger and M. B. Berenbaum, *ibid.*, **73**, 2618 (1951).

and it is probable that isomerization to the hydrazone is the competing reaction. An indication of this was the isolation from the chromatographic column of an oil containing nitrogen with an N–H stretching frequency at 3400–3600/cm. The product analysis resulted in four solid compounds, all of which were shown to be coupled product, 3,5,6,8-tetraphenyldecane. The disproportionated products were prepared independently as mentioned previously and shown to be liquids at 0°. The possibility that the product obtained in the decomposition resulted from the addition of a radical formed on decomposition to 1,3-diphenyl-1-pentene, which would result from a disproportionation reaction, followed by stabilization by hydrogen abstraction, is unlikely since the disproportionation reaction must produce 1,3-diphenylpentane, and this compound could not be isolated from the reaction mixture. The possibility that a small amount of 1,3-diphenylpentane would escape detection cannot be overruled although it is unlikely that it was present in any large amount. The amount of coupled product isolated was 95.4% (Table I) based on the 72.7% value of nitrogen evolution. These data strongly suggest that at 89.7° the combination of radicals is the exclusive manner of termination.

The decomposition of 1,1′-azo-bis-(1,3-diphenylpentane) at 144.4° gave a theoretical evolution of nitrogen and the same four compounds found at the lower temperature were isolated. Since the rate of decomposition is probably much faster, the competing reaction of isomerization may be negligible. A total of 89.3% (Table I) of 3,5,6,8-tetraphenyldecanes were obtained, again strongly suggesting that coupling of two radicals was the method of termination.

It is recognized that the total number of radical collisions that occur in a polymer system is less than the number that occur in a model system of the type studied here. However, the ratios of the rate of coupling to the rate of disproportionation will be comparable at the same temperature, so long as the steric and polar factors affecting the radical in each system are similar. Since the radical produced from the decomposition of the azo compound is attached to two distinct styrene units, the polar and steric factors should be nearly identical to that of the polymer radical.

The rate of decomposition of 1,1′-azo-bis-(1,3-diphenylpentane) at 118.8° closely corresponds to the rate of decomposition of 1-azo-bis-1-phenylethane corrected to the same temperature. This is an indication that the group ($CH_3CH_2CH(C_6H_4)CH_2$) does not provide any additional steric interaction between the two halves of the molecule than does the simple (CH_3) group. Unlike the situation with tertiary aliphatic azo compounds,[8,13] steric factors between the two halves of the molecules do not seem to be as important in the secondary azo types.

Although some of the radicals produced may not leave the solvent cage on decomposition, this in no way changes the reactivity of the radicals; that is, the reactivity of radicals which have escaped or are retained should be the same. This compound catalyzes the polymerization of styrene at 110°, again strongly indicating that free radicals are formed on decomposition.

The results obtained in this work, together with the reported results of Bevington, Melville and Taylor and Bickel and Kooyman for the bimolecular termination of polystyrene at 25, 60 and 125° clearly indicate that combination of polystyrene radicals occurs exclusively from 25 to 144°

Experimental[9,10]

β-Phenylvalerophenone.—This compound was prepared according to the procedure of Kohler.[11] Distillation of the crude ketone through a short path column gave the pure ketone, 59%, b.p. 135° (0.3 mm.), m.p. 60–61° uncor., m.p. 63°.[11]

Anal. Calcd. for $C_{17}H_{18}O$: C, 85.72; H, 7.56. Found: C, 85.76; H, 7.37.

β-Phenylvalerophenone Azine.—This compound was prepared from 47.5 g. (0.199 mole) of β-phenylvalerophenone, 5.0 g. (0.10 mole) of 64% aqueous hydrazine in 300 ml. of benzene and 10 ml. of ethanol. The reaction mixture was refluxed for 5 days and the water removed by a Dean–Stark trap. The solvents were removed under reduced pressure, and the residue distilled through a small fractionating column to give 30.3 g. (64.2%), b.p. 238° (0.3 mm.), of azine.

Anal. Calcd. for $C_{34}H_{36}N_2$: C, 86.39; H, 7.68; N, 5.93. Found: C, 86.46; H, 7.94; N, 5.75.

1,1′-Azo-bis-(1,3-diphenylpentane).—This compound was prepared according to the general procedure of Cohen, Groszos and Sparrow.[6] β-Phenylvalerophenone azine, 31 g. (0.131 mole), was added to 50 ml. of glacial acetic acid and 0.5 g. of platinum oxide. The reaction mixture was placed in a Parr apparatus and subjected to a pressure of 2.5 atm. of hydrogen until the theoretical amount of hydrogen was absorbed. Acetic acid was removed under reduced pressure and the residue neutralized with 10% sodium hydroxide. Attempts to isolate a pure product failed. Distillation generally resulted in decomposition of the product. To the crude 1,2-disubstituted hydrazine in 15 ml. of petroleum ether (b.p. 28–38°) was added 100 ml. of 30% hydrogen peroxide and sufficient sodium bicarbonate (8 g.) to saturate the solution. The reaction mixture was vigorously stirred for three hours at room temperature. The azo compound was extracted with ether and dried over magnesium sulfate, the ether removed under reduced pressure and the residue taken up in petroleum ether (b.p. 28–38°). The azo compound crystallized at −20°, 0.8 g., 2.5% (based on the initial azine), m.p. 121–121.5° dec. Reoxidation of the reaction mixture gave an additional 1.3 g. of azo compound, total yield 6.7%.

Anal. Calcd. for $C_{34}H_{38}N_2$: C, 86.03; H, 8.07; N, 5.90. Found: C, 85.97; H, 7.91; N, 6.02.

1,3-Diphenyl-1-pentene.—β-Phenylvalerophenone, 24 g. (0.101 mole) was added slowly to a stirred, refluxing ether solution of 7.5 g. (0.2 mole) of lithium aluminum hydride. The reaction mixture was refluxed for three hours after the completion of the addition of the ketone. The reaction mixture was then decomposed with ethanol and the ether solution separated and dried over anhydrous magnesium sulfate. The ether was removed under reduced pressure and the crude alcohol dehydrated directly.

The alcohol was dropped onto 12 g. of fused potassium hydrogen sulfate which was maintained at a temperature of 230–250°. After the addition was complete the temperature was maintained for 1.5 hours and the reaction mixture was cooled and washed with ether. The ether solution was dried over anhydrous magnesium sulfate, the ether removed under reduced pressure and the residue distilled to give 10.8 g. (48.5%) of olefin based on ketone, b.p. 120° (0.7 mm.), $n^{27}D$ 1.5802.

Anal. Calcd. for $C_{17}H_{18}$: C, 91.84; H, 8.16. Found: C, 92.14; H, 8.10.

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(8) C. G. Overberger, W. F. Hale, M. B. Berenbaum and A. B. Finestone, This Journal, **76**, 6185 (1954).

(9) All melting points are corrected unless otherwise stated.

(10) Analyses by Dr. K. Ritter, Zurich, Switzerland, and Dr. F. Schwarz-kopf, New York, N. Y.

(11) E. P. Kohler, *Am. Chem. J.*, **38**, 548 (1907).

1,3-Diphenylpentane.—1,3-Diphenyl-1-pentene, 9.5 g. (0.0426 mole), was added to 75 ml. of ethanol and 1 g. of Raney nickel W-2 catalyst.[12] The reaction mixture was placed in a Parr apparatus and subjected to a pressure of 3 atm. of hydrogen. The uptake of hydrogen was rapid and the theoretical volume of hydrogen was absorbed. The catalyst was removed by filtration, the ethanol removed under reduced pressure and the residue distilled to give 6.2 g. (65.5%) of product, b.p. 113° (0.8 mm.), $n^{25.5}\text{D}$ 1.5445.

Anal. Calcd. for $C_{17}H_{20}$: C, 91.01; H, 8.99. Found: C, 91.04; H, 8.88.

Product Analysis for the Thermal Decomposition of 1,1'-Azo-bis-(1,3-diphenylpentane).—1,1'-Azo-bis-(1,3-diphenylpentane) was decomposed in 300 ml. of bromobenzene at two different temperatures, (1) 89.7° and (2) 144.25°, and the amount of nitrogen evolved observed.[13] The procedure for product analysis was basically the same in each experiment.

After decomposition was complete (89.7°, 69 hr.; 144.25°, 1 hr.) the solvent was fractionally distilled at reduced pressure and residual bromobenzene was removed by maintaining the flask temperature at 30° and reducing the pressure to 0.5 mm. The residue was then passed through a chromatographic column packed with activated alumina. The residue was placed on the column with *n*-hexane and eluted with *n*-hexane. The column was then washed with 2 liters of hexane and 50-ml. samples were removed. The hexane was removed from each fraction and the wax residues present in 8 fractions were diluted with acetone. Two distinctly different solids were obtained in this manner, the first, solid 1, melted at 167.5–169°, gave negative tests with bromine and permanganate for unsaturation, and the infrared spectrum indicated a saturated hydrocarbon with the exception of aromatic frequencies.

Anal. Calcd. for $C_{34}H_{38}$: C, 91.42; H, 8.58; mol. wt., 447. Found: C, 91.33; H, 8.35; mol. wt., 422, 467 (Rast).

This compound is undoubtedly an isomer of 3,5,6,8-tetraphenyldecane obtained from the coupling reaction of two 1,3-diphenyl-1-pentyl radicals (II).

Solid 2, m.p. 141.5–142°, showed no unsaturation with bromine and permanganate, and the infrared spectrum was identical with solid 1.

Anal. Calcd. for $C_{34}H_{38}$: C, 91.42; H, 8.58; mol. wt., 447. Found: C, 91.57; H, 8.35; mol. wt., 458, 467 (Rast).

Solid 2 is, apparently, a stereoisomer of solid 1.

After removal of solids 1 and 2, the remaining wax was dissolved in isopropyl alcohol and on cooling to −5° overnight, a solid crystallized from solution, 3, m.p. 93.5–98°. The tests for unsaturation were negative and the infrared spectrum was identical with solids 1 and 2.

Anal. Calcd. for $C_{34}H_{38}$: C, 91.42; H, 8.58; mol. wt., 447. Found: C, 91.15; H, 8.88; mol. wt., 423, 431 (Rast).

Another isomer of 3,5,6,8-tetraphenyldecane is strongly indicated. Solid 3 was further recrystallized from isopropyl alcohol and gave a new solid 4, m.p. 99.5–100°, mol. wt. 428, 465 (Rast). Tests for unsaturation with permanganate and bromine were negative, and the infrared spectrum was identical with solids 1, 2 and 3.

Compound 3 was recovered from the solvent, isopropyl alcohol, m.p. 93.2–97.8°.

Table I outlines the amount of coupled product accounted for at both temperatures.

TABLE I

THERMAL DECOMPOSITION OF 1,1'-AZO-BIS-(1,3-DIPHENYLPENTANE)

	M.p., °C.	Decompn. temp., °C. 89.7 ± 0.1	 144.25 ± 0.05
Amt. azo compd. decomp., g.		1.495	1.273
Percentage decomp.		72.70	101.0
Total solid 1, g.	167.5–169	0.073	0.068
Total solid 2, g.	141.5–142	.052	.048
Total solid 3, g.	93.5–98	.836	.938
Total solid 4, g.	99.5–100	.014	.016
Total solid, g.		.975	1.070
Percentage coupled products based on percentage decomp.		95.40	89.30
Total percentage unaccounted for based on percentage decomp.		4.60	10.70

In the decomposition run at 89.7° a yellow oil was isolated (0.275 g.) from the chromatographic column, on stirring the alumina in acetone. A sodium fusion indicated the presence of nitrogen. Attempts to make a solid derivative were unsuccessful. This oil would represent 67.2% of the 27.3% that was undecomposed. An infrared spectrum indicated the presence of a carbonyl group, 1680–1695/cm. an N–H stretching frequency, 3400–3600/cm., and an $N{=}C$ group, 1630–1660/cm.

BROOKLYN, N. Y.

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[12] R. Mozingo, "Organic Syntheses," Coll. Vol. III, John Wiley and Sons, Inc., New York, N. Y., p. 181.

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

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF WASHINGTON]

The Stereochemistry of the Wolff Rearrangement

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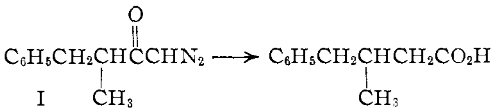
The Wolff rearrangement of *sec*-butyl diazomethyl ketone using silver benzoate–triethylamine, silver oxide, silver thiosulfate or ultraviolet light as catalysts gave the expected products with 97 ± 3% retention of configuration. The rearrangement of benzylmethyldiazoacetone also gave mainly retention of configuration in contrast to a previous report. It is concluded that the rearrangement of *sec*-alkyl diazomethyl ketones proceeds largely with retention of configuration.

In 1940, Wallis and co-workers[2] reported that the rearrangement of optically active benzylmethyldiazoacetone (I) using silver thiosulfate gave the expected acid, which was however optically inactive. When ammoniacal silver nitrate in methanol was used as the catalyst, the amide obtained was found to be partially racemized. Since compound I was optically stable for long periods of time, even on distillation, and could be converted to an optically active ketol on treatment with aqueous formic acid, it was felt that enolization of the diazoketone was not responsible for the observed racemization.



$$\mathrm{C_6H_5CH_2}\underset{\mathrm{CH_3}}{\mathrm{CH}}\overset{\mathrm{O}}{\overset{\|}{\mathrm{C}}}\mathrm{CHN_2} \longrightarrow \mathrm{C_6H_5CH_2}\underset{\mathrm{CH_3}}{\mathrm{CH}}\mathrm{CH_2CO_2H}$$

I

Later, Lane and Wallis[3] described the rearrange-

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[1] Taken from part of a thesis submitted by T. W. Hutton to the University of Washington in partial fulfillment of the requirements for the degree of Doctor of Philosophy, 1954. Allied Chemical and Dye Corp. Fellow, 1952–1953.

[2] J. F. Lane, J. Willenz, A. Weissberger and E. S. Wallis, *J. Org. Chem.*, **5**, 276 (1940).

[3] J. F. Lane and E. S. Wallis, *ibid.*, **6**, 443 (1941).