

centrations. The direct correlation between reaction rate constant and salicylonitrile  $pK_a$  provides a built-in measure of the expected effects of substitution on reactivity. (In fact, if more refined thermodynamic measurements can establish that substituent effects on the benzisoxazole-salicylonitrile equilibrium constant are very small, then the salicylonitrile  $pK_a$  values must provide an exact measure of the effect of substituents on equilibria for the conversion of benzisoxazoles to salicylonitrile anions.) The predictability of the effect of benzo substitution on rate, together with the rigidity of the benzisoxazole function and the large separation of the 3 position and the reactivity-influencing benzo sites, implies that the leaving group properties of the benzisoxazole can be varied predictably and independently, with minimal idiosyncratic interaction with the region of reacting bonds adjacent to the 3 position. Because of this property, we feel that families of substituted benzisoxazoles offer much promise as experimental tools for the analysis of a variety of subtle mechanistic questions. In an initial study of this kind,<sup>6,36</sup> we have approached the problem of the existence of intrinsic curvature of Brønsted plots by deter-

mining the joint effects of base strength and ring substitution on the rates of proton transfer from benzisoxazoles. Other studies of solvent effects have been completed or are in process.<sup>6,18</sup> The ready availability of 3-acylbenzisoxazoles and their rapid cleavage by nucleophiles suggest an obvious application to acyl transfer chemistry which remains to be explored.

**Registry No.**—Hydroxylammonium *O*-sulfate, 2950-43-8; 4-chlorosalicylaldehyde, 2420-26-0; 5-chlorosalicylaldehyde, 635-93-8; 5-methoxysalicylaldehyde, 672-13-9; 4-methoxysalicylaldehyde, 673-22-3; 4-nitrosalicylaldehyde, 2460-58-4; benzisoxazole, 271-95-4; 5-nitrobenzisoxazole, 39835-28-4; [3-<sup>2</sup>H]-5-nitrobenzisoxazole, 39835-29-5; [formyl-<sup>2</sup>H]-5-nitrosalicylaldehyde, 39835-30-8; 5,7-dinitrobenzisoxazole, 39835-31-9; trimethylamine, 75-50-3; methyldiethanolamine, 105-59-9.

**Acknowledgment.**—Support for this work was provided by the National Science Foundation, Grants GP 8329 and 33265x. Fellowship support from the National Institutes of Health (M. L. C.) and the National Science Foundation (K. G. P.) is gratefully acknowledged.

(36) D. S. Kemp and M. L. Casey, submitted to *J. Amer. Chem. Soc.*

## Chemistry of Diarylazoalkanes. IV. Effect of Substituents on the Thermal Decomposition of Symmetrically Disubstituted 1,1'-Diphenyl-1,1'-azoethanes<sup>1,2</sup>

J. REID SHELTON\* AND C. K. LIANG

Department of Chemistry, Case Western Reserve University, Cleveland, Ohio 44106

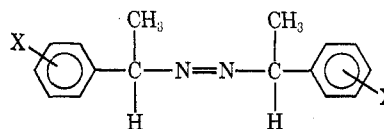
Received August 15, 1972

The effect of substituents upon the first-order thermal decomposition of symmetrically disubstituted 1,1'-diphenyl-1,1'-azoethanes was studied in *p*-cymene using a spectroscopic method. The observed effects can best be explained in terms of the relative importance of inductive and resonance effects (including hyperconjugation). Steric factors resulting from electrostatic repulsions are also involved in some cases. The importance of steric effects was especially evident in the increased rate of decomposition with an *o*-methoxy substituent on each phenyl group. The substituted  $\alpha$ -phenylethyl radicals, formed by thermal decomposition of the respective azo compounds in *o*-dichlorobenzene, coupled to form disubstituted 2,3-diphenylbutanes. Minor amounts of substituted ethylbenzenes were also produced, probably by disproportionation. The corresponding substituted styrenes were not found and presumably were polymerized under the conditions of the reaction. Activation parameters were determined for most of the thermal decompositions.

Shelton and coworkers<sup>2,3</sup> investigated the effect of substituents upon the thermal decomposition of disubstituted azocumenes  $[XC_6H_4(CH_3)_2CN=]_2$ , X = H, *p*-CH<sub>3</sub>, *p*-CH<sub>2</sub>CH<sub>3</sub>, *p*-(CH<sub>3</sub>)<sub>2</sub>CH, *p*-(CH<sub>3</sub>)<sub>3</sub>C, *p*-F, *p*-Br, *p*-Cl, and *m*-Cl, as part of their continuing study of the behavior of radical species.<sup>4</sup> The effects of the substituents upon the rates were small but significant, as also observed in the similar systems of the previous investigations.<sup>5</sup>

The availability in this laboratory of a modified synthetic method<sup>6</sup> suggested the possible preparation

of a series of symmetrically disubstituted 1,1'-diphenyl-1,1'-azoethanes (A) by oxidation with freshly



A, X = H, *o*-CH<sub>3</sub>O, *p*-CH<sub>3</sub>, *p*-CH<sub>2</sub>CH<sub>3</sub>, *p*-Cl, *p*-F, *p*-CH<sub>3</sub>O, *m*-CH<sub>3</sub>, *m*-CH<sub>2</sub>O, *m*-Cl, *m*-F, *m*-CF<sub>3</sub>

(1) Taken from the Ph.D. Thesis of C. K. Liang, Case Western Reserve University, 1969.

(2) Paper III of the series: P. Kovacic, R. R. Flynn, J. F. Gormish, A. H. Kappelman, and J. R. Shelton, *J. Org. Chem.*, **34**, 3312 (1969).

(3) J. R. Shelton, C. K. Liang, and P. Kovacic, *J. Amer. Chem. Soc.*, **90**, 354 (1968).

(4) J. R. Shelton and C. W. Uzelmeier, *J. Amer. Chem. Soc.*, **88**, 5222 (1966).

(5) S. G. Cohen, S. J. Groazes, and D. B. Sparrow, *J. Amer. Chem. Soc.*, **72**, 3947 (1950); S. Solomon, C. H. Wang, and S. G. Cohen, *ibid.*, **79**, 4104 (1957).

(6) J. R. Shelton and C. K. Liang, *Synthesis*, (4), 204 (1971).

made mercuric oxide of appropriately substituted hydrazines.

It was the purpose of this study to investigate the effects of the various substituted groups on the rate of decomposition and product distributions of these azo compounds. Some known derivatives are included in the series as a basis for comparison with prior studies.<sup>5</sup>

TABLE I  
 THERMAL DECOMPOSITION OF DISUBSTITUTED 1,1'-DIPHENYL-1,1'-AZOETHANES IN *p*-CYMENE

Registry no.	X in $[XC_6H_4CH(CH_3)N=]_2$	$k_1 \times 10^4, \text{sec}^{-1}$			Rel reactivity	
		85°	95°	105°	95°	105°
32234-19-8	<i>m</i> -CH <sub>3</sub> O		1.53 <sup>a</sup>	6.91 ± 0.04	0.56	0.84
32234-16-5	<i>p</i> -F	0.55 ± 0.12	2.35 ± 0.02	7.85 ± 1.10	0.86	0.96
5661-68-7	H		2.74 ± 0.06	8.21 ± 0.01	1.00	1.00
32234-18-7	<i>m</i> -CH <sub>3</sub>			8.17 ± 0.07		1.00
32234-14-3	<i>p</i> -CH <sub>3</sub> CH <sub>2</sub>		3.02 ± 0.05	9.14 ± 0.13	1.10	1.11
32234-13-2	<i>p</i> -CH <sub>3</sub>		3.06 ± 0.19	9.35 ± 0.10	1.12	1.15
32234-15-4	<i>p</i> -CH <sub>3</sub> O		3.56 ± 0.03	10.90 ± 0.09	1.30	1.33
32234-20-1	<i>m</i> -F			11.21 ± 0.01		1.37
32234-21-2	<i>m</i> -Cl		4.13 ± 0.02	12.18 ± 0.01	1.51	1.46
32234-22-3	<i>m</i> -CF <sub>3</sub> <sup>b</sup>		4.13	13.57	1.51	1.66
32234-17-6	<i>p</i> -Cl	1.45 ± 0.00	4.82 ± 1.20	16.50 ± 0.00	1.75	2.01
32234-23-4	<i>o</i> -CH <sub>3</sub> O	1.69 <sup>c</sup>	6.11 ± 1.00	19.75 ± 0.25	2.23	2.42

<sup>a</sup> Value may be low on the basis of higher relative rate observed at 105°. <sup>b</sup> Compound melted at 9–10° and was not recrystallized. <sup>c</sup> Measured at 84.6°.

### Results and Discussion

**Thermal Decomposition Rates.**—Cohen and co-workers<sup>5</sup> studied the rates of decomposition of para-, para'-disubstituted 1,1'-diphenyl-1,1'-azoethanes by measuring gas evolution. In our study, rates of decomposition were determined by following the disappearance of visible absorption due to the azo linkage of this series of compounds, which has a characteristic wavelength of 359 m $\mu$  and follows Beer's law.<sup>7</sup> No absorbance was shown in this region by either the solvent, *p*-cymene, or the decomposition products. In order to minimize the possible absorption interference due to a trace of acetophenone azines resulting from oxidation of azo compounds, the Guggenheim method<sup>8</sup> was employed to calculate the rate constants. The kinetic results are shown in Table I.

It is of particular interest that the rate of decomposition of 1,1'-diphenyl-1,1'-azoethane at 105° observed in this laboratory agrees with the previous findings,<sup>5,9</sup> within 3%. Molecular models indicate that the *cis* configuration of this compound would exhibit considerable steric strain, and it is generally accepted that the *trans* azo configuration is preferentially formed.<sup>9</sup>

It is helpful to compare the results obtained previously in this laboratory<sup>2,3</sup> for the thermal decomposition of disubstituted azocumenes (shown in Table II)

TABLE II

RELATIVE REACTIVITIES FOR THERMAL DECOMPOSITION OF DISUBSTITUTED AZOCUMENES AT 42.8° IN TOLUENE<sup>a</sup>

X in $[XC_6H_4(CH_3)_2N=]_2$	Rate constant $k_1 \times 10^5, \text{sec}^{-1}$	$\Delta H^\ddagger, \text{kcal/mol}$	$\Delta S^\ddagger, \text{cal/deg mol}$	Relative reactivity
H	1.13	29.3	11.4	1.00
<i>p</i> -(CH <sub>3</sub> ) <sub>2</sub> CH	1.13	29.7	14.9	1.00
<i>p</i> -(CH <sub>3</sub> ) <sub>3</sub> C	1.16	29.5	13.9	1.02
<i>p</i> -CH <sub>3</sub> CH <sub>2</sub>	1.29	29.0	14.6	1.13
<i>p</i> -F <sup>c</sup>	1.31	27.7	9.0	1.16
<i>p</i> -CH <sub>3</sub>	1.66	28.8	10.2	1.46
<i>m</i> -Cl <sup>c</sup>	2.46	27.7	7.6	2.18
<i>p</i> -Br	2.72	28.1	8.7	2.40
<i>p</i> -Cl <sup>c</sup>	2.90	26.9	6.5	2.67

<sup>a</sup> Reference 3. <sup>b</sup> Reference 10a. <sup>c</sup> Reference 2.

(7) S. Seltzer, *J. Amer. Chem. Soc.*, **83**, 2625 (1961).

(8) E. A. Guggenheim, *Phil. Mag.*, **2**, 538 (1926).

(9) S. Seltzer and E. R. Hamilton, Jr., *J. Amer. Chem. Soc.*, **88**, 3775 (1966).

with the data obtained in this study (Table I). It can be seen that the effects of the substituents in both systems on the rates of decomposition are relatively small (as expected for a radical mechanism) but significant. The results obtained in both studies indicated that the Hammett relation was not applicable, since there was mutual conjugation between the substituents and the reaction center (developing radical) in the transition state for the decomposition of the para-substituted azo compounds.

The relative reactivities in Tables I and II show that for those substituents which produced significant changes in the rate of thermal decomposition the relative order is the same in both series: azocumene series, *p*-Cl (2.7) > *m*-Cl (2.2) > *p*-CH<sub>3</sub> (1.5) > H (1.0); azo- $\alpha$ -phenylethane series, *p*-Cl (2.0) > *m*-Cl (1.5) > *p*-CH<sub>3</sub>, H (1.0).

Comparing the relative effect of a given substituent in the two series shows a much greater effect upon the rate of thermal decomposition of an azocumene as compared to the same substituent on the phenyl groups of a 1,1'-diphenyl-1,1'-azoethane. This trend has been confirmed by Timberlake<sup>10a</sup> and extended to include a series of phenylazomethanes which exhibit even smaller substituent effects. These results are contrary to the order which would be expected from consideration of activation energies, which predict more bond breakage in the transition state for phenylazomethanes and phenylazoethanes as compared to the azocumenes. It seems probable that steric factors may account for the faster rates and greater susceptibility to substituent effects as methyl groups replace hydrogen on the methylene groups of the phenylazomethanes. Overberger and coworkers<sup>11</sup> used a steric argument to rationalize the increased rate observed with isobutyl compared to *n*-butyl in azonitriles.

The  $\alpha$ -methylbenzylic radicals generated in the present system would be expected to be more reactive than the cumyl radicals (generated from the azocumenes), since the latter radicals have an additional methyl group to aid in the stabilization. Weiner and Hammond<sup>12</sup> found that the relative rate of bimolecular

(10) (a) J. W. Timberlake, private communication. (b) J. W. Timberlake and M. L. Hodges, *Tetrahedron Lett.*, 4174 (1970).

(11) C. G. Overberger, M. T. O'Shaughnessy, and H. Shalit, *J. Amer. Chem. Soc.*, **71**, 2661 (1949).

(12) S. A. Weiner and G. S. Hammond, *J. Amer. Chem. Soc.*, **91**, 986 (1969).

combination plus disproportionation is  $C_6H_5\dot{C}HCH_3$  (5.0)/ $C_6H_5\dot{C}(CH_3)_2$  (1.0).

The rates of decomposition of the symmetrically disubstituted 1,1'-diphenyl-1,1'-azoethanes in Table I decrease in the order  $o\text{-CH}_3O > p\text{-Cl} > m\text{-CF}_3 > m\text{-Cl} > p\text{-CH}_3O$ ,  $m\text{-F} > p\text{-CH}_3$ ,  $p\text{-CH}_2CH_3 > m\text{-CH}_3$ ,  $H$ ,  $p\text{-F} > m\text{-CH}_3O$ .

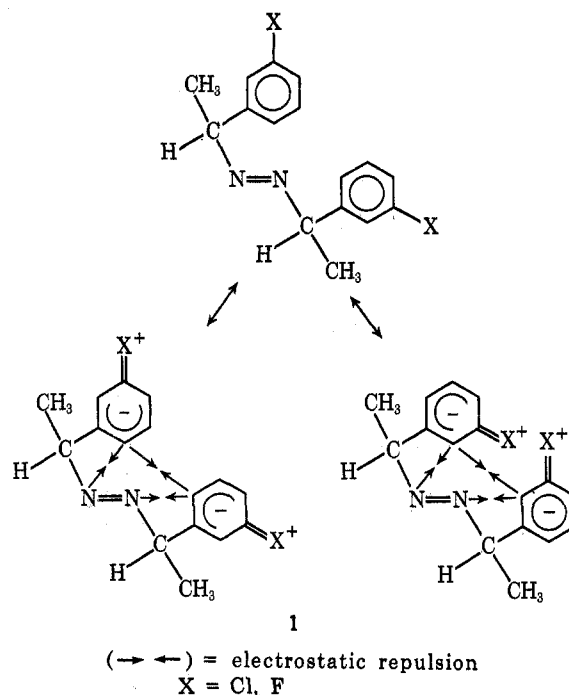
The net effect upon rate appears to be the resultant of a combination of inductive, resonance, and steric effects. A detailed analysis is not justified in view of the small differences observed, but some interpretation can be made consistent with the comparable effects observed in the azocumene work.<sup>2,3</sup>

The net outcome from the combined inductive and resonance influences appears to determine the observed rate order for the para-substituted azo compounds. The favorable resonance contribution of  $p\text{-Cl}$  and  $p\text{-CH}_3O$  outweighs the adverse inductive effect. The lesser effect of the methoxy group is consistent with a recent observation by Timberlake "that the stabilizing effect of the methoxy group in a pure radical system is small."<sup>10</sup> In the case of  $p\text{-F}$  any stabilization from resonance appears to be offset by induction; so the observed rate is very close to that of the parent compound, as was also observed in the azocumene study (Table II).

It is interesting that the  $m\text{-F}$ ,  $m\text{-Cl}$ , and  $m\text{-CF}_3$  substituted azo- $\alpha$ -phenylethanes decomposed at rates comparable to the  $p\text{-Cl}$  and  $p\text{-CH}_3O$  derivatives. In our discussion of the similar activating effect of  $m\text{-Cl}$  in azocumene,<sup>2</sup> we noted two possible hypotheses: (1) the adverse inductive effect should be negligible when the halogen is attached to a carbon which does not possess radical character in the transition state; and (2) a resonance effect may be indirectly involved.

The effects of meta substituents, often thought to be mainly inductive factors, may result in part from the charges, positive or negative, which they inject into the benzene rings to which they are attached. In symmetrically substituted diarylazoalkanes, the resulting electrostatic repulsions between the two halves of the molecule, as indicated in structures 1, could contribute to the observed increased rate of decomposition observed with the  $m\text{-F}$ ,  $m\text{-Cl}$ , and  $m\text{-CF}_3$  compounds. In the latter case, C-F hyperconjugation<sup>13</sup> would impart a positive charge on the benzene rings with a resultant electrostatic repulsion. Alternatively, direct repulsions due to the electrons surrounding the halogen atoms may be a more important factor in the observed activating effects of  $m\text{-F}$ ,  $m\text{-Cl}$ , and  $m\text{-CF}_3$  substituents. Marvel and coworkers<sup>14</sup> observed a similar activating effect of  $m\text{-Cl}$  in the decomposition of hexarylethanes, which they explained in terms of electrostatic repulsions resulting from resonance interactions of the type illustrated in 1.

The somewhat slower rate of decomposition of the  $m\text{-CH}_3O$  derivative than the parent compound is not consistent with the above resonance interpretation. Marvel<sup>14</sup> observed a similar lower reactivity for me-



thoxy compared to other substituents in hexarylethanes [ $m\text{-Cl}$  (8.18)/ $m\text{-CH}_3O$  (1.27)]. Thus, direct repulsions between the halogen atoms in these meta derivatives may be the major factor in the observed activating effects rather than an indirect effect involving partial charges resulting from resonance delocalization.

The  $o$ -methoxy derivative was the most reactive of the compounds studied. The much faster rate of decomposition as compared to  $p\text{-CH}_3O$  suggests a rather large steric effect. This view is supported by the unexpected doubling of the nmr spectra of the  $o\text{-CH}_3O$  derivative, as shown in Figure 1.<sup>15</sup> Doubling was also observed in the nmr spectra of the  $m\text{-CF}_3$  compound (Figure 2).<sup>15</sup> In both cases, the methyl protons  $\alpha$  to the azo group gave two sets of doublets which were centered at  $\delta$  1.38 and 1.42 for the  $o\text{-CH}_3O$  compound and at  $\delta$  1.50 and 1.56 for the  $m\text{-CF}_3$  derivative. In contrast, all the other azo compounds in the series showed only the expected doublet for the corresponding methyl protons, as shown in Figures 3 and 4<sup>15</sup> for the  $m\text{-Cl}$  and  $m\text{-CH}_3O$  compounds. The methoxy protons appeared as the expected singlet in Figure 4 and also in the  $p\text{-CH}_3O$  isomer, but two singlets are seen in Figure 1, centered at  $\delta$  3.71 and 3.76, for the  $o\text{-CH}_3O$  protons. The methine protons are not affected and appear as the expected quartet centered at  $\delta$  4.70 and 5.07 for  $m\text{-CF}_3$  and  $o\text{-CH}_3O$ , respectively.

Similar doubling of nmr spectra has been observed by others. This is an expected effect "when the rate of rotation about a given bond is intermediate between free rotation about unhindered bonds and the severely hindered rotation about formal double bonds, so that the nmr spectrum usually consists of a superposition of

(13) W. A. Sheppard and C. M. Shorts, "Organic Fluorine Chemistry," W. A. Benjamin, New York, N. Y., 1969, Chapter 3.

(14) M. F. Roy and C. S. Marvel, *J. Amer. Chem. Soc.*, **59**, 2622 (1937); C. S. Marvel, J. F. Kaplan, and C. M. Himel, *ibid.*, **63**, 1892 (1941); C. S. Marvel, J. Whitson, and H. W. Johnston, *ibid.*, **66**, 415 (1945); C. S. Marvel, F. C. Deitz, and C. M. Himel, *J. Org. Chem.*, **7**, 392 (1942).

(15) Figures 1-4 showing the nmr spectra of  $o\text{-CH}_3O$ ,  $m\text{-CF}_3$ ,  $m\text{-Cl}$ , and  $m\text{-CH}_3O$  disubstituted 1,1'-diphenyl-1,1'-azoethane will appear following these pages in the microfilm edition of this volume of the journal. Single copies may be obtained from the Business Operations Office, Books and Journals Division, American Chemical Society, 1155 Sixteenth St., N.W., Washington, D. C. 20036. Remit check or money order for \$3.00 for photocopy or \$2.00 for microfiche, referring to code number JOC-73-2301.

spectra resulting from the two (or more) rotational isomers that are present in equilibrium."<sup>16</sup>

Alternatively, the observed doubling of the nmr spectra in the present study could be due to a mixture of meso and *dl* isomers which, having magnetically nonequivalent methyl groups, would give rise to two sets of doublets. It is possible that pure meso compounds were isolated in all the other cases, since they would be expected to be the least soluble of the diastereoisomers.<sup>17</sup> The presence of a second diastereoisomer in the *m*-CF<sub>3</sub> case is probable in view of the low melting point (9–10°)<sup>6</sup> and the weak intensity of one of the doublets, consistent with contamination by a small amount of another isomer. In contrast, both methyl doublets and the two methoxy singlets observed with *o,o'*-dimethoxy-1,1'-diphenyl-1,1'-azoethane are major peaks, and this compound was a crystalline solid (mp 56.5–58°).<sup>6</sup> It seems improbable that the same experimental procedures would yield essentially pure isomers of all the other crystalline compounds, and a mixture of diastereoisomers in this one case.

In order to test the restricted rotation hypothesis in this case, nmr spectra were also determined at other temperatures. Lowering the temperature produced no change, and higher temperatures caused decomposition, which gave very complex spectra. The nmr data are thus inconclusive, but the evidence of a rather large steric contribution to the increased rate of decomposition of the *o*-CH<sub>3</sub>O disubstituted diphenylazoethane supports the interpretation that nonbonding interactions between these ortho methoxy groups and the azo  $\alpha$ -methyl group may be strong enough to restrict rotation and cause the  $\alpha$ -CH<sub>3</sub> to give rise to two different sets of doublets, and the CH<sub>3</sub>O group to show two singlets as seen in Figure 1.<sup>15</sup>

Activation parameters for the thermal decomposition of disubstituted 1,1'-diphenyl-1,1'-azoethanes were calculated for all compounds in Table I for which rate constants were determined at two or more temperatures. The relative reactivity increases going down in Table I, and both enthalpy of activation and entropy of activation tend to lower values going down the series in the same order in Table III. (The values for the *m*-CH<sub>3</sub>O compound are less reliable than the others, since the rate constant at 95° in Table I may be low.) The values for the *p*-F, *p*-Cl, and *o*-CH<sub>3</sub>O compounds are the most reliable, as they represent rate constants determined at three temperatures over a wider range.

Bartlett and Hiatt<sup>18</sup> observed a similar tendency for a lowering of the activation energy associated with a lowering of activation entropy in their study of perester decomposition. Since these effects oppose each other, the net result in their series, and in the present study of the decomposition of diarylazoalkanes, was found to be in the direction indicated by the enthalpies of activation.

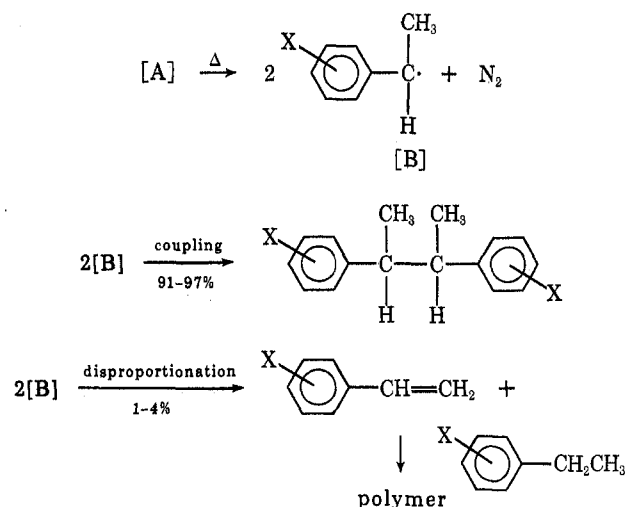
**Product Analysis.**—The organic products of the thermal decomposition of disubstituted 1,1'-diphenyl-1,1'-azoethanes in *o*-dichlorobenzene are mainly the coupling products of the substituted  $\alpha$ -phenylethyl

TABLE III

X in [XC <sub>6</sub> H <sub>4</sub> CH-(CH <sub>3</sub> )N=] <sub>2</sub>	$\Delta H^\ddagger$ , kcal/mol	$\Delta S^\ddagger$ , cal/deg mol	$\Delta\Delta H^\ddagger$ , kcal/mol	$\Delta\Delta S^\ddagger$ , cal/deg mol
<i>m</i> -CH <sub>3</sub> O	41.0 <sup>b</sup>	30.3 <sup>b</sup>	11.4	29.7
<i>p</i> -F	35.1	15.0	5.5	14.4
H	29.6	0.6	0.0	0.0
<i>p</i> -CH <sub>3</sub> CH <sub>2</sub>	29.9	1.6	0.3	1.0
<i>p</i> -CH <sub>3</sub>	30.2	2.3	0.6	1.7
<i>p</i> -CH <sub>3</sub> O	30.2	2.8	0.6	2.2
<i>m</i> -Cl	29.2	0.4	-0.4	-0.2
<i>m</i> -CF <sub>3</sub>	32.2	8.5	2.6	7.9
<i>p</i> -Cl	32.0	8.2	2.4	7.6
<i>o</i> -CH <sub>3</sub> O	32.4	9.7	2.8	9.1

<sup>a</sup> Estimated error  $\pm 2$  cal/deg mol. <sup>b</sup> See footnote *a* in Table I.

radicals plus some disproportionation products. A reaction scheme similar to that proposed for the azocumene system<sup>3,19</sup> follows.



The products were analyzed by gas-liquid partition chromatography (glpc) and only disubstituted 2,3-diphenylbutanes and minor amounts of substituted ethylbenzenes were observed in the reaction mixtures. Any substituted styrenes, formed by disproportionation, were evidently polymerized, since the  $\alpha$ -phenylethyl radicals are excellent initiators, as was demonstrated in the polymerization of styrene by Cohen and coworkers.<sup>5</sup>

The distribution of the substituted  $\alpha$ -phenylethyl radicals to observed products is listed in Table IV. Coupling to form substituted diphenylbutanes accounted for 91–97% of the radicals produced. This is in good agreement with a similar study done by Seltzer<sup>7</sup> with the deuterio derivative, 1,1'-diphenyl-1,1'-azoethane-1,1'-*d*<sub>2</sub>. He found that the atom % D in the only identified product, 2,3-diphenylbutane-2,3-*d*<sub>2</sub>, from the thermal decomposition of the azo compound in ethylbenzene is the same, within 15%, as that in the starting material. He did not detect the disproportionation product, since it would have been the same as the solvent, ethylbenzene. The formation of up to 2% of the substituted ethylbenzene in the present study indicates that up to 4% of the

(16) J. R. Dyer, "Application of Absorption Spectroscopy of Organic Compounds," Prentice-Hall, Englewood Cliffs, N. J., 1965, p 113.

(17) F. D. Greene, M. A. Berwick, and J. C. Stowell, *J. Amer. Chem. Soc.*, **92**, 867 (1970).

(18) P. D. Bartlett and R. R. Hiatt, *J. Amer. Chem. Soc.*, **80**, 1398 (1958).

(19) S. F. Nelson and P. D. Bartlett, *J. Amer. Chem. Soc.*, **88**, 137 (1966).

TABLE IV  
DISTRIBUTION OF RADICALS<sup>a</sup> TO OBSERVED PRODUCTS.  
THERMAL DECOMPOSITION OF DISUBSTITUTED

1,1'-DIPHENYL-1,1'-AZOETHANES IN <i>o</i> -DICHLOROBENZENES, 120°			
X in [XC <sub>6</sub> H <sub>4</sub> CH-(CH <sub>2</sub> )N=]	XC <sub>6</sub> H <sub>4</sub> CH <sub>2</sub> CH <sub>3</sub> , %	[XC <sub>6</sub> H <sub>4</sub> CH(CH <sub>3</sub> )-] <sub>2</sub> , %	Overall yield, %
<i>m</i> -CH <sub>3</sub> O	<i>b</i>	97 ± 0.2	97
<i>p</i> -F	<2	96 ± 0.6	98
H	2.2	91 ± 3	93
<i>m</i> -CH <sub>3</sub>	<2	93 ± 1	95
<i>p</i> -CH <sub>2</sub> CH <sub>2</sub>	<i>b</i>	97 ± 1	97
<i>p</i> -CH <sub>3</sub>	1.3	96 ± 1	97
<i>m</i> -F	<2	95 ± 0.5	97
<i>m</i> -Cl	<i>b</i>	97 ± 1.5	97
<i>p</i> -CH <sub>3</sub> O	<i>b</i>	92 ± 0.5	92
<i>o</i> -CH <sub>3</sub> O	<i>b</i>	93 ± 2	93

<sup>a</sup> Mole percentage of radicals accounted for after 24 hr of decomposition based on amount of azo compounds before reactions.  
<sup>b</sup> Glpc showed no peak for this product, estimated to be less than 1%.

radicals were involved in disproportionation, since an equivalent amount of the substituted styrene would be expected. It is also apparent that the effect of the substituents on the product distribution is negligible, consistent with the azocumene findings.<sup>3</sup>

### Experimental Section

Syntheses of the azo compounds are reported elsewhere by Shelton and Liang,<sup>6</sup> including yields, melting points, analysis, and nmr data.

**Decomposition Rate Measurements.**—The solvent, *p*-cymene (Fisher), was distilled over calcium hydride and the middle fraction, bp 174–174.5°, was collected. Nitrogen, passed through a drying tube filled with Drierite, was bubbled through the *p*-cymene for at least 30 min at room temperature to expel the oxygen. A 180-ml portion of this *p*-cymene was transferred to the reaction vessel which was immersed in a constant-temperature bath (Lauda Thermostat, Type NBss15122) and purged with nitrogen throughout the entire reaction. After the temperature of the whole system was equilibrated, a 20-ml solution of azo compound (0.4–0.5 g, recrystallized before use, in 20 ml of pure dried *p*-cymene) was injected with a 50-ml syringe into the reaction vessel through a septum. After the contents came to temperature equilibrium with the bath (generally 5 min), sampling was started using a 10-ml syringe with a 12-in. needle.

Ten samples were taken at intervals of 30 min by puncturing the septum and withdrawing approximately 8 ml of the reaction mixture. The samples were transferred immediately into small brown bottles and quenched in an ice-water bath. The second set of ten samples was obtained in the same manner after about 1–2 half-lives. Then each sample was transferred to an uv cell (2-cm quartz) and absorbance was measured at a fixed wavelength, 359 m $\mu$ , with an A. P. C. Cary 14 recording spectrophotometer.

Excellent linear first-order plots were obtained using the Guggenheim method<sup>8</sup> by plotting  $\ln(A_t - A_{T+t})$  vs. time, where  $A$  is absorbance at 359 m $\mu$ ,  $T$  is the time between the starts of the two series of samples, and  $t$  is the time interval (30 min). From these data rate constants were calculated. Activation parameters were obtained from decomposition rates measured at 105, 95, and in some cases 85°.

**Product Analysis.**—A 10–15-ml sample of the disubstituted 1,1'-diphenyl-1,1'-azoethane in *o*-dichlorobenzene solution (concentration ~0.07 *M*) was placed in a 50-ml flask fitted with reflux condenser and nitrogen inlet to give approximately 0.7–1.0 mmol of the azo compound. This flask was flushed with nitrogen and then immersed in a constant-temperature oil bath (120°) for about 24 hr under positive nitrogen pressure.

The raw reaction mixtures were analyzed by a Matronic Model 500 dual-column gas chromatograph. For the high-boiling products, a 2 ft  $\times$  0.25 in. column packed with 20% SF-96 on acid-washed Chromosorb P (30–60 mesh) was used, and, for the lower molecular weight materials, a 10 ft  $\times$  0.125 in. column packed with 5% diisodecyl phthalate and 5% Bentone-34 on Chromosorb G (60–80 mesh) was employed.

The reaction products from the decomposition of *p,p'*-dimethyl-1,1'-diphenyl-1,1'-azoethane and the parent compound were identified by comparison of glpc retention times with those of authentic samples which were either made by other routes or obtained commercially. Based on this information, the coupling and disproportionation products for the other derivatives could be easily identified by the relative retention times observed in each case. The coupling products of the methoxy isomers, for example, showed the following retention times: *p*-CH<sub>3</sub>O (2.7 min)/*m*-CH<sub>3</sub>O (2.1 min)/*o*-CH<sub>3</sub>O (2.0 min). Since only a single peak was observed on each gas chromatogram, the identification was definite in every case.

**Acknowledgment.**—The authors are indebted to Miss Frances Chang for her contribution in obtaining rate data at additional temperatures for several of the azo compounds to permit calculation of the activation parameters. This work is part of a series of studies of free-radical reactions supported by the Goodyear Tire and Rubber Co., Akron, Ohio.