

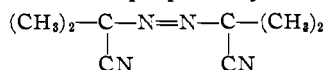
[CONTRIBUTION FROM THE CHEMICAL RESEARCH LABORATORY OF POLAROID CORPORATION]

1-Azo-bis-1-arylalkanes and their Decomposition¹

BY SAUL G. COHEN, STEPHEN J. GROSZOS AND DONALD B. SPARROW

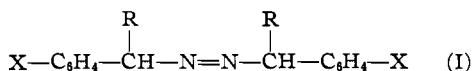
Simple aliphatic azo compounds^{2,3} are rather stable materials, which decompose at elevated temperatures (about 300°) in unimolecular reactions⁴ to form nitrogen and free alkyl radicals.⁵ Comparison of azo-bis-methane^{3,4,6} with azo-bis-2-propane^{3,4,6} indicates that this substitution of methyl groups for alpha hydrogen atoms decreases the activation energy of the decomposition from 51 kilocalories to 41 kilocalories and leads to more rapid decomposition at low temperatures.

Azo-bis-isobutyronitrile, which is formally derived from azo-bis-2-propane by substitution of



cyano groups for the remaining two alpha hydrogen atoms, is representative of a group of compounds^{7,8} which show moderate rates of decomposition at still lower temperatures, with activation energies of about 30 kilocalories. They are useful polymerization initiators because of the free radicals formed in their decomposition.

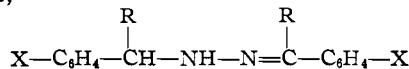
There are descriptions in the literature of a few 1-azo-bis-1-aryl-alkanes,⁹⁻¹³ formula I



in which R = H, CH₃, C₂H₅, and X = H, CH₃-COO, CH₃O. Such formal substitution of aryl-groups for alpha hydrogen atoms of the aliphatic azo compounds leads to increased reactivity. These compounds were reported to decompose at 100-160°, leading to the 1,2-diarylethanes



and to rearrange to their hydrazone tautomers more readily than the simple aliphatic compounds,^{2,3,10,13}



(1) This work was sponsored by the Signal Corps, Department of the Army, and the Air Material Command, Electronics Subdivision, U. S. Air Force.

(2) Thiele, *Ber.*, **42**, 2578 (1909).

(3) Lochte, Noyes and Bailey, *THIS JOURNAL*, **44**, 2556 (1922).

(4) Ramsperger, *ibid.*, **49**, 913 (1927); **50**, 714 (1928); **51**, 918, 2134 (1929).

(5) (a) Leermakers, *ibid.*, **55**, 3499 (1933); (b) Rice and Evering, *ibid.*, **55**, 3899 (1933).

(6) Gershinowitz and Rice, *J. Chem. Phys.*, **2**, 273 (1934).

(7) Lewis and Matheson, *THIS JOURNAL*, **71**, 747 (1949).

(8) Overberger, O'Shaughnessy and Shalit, *ibid.*, **71**, 2661 (1949).

(9) Thiele, *Ann.*, **376**, 265 (1910).

(10) Schulze and Lochte, *THIS JOURNAL*, **48**, 1031 (1926).

(11) Bretschneider, de Jonge, Bretschneider and Ajtai, *Ber.*, **74B**, 571 (1941).

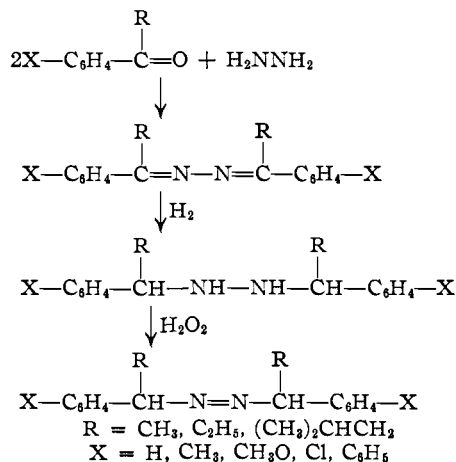
(12) Foldi and Fodor, *ibid.*, **74**, 589 (1941).

(13) Fodor and Szarvas, *ibid.*, **76B**, 334 (1943).

These azo-bis-arylalkanes were of interest to us since it seemed that free radicals were almost certainly formed in these decompositions also, and that these materials would be a convenient source of useful α -phenylethyl or styrene type radicals, and that the effects of the substituents X and R on the rates of decomposition would be worthy of study. They would be polymerization initiators which would introduce no polar fragments into the polymers. In the special case that the α -phenylethyl radical, C₆H₅-(CH₃)CH·, is generated in styrene, the polymerization would have the advantages of catalysis while the polymer would be essentially pure polystyrene.

We are reporting the preparation of some 1-azo-bis-1-arylalkanes, their absorption spectra, the rates of decomposition in ethylbenzene at 100° and 110° and the activation energies, the quantitative evolution of nitrogen during their decomposition in the presence of styrene and their use as initiators of the polymerization of styrene.

Preparation.—The 1-azo-bis-1-arylalkanes were prepared from the corresponding ketones via the azines and hydrazines by the general method which had been described previously.⁹⁻¹³



Detailed procedures were worked out anew and are described in the experimental section. Azines were prepared from acetophenone, *p*-methyl-, *p*-methoxy-, *p*-chloro- and *p*-phenylacetophenones, propiophenone and isovalerophenone. The azines were hydrogenated to the hydrazines, which in our final procedure were obtained as crude oils, wet with solvent, which were oxidized directly to the azo compounds. The azo compounds were obtained from all these azines, except that from *p*-phenylacetophenone, in 30-40% yield, as colorless crystalline materials; that from *p*-chloroacetophenone was light yellow. The data are summarized in Table I.

TABLE I
 1-AZO-BIS-1-ARYLALKANES

No.	[X-C ₆ H ₄ -CH-N=] ₂		M. p., °C.	Recryst. solvent	Yield, %	log ε, 335 mμ	Carbon, %		Hydrogen, %	
	X	R					Calcd.	Found	Calcd.	Found
1	H	CH ₃	72-73	Ethanol	34	1.77	a			
2	H	CH ₂ CH ₂	58-59	Ethanol	31	2.64	81.2	81.1	8.3	8.4
3	CH ₃	CH ₃	78-79	Ethanol-ligroin	44	1.74	81.2	81.2	8.3	8.4
4	H	(CH ₃) ₂ CHCH ₂	83-84	Methanol-ligroin	30	1.66	81.9	82.0	9.4	9.4
5	CH ₃ O	CH ₃	91-92	Methanol	34	1.85	72.4	72.3	7.4	8.5
6	Cl	CH ₃	108-109	Methanol-ligroin	44		62.6	62.9	5.2	5.4

^a Schulze and Lochte, ref. 10.

Absorption spectra of these materials were obtained in ethanol and all except the one derived from *p*-chloroacetophenone showed characteristic absorption maxima at 355 mμ. Log ε values at these wave lengths, varying from 1.66 to 2.64, are included in Table I. These spectra are reproduced in Figs. 1 and 2. Such absorption spectra have been used to distinguish azo-toluenes from the corresponding isomeric benzyl benzaldehydes.¹³ The para-chloro compound showed only a shoulder at about 355 mμ. It may well be that this material, which melted sharply and appeared pure, either was partly the tautomeric hydrazone or isomerized readily in the hydroxylic solvent to the hydrazone, the absorption spectrum of which masked the mini-

mum at about 300 mμ which is characteristic of these azo compounds.

Decomposition in the Presence of Styrene.— Since a primary object of this research was to prepare polymerization initiators which would introduce no polar fragments into polystyrene, the evolution of nitrogen was measured during the decomposition of these azo compounds in dilute solution in 3.46 m./l. styrene in ethylbenzene at 120°. The azo compounds would fail in this property if they rearranged in part to the tautomeric hydrazones which would be included mechanically in the polymer, or if a nitrogen containing free radical should be in part the initiating species, *i. e.*, X-C₆H₄-CHR-N=N. The latter seems an unlikely cause for permanent

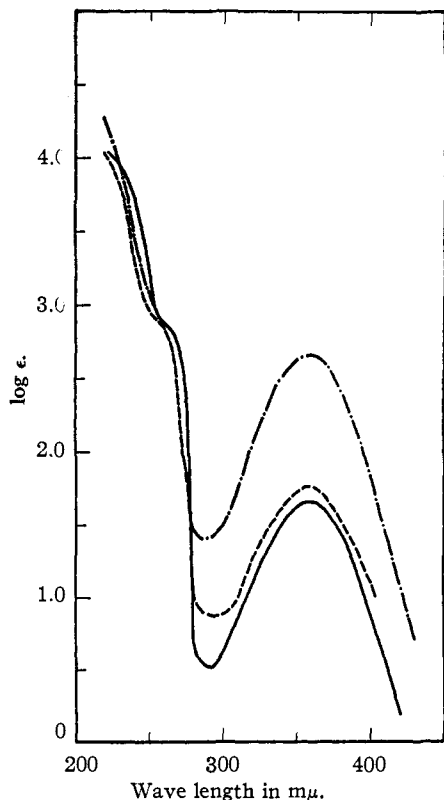


Fig. 1.—Absorption spectra of 1-azo-bis-1-arylalkanes, [C₆H₄-CRH-N=]₂: —, R = (CH₃)₂CH-CH₂-; ---, R = CH₃-; ····, R = C₂H₅-.

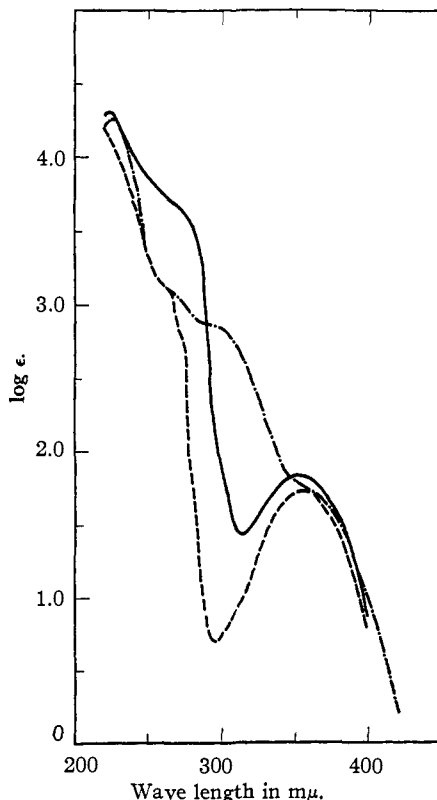


Fig. 2.—Absorption spectra of 1-azo-bis-1-arylalkanes, [X-C₆H₄-CCH₂H-N=]₂: —, X = CH₃O-; ---, X = CH₃-; ····, X = Cl.

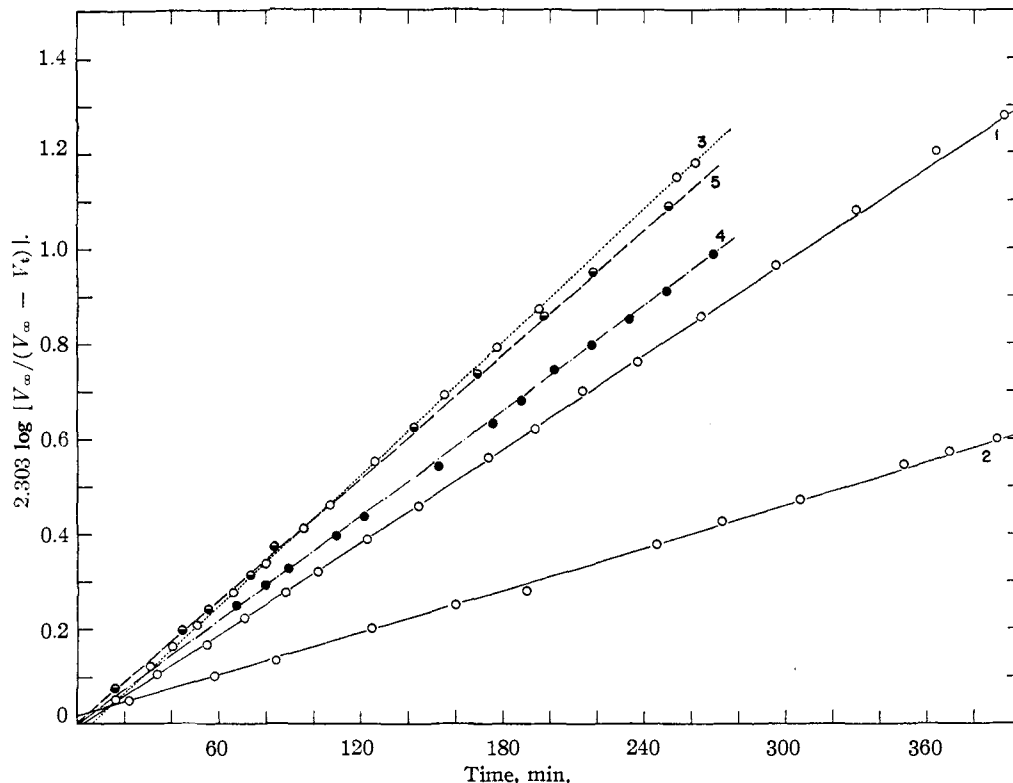


Fig. 3.—Decomposition of 1-azo-bis-1-arylalkanes in ethylbenzene at 100.4°: curve 1, $[\text{C}_6\text{H}_5\text{—CCH}_2\text{H—N=}]_2$; curve 2, $[\text{C}_6\text{H}_5\text{—CHC}_2\text{H}_5\text{—N=}]_2$; curve 3, $[\text{C}_6\text{H}_5\text{—CH}(\text{CH}_2\text{CH}(\text{CH}_3)_2)\text{—N=}]_2$; curve 4, $[\textit{p}\text{—CH}_3\text{—C}_6\text{H}_4\text{—CHCH}_3\text{—N=}]_2$; curve 5, $[\textit{p}\text{—CH}_3\text{O—C}_6\text{H}_4\text{—CHCH}_3\text{—N=}]_2$.

retention of nitrogen since the product of addition of such a radical to styrene monomer would be an azo compound of similar structure and if any nitrogen at all evolved, then ultimately all would. The six azo compounds listed in Table I were examined. With one exception, all led to quantitative evolution of nitrogen ($100.5 \pm 1.5\%$), under the conditions of the experiment and initiated polymerization of styrene. The exception, as with the absorption spectrum was 1-azo-bis-1-*p*-chlorophenylethane which led to 68% of the theoretical evolution of nitrogen, probably because of rearrangement to the more stable tautomeric hydrazone.

Rates of Decomposition.—The rates of decomposition of the azo compounds (except 1-azo-bis-1-*p*-chlorophenylethane) were determined in ethylbenzene at $100.4 \pm 0.1^\circ$ and $110.3 \pm 0.1^\circ$ by measurement of the volume of evolved nitrogen as a function of time (V_t). The solutions were about 0.02 molar. The equipment and procedure were similar to that described recently by Overberger, *et al.*⁸ In our equipment the tube connecting the reaction flask to the gas buret was 3 mm. i.d. instead of capillary, and most of this tube and the buret were maintained at 30° by water circulating from a thermostat bath. A mechanical vibrator was used to prevent supersaturation of the solvent with

nitrogen. Short apparent induction periods were observed in many of the reactions. Since these were probably due to gas shrinkage caused by reaction of radicals with traces of oxygen^{7,8} the effective zero time volumes were determined by extrapolation of early volume readings back to zero time. This method of determining V_t led to V_∞ 's which checked the calculated values and to plots of $\ln \frac{V}{(V_\infty - V_t)}$ vs. time which were straight lines which passed through the origin. The first order rate constants were obtained from these plots. At least two runs were made for each compound at both temperatures. The data are summarized in Table II and Figs. 3 and 4.

TABLE II
DECOMPOSITION OF 1-AZO-BIS-1-ARYLALKANES IN ETHYL-
BENZENE

$\frac{[\text{X—C}_6\text{H}_4\text{—CHN=}]_2}{\text{R}}$	$\frac{\text{R}}{\text{R}}$	$k_1 \times 10^5, \text{sec.}^{-1}$		$E_A, \text{kcal./mole}$
		100.4°	110.3°	
H	CH ₃	5.45 ± 0.05	16.9 ± 0.1	32.6 ± 0.5
H	CH ₂ CH ₂	2.35 ± 0.1	7.2 ± 0.2	32.3 ± 2.8
CH ₃	CH ₃	5.9 ± 0.2	18.5 ± 0.5	32.9 ± 1.8
H	(CH ₃) ₂ CHCH ₂	7.6 ± 0.05	24.2 ± 0.4	33.3 ± 1.0
CH ₃ O	CH ₃	7.15 ± 0.1	24.8 ± 0.2	35.8 ± 1.0

If 1-azo-bis-1-phenylethane, derived from acetophenone, is taken as the reference compound, it is seen that the presence of para-methoxyl

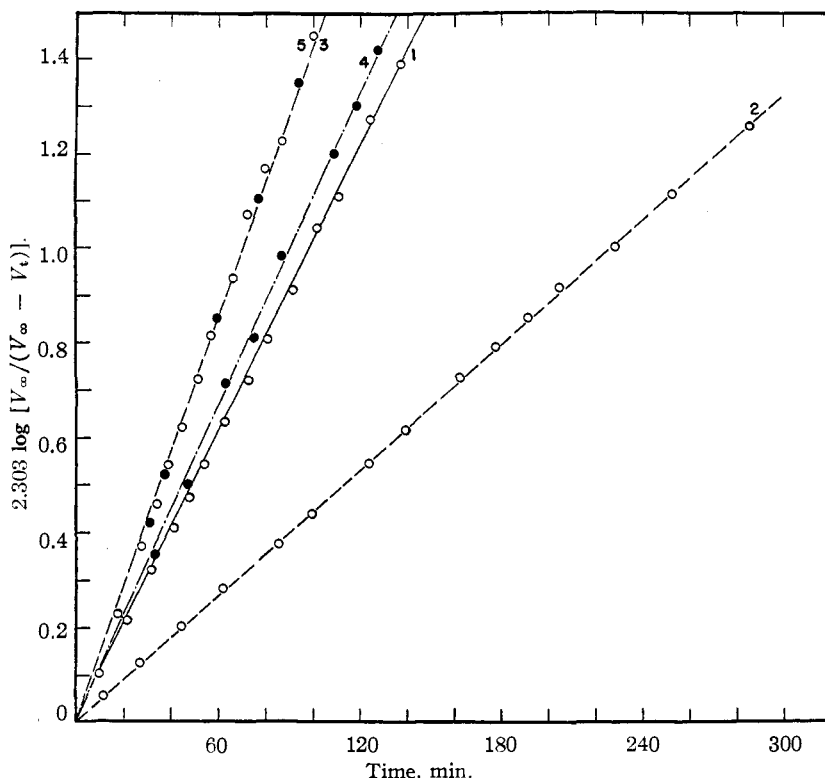


Fig. 4.—Decomposition of 1-azo-bis-1-arylalkanes in ethylbenzene at 110.3°: curve 1, $[\text{C}_6\text{H}_5-\text{CCH}_3\text{H}-\text{N}=\text{N}]_2$; curve 2, $[\text{C}_6\text{H}_5-\text{CHC}_2\text{H}_5-\text{N}=\text{N}]_2$; curve 3, $[\text{C}_6\text{H}_5-\text{CH}(\text{CH}_2\text{CH}(\text{CH}_3)_2)-\text{N}=\text{N}]_2$; curve 4, $[\text{p}-\text{CH}_3-\text{C}_6\text{H}_4-\text{CHCH}_3-\text{N}=\text{N}]_2$; curve 5, $[\text{p}-\text{CH}_3\text{O}-\text{C}_6\text{H}_4-\text{CHCH}_3-\text{N}=\text{N}]_2$.

groups, or alpha-isobutyl in place of alpha-methyl groups, leads to about 40% increase in the rates of decomposition, para-methyl groups lead to a very slight increase, while alpha-ethyl in place of alpha-methyl groups lead to rates slightly less than half of those of the reference compound. The effects of the para-methoxy and para-methyl groups are probably due to their electron release property, which may stabilize the radicals. The effect of the alpha isobutyl groups is probably steric, while the nature of the retarding effect of the ethyl group is obscure, an explanation being possible in terms of reduced hyperconjugation. However, the range in rate constants is small, slightly more than three fold, and the number of compounds examined is as yet inadequate for detailed discussion. The rates at 110° were comparable to those of the azo-isobutyronitriles at 80°,^{7,8} while the activation energies were similar in the two series.

Polymerization of Styrene.—The activity of these azo-bis-arylalkanes in initiating the polymerization of styrene was examined briefly. Dilute solutions of the azo compounds in 3.46 m./l. styrene in ethylbenzene were heated at 100.4° for one hour in vacuum and the polymers were precipitated in methanol. The results are summarized in Table III. The extents of poly-

merization varied from 9.5 to 18.8%, increasing with increasing average rates of decomposition (k_1c) of the initiators. The intrinsic viscosities decreased with increasing rates of polymerization. If the rates of polymerization are proportional to the square roots of the rates of initiator decomposition, the quotient of these two terms leads to the proportionality factors which are measures of the efficiencies of the compounds in initiating polymerization by their decomposition. These factors have been estimated, corrections being applied for changes in the concentrations of monomer and initiator during the time of polymerization. They are listed in the last column, Table III, and range from 0.23 to 0.27 $(\text{m./l./sec.})^{1/2}$.

Thus these initiators which, to be sure, are all closely related structurally, appear to have quite similar efficiencies ($\pm 8\%$) as polymerization initiators. It may be that the efficiencies are equal because all are high, possibly quantitative, in systems in which the initiator radicals are closely related structurally to the monomer, which is in turn capable of being converted to polymers of high molecular weight. Factors which might

TABLE III
POLYMERIZATION OF 3.46 M./L. STYRENE IN ETHYLBENZENE, 100°, BY 1-AZO-BIS-1-ARYLALKANES

X	R	[X-C ₆ H ₄ -CH(N)=N] ₂		Polymer		$-\frac{dM}{dt}$ $\frac{\sqrt{k_1c}}{\sqrt{k_1c}}$ ^{1/2}
		<i>c</i> , m./l.	<i>k</i> ₁ <i>c</i> , × 10 ⁶	%	η	
H	CH ₃	0.0102	0.510	15.6	0.33	0.23
H	C ₂ H ₅	.0080	.179	9.5	.36	.23
CH ₃	CH ₃	.0080	.424	15.5	.34	.25
H	(CH ₃) ₂ CHCH ₂	.0083	.562	18.8	.28	.27
CH ₃ O	CH ₃	.0082	.526	17.8	.32	.26

lower the efficiency of initiation are possible simultaneous decomposition of the azo compound and dimerization of the radicals, or ineffective decomposition in a cage of solvent molecules.¹⁴ If such compounds do initiate polymerization quantitatively a convenient method of measuring the rates of chain initiation in these systems becomes available.

(14) Matheson, *J. Chem. Phys.*, **13**, 584 (1945).

Experimental

Preparation of Ketone-Azines.—Propiophenone, *p*-methyl-, *p*-chloro-, *p*-methoxy-, and *p*-phenyl-acetophenones were obtained from Eastman Kodak Co. Isovalerophenone was prepared by the Friedel-Crafts reaction of isovaleryl chloride and benzene, 91% yield, b. p. 85–88° at 2–3 mm. Each ketone, 1 mole, and hydrazine hydrate, 0.5 mole, were boiled under reflux for several hours in ethanol which contained 0.5% acetic acid. The azines either precipitated or were obtained after concentration and were recrystallized. The products included acetophenone azine,¹⁵ 65% yield, m. p. 124° (from alcohol); propiophenone azine,¹⁶ 78% yield, m. p. 66–67° (from ethanol); *p*-methylacetophenone azine,¹⁷ 81% yield, m. p. 137–138°; isovalerophenone azine, 44% yield, m. p. 69–71° (from methanol). *Anal.* Calcd. for C₂₂H₂₈N₂: C, 82.5; H, 8.8. Found: C, 82.8; H, 8.8; *p*-phenylacetophenone azine, 85% yield, m. p. > 250°. *Anal.* Calcd. for C₂₃H₂₄N₂: C, 86.6; H, 6.2. Found: C, 86.6; H, 6.2; *p*-chloroacetophenone azine,¹⁸ 69% yield, m. p. 153–154° (from ethyl acetate-ethanol); *p*-methoxyacetophenone azine,¹⁹ 83% yield, m. p. 200–202° (from benzene). *Anal.* Calcd. for C₁₉H₂₀O₂N₂: C, 73.0; H, 6.8. Found: C, 73.3; H, 7.0.

Preparation of 1-Azo-bis-1-arylalkanes.—After a number of preliminary experiments it was found that the hydrogenation of the azines proceeded satisfactorily in acetic acid solution in the presence of Adams catalyst at 30 p.s.i., slowing down after absorption of two moles of hydrogen.

In early experiments hydrochloric acid was added at this point, the catalyst was removed and the solvent was evaporated. The hydrazine hydrochloride was washed with ether and oxidized to the azo compound with bromine water. It was subsequently found more convenient to remove the catalyst, boil off the acetic acid in vacuum, leaving the hydrazine as an oil, neutralize residual acetic acid with sodium hydroxide, and treat with excess saturated sodium bicarbonate and a 10% excess of 30% hydrogen peroxide with stirring at room temperature for several hours. The azo compound was extracted with ether, dried over magnesium sulfate, concentrated in vacuum and recrystallized.

Quantitative Nitrogen Evolution.—A weighed sample of the azo compound, about 0.2 g., was dissolved in 40 cc. of 40% styrene in ethylbenzene and swept with carbon dioxide until micro bubbles appeared in 50% potassium hydroxide solution in a nitrometer. The solution was then heated in vapors of boiling tetrachloroethylene in a

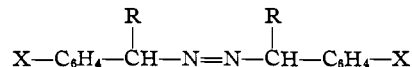
stream of carbon dioxide until the volume of nitrogen reached a constant value (about four hours). The azo compounds led in the order listed in Table I to 100.9, 99.1, 99.0, 101.8, 102 and 68% of the theoretical nitrogen content. The last two compounds were analyzed for nitrogen by Dr. C. K. Fitz. *Anal.* Calcd. for C₁₈H₂₂O₂N₂: N, 9.4. Found: N, 9.4. *Anal.* Calcd. for C₁₈H₁₈N₂Cl₂: N, 9.1. Found: N, 9.1.

Polymerization of Styrene.—Portions (10 ml.) of 3.46 m./l. styrene in ethylbenzene were pipetted into glass test-tubes into which small quantities (*ca.* 0.025 g.) of the five azo compounds, listed in Table III, had been accurately weighed. The tubes were cooled in *Dry-Ice* and sealed in vacuum. The tubes were warmed to room temperature, shaken until a clear solution resulted and heated at 100.4 ± 0.1% for one hour. The tubes were cooled and opened, and weighed quantities (about 8.5 g.) of the solutions were added to excess methanol. The precipitated polystyrene samples were washed with methanol, dried in vacuum, and weighed to the nearest milligram. The polymer weights ranged from 0.33 g. to 0.66 g.

Intrinsic Viscosities were determined in benzene at 30°.

Summary

Six azo compounds of structure



have been prepared by oxidation of the corresponding hydrazines, in which X and R are, respectively, H and CH₃, H and CH₂CH₃, CH₃ and CH₃, H and (CH₃)₂CHCH₂, CH₃O and CH₃, Cl and CH₃. All except the last compound showed characteristic minima in absorption at about 300 mμ, and maxima at 355 mμ, and decomposed in the presence of styrene at 120° with quantitative evolution of nitrogen. The rates of decomposition at 100° and 110° and the activation energies were determined in ethylbenzene. The rates were first order and the activation energies were 32–36 kcal. These compounds initiate the polymerization of styrene, introduce no polar end groups into the polystyrene and show essentially identical efficiencies in this initiation, which may be quite high.

CAMBRIDGE 39, MASSACHUSETTS

RECEIVED DECEMBER 15, 1949

(15) Curtius and Thun, *J. prakt. Chem.*, [2] **44**, 167 (1891).

(16) Mazurewitsch, *Bull. Soc. Chim.*, [4] **37**, 1165 (1925).

(17) Curtius and Kof, *J. prakt. Chem.*, [2] **86**, 114 (1912).

(18) Loch and Stach, *Ber.*, **77B**, 293 (1944).

(19) Vorlander, *Z. physik. Chem.*, **87**, 360 (1907).