Substituent Effects in Radical Reactions. III.[1] Thermolysis of Substituted Phenylazomethanes, 3,5-Diphenyl-1-pyrazolines, and Azopropanes

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Abstract: Activation parameters have been determined for the thermolysis of substituted phenylazomethanes (**7a–e**), 3,5-diphenyl-1-pyrazolines (**8a–d**), and azopropanes (**10b,f,g,k–m,o**). The order of substituent effects in the three series is the same and similar tc those previously reported for azocumenes (**22**) and diphenylazoethanes (**23**). The rate differences of 10^9 for the azopropar.e model are evaluated in terms of steric and electronic interactions and are related to the question of polarized vs. nonpolarized transition states in other radical systems.

The concept of polarized transition states in radical reactions has been known for years.[2] Support for this mechanism can be found in hydrogen abstraction reactions where Hammett linear free energy correlations using σ^+ parameters give negative ρ values. Table I lists in order of increasing ρ a number of radicals used in substituted toluene studies.

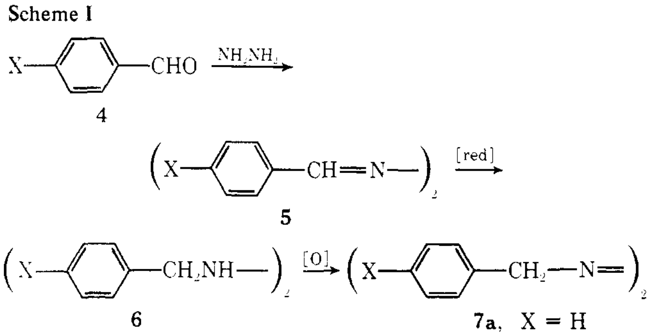
Recently, arguments against the "polar effect" have been advanced.[13] A linear correlation between ρ and ΔH for the hydrogen abstraction of substituted toluenes and the lack of correlation between the magnitude of ρ and the electron affinity of abstracting radical were offered in support of a "nonpolar mechanism". Zavitsas and coworkers[13] believe that ". . . . ρ reflects differences in the bond dissociation energies of substituted toluenes and that its magnitude is a measure of the sensitivity of the abstracting radical to these differences". However, it has been argued that the ρ vs. ΔH relationship with only five radicals is fortuitous[9] as both t-BuOO· (ρ = −0.56)[9] and t-Bu· (ρ = +0.99)[12] have much larger ρ values than the Zavitsas correlation would predict.

This study was initiated to find a better model for evaluation of radical substituent effects, and the data reported herein support the "polar" mechanism for radical abstractions from substituted toluenes but not in azoalkane decompositions.

Results and Discussion

Synthesis. (1) 1,1′-Diarylazomethanes. Compounds 1,1′-diphenylazomethane (**7a**), 1,1′-bis(p-tolyl)azomethane (**7b**), 1,1′-bis(p-anisyl)azomethane (**7c**), 1,1′-bis(p-chlorophenyl)azomethane (**7d**) and 1,1′-bis(p-biphenyl)azomethane (**7e**) were all prepared according to Scheme I.[14]

Scheme I

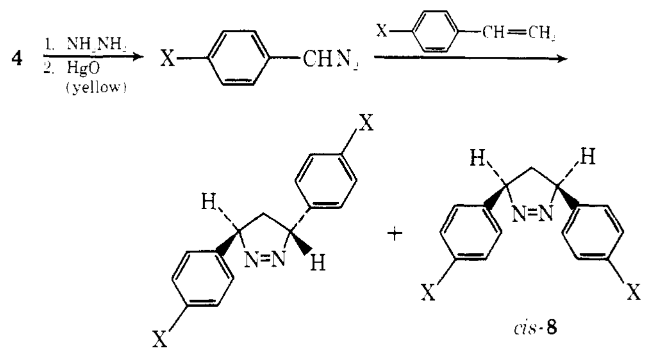


7a, X = H
b, X = CH_3
c, X = OCH_3
d, X = Cl
e, X = C_6H_5

Para-substituted benzalazines (**5a–c**) were hydrogenated using 10% Pd/C to give the corresponding hydrazines (**6**). The p-chloro and p-phenyl derivatives (**5d,e**) could not be reduced in this fashion, perhaps because of solubility factors, and required sodium amalgam in ethanol. Oxidation to the arylazomethanes was effected using commercial yellow mercuric oxide.[14] The yields based on benzaldehydes were approximately 40%.

2. 3,5-Diaryl-1-pyrazolines. *trans*-3,5-Diphenyl-1-pyrazoline (**8a**), *trans*-3,5-bis(p-tolyl)-1-pyrazoline (**8b**), *trans*-3,5-bis(p-anisyl)-1-pyrazoline (**8c**), and *trans*-3,5-bis(p-chlorophenyl)-1-pyrazoline (**8d**) were all prepared according to the method of Overberger and workers (Scheme II), and all except **8b** are known compounds.[15]

Scheme II



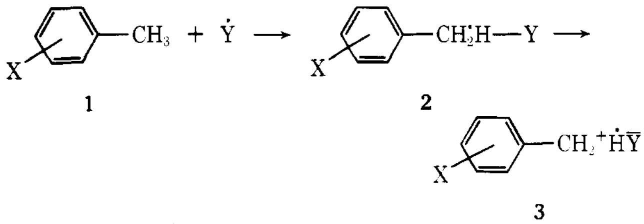
trans-8 *cis*-8

a, X = H
b, X = CH_3
c, X = OCH_3
d, X = Cl

The addition of substituted styrenes to phenyldiazomethane and p-chlorophenyldiazomethane gave only *trans*-1-pyrazolines **8a** and **8d.** Mixtures of *cis*- and *trans*-**8b** and **8c** were obtained from substituted styrenes and p-tolyldiazomethane and p-anisyldiazomethane. The pure trans isomers **8b** and **8c** were isolated from partially decomposed solutions of mixtures of cis and trans by virtue of the much more rapid decomposition of *cis*-**8b** and **8c** (see Experimental Section).[16]

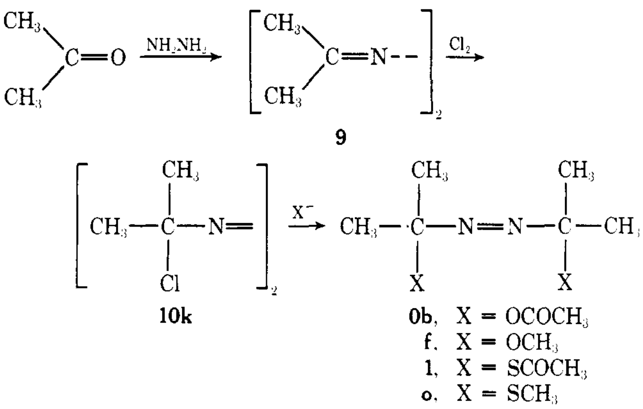
3. 2,2′-Disubstituted Azopropanes. The chloro (**10k**),[17] methoxy (**10f**),[1a] and thiomethyl **10o**[1b,17b] acetate (**10b**), and thioacetate (**10l**) derivatives were all prepared according to Scheme III. An interesting aspect of this synthetic procedure is the ability of a tertiary halide to undergo substitution rather than elimination. A number of other substitutions on this system are known,[17,18] although in some

Table I. ρ Values for Hydrogen Abstraction of Substituted Toluenes



Abstracting radical, Y	ρ value	Ref
Br·	−1.78	3
$Cl_3C\cdot$	−1.46	4
	−1.36	5
t-BuO·	−0.83 to −0.65	6a–c
Cl·	−0.66	7
$HO_2CCH_2\cdot$	−0.63	8
t-BuOO·	−0.56	9
$CH_3\cdot$	−0.1	10
$C_6H_5\cdot$	−0.3, −0.1	11a,b
t-Bu·	+0.99	12

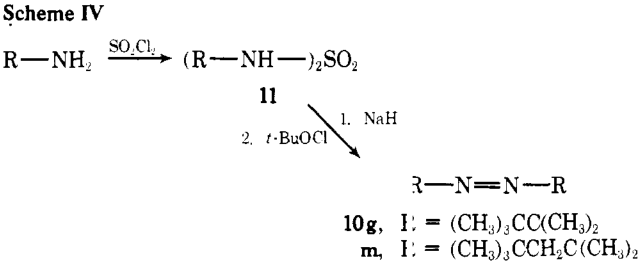
Scheme III



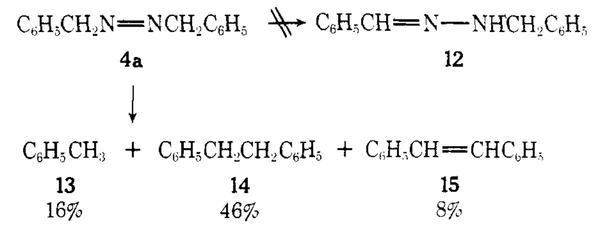
cases nucleophiles convert **10k** back to acetone azine (**9**).[17,18]

The two tertiary alkyl azoalkanes were prepared by modification of a procedure introduced by Ohme, Schmitz, and Preuschhof[19] (Scheme IV) and are described elsewhere.[20]

Scheme IV



Decomposition Products. The organic products formed from the thermal decomposition of 1,1′-diphenylazomethane in diphenyl ether at 170° were determined by GLC using an internal standard. The primary products were bibenzyl (45.6%), toluene (15.7%), and stilbene (8.1%). These same products were observed by Bickel and Waters[21] in decalin in 39, 12.5, and 10.5%, respectively. None of these products is the result of prior or concomitant isomerization of diphenylazomethane to the corresponding hydrazone (**12**).[22] We have determined that the hydrazone is stable to temperatures up to 180°, and a volumetric determination of nitrogen for diphenylazomethane shows it to be quantitative. The actual mechanism of stilbene formation has not been determined, but the yield is reduced to less than 2% when diphenylazomethane is decomposed in cumene. The rate of decomposition with cumene added is essentially the same.

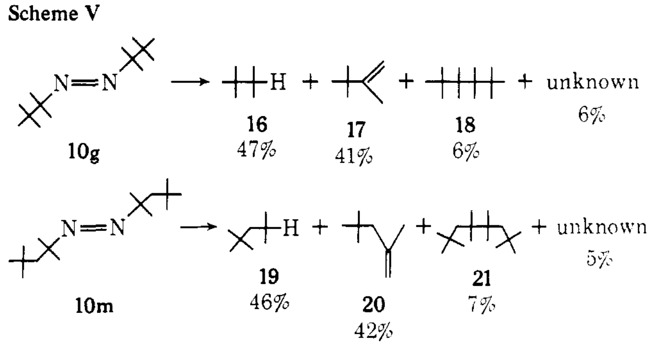


The products of decomposition of *p*-substituted 3,5-diphenyl-1-pyrazolines in benzene are mixtures of *cis*- and *trans*-1,2-diarylcyclopropanes.[15] The ratio of trans to cis cyclopropene products is temperature dependent and varies from 15.7 at 50° (94% trans, 6% cis) to 10.4 at 80° (91.2% trans, 8.8% cis) for the decomposition of 3,5-diphenyl-1-pyrazoline in benzene. The trans to cis cyclopropane ratios for *trans*-3,5-bis(*p*-tolyl)-1-pyrazoline and *trans*-3,5-bis(*p*-anisyl)-1-pyrazoline at 80° are 13.3 (93% trans, 7% cis) and 21.2 (95% trans, 4.5 cis). While these ratios are probably no more accurate than ±1%, the trend is for the more stable diradical (p-OCH_3 > p-CH_3 > p-H) to reflect more of its original stereochemistry in the products. This will be discussed in greater detail later.

cis-3,5-Bis(*p*-anisyl)-1-pyrazoline gave a trans to cis cyclopropane ratio of 0.78.

Products were determined for only four of the seven 2,2′-disubstituted azopropanes. The products for the methoxyazopropane (**10f**)[1a] and thiomethyl (**10o**)[1b] have been reported previously and will not be discussed further here. The *tert*-heptyl- (**10g**) and *t*-octyl- (**10m**) azopropanes were analyzed by GLC collection and compared with known compounds. The spectral relative yields of hydrocarbon products are shown in Scheme V, and the absolute yields of identified products were roughly 90% of the theoretical amounts. The fate of the tertiary radicals is as expected. The ratio of $k_{disproportionation}$ to $k_{coupling}$ for the *tert*-butyl radical, determined for 2,2′-azoisobutane, is 4.5.[23] The values of 6.5 to 7.5 for the sterically more bulky tertiary radicals from **10g** and **10m** reflect the slightly greater ease of disproportionation over coupling.

Scheme V

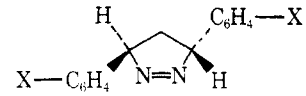


Discussion

Rate constants and activation parameters for para-substituted *trans*-3,5′-diphenyl-1-pyrazolines (**8a–d**) are recorded in Table II, para-substituted diphenylazomethanes (**7a–e**) in Table III, and 2,2′-disubstituted 2,2′-azopropanes (**10,b,f,g,k,l,m,o**) in Table IV.

Many radical systems have been evaluated in terms of substituent effects. For the most part, they show pronounced polar effects (vide ante) which may be completely overshadowing any radical character (i.e., 3 is more significant than **2**). Supportive evidence can be seen in Table V.

Table II. Rate Data for Para-Substituted *trans*-3,5-Diphenyl-1-pyrazolines in Toluene



Temp, °C	8a X = H $k \times 10^4$, sec^{-1}	8b X = CH_3 $k \times 10^4$, sec^{-1}	8c X = OCH_3 $k \times 10^4$, sec^{-1}	8d X = Cl $k \times 10^4$, sec^{-1}
55.0				0.92 ± 0.03[a]
60.0	0.777 ± 0.04[a]	1.09 ± 0.01[a]	1.08 ± 0.01[a]	
65.0	1.42 ± 0.01[b]	2.03 ± 0.01[a]		2.79 ± 0.02[a]
70.0	2.73 ± 0.1[b]	3.43 ± 0.01[a]	3.97 ± 0.01[a]	5.43 ± 0.01[a]
75.0	4.23 ± 0.01[a]	6.13 ± 0.1[b]		8.76 ± 0.02[a]
80.0	7.71 ± 0.2[b]	10.1 ± 0.2[b]	10.9 ± 0.01[a]	14.1 ± 0.1[b]
83.5	12.7 ± 0.1[a]			
85.0	15.2 ± 0.4	15.5 ± 0.5[b]	18.1 ± 1.0[b]	24.0 ± 0.2[a]
90.0	23.6 ± 0.5	27.2 ± 0.5[b]	24.5 ± 0.1[a]	
ΔH^*, kcal/mol	27.0 ± 0.4	24.7 ± 0.4	25.4 ± 0.5	24.6 ± 0.4
ΔS^*, eu	3.4 ± 1.3	−2.8 ± 1.0	0.0 ± 1.6	−2.1 ± 1.1

[a] Standard deviation of one run. [b] Average value and error of two or more runs.

Table III. Rate Data for Para-Substituted Diphenylazomethanes in Diphenyl Ether

$X—C_6H_4CH_2N{=}NCH_2C_6H_4—X$

Temp, °C	7a X = H $k \times 10^4$, sec^{-1}	7b X = CH_3 $k \times 10^4$, sec^{-1}	7c X = CH_3O $k \times 10^4$, sec^{-1}	7d X = Cl[c] $k \times 10^4$, sec^{-1}	7e X = C_6H_5 $k \times 10^4$, sec^{-1}
135.0					1.23 ± 0.05[a]
145.0	1.72 ± 0.1[b]	2.00 ± 0.01[a]	2.23 ± 0.03[a]	2.30 ± 0.02[a]	3.58 ± 0.02[a]
150.0	3.00 ± 0.05[a]	3.16 ± 0.01[b]	3.86 ± 0.07[a]	3.88 ± 0.02[a]	5.49 ± 0.02[a]
155.0	4.93 ± 0.1[b]	4.69 ± 0.1[b]	5.67 ± 0.07[a]	7.60 ± 0.03[a]	7.76 ± 0.02[a]
160.0	6.38 ± 0.1[b]	6.46 ± 0.04[a]	9.86 ± 0.01[a]	12.1 ± 0.1[a]	12.8 ± 0.3[a]
165.0	11.2 ± 0.04[a]	12.2 ± 0.2[b]	16.1 ± 0.7[b]	14.9 ± 0.4[a]	20.9 ± 0.6[a]
170.0	19.4 ± 0.05[a]	19.1 ± 0.1[b]	23.4 ± 0.5[a]	28.2 ± 0.1[a]	
175.0	28.4 ± 0.1[a]	34.5 ± 0.6[b]	37.9 ± 0.3[a]	44.0 ± 0.1[a]	
ΔH^*, kcal/mol	34.3 ± 1.1	34.7 ± 0.8	34.6 ± 0.6	35.0 ± 1.5	32.0 ± 0.8
ΔS^*, eu	5.6 ± 2.5	6.5 ± 1.9	6.7 ± 1.5	8.0 ± 3.0	1.4 ± 2.0

[a] Standard deviation of one run. [b] Value and error of two or more runs. [c] All temperatures of Cl derivative are 0.56° higher than reported.

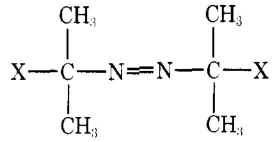
In radical abstraction reactions of para-substituted benzylic hydrogens, $k_{OCH_3}/k_H > 1$ and $k_{Cl}/k_H < 1$, thereby making $k_{OCH_3}/k_{Cl} > 1$. This is as expected for reactions with positive character being built up in the transition state. A methoxy substituent is a better cation stabilizer than is a chloro substituent ($\sigma^+_{p\text{-}CH_3O} = -0.78$, $\sigma^+_{p\text{-}Cl} = +0.11$). For the three series **7**, **8**, and **10**, $k_{OCH_3}/k_{Cl} < 1$. This clearly points to a different stabilization mechanism.

Substituted azocumenes (**22**)[24,25] and phenylazoethanes (**23**)[26] (cf. Table V) show very little sensitivity toward substituent change. Initially we believed that these small rate differences observed by Kovacic and Shelton et al.[24-26] might simply be due to the inherent stability of the radicals studied. The tertiary and secondary radicals might require little interaction with substituent. Apparently this is not the case since the phenylazomethanes show less sensitivity to substituent change than do either azocumenes or diphenylazoethanes.[27] Since the order of substituent effects is the same in all three series (H < CH_3 < CH_3O < Cl), it is unlikely that the trend of decreased sensitivity in going from **22** to **23** to **7** is not real. This is contrary to what is expected for several reasons. First, the ρ value for hydrogen abstraction by Br· from substituted azocumenes, ethylbenzenes, and toluenes decreases from −0.38 to −0.53 to −1.46.[28] This shows a greater substituent interaction or more "intermediate character" (carbenium ion or radical), in the transition state for production of a primary radical over a secondary or tertiary. Secondly, the ΔG^*_{100} (kcal/mol) increases from 25.0(**22**)[23-25] to 29.5 (**23**)[23] to 32.1 (**7**) which, according to the Hammond postulate,[29] means more bond breakage in transition state for thermolysis of phenylazomethanes. Intuitively one would therefore expect larger not smaller substituent interactions. Shelton and Liang[26] believe 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." We fail to see how this explanation applies but cautiously add no alternative rationalizations at this time. However, we don't believe the results are artifacts since parts of these three systems were determined independently by two groups using different methods of analysis.[1a,24-26]

A detailed analysis of substituent effects in quantitative terms based on results from azocumenes (**22**),[24,25] phenylazoethanes (**23**),[26,31] and phenylazomethanes (**7**) is probably not warranted. First, substituent rate differences are too small to accurately determine any sort of radical substituent parameter ($\sigma\cdot$).[30,31] Secondly, determining the amount of inductive (σ_I) or resonance contribution (σ_R) would imply some knowledge of the type of transition state involved.[24] For example, is it electron deficient (carbenium ion like) or electron sufficient (carbanion like)? Since a radical is, in theory, intermediate in oxidation state between R^+ and R^-, very subtle changes in method of generation could swing the transition state toward one or the other. For this reason, one should be cautious in anticipating the effect of an inductively electron-withdrawing substituent based on a limited series.[24,25] While multiparameter equations could no doubt be used,[32a,b] we reject the idea that any simple parameter (σ, σ^+, σ^-, σ_I, σ_R, etc.) fits the phenylazomethanes (**7**) and, by implication, azocumenes (**22**)[24,25] and phenylazoethanes (**23**).[26,33]

To alleviate this problem, we selected 2,2′-disubstituted azopropanes as a model system. This system is related to

Table IV. Rate Data for Disubstituted Azopropanes in Diphenyl Ether



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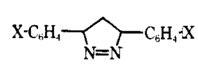
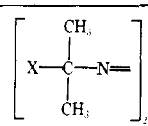
10g X = $(CH_3)_3C$– Temp, °C	$k \times 10^4$, sec^{-1}	10m X = $(CH_3)_3CCH_2$– Temp, °C	$k \times 10^4$, sec^{-1}	10b X = $CH_3C(=O)$–O– Temp, °C	$k \times 10^4$, sec^{-1}
170.0	2.37 ± 0.07[b]	130.2	1.82 ±0.04[b]	190.0	0.823 ± 0
175.0	3.86 ± 0.3[b]	135.0	2.95 ± 0.08[b]	200.1	2.61 ± 0.01[a]
180.0	5.29 ± 0.1[b]	140.0	4.51 ± 0.08[b]	205.1	4.10 ± 0.01[a]
185.0	8.01 ± 0.3[b]	145.0	7.97 ± 0.1[b]	210.3	6.38 ± 0.01[a]
190.0	10.0 ± 0.3[b]	150.0	12.8 ± 0.4[b]	215.4	8.97 ± 0.1[b]
195.0	21.7 ± 0.9[b]	155.0	20.6 ± 0.8[b]	220.5	14.7± 0.01[a]
200.0	36.8 ± 1.0[b]	160.0	28.1 ± 0.5[b]	223.1	18.7 ± 0.01[a]
ΔH^*, kcal/mol	37.4 ± 0.9		31.7 ± 0.6		40.9 ± 1.2
ΔS^*, eu	8.4 ± 1.9		2.4 ± 1.4		10.3 ± 2.5

10l X = CH_3COS Temp, °C	$k \times 10^4$, sec^{-1}	10f X = CH_3O Temp, °C	$k \times 10^4$, sec^{-1}	10k X = Cl Temp, °C	$k \times 10^4$, sec^{-1}		10o X = CH_3S Temp, °C	$k \times 10^4$, sec^{-1}	
130.0	1.33 ± 0.06[a]	150.1	0.402 ± 0.004[a]	158.5	1.03		125.0	3.40	
135.0	2.29 ± 0.05[a]	155.0	0.770 ± 0.006[a]	166.5	2.86		130.0	6.80	
140.0	4.40 ± 0.03[a]	159.9	1.50 ± 0.01[a]	167.9	4.54		135.0	7.10	12.5[c]
145.0	6.83 ± 0.02[a]	169.7	3.76 ± 0.01[a]	175.0		4.95[c]	140.0	10.0	13.9[c]
149.4	11.9 ± 0.2[a]	174.6	6.67 ± 0.01[a]	178.5	8.08		145.0	11.5	20.5[c]
155.0	18.3 ± 0.7[a]	179.5	10.6 ± 0.4[b]	180.0		7.20[c]	150.0	16.9	26.6[c]
159.4	30.1 ± 0.5[a]	184.3	18.0 ± 0.5[b]	184.8	12.5		155.0	28.3	40.8[c]
				185.0		9.20[c]	160.0	38.0	60.0[c]
				191.0	19.7		165.0	51.7	69.1[c]
				195.0		14.2[c]	ΔH^*, kcal/mol	20.2 ± 1.2	21.4 ± 1.4
				200.0		20.9[c]	ΔS^*, eu	−24.0 ± 3.0	−20.0 ± 3.0
ΔH^*, kcal/mol	36.1 ± 0.6		41.0 ± 0.8		33.0 ± 3.2	21.9 ± 1.3			
ΔS^*, eu	12.7 ± 1.5		17.6 ± 1.8		−0.5 ± 4	−25.0 ± 3			

[a] Standard deviation of one run. [b] Average value and error of two or more runs. [c] Values obtained with a layer of Nujol covering the mercury to assure that no mercury vapors are affecting the rate. The large deviations in precision between the two methods and in values determined twice at the same temperature leave us very skeptical of the accuracy of values for **10k** and **10o**.

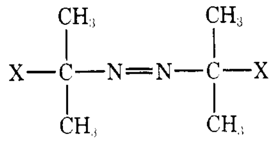
Table V. Relative Rates of Substituted Arylazoalkanes, Pyrazolines, and Azoalkanes

X	$[X\text{-}C_6H_4C(CH_3)_2N{=}]_2$ **22** Relative rate, 40° [25,26]	$[X\text{-}C_6H_4CHCH_3N{=}]_2$ **23** Relative rate, 95° [26,33]	$[X\text{-}C_6H_4CH_2N{=}]_2$ **7** Relative rate, 150°	 **8** Relative rate, 80° [16]	 **10** Relative rate, 100°
H	1.0	1.0 (1.0)	1.0	1.0	1.0
CH_3	1.46	1.12 (1.16)	1.07	1.38	5.6×10^2
CH_3O	2.06[1a]	1.30 (1.39)	1.30	1.48	5.8×10^3
Cl	2.67	1.75	1.50	1.92	7.2×10^4
C_6H_5			2.04		2.3×10^9

the azocumenes except that the removal of the phenyl group allows maximum interaction of the substituent with the incipient radical center. However, in addition to increased resonance and inductive interactions, steric effects might be increased.

Table VI is a composite of all such compounds that have been studied. The relative rates span a range of $>10^9$ ($\Delta\Delta G^* = 16$ kcal/mol) which supports the contention that azoalkanes in general are excellent radical precursors[43] and in particular that azopropanes are much more sensitive models than azocumenes (**22**), diphenylazoethanes (**23**), or diphenylazomethanes (**7**). We believe these rate differences, for the most part, reflect electronic (resonance and inductive) contributions to radical stability with qualitatively predictable amounts of steric contributions. A plot of the log of the rate constants for azopropanes **10a**, **10c**, **10f**, **10k**, and **10s** vs. the corresponding disubstituted diphenylazomethanes is roughly linear. This indicates a similarity in mechanism of stabilization or a fortuitous correlation of electronic and steric contributions in **10** with electronic effects in phenylazomethanes. Furthermore, with the exception of **10m** (discussed below) all groups in Table VI are sterically less demanding than **10g**. The rate difference between **10g** and **10c** is only a factor of 12. Since the stabilities of the two tertiary radicals should be similar, ignoring small hyperconjugative differences, the $\Delta\Delta G^* = 1.9$ kcal/mol is probably mostly a difference in ground state energies. This difference of 1.9 is small compared with the total

Table VI. Composite of Rate Data for 2,2′-Disubstituted 2,2′-Azopropanes



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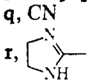
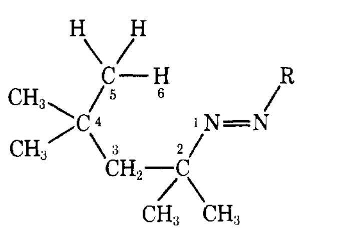
X	Relative rate, 100°	ΔG^* (100°), kcal/mol	ΔS^*, eu	Ref
a, H	1.0	40.8	17.0	34
b, CH_3CO_2	3.9×10^2	37.0	10.3	This work
c, CH_3	5.6×10^2	36.2	16.1	35, see also ref 34 and 36
d, CH_3COOCH_2	6.7×10^2	36.1	15.0	37
e, $CH_3CH_2CH_2$	1.4×10^3	34.5	14.4	36
f, CH_3O	5.8×10^3	34.4	17.6	This work
g, $(CH_3)_3C$	7.0×10^3	34.3	8.3	This work
h, $C_6H_5CH_2$	8.9×10^3	34.1	4.1	38
i, C_6H_5O	2.8×10^4	33.2	−2.5	38
j, c-C_3H_5	3.0×10^4	33.2	12.3	35
k, Cl	$\sim 7 \times 10^4$	~32.5	~8.5	This work
l, CH_3COS	3.6×10^5	31.4	12.7	This work
m, $(CH_3)_3CCH_2$	7.2×10^5	30.8	4.0	This work
n, C_6H_5S	3.7×10^6	29.6	−12.6	38
o, CH_3S	$\sim 1 \times 10^7$	~29	~ −20	This work
p, $CO_2C_2H_5$	1.4×10^8	26.9	4.8	39
q, CN	1.7×10^8	26.8	10.4	40
r, 	3.0×10^8	26.4	7.0	41
s, C_6H_5	2.3×10^9	24.9	11.2	23, see also ref 26
t, $H_2C{=}CH$	5.0×10^9	24.3	5.0	42
u, $HC{\equiv}C$	5.1×10^9	24.2	7.0	42

$\Delta\Delta G^*$ of 16 kcal/mol for **10a** to **10u**. Furthermore, it is unlikely that substituents like CH≡C- (**10u**) and CN (**10q**) would have nearly the steric effect of a *tert*-butyl group (**10g**).

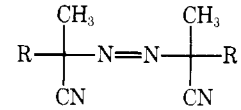
The relative rate of 1300 for **10m**/**10c** (*tert*-octyl/*tert*-butyl) is striking and larger than might have been expected based on the classic work of Overberger et al.[44] From the data in Table VII, it can be seen that simple bulk on the α carbon is not sufficient to cause substantial rate acceleration. For example, the bulkier **24b** is slower than **24a.** It apparently depends on the branching at the γ carbon, although not in a linear fashion. Compound **24d** with two methyl groups in the γ position is 6 times faster than **24a,** and **24e** with three methyl groups is 90 times faster than **24a.** The actual size of the group at the γ-C is only moderately important as **24e** $\simeq$ **24f.**[45] In a qualitative sense, however, the more "Newman rule of six" interactions (**25**), the faster the rate.[46]



25

The substituents that show the greatest rate enhancement in the azopropane series (Table VI) are those which have available π systems for delocalization of the odd electron. The general trend is to observe faster rates with good carbanion stabilizing groups than with good carbocation groups (**10p–u**). This is not to say that the relationship is quantitative, but it does indicate that transition states for

Table VII



24

R	k_{rel} (80°)
a, methyl	1.0
b, isopropyl	0.8
c, *n*-pentyl	1.0
d, isobutyl	6
e, neopentyl	~92
f, Ph-$C(CH_3)_2CH_2$−	~93

decomposition of azoalkanes are completely unlike those obtained from hydrogen abstraction of toluene. The latter seem to be highly dependent on the nature of abstracting radical and reflect electron-deficient transition states. They are therefore probably not indicating true radical stabilities. Within limits, we believe the azoalkanes are better models for evaluation of radical substituent effects.

One object of this work was to compare heteroatom stabilization of radicals. The effects of oxygen and sulfur participation have been discussed in two earlier communications.[1a,b] The relative rate difference between **10f** and **10c,** a factor of ~10, is small compared with the overall effect of $\sim 10^8$ between **10u** and **10c.** The stability usually attributed to ether radicals, based on the preference for α-hydrogen abstraction, is probably more a function of the *abstracting* radical species than of actual stability of the product ether radical. It would be interesting, for example, to test the competition of the α and β hydrogens of ethyl ether with a less electronegative radical like methyl or *tert*-butyl.

The relative rate difference between **10b** and **10l,** a factor of $\sim 10^3$, makes a convenient comparison of oxygen with sulfur, the latter having d orbitals.

Two compounds in Table IV, **10k** and **10o,** deserve special attention. For **10k,** completely different activation parameters were obtained in presence of mercury vapor and in the absence of it. This is quite probably due to its penchant for elimination of HCl. The same is true for **10o,** although for different reasons, perhaps catalysis by mercury vapor (footnote *c,* Table IV). We therefore attach very little reliability to the values reported.

With the exception of the methyl substituent, the para-disubstituted 3,5-diphenyl-1-pyrazoline (**8a–d**) series has been discussed previously.[16,47] The order of substituent interaction is the same as in azocumenes (**22**), phenylazoethanes (**23**), and phenylazomethanes (**7**). The sensitivity appears to lie between that of **7** and **22,** although it would be hard to predict, a priori, what one might expect. Diphenyl-1-pyrazolines (**8**) give a sort of quasi-secondary radical similar to **23,** but the geometry of the decomposing azo linkage is cis compared with the expected trans geometry in **7, 22,** and **23.**

One interesting aspect of the 1-pyrazoline series is the highly stereoselective nature of the thermal products. The *trans*-3,5-diphenyl-1-pyrazolines give >90% *trans*-1,2-diphenylcyclopropanes. This retention of configuration is completely contrary to what has been observed in a number of other "pyrazoline" systems. For example, Crawford and coworkers have observed a reversal of stereochemistry for thermolysis of *cis*- and *trans*-3,5-dimethyl-1-pyrazoline. *cis*-3,5-Dimethyl-1-pyrazoline gives 33.2% *cis*- and 66.1% *trans*-1,2-dimethylcyclopropanes. *trans*-3,5-Dimethyl-1-pyrazoline gives 72.6% *cis*- and 25.4% *trans*-1,2-dimethylcyclopropanes. These results and a number of other experimental and theoretical studies[48-53] seem to implicate a π-cyclopropane intermediate. It is our feeling that the 1,3-

diphenyl diradicals derived from the diphenylpyrazolines are not of this type. The products are best accounted for in terms of pure (or nearly so) diradical intermediates. The additional stabilization derived from 1-3 orbital interaction may not be required for these sufficiently stable benzylic diradicals. However, the product-forming step is apparently highly sensitive to steric control. For example, *cis*-3,5-bis(*p*-anisyl)-1-pyrazoline gives 44% *cis*- and 56% *trans*-1,2-dianisylcyclopropane. The activation energy for decomposition of *cis*-3,5-dianisyl-1-pyrazoline[54] is at least 6 kcal/mol less than that of the trans isomer which is consistent with this supposition.

Experimental Section

Kinetics. The rates of decomposition of 3,5-diaryl-1-pyrazolines (in toluene, Table II), phenylazomethanes (in diphenyl ether, Table III), and 2,2′-azopropanes (in diphenyl ether, Table IV) were followed on a constant volume, variable pressure kinetics apparatus which records pressure automatically and continuously. Its construction and operation are described elsewhere.[55] The reactions were, with two exceptions (**10k** and **10o**), well behaved first-order decompositions, and data points were collected for at least 2.5 half-lives for calculation of rate constants. Activation parameters were determined in the standard fashion,[56] and values and errors are reported in Tables II, III, and IV. Normally, runs were made on solutions of ~0.01 *M* (20–30 mg of azo to 10 ml of solvent).

Synthesis of Azines 5a–e. The azines **5a–e** were prepared according to the literature from anhydrous hydrazine and the corresponding benzaldehydes. All were recrystallized from ethanol and had the following properties: **5a**, X = H, in 80% yield, mp 93° (lit.[57] mp 93°); **5b**, X = CH_3, in 78% yield, mp 153° (lit.[58] mp 154–155°); **5c**, X = OCH_3, in 70% yield, mp 171° (lit.[59] mp 168°); **5d**, X = Cl, in 73% yield, mp 212–213° (lit.[60] mp 208°); and **5e**, X = C_6H_5, in 75% yield, mp 258–260° (lit.[61] mp 230–245°).

Synthesis of *N,N′*-Dibenzylhydrazines. Azines **5a**, **5b**, and **5c** were hydrogenated overnight in a Parr hydrogenator under 50 lb of pressure using ether as a solvent and 10% Pd/C as the catalyst. Azines **6d** and **6c** were reduced with sodium amalgam in refluxing ethanol according to the literature.[62] All hydrazines were used in the subsequent oxidation without further purification.

Synthesis of Para,para-Disubstituted Diphenylazomethanes. All *N,N′*-dibenzylhydrazines were oxidized at room temperature (24 hr) in ether using a 3 *M* excess of *commercial* yellow mercuric oxide (Matheson, Coleman and Bell).[63] All diphenylazomethanes were recrystallized from methanol, and physical data are listed in Table VIII.

Synthesis of 3,5-Diaryl-1-pyrazolines. The *trans*-3,5-diaryl-1-pyrazolines (**8a–d**) were prepared according to the method of Overberger and coworkers, with one modification. *trans*-3,5-Diphenyl-1-pyrazoline (**8a**), mp 107–108° dec (lit.[15a] mp 109–110° dec), and *trans*-3,5-bis(*p*-chlorophenyl)-1-pyrazoline (**8d**), mp 118° dec (lit.[15a] mp 120–121° dec), were obtained in 23 and 24% yields from the corresponding styrenes and phenyldiazomethanes. NMR indicated no cis isomer to be present.[15] The mixtures of *cis*- and *trans*-3,5-bis(*p*-anisyl)-1-pyrazoline (**8c** in 33% yield) and *cis*- and *trans*-3,5-bis(*p*-tolyl)-1-pyrazoline (**8b** in 32% yield) were converted into pure trans isomers by decomposing the less stable cis isomers in refluxing ether (8 hr), washing out the cyclopropanes with cold pentane and recrystallizing the product from ether. *trans*-3,5-Bis(*p*-anisyl)-1-pyrazoline [**8c**, mp 121–122° dec (lit.[15] mp 129° dec)] and *trans*-3,5-bis(*p*-tolyl)-1-pyrazoline (**8b**, mp 105–106° dec) were obtained in approximately 10% yield. It has subsequently been found that preheating the melting point apparatus decreases the amount of decomposition and increases the melting point by 3–4°.

Anal. Calcd for *trans*-3,5-bis(*p*-tolyl)-1-pyrazoline ($C_{17}H_{18}N_2O_2$): C, 72.32; H, 6.43; N, 9.92. Found: C, 72.23; H, 6.65; N, 10.05. NMR: δ 7.05 (m, 10 H), 5.65 (t, J = 8.0 Hz, 2 H), 1.95 (t, J = 8.0 Hz, 2 H), and 2.32 ppm (s, 6 H).

Synthesis of 2,2′-Disubstituted 2,2′-Azopropanes. 2,2′-Dichloro-2,2′-azopropane (**10k**) was prepared according to the method of Benzing[66] in yields ranging from 60 to 80% and was recrystallized at low temperatures from pentane, mp 58–60° (lit.[66] 59°).

Table VIII. Physical Data for Phenylazomethanes 7a–c

Compd	Aromatic protons	Benzlic protons	Remaining protons	% yield, based on azine	Mp, °C
7a	7.16 (s)	4.82 (s)		50	32–34 (lit.[64] 27–29)
7b	7.10 (s)	4.82 (s)	2.30 (s)	53	63–65 Anal. Calcd for $C_{16}H_{18}N_2$: C, 80.63; H, 7.61; N, 11.75. Found: C, 80.25; H, 7.61; N, 11.54
7c	6.97 (q)	4.80 (s)	3.75 (s)	60	92–93 (lit.[65] 92–93)
7d	7.63 (m)	5.11 (s)		45	90–91 (lit.[62] 89–90)
7e	7.75 (m)	5.15 (s)		61	161–162.5 Anal. Calcd for $C_{16}H_{22}N_2$: C, 86.15; H, 6.11; N, 7.72. Found: C, 85.91; H, 6.13; N, 7.80

2,2′-Diacetoxy-2,2′-azopropane (**10b**) was prepared from 2,2′-dichloro-2,2′-azopropane (**10k**) according to the literature in 52% yield, mp 102–104° (lit.[66] mp 103°).

2,2′-Diacetylthio-2,2′-azopropane (**10l**) was prepared in 27% yield according to the literature, mp 35–36° (lit.[66] 37.5–38°).

2,2′-Dimethylmercapto-2,2′-azopropane (**10o**). 2,2′-dichloro-2,2′-azopropane (55 g, 0.3 mol) was added portionwise to a solution of methanethiol (39 g, 0.8 mol), sodium hydroxide (32 g, 0.8 mol), water (2000 ml), and ethanol (600 ml) over a period of 0.5 hr at 0°. The mixture was stirred for 1 hr at room temperature, poured into 2 l. of ice-water, and extracted with ether. The extracts were dried over magnesium sulfate and concentrated and the product recrystallized from cold hexane to give 21 g (33%) of 2,2′-dimethylmercapto-2,2′-azopropane: mp 39–39.5°; NMR (CCl_4) δ 1.50 (s, 12 H) and 1.92 ppm (s, 6 H); λ_{max} 367 nm (ϵ 118), 268 (1560).

Anal. Calcd for $C_8H_{18}S_2N_2$: C, 46.60; H, 8.74; N, 13.59. Found: C, 46.43; H, 8.74; N, 13.56.

2,2′-Dimethoxy-2,2′-azopropane (10f). To a solution of sodium methoxide (6.1 g of sodium, 0.27 g-atom in 150 ml of methanol) at 0° was added portionwise 2,2′-dichloro-2,2′-azopropane (**10k**) (9.3 g, 0.051 mol). The solution was stirred at room temperature for 3 hr. The methanol was distilled off. Water was added, and extraction with ether and concentration gave, after distillation [bp 75° (22 mm)], 4.9 g (55%) of 2,2′-dimethoxy-2,2′-azopropane (**10f**): NMR (CCl_4) δ 1.28 (s, 12 H) and 3.42 ppm (s, 6 H).

Anal. Calcd for $C_8H_{18}N_2O_2$: C, 55.13; H, 10.43. Found: C, 55.23; H, 10.27.

2,2′,3,3,3′,3′-Hexamethyl-2,2′-azobutane (**10g**) was prepared in 36% yield from *N,N′*-bis[2,3,3-trimethyl-2-butyl]sulfamide (**11g**) as previously described.[20]

Anal. Calcd for $C_{14}H_{30}N_2$ (**10g**): C, 74.25; H, 13.36; N, 12.38. Found: C, 74.15; H, 13.40; N, 12.48.

Anal. Calcd for $C_{14}H_{32}N_2SO_2$ (**11g**): C, 57.47; H, 11.03; N, 9.58. Found: C, 57.71; H, 10.93; N, 9.59.

2,2′-4,4′,4′-Hexamethyl-2,2′-azopentane (**10m**) was prepared in 78% yield from *N,N′*-bis[2,4,4-trimethyl-2-pentyl]sulfamide (**11m**) as previously described.[20]

Anal. Calcd for $C_{16}H_{34}N_2$ (**10m**): C, 75.59; H, 13.38; N, 11.02. Found: C, 75.65; H, 13.53; N, 11.20.

Anal. Calcd for $C_{16}H_{36}N_2SO_2$ (**11m**): C, 59.93; H, 11.34; N, 8.73. Found: C, 60.07; H, 11.39; N, 8.63.

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Photochemical Transformations. XIII. Photorearrangements of 3-Phenylcycloheptene and Some Phenylnorcaranes[1,2]

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Abstract: While irradiation of 3-phenylcycloheptene (**12**) in cyclohexane or acetonitrile did not lead to isomeric products, that in benzene led to a mixture of 2-phenylmethylenecyclohexane (**15**) and *cis*- and *trans*-2-phenylnorcarane (**16** and **17**) rather than to the anticipated di-π-methane product, *endo*- (or *exo*-)-7-phenylnorcarane. *endo*-7-Phenylnorcarane (**13**) isomerized to the exo isomer (**14**) when irradiated in ketonic solutions (or by base-catalyzed isomerization) and to benzylidenecyclohexane (**18**) and 1-benzylcyclohexene (**19**) upon irradiation in benzene or acetonitrile. 1-Phenylnorcarane (**23**) gave 3-phenylcycloheptene (**12**) and 1-phenylcycloheptene upon irradiation in benzene. Irradiation of *o*-(3-cycloheptenyl)phenol (**32**) gave cyclization products from addition of the hydroxyl group to the double bond. Plausible reaction paths for the photoreactions of **12** are discussed; it is concluded that the epimeric 2-phenylcarbenes (**28**) are the most plausible intermediates.

Photochemical 1,2-migrations of allylic substituents, accompanied by a ring-closure process, provide general synthetic methods for cyclopropanes. A good deal of attention in this laboratory has been focused on the photosensitized rearrangement-cyclization of allylic halides (**1**) to halocyclopropanes (**2**), which is a quite general reaction,[3] with only a few failures. These reactions, which involve sensitization with triplet sensitizers, have stereochemical consequences, which are observable in appropriate cases. Thus 3-chlorocycloheptene (**3**) gives[3d,f] exclusively *endo*-7-chlo-