Chemistry of Diarylazoalkanes. III. Effect of Structural Variation on Rate and Nature of the Thermal Decomposition

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Received February 11, 1969

A kinetic study of the thermal decomposition in toluene of various diarylazoalkanes [p,p'-difluoro-, p,p'dichloro-, and m,m'-dichloroazocumenes and 1,1'-di(4-tolyl)azocyclohexane] showed that the rates were all The effects of the structural variations were small but significant. The influence of substituents first order. on the aromatic nucleus is discussed in terms of resonance and induction theory. A steric argument is used to rationalize the rate increase produced by changing the alkyl substituents on the side chain from dimethyl to pentamethylene. The radicals formed in the azo decompositions primarily coupled to form the expected dimers, with disproportionation occurring to a small extent. Activation energies for the thermal decompositions were determined.

The discovery in this laboratory of a convenient method for the preparation of t-benzylamines^{4,5} made available the precursors of the corresponding azo compounds. Following the initial studies by Nelsen and Bartlett^{6,7} on the thermal decomposition of azocumene, we ascertained the effect of various para substituents on the kinetics and course of the breakdown.8 This report deals with the influence of additional structural variations on the rate and nature of the thermal decomposition in the diarylazoalkane series.

Results

The azo compounds [p,p'-diffuoro-, p,p'-dichloro-, and <math>m,m'-dichloroazocumenes and 1,1'-di(4-tolyl)azocyclohexane] were prepared by oxidation of the corresponding amines with iodine pentafluoride according to a modification⁹ of the procedure of Nelsen and Bartlett.⁶ The yields and physical properties are listed in Table I. Rates of decomposition were obtained by following the disappearance in the ultraviolet (uv) spectrum of the characteristic peak at 367 m μ due to absorption by the azo linkage.⁸ This technique is similar to the spectrophotometric method used by Talat-Erben and Bywater in the azonitrile series.¹⁰ One example of an Eyring plot of the rate data is shown in Figure 1 (the other azo compounds gave similar plots). The kinetic results are summarized in Tables II and III. Pertinent data from previous work are included for comparison. Examination of the kinetics reveals that the structural alterations produced small, but nevertheless significant, differences in the rates. The differences in the activation energies were minor, probably not significant in most cases.

In keeping with the prior studies^{6,8} on diarylazoalkanes, the organic products from thermal decomposi-

(2) Supported by the National Science Foundation Research Participation for College Teachers Program.

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tion resulted mainly from coupling of the t-benzyl radicals (Table IV). Disproportionation constituted a minor, competing pathway. From the total yield (84 to >96%) of these products, 86 to >96% was derived from the dimerization reaction.

Identification of the predominant components was generally accomplished by comparison (glpc and infrared (ir) spectra) with authentic materials prepared from the corresponding substituted cumene and di-tbutyl peroxide. In addition, this correlation served to verify the structure of the *t*-benzylamine. An exception to the peroxide method was observed in the case of p-cyclohexyltoluene since C-H bonds other than the *t*-benzyl one appeared to undergo preferential attack.

Although the two disproportionation products should theoretically be present in equal amounts, larger quantities of the substituted α -methylstyrenes were obtained in the case of the *p*-chloro and *p*-fluoro derivatives. This is analogous to the behavior reported⁸ for the *p*-bromo analog.

We found it critically important to control the conditions of decomposition carefully; otherwise the intermediate radicals were quite readily scavenged, presumably by oxygen. For example, intimate exposure to large volumes of nitrogen proved deleterious, apparently because of the presence of trace quantities of oxygen in the gas. When the reaction mixture was in contact with an ordinary atmosphere, the yield of coupled product diminished drastically. Decrease in yield of the desired material was accompanied by an increase in the amount of unidentified components which seem to arise from oxidation. Cumene is known to undergo autoxidation with ease in the presence of azobisisobutyronitrile as initiator.¹¹

Discussion

Some insight is gained from a theoretical treatment of the results and comparison with related studies from the prior literature. The net outcome from interaction of the inductive and resonance influences appears to determine the observed rate order, $Cl > Br > CH_3 >$ F > H, for the *para*-substituted azocumenes. Both effects decrease in the halogen series as indicated, F > Cl > Br. In all cases the favorable resonance contribution by halogen outweighs the adverse induction, although to the least degree with fluorine.

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TABLE I Synthesis and Properties of Diarylazoalkanes

					Product		
_	R"/2		Registry		Yield ^a	Mp, dec,	λ_{max} ,
R	R'	R''	no.	Temp, °C	%	۰Co	mμ (ε)
p-Methyl	Methyl	Methyl	18344-79-1	-20 to -10	39°,ª		
p-Chloro	Methyl	Methyl	21317-34-0	-25 to -10	47	106 - 107.5	367 (53.)
p-Fluoro	Methyl	Methyl	21317-35-1	-25 to -10	36	98.5-99	367 (44.)
m-Chloro	Methyl	Methyl	21317-36-2	-30 to -20	50	37.5-38.5	371 (48.
p-Methyl	Pentame	ethylene	21317-37-3	-25 to -10	40	90-91	380 (57.)

^a Crude product. ^b Pure material; elemental analyses (all elements) were within 0.2% of theory. ^c An 18% yield was obtained at room temperature. ^d When the amine in methylene chloride was added to a solution of iodine pentafluoride in methylene chloride, a yield of 17% resulted. ^eWithout decomposition.

	TABLE II	
RATES A	AND ACTIVATION ENERGIES FO	R THE
THERMAL I	DECOMPOSITION OF DIARYLAZO	ALKANES
Temp, °C	$k_1 \times 10^{5}$, sec ⁻¹	$E_{\rm A}{}^a$, kcal/mol
	p, p'-Dimethylazocumene	
36.0 ± 0.1	0.84	26.3 ^b
42.8 ± 0.1	1.62	
61.1 ± 0.5	20.80	
	p, p'-Difluoroazocumene	
36.0 ± 0.1	0.57	27.7
42.8 ± 0.1	1.31°	
48.2 ± 0.1	2.94	
61.1 ± 0.5	18.80	
	p, p'-Dichloroazocumene	
36.0 ± 0.1	1.11	26.9
42.8 ± 0.1	2.90°	
48.2 ± 0.1	6.52	
61.1 ± 0.5	32.80	
	m,m'-Dichloroazocumene	
36.0 ± 0.1	0.88	27.7
42.8 ± 0.1	2.46 ± 0.14^{d}	
48.2 ± 0.1	5.55	
61.1 ± 0.5	27.96	
1	,1'-Di(4-tolyl)azocyclohexane	
36.0 ± 0.1	0.87	25.6
42.8 ± 0.1	2.01 ± 0.13^{d}	
61.1 ± 0.5	20.09	

^a The error is estimated to be 1-2 kcal/mol. ^b Compare with 28.8.^d ^c Average of triplicate runs. The individual values deviated by <7% from the average. ^d Average of duplicate runs.

TABLE III Relative Rates of Decomposition of Diarylazoalkanes at 42.8°

R	R'	R"	$K_1 \times 10^{6},$ sec ⁻¹	Relative reactivity	
Hvdrogen	Methyl	Methyl	1.13ª	1.00	
p-Bromo	Methyl	Methyl	2.72^{a}	2.40ª	
p-Chloro	Methyl	Methyl	2.90	2.67	
p-Fluoro	Methyl	Methyl	1.31	1.16	
m-Chloro	Methyl	Methyl	2.46	2.18	
<i>p</i> -Methyl	Methyl	Methyl	1.62	1.43	
<i>p</i> -Methyl	Pentame	ethylene	2.01	1.78	
- 0 - 0 0		41. 1.00.4			

^a See ref 8. ^b Compare with 1.66.⁸

The same order of reactivity, $Cl > Br > CH_3$, was observed in the polymerization of *para*-substituted α -methylstyrenes,¹² which is not surprising in view of

(12) V. V. Korshak, A. M. Polyakova, and I. M. Stoletova, *Izvest. Akad.* Nauk SSSR, Otdel. Khim. Nauk, 1471 (1959); Chem. Abstr., 54, 1368 (1960).



Figure 1.—Eyring plot for decomposition of p,p'-dichloroazo- \bullet cumene.

TABLE IV DISTRIBUTION OF RADICALS IN THE DECOMPOSITION PRODUCTS FROM DIARYLAZOALKANES

			Yield. %			
R	B.'	R″	R' - RC ₅ H,CH - R''	$RC_{g}H_{4}C = CH_{2}$	$\begin{pmatrix} \mathbf{R}' \\ \mathbf{L} \\ \mathbf{R} \\ \mathbf{C}_{\mathbf{\theta}} \mathbf{H}_{4} \\ \mathbf{C} \\ \mathbf{L} \\ \mathbf{R}'' \\ \mathbf{R}'' \end{pmatrix}_{2}$	
p-Chloro	Methyl	Methyl	2.5	6.8	74.7ª	
p-Chloro	Methyl	Methyl	2.9	10.0	61.1ª,b	
<i>p</i> -Chloro	Methyl	Methyl	1.0	8.2	48ª,c	
p-Fluoro	Methyl	Methyl	5.1	8.1	78.9ª	
<i>m</i> -Chloro	Methyl	Methyl	d	d	93.2ª	
<i>p</i> -Methyl	Pentan	nethylene	d	d	95.7	

^a Glpc analysis indicated the presence of other components which were not examined further. ^b Nitrogen was passed through the solution during the entire decomposition period. ^c Nitrogen purge was omitted. ^d Not determined.

the similarity between the t-benzyl radicals in the two systems. Furthermore, despite the fact that the exact order is not duplicated, there are basic likenesses to the relative rates of radical phenylation¹³ of monosubstituted aromatic substrates, Br (1.29) > CH₃ (1.23) > Cl (1.06) > F (1.03) > H (1). It is apparent that the substituent would interact similarly with both types of radicals, t-benzyl and σ complex. Shelton and Uzelmeier¹⁴ reported the following relative reactivities in homolytic substitution by the nucleophllic cyclohexyl radical, C₆H₅Cl (3.5) > C₆H₅F (1.9) > C₆H₆ (1) > C₆H₅CH₃ (0.76). Mechanistic considerations indicate

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

certain correlations between our data and the relative tendencies of 1,2-aryl migration in the neophyl radical derived from ZC₆H₄C(CH₃)₂CH₂CO₃C(CH₃)₃ or ZC₆H₄- $C(CH_3)_2CH_2CHO$, for which 1 is postulated to be involved.^{15,16} Although more migration occurred with



the *p*-chloro and *p*-bromo compounds than in the unsubstituted case. Rüchardt and Hecht noted that the amount of rearrangement was reduced for p-fluoro and p-methyl.¹⁵ As a rationalization of the results, it was pointed out that the formation of 1 involves a nucleophilic radical in a transition state that is apparently characterized by a certain degree of polarity.¹⁶

On the other hand, in certain situations entailing generation of benzyl radicals, e.g., by means of peroxy radicals, p-halo substituents are generally rate retarding.¹⁷ In the mechanistic considerations, participation of polar influences in the transition state has been invoked.17,18

It is interesting that m,m'-dichloroazocumene decomposed almost as rapidly as the para, para' isomer. For comparison, in the phenylation category the partial rate factor for the meta position of chlorobenzene is 1. Several possible hypotheses can be invoked in our case: (1) the adverse inductive effect should diminish when halogen is affixed to a carbon which does not possess radical character in the transition state; and (2) a resonance effect (2) may be indirectly involved.¹⁹ This



latter type of approach has been used previously to explain the greater acidity of β -picoline vs. toluene,²⁰ and the order of reactivity, F > Cl, Br, in the protode-triethylgermylation of the *m*-halo compounds.²¹ A similar situation prevails in aryl migration within the neophyl radical; the *m*-chloro and *m*-bromo derivatives are more prone to rearrange than the unsubstituted parent compound.¹⁵

We observed that a change in the α -alkyl substituents from dimethyl to pentamethylene produced a slight rate enhancement. This appears reasonable on the basis of steric factors since Stuart models reveal more crowding between the two halves of the molecule (certain conformations) for the cyclohexane-containing compound. From a study of the decomposition kinetics for azonitriles, Overberger and coworkers used

$$\begin{pmatrix} CH_{\vartheta} \\ \downarrow \\ RCN = \\ \downarrow \\ CN \end{pmatrix}_{\mathbf{s}}$$

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York, N. Y., 1962, p 114.

a steric argument to rationalize the enhanced rate when R = isobutyl compared with <math>R = n-butyl.²² If hyperconjugative stabilization of the intermediate radical were important in our case, one would expect an order opposite that which was observed. Hyperconjugative and inductive effects were not involved to any significant extent in the breakdown of simple azonitriles.²² Interpretation of the data for the alicyclic types is further complicated by the concept of I strain which postulates an increase in the steric factor on conversion of a cyclohexane ring to the corresponding radical.²³ Although this is not a predominant consideration in our case, it could well contribute to the 20fold decrease in rate for the azo compound from cyclohexanone as compared with the azonitrile in which $R = methvl.^{22}$

Experimental Section

Melting points and boiling points are uncorrected. Microanalyses and molecular weight determinations (vapor pressure osmometry) were performed by Galbraith Laboratories, Knoxville, Tenn.

Diarylazoalkanes.--These compounds were prepared from the corresponding amines^{4,5} by oxidation with iodine pentafluoride according to the previously reported procedure.9

Decomposition Rate Measurements .- A modification of a published procedure was used.⁸ Solutions of the azo compound in toluene (about 0.015 M) were placed in a constant-temperature bath. Periodically samples were removed and immersed in a Dry Ice-carbon tetrachloride-chloroform bath to quench the reaction. Time was recorded the instant the tube was plunged into the bath. The absorbancies were then measured with a Beckman DB-G spectrophotometer. Since the change of absorbance with concentration of the azo compound follows Beer's law quite well, it was convenient to plot the absorbance at 367 m μ directly on semilogarithmic paper. First-order plots were obtained from which the rate constants were calculated.

Product Analysis.-Nitrogen was passed through a toluene solution (6-10 ml) ($\sim 0.03 M$) of the azocumene in a flask fitted with a reflux condenser. The flask was then immersed in a constant-temperature bath (60°) for 24 hr, while nitrogen was slowly passed over the surface of the liquid. The reaction mixture was then concentrated to ~ 1 ml by distillation followed by analysis, in most cases, with a Matronic Model 500 dual-column gas chromatograph. For the high boiling products, a 2 ft by 0.25 in. column packed with 20% SF-96 on acid-washed Chromosorb P (30-60 mesh) was used at 200° and, for the lower molecular weight material, a 6 ft by 0.25 in. column packed with 20% SF-96 on acid-washed Chromosorb P (30-60 mesh) was used at 160°. Bibenzyl was selected as the internal standard. Calibration was accomplished with mixtures of the authentic materials and bibenzyl. We were not able to analyze the products from 1,1'di(4-tolyl)azocyclohexane by glpc. The dicumyls from the azo decomposition were collected by glpc and compared with authentic materials (glpc retention time and infrared spectrum).

p,p'-Difluorobicumyl.—A mixture of p-fluorocumene (3 g) and di-t-butyl peroxide (1.46 g) was heated at 120-130° for 3 days. The material boiling below 40° (0.6 mm) was removed by distillation and 2 ml of absolute ethanol was added to the residue. The crystals which separated on cooling in Dry Ice-acetone were recrystallized first from ethanol and then from ethanol-water: 0.1 g, mp 121.5-123° (lit.²⁴ mp 124.5-125°). p,p'-Dichlorobicumy1.—The reaction of p-chlorocumene and

di-t-butyl peroxide was carried out in essentially the same manner as for p, p'-difluorobicumyl. After addition of acetone to the cooled reaction mixture, the resulting solid was collected: mp 168.5-170°. Purification by glpc gave material melting at 170-171° (lit.²⁴ mp 170–171°).

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m,m'-Dichlorobicumyl.—The reaction of m-chlorocumene and di-t-butyl peroxide was carried out as in the preceding section. On cooling of the reaction mixture, crystals formed which were removed by filtration, washed with acetone, and recrystal.ized from absolute ethanol: mp 134-135°. Characteristic meta-substitution bands were observed in the ir region at 11.3 and 12.8 μ . The nmr spectrum (CS₂ solution) possessed signals at δ 1.3 (singlet, CH₂, 12 H) and 7.08 (multiplet ArH, 7.8 H).

Anal. Calcd for $C_{18}H_{20}Cl_2$: C, 70.36; H, 6.56; Cl, 23.08. Found: C, 70.40; H, 6.50; Cl, 23.11.

1,1'-Di-p-tolyldicyclohexyl.—A solution of 0.1343 g of 1,1'-dip-tolylazocyclohexane in 13 ml of toluene was heated under nitrogen at 60° for 24 hr. The solid remaining after the solution was evaporated to dryness weighed 0.1188 g (95% yield). Purification was accomplished by dissolving the solid in a minimum amount of carbon disulfide, adding 3 ml of pentane, cooling in Dry Ice, and isolating the crystallized solid. After repeated recrystallization in this manner, followed by drying at 100° (6 mm), the material melted at 207-208°, apparently with decomposition. In the nmr spectrum (CS₂ solution) signals were present at δ 0.95-2.4 (multiplet, CH₂, 2.28 (singlet, CH₃), and 6.8 (doublet, ArH). The ratio of ArH to RH was 4:13.2 (theory, 4:13). In the ir spectrum, absorption occurred at 12.3 μ (para substitution) and 12.1, 12.7, and 13.45 μ (assigned to the 1,1-disubstituted cyclohexane ring). A similar three-band pattern (11.9, 12.25, and 12.6 μ) is exhibited by bicyclohexyl-1,1'-diol.²⁶ In the mass spectrum, no peak appeared in the molecular ion region (m/e 346), but a strong one was present at m/e 173, conceivably due to thermal dissociation.

Anal. Calcd for C28H34: C, 90.11; H, 9.89, mol wt, 346.
 Found: C, 90.28; H, 9.82; mol wt, 330.
 p-Cyclohexyltoluene and Di-t-butyl Peroxide.—A mixture of

p-Cyclohexyltoluene and Di-t-butyl Peroxide.—A mixture of p-cyclohexyltoluene (6.44 g) and di-t-butyl peroxide (2.68 g) was heated at $125-149^{\circ}$ for 26 hr. After an additional 1.4 g of di-tbutyl peroxide was added, the mixture was heated at $120-140^{\circ}$ for 24 hr longer. Dilution of the cooled mixture with acetone (50 ml) precipitated a yellow solid. Purification was effected several times by dissolving the filtered solid in benzene and reprecipitating with acetone. The material was dried at 100° (6 mm); it softened at 180° , turned to a clear orange gel at $200-220^{\circ}$, then melted at $220-290^{\circ}$. The product showed a broad

(25) The Sadtler Standard Spectra, No. 25042.

band at 12.25 μ (para substitution) in the ir spectrum, with no other absorption in the 12-13.5- μ region. The nmr spectrum gave a broad complex signal from δ 0.8 to 3.5 (RH) and 6.5-7.5 (ArH), with a ArH/RH ratio of 4:12.7 (theory, 4:13).

Anal. Found: C, 88.66; H, 8.94; mol wt, 4400.

m-Chlorocumene.—m-Cumidine hydrochloride was prepared by passing hydrogen chloride through a solution of m-cumidine⁴⁶ (6 g) in ether (200 ml). Isoamyl nitrite²⁷ (6.3 g) was added dropwise as rapidly as possible to a suspension of the salt in 200 ml of refluxing carbon tetrachloride. After being washed with water, dilute sodium hydroxide, and water, the mixture was distilled: 2.2 g, bp 70-72 (7.2 mm), n^{20} D 1.5015 [lit.²⁸ bp 66-68° (8 mm), n^{20} D 1.5136.

p-Chloro- α -methylstyrene.—The synthesis from p-chloro-acetophenone was accomplished by adaptation of the method of Benkeser and coworkers.²⁹ Dehydration of the p-chlorocumyl alcohol was carried out with iodine.³⁰

p-Fluoro- α -methylstyrene.—p-Fluoroacetophenone, bp 81-83° (6.5-7.2 mm), lit.³¹ bp 79° (10 mm), was produced by Friedel-Crafts acylation³¹ of fluorobenzene. Treatment of the ketone with 1 equiv of methyl Grignard reagent afforded crude *p*-fluorocumyl alcohol.³² Dehydration by heating with iodine³⁰ furnished *p*-fluoro- α -methylstyrene, bp 50-51° (6.6-7 mm) [lit.³² bp 93-94° (80 mm)].

p-Chlorocumene.—The preparation from p-chloroacetophenone has been described.⁵

Acknowledgment.—We are grateful to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of a portion of this work, and to Mr. C. K. Liang for helpful discussions.

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Linear Free-Energy Relations (LFER) for Amphoteric 5- (or 6-) Substituted Benzimidazoles

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Received April 28, 1969

Aqueous thermodynamic pK_a values at 25° have been obtained spectrophotometrically for a series (Br, CH₃, CF₃, Cl, F, H, NH₂, and NO₂) of 5- (or 6-) substituted benzimidazoles. ΔpK_a (acidity) values are excellently correlated with corresponding ΔpK^+ (basicity) values with $\Delta pK^+ = (1.16 \pm 0.05)\Delta pK_a - 0.02 (\pm 0.04)$ with standard error in ΔpK^+ of 0.09 and correlation coefficient 0.995. ΔpK^+ and ΔpK_a give good correlations with Taft's σ_I and σ_R^0 and Lupton and Swain's \mathfrak{F} and \mathfrak{R} . The relative importance of resonance and nonresonance effects is near the same for ΔpK^+ and ΔpK_a . The composite substituent constant ($\sigma_I + 0.8 \sigma_R^0$) or ($\mathfrak{F} + \mathfrak{R}$) lies midway between σ_m and σ_p^0 in the importance of resonance. Both the ΔpK_a and ΔpK^+ series show a sensitivity to the polar (*i.e.*, nonresonance) effects of substituents that is characteristic of benzene derivatives undergoing a change in formal charge of one on the first atom of a side-chain reaction site. Hammett indicator plots of log [(anion)/(molecule)] vs. log C_{0H} give slopes of unity for the title compounds.

In an earlier paper² aqueous thermodynamic cation acidity constants (pK^+) as a measure of the basicity of some 5- (or 6-) substituted benzimidazoles were reported. Since there is a paucity of data in the literature³ in which a series of ampholytes have had both teeir acid and base strengths measured by precise methods and under the same conditions and have had substituent effects on both acidity and basicity correlated, we felt it would be of interest to determine the aqueous thermodynamic molecule acidity constants (pK_a) of the title compounds.

We also wished to establish whether molecule acidity constant changes would lend themselves to quantitative

⁽¹⁾ Work performed as National Science Foundation Undergraduate Research Participant and in partial fulfillment of the requirements for the B.S. degree in chemistry.

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