Neighboring-Group Effects in Free-Radical Reactions. The Thermal Decomposition of 1,1′,2,2′-Tetraphenylazoethane and 1,1′,2,2′-Tetraphenylazoethane-1,1′-d_2[1]

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Abstract: α-Secondary deuterium isotope effects are reported at 106.47° for the thermal decomposition of *meso*- and *dl*-1,1′,2,2′-tetraphenylazoethane (I) and *meso*- and *dl*-1,1′,2,2′-tetraphenylazoethane-1,1′-d_2 (II). The smaller α effect observed for *meso*- and *dl*-II compared to 1,1′-diphenylazoethane is discussed in terms of either steric effects or participation by neighboring phenyl. Activation parameters for both *meso*- and *dl*-I are consistent with a simultaneous one-step decomposition mechanism. The rate enhancement observed for *dl*-I over *meso*-I is probably of steric origin.

The mechanism of vicinal migrations of aryl groups to carbon in free-radical reactions has been investigated largely by product and isotopic labeling studies.[2] From these results the rearrangement mechanism has been interpreted as involving (a) formation of the classical radical and its subsequent rearrangement, and (b) the absence of free-radical analogs of phenonium ions.[2a]

The neophyl radical generated by a number of reactions undergoes partial phenyl migration, 50% from the Kharasch reactions,[3] 57% from aldehyde decarbonylation,[4] and 49% from acyl peroxide decomposition.[5] The extent of rearrangement accompanying decarbonylation is concentration[6] and temperature dependent.[7] The ease of rearrangement is dependent upon substituents in the aromatic ring and nearly independent of the radical-producing reaction.[7,8] The "neophyl" radical produced by decarbonylation of 1-phenylcyclopentylacetaldehyde and 1-phenylcyclohexylacetaldehyde undergoes 63 and 89% rearrangement, respectively, at 140°.[9] The extent of rearrangement is dependent upon temperature and radical lifetime, and consequently inversely proportional to aldehyde concentration and decreased by addition of benzyl mercaptan.

The extent of vicinal migration accompanying decarbonylation is dependent upon the substrate structure. The disparity in products from decarbonylation of various aldehydes under almost identical conditions suggests differing degrees of stability for the intermediate radicals. For example, radicals produced by decarbonylation of β-phenylisovaleraldehyde react by hydrogen abstraction from the aldehyde (57% rearrangement),[4] those from 3,3-diphenylbutanal (100% rearrangement) undergo disproportionation,[10] those from 2-methyl-3,3,3-triphenylpropanal (100% rearrangement) also undergo disproportionation,[10] and those from 3,3,3-triphenylpropanal (100% rearrangement) give only 1,1,2-triphenylethane.[10]

The aforementioned rearrangements all produce radicals of enhanced stability. However, enhanced stability of the rearranged radical and/or relief of strain cannot be the sole driving force for the rearrangement. The phenylethyl-1-C^{14} radical produced by decarbonylation of 3-phenylpropanal-2-C^{14}[11] and by the Kharasch reaction with 2-phenylethyl bromide-1-C^{14}[12] undergoes 3.3 and 20% rearrangement, respectively, to yield a radical of equivalent energy. The extent of rearrangement in the decarbonylation reaction increases with increasing temperature and is decreased 30% upon addition of thiophenol.

Walling,[2a] using the predictions of simple Hückel theory, suggests that the bridged radical should be less stable with respect to the initial or rearranged radical but that the transition state for phenyl migration is stabilized by delocalization of the odd electron over the π system of the aromatic nucleus. However, more extensive calculations suggest that the stability of the classical radical with respect to the bridged phenyl radical is dependent upon the groups at the origin and presumably the terminus of migration.[13]

Since participation should alter the potential energy of the transition state preceding radical formation its importance is perhaps best assessed by direct measurement of transition-state energies. The pyrolysis of 2,2′-diphenyl-1,1′,2,2′-tetramethylazopropane at 255° is apparently the only kinetic study of a reaction both yielding radicals in a primary step and involving phenyl migration.[14] From the small substituent effect it was concluded that the decomposition was unattended by major amounts of participation.[14] However, the high temperature might be expected to reduce the substituent effect. Suggestive perhaps of either steric acceleration and/or participation in its decomposition is the fourfold rate enhancement exhibited over 1,1′-di-

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[1] Research performed under the auspices of the U. S. Atomic Energy Commission.

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[8] (a) C. Rüchardt, *ibid.*, **94**, 2609 (1961); (b) C. Rüchardt and S. Eichler, *ibid.*, **95**, 1921 (1962); (c) C. Rüchardt and H. Trautewein, *ibid.*, **95**, 1197 (1962); (d) *ibid.*, **96**, 160 (1963); (e) C. Rüchardt and H. Hecht, *Tetrahedron Letters*, 961 (1962).

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[13] H. E. Zimmerman and A. Zweig, *ibid.*, **83**, 1196 (1961).

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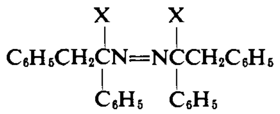
methylazoethane. Since the rate for the latter was determined in the gas phase a direct comparison may not be completely valid. The authors suggest that its rate would be higher in solution, thus reducing the rate discrepancy. Although current evidence argues against bridged phenyl radicals as intermediates it does not seem to exclude degrees of participation; the transition states preceding formation of the neophyl and 2-phenylethyl radicals might involve some degree of phenyl participation. Conceivably, the loss of carbon monoxide from the 3,3,3-triphenylpropanoyl radical and phenyl migration could be concerted. If the rearrangement mechanism involved initial formation of classical unrearranged radicals, the degree of bond breaking in the transition state should be largely structure independent for similar compounds. The lack of detailed kinetic studies appeared to warrant a further investigation of the energetics of radical formation.

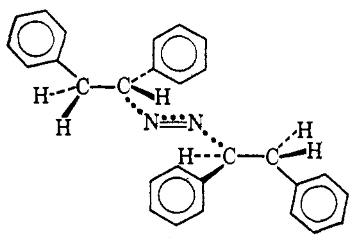
As the initial part of a study of the role of neighboring phenyl participation in radical reactions we report the secondary α-deuterium isotope effects in the thermal decomposition of *meso*- and *dl*-I and -II.



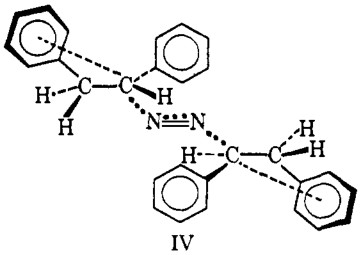
$$C_6H_5CH_2\overset{X}{\underset{C_6H_5}{C}}N{=}N\overset{X}{\underset{C_6H_5}{C}}CH_2C_6H_5$$

I, X = H, *meso* and *dl*
II, X = D, *meso* and *dl*

The mechanism of the thermal decompositions of symmetrically substituted azo compounds containing two α-benzylic carbons is known to involve simultaneous rupture of both carbon–nitrogen bonds.[15] Because of this mechanistic simplicity the α-deuterium effect in *meso*- and *dl*-II can be directly related to the bonding changes accompanying formation of the transition state leading to the 1,2-diphenylethyl radical. Two possible transition states in the decomposition of I(II) are (a) III, classical and (b) IV, involving stabilization of the developing p electron by the π electrons of neighboring phenyl. III and IV differ in the hybridization of C-α or alternatively in the bonding at C-α.



III



IV

Decomposition of I *via* III results in a greater hybridization change or loss in bonding at C-α than *via* IV (interaction between β-phenyl and C-α partially compensating for reduction of the H–C–N bending force constant). Consequently, the α-isotope effect (k_H/k_D) should be larger for the former than for the latter.[16] We would expect III to closely resemble the transition state in the decomposition of 1,1′-diphenylazoethane (V). Decomposition of I *via* III would then be expected to show an isotope effect of the same magnitude as V (k_H/k_D = 1.27).[15c] It is interesting that in another reaction leading to the formation of the α-phenylethyl radical, the pyrolysis of *t*-butyl-2-phenylperpropionate-2-*d*, the α effect (k_H/k_D = 1.14/D) is virtually the same.[17]

Results and Discussion

Similar to the results of Overberger and co-workers[18] we obtained two forms of I and II. On the basis of a symmetry argument[19] the higher melting isomer is tentatively assigned the *meso* configuration and the low melting, the *dl* configuration. The similarities of the ultraviolet spectra for the two forms (*meso*-I ϵ_{362} 54.6; *dl*-I ϵ_{364} 56.3) and the small rate differences between them (*vide infra*) argues against the two forms being *cis–trans* isomers. Models indicate the *cis* configuration of I would suffer enormous strain. The ultraviolet spectra of *cis*- and *trans*-azobenzene exhibit marked differences (*cis*, log ϵ_{432} 3.1; *trans*, log ϵ_{450} 2.6).[20] The differences in the ultraviolet between the two isomeric forms of 2,2′-diphenyl-1,1′,2,2′-tetramethylazopropane (ϵ_{366} 29.4, mp 83–84°, ϵ_{364} 24.2)[18b] are similar to those between *meso*- and *dl*-I.

All attempts to purify the *dl* isomer by recrystallization failed. Purification was accomplished by column chromatography using silica gel as the support. Considerable effort was expended to ensure that the *dl* isomer was uncontaminated by the *meso*.

The nmr spectrum of *meso*-I shows aromatic absorptions at δ 7.1. The proton at C-α appears as a triplet at δ 4.7. The C-β protons appear as two sets of doublets of slightly unequal intensity centered at δ 3.2. At a sweep width of 100 cps eight lines are observed for the protons at C-β and two peaks are discernible for the center line of the apparent triplet, indicative of an ABX pattern for the three protons.[21] The AB portion yields $|J_{AB}|$ = 13.8 cps and $|J_{AX} + J_{BX}|$ = 14.4 cps. The X portion also yields $|J_{AX} + J_{BX}|$ = 14.4 cps. *dl*-I reveals aromatic absorptions centered at δ 7.0, a triplet for the C-α proton at δ 4.7, and a unsymmetrical doublet at δ 3.1 for the two protons at C-β. The patterns remain unchanged at a sweep width of 50 cps.

Table I contains rate constants, relative rates, and activation parameters for *meso*- and *dl*-I. Actual fluctuations in the bath temperature and the errors associated with the thermocouple calibration contribute

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[15] (a) S. G. Cohen and C. H. Wang, *J. Am. Chem. Soc.*, 77, 3628 (1955); (b) C. G. Overberger and A. V. DiGiulio, *ibid.*, 81, 2154 (1959); (c) S. Seltzer, *ibid.*, **83**, 2625 (1961).

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Table I. Rate Constants and Activation Parameters for Decomposition of 1,1′,2,2′-Tetraphenylazoethane in Ethylbenzene

Compd	Temp, °C	$k \times 10^{-3}$, min^{-1}	Rel rate	E_A, kcal/mole	$\Delta S^{\ddagger}$, eu
meso-I	115.28 ± 0.05	14.6 ± 0.1	1		
	106.47 ± 0.04	5.44 ± 0.08[b]	1	33.1 ± 0.2	7.6 ± 0.5
	96.56 ± 0.04	1.66 ± 0.00[a]	1		
	106.47 ± 0.04	5.36[c]	1	33.1 ± 0.1	7.6 ± 0.2
dl-I	115.28 ± 0.05	17.1 ± 0.1[a]	1.18		
	106.47 ± 0.04	6.27 ± 0.03[b]	1.15	33.2 ± 0.1	8.2 ± 0.3
	96.56 ± 0.04	1.94 ± 0.01[a]	1.17		
	106.47 ± 0.04	6.27[c]	1.17	33.2 ± 0.2	8.2 ± 0.4

[a] Average of two competitive determinations for *meso* and *dl*. [b] Average of rate constants from isotope studies and footnote *c*. [c] Value from one competitive determination.

equally to the deviations in the temperatures, as shown in Table I. At 106.47° the average for all rate constants for *meso*-I and the single value obtained from the one competitive determination agree within the limits of experimental error. The agreement is even better for *dl*-I. These rate studies, extending over a period of weeks, indicate that actual deviations associated with the measured *k*'s are less than 2%.

The data in Table II indicate that within the precision of the measurement of the *k*'s the plot of log *k vs.* 1/*T* is linear.

Table II. Comparison of Observed and Calculated Rate Constants for Decomposition of *meso*- and *dl*-I

Compd	Temp, °C	$k_{\text{obsd}} \times 10^3$, min^{-1} [a]	% dev, k_{obsd}	$k_{\text{calcd}} \times 10^3$, min^{-1}	% dev, k_{calcd}
meso-I	115.28	14.547 ± 0.106[b]	±0.73	14.600	−0.36
	106.47	5.441 ± 0.078[c]	1.4	5.400	0.74
	96.28	1.662 ± 0.004[b]	0.20	1.667	−0.32
	115.28	14.547 ± 0.106[b]	0.73	14.514	0.22
	106.47	5.356[d]		5.371	0.28
	96.28	1.662 ± 0.004[b]	0.22	1.659	0.19
dl-I	115.28	17.152 ± 0.088[b]	0.51	17.100	0.25
	106.47	6.274 ± 0.029[c]	0.46	6.305	−0.50
	96.28	1.944 ± 0.014[b]	0.71	1.940	0.25
	115.28	17.152 ± 0.088[b]	0.51	17.097	0.26
	106.47	6.268[d]		6.305	−0.58
	96.28	1.944 ± 0.014[b]	0.71	1.939	0.32

[a] Not rounded for computational purposes. Deviations are standard deviations. [b] Average of two competitive determinations for *meso* and *dl*. [c] Average of rate constants from isotope studies and footnote *d*. [d] Value from one competitive determination.

Table III. Isotope Effects in the Decomposition of 1,1′,2,2′-Tetraphenylazoethane-1,1′-d_2 at 106.47 ± 0.03° in Ethylbenzene[a]

Compd	Atoms of α-D[b]	$(k_H/k_D)_{\text{obsd}}$[c]	(k_H/k_D)[f] cor
meso-II	1.375 ± 0.035	1.1493 ± 0.0017[d]	1.224 ± 0.006
dl-II	1.395 ± 0.028	1.1367 ± 0.0025[d]	1.202 ± 0.006
meso-II	1.853 ± 0.009	1.1935[e]	1.210

[a] The first two columns are not rounded for computational purposes; the last is. [b] Determined by nmr; combustion gives in order of entry 1.404, 1.397, and 1.905 atoms of D. [c] Measured competitively. [d] Average of four determinations. [e] One determination. [f] k_H/k_D observed corrected to 2.0 atoms of D.

Table III contains the observed and corrected isotope effects and the deuterium content of each compound determined by both nmr and combustion. The agreement in the total deuterium content for the first two entries between the two methods is excellent. The source of the 2% discrepancy between the two methods for entry three is not known. Proton ratios were determined by integration following repetitive scanning with a computer of average transients (Varian C-1024). Deviations in the measured isotope effects and the deuterium determinations contribute about equally to the deviations in the corrected isotope effects.

dl-I decomposes 17% faster than *meso*-I, in qualitative agreement with predictions based on inspection of Dreiding models which suggest the *dl* isomer to be slightly more hindered. Although similar rate differences between isomeric forms of azo compounds have been reported[14,18a] it is disconcerting that the rate differences do not in all cases parallel the melting point behavior[18a] and questions the validity of the symmetry argument[19] for assignment of configuration. Although the relative rate difference between *dl*- and *meso*-I appears to be temperature independent, $\Delta\Delta S^{\ddagger}$ is almost equal to the combined errors.

α-Isotope effects in the series V,[15c] 1-methyl-1′-phenylazoethane (VI),[22] and α-phenylethylazomethane (VII)[23] reveal that the decomposition mechanism changes from symmetrical to unsymmetrical one-step cleavage to two-step cleavage. The alteration in mechanism is reflected in E_a (kcal/mole) and $\Delta S^{\ddagger}$ (eu), 32.6 and 7.0 for V,[24] 36.5 and 9.3 for VI,[15b] and 38.6 and 14.0 for VII.[23] Introduction of dissymmetry into the transition state of VI results in a 4-kcal increase in E_a suggestive of different degrees of resonance stabilization.[15b,23,25] The observed trend in $\Delta S^{\ddagger}$ results from loss of restricted rotation in the isopropyl and methyl groups in the transition states of VI and VII.[23] The similarity in the activation parameters especially E_a for *meso*- and *dl*-I strongly supports a symmetrical one-step mechanism for I.

The α effect (Table II, corrected to 2.0 atoms of D) for V (1.27) is approximately 5% larger than for *meso*-II (1.224) and 7% larger than for *dl*-II (1.202). Only one determination of the isotope effect for *meso*-II (at the level of 1.853 atoms of D per molecule) was made and therefore the observed errors associated with it are unknown. If the mean deviations for the isotope effects for *dl*- and *meso*-II are used, however, the isotope effects for *meso*-II at two different levels of deuterium content are very close. The mean value of all isotope effects for *meso*-II (1.221) is approximately 2% greater than the mean isotope effect for *dl*-II.

Three possible interpretations of the observed results need to be considered. A possibility which appears implausible is that all other things being equal, the

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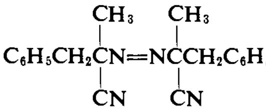
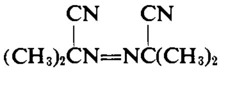
substitution of phenyl for hydrogen in V, to arrive at structure I, markedly affects the force constants associated with the α-benzylic hydrogens in both the reactant (I) and transition state (III), resulting in a smaller α effect in the decomposition of I. It has been shown, however, that upon substitution, force constant values in alkanes are maintained.[26]

Possible steric interference between the ends of I resulting from substitution of benzyl for methyl in V might be expected to result in a rate increase.[27] Hence, the transition state for I, decomposition *via* III, would be more reactant like than that for V,[28] resulting in a decrease in the α effect. Rates of decomposition of VIII (1.16×10^{-4} sec^{-1}) and IX (1.60×10^{-4} sec^{-1}), however, led Overberger and Biletch[29] to conclude that



$C_6H_5CH_2\overset{CH_3}{\underset{CN}{C}}N{=}N\overset{CH_3}{\underset{CN}{C}}CH_2C_6H_5$

VIII



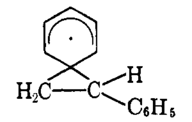
$(CH_3)_2\overset{CN}{C}N{=}N\overset{CN}{C}(CH_3)_2$

IX

in these compounds benzyl and methyl exhibit comparable steric effects. The structural change from VIII to IX is analogous to that encountered in going from I to V and this together with the near identity of rates between V and *meso*-I argues against a steric effect.

The reduction in the α effect observed for *meso*- and *dl*-II is at least consistent with neighboring-group participation, *i.e.*, decomposition *via* IV. α-Isotope effects (corrected to 106.47° for 2 atoms of D) consistent with neighboring phenyl participation have been reported in the formolysis of 2-phenylethyl[30] (X) (1.17) and 2-anisylethyl tosylates[31] (XI) (1.17). In harmony with this picture is the insignificance of hyperconjugation as shown by the absence of secondary β-deuterium isotope effects in these solvolyses. Participation in I, if it occurs, involving interaction between the π electrons of the aromatic ring and the incipient odd electron in the transition state as indicated in IV, is similar in nature to that proposed for the formolysis of β-arylethyl systems.[32]

Since in a highly endothermic process the transition state leading to the intermediate is expected to resemble that intermediate closely,[28] some comment, assuming participation, on the bonding in the intermediate 1,2-diphenylethyl radical is appropriate. The α effect for *meso*- and *dl*-II compared to that for V argues against a bridged phenyl radical intermediate XII. This conclusion is supported by the α effects observed for X and XI and is interpreted in terms of weak C-α-Ar and strong C-β-Ar bonds.[31] An attractive possibility is interaction between the π electrons of the β-phenyl and the odd electron similar to that observed in complexing between halogen atoms and aromatic solvents.[33] The absence of 1,2-hydrogen migrations in radical reactions[2] except for one reaction involving diradicals[34] seems to eliminate the possibility of hydrogen participation.



XII

Dreiding models suggest that participation should be equally probably for *meso*- and *dl*-I. If the 17% rate enhancement for *dl*-I is a result of a more hindered reactant conformation, then it might be expected that the *dl*-I transition state lies closer to reactant than does the *meso*-I transition state. This could account for the 2% difference in isotope effects between *meso*- and *dl*-I. These results represent a dichotomy since either steric effects[35] or participation[32a,36] should be reflected by enhanced rates of decomposition for both *meso*- and *dl*-I. The primary nitrogen isotope effect (k_{14}/k_{15}) observed in the decomposition of *meso*-I[37] is smaller than for V,[38] suggesting that (a) the bonding in the transition state of I is different from V, and (b) the transition state for I is probably reached earlier along the reaction coordinate than V. Hence, in some instances, isotope effects may be a more sensitive tool than a comparison of rates for probing for the possibility of neighboring-group effects in reactions of structurally related compounds.

Although the isotope effects are in accord with a more reactant-like transition state for *meso*- and *dl*-I compared to V resulting from the substitution of phenyl for hydrogen and is reflected in the reaction as either steric acceleration or participation, consideration of all the data suggests that the latter is the better explanation. Further work is currently in progress.

Experimental Section[39]

***meso*-1,1′,2,2′-Tetraphenylazoethane (I).** Desoxybenzoin azine was prepared by the method of Goldschmidt and Acksteiner,[40] mp 164.4–165.3° (lit. 160–162.5°,[40] 164°[41]). Five per cent palladium on charcoal, 3.6 g, suspended in 210 ml of tetrahydrofuran was equilibrated with hydrogen gas; 9.00 g of the azine was then reduced at atmospheric pressure. Six to seven hours were required for uptake of 2 moles of hydrogen. The reaction mixture was filtered through a fine-grade sintered-glass funnel and the tetrahydrofuran evaporated under reduced pressure. The hydrazine was taken up in 100 ml of benzene and oxidized with yellow mercuric oxide; the suspension was filtered and the benzene evaporated under reduced pressure. The crude azo compound was dissolved in carbon tetrachloride (50°) and crystallized at 0°, mp 127–131°. *meso*-I was then repeatedly recrystallized (0 to −10°) from AR grade acetone: mp 131.5–132.9° dec, immersion at 129°, ϵ (benzene) 54.6, λ_{max} 362 mμ.

Anal. Calcd for $C_{28}H_{26}N_2$: C, 86.12; H, 6.71; N, 7.17. Found: C, 85.99; H, 6.81; N, 7.50.

***dl*-1,1′,2,2′-Tetraphenylazoethane (I).** Crude *dl*-I was obtained upon addition of petroleum ether to the carbon tetrachloride mother liquor from *meso*-I at 0°, mp 95–106°. The crude product was purified by column chromatography using Baker AR grade

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[39] (a) All melting points are uncorrected. (b) Analyses performed by Schwarzkopf Microanalytical Laboratory.

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[41] V. Sprio, *Gazz. Chim. Ital.*, **85**, 569 (1955).

silica gel as the substrate and benzene–petroleum ether (bp 30–60°) as the eluting solvent. In one separation, 1.22 g of material (column dimensions, 77 × 2.4 cm) was eluted with solvent mixtures of 35:65 and 45:55 (v/v) %. Dissolving the chromatographed material in ether and cooling to $-30°$ yielded a crop of crystals, mp 131.5–132.8°. Cooling to $-40°$ yielded a second crop, mp 131–132.6°. The volume of the filtrate was then reduced by about 25% and a volume of petroleum ether equivalent to approximately one-fourth of the final volume was added. Crystallization at $-76°$ yielded 0.42 g of *dl*-I, mp 102.1–103.1°. In a second separation 1.0 g of crude product (colunm dimensions, 80 × 2.4 cm) was eluted with 38:62 (v/v) % benzene–petroleum ether. Dissolving the chromatographed product in ether and cooling to $-40°$ yielded 0.07 g of material, mp 130.8–132.4°. The volume of the filtrate was slightly reduced. Crystallization at $-76°$ yielded 0.06 g of material, mp 125–130°. The volume of the resulting filtrate was reduced further and an equivalent volume of petroleum ether was added. Crystallization at $-50°$ gave 0.38 g of *dl*-I: mp 102–102.8°, immersion 98.6 and 100°, ϵ (benzene) 56.3, $\lambda_{\max}$ 364 mμ.

Anal. Calcd for $C_{28}H_{26}N_2$: C, 86.12; H, 6.71; N, 7.17. Found: C, 86.48; H, 6.49; N, 7.26.

***meso*-1,1′,2,2′-Tetraphenylazoethane-1,1′-d_2 (II).** Five per cent palladium on charcoal, 3.6 g, suspended in 425 ml of tetrahydrofuran was equilibrated with gaseous deuterium; 9.06 g of azine was then reduced at 0° and atmospheric pressure. After the requisite volume of gas had been taken up the reaction mixture was worked up by the usual procedure; the hydrazine oxidation was carried out at 0°. The combined product from three reductions was recrystallized from 300–400 ml of AR grade acetone (-10 to $-20°$). Reducing the volume of the filtrate to approximately 175 ml and cooling to $-10°$ gave a second crop of crystals. The combined fractions were recrystallized ($-10°$) two additional times from acetone (50°): yield 7.63 g, mp 132.2–133.6° dec, immersion 130°, ϵ (benzene) 55.0, $\lambda_{\max}$ 362 mμ.

***dl*-1,1′,2,2′-Tetraphenylazoethane-1,1′-d_2 (II).** The filtrate from the first recrystallization of *meso*-II was concentrated to 150 ml. Crystallization at $-20°$ yielded 6.3 g of crude *dl*-II, mp 93–96°. An additional 9.7 g was obtained upon evaporation of the filtrate. Two samples of crude *dl*-II (1.16 and 1.46 g) were purified by column chromatography (column dimensions, 2.4 × 78 cm and 2.4 × 74 cm) by using 30:70 (v/v) % benzene–petroleum ether as the eluting solvent, combined yield 1.44 g. No precipitate was obtained upon cooling chromatographed *dl*-II dissolved in ether to $-40°$. Addition of petroleum ether and crystallization at $-40°$ yielded 1.14 g of *dl*-II: mp 103.0–103.8°, ϵ (benzene) 57.0, $\lambda_{\max}$ 364 mμ.

Ethylbenzene was distilled from sodium at atmospheric pressure through a 12-in. HeliPak column. The refractive index was measured; $n^{25}\text{D}$ 1.4932, lit.[42] 1.4933.

Kinetics. Approximately 0.024 g of azo compound was dissolved in 3 ml of ethylbenzene and the resulting solution transferred to a fused quartz ultraviolet cell fitted with a quartz 10/30 inner joint. The kinetic solution was degassed at Dry Ice temperature under high vacuum (<1 μ of pressure) by a standard degassing procedure. The degassing procedure was repeated until the pressure was that of ethylbenzene. The cells were then sealed under vacuum by allowing the heated quartz tube, below the joint, to collapse. Excellent first-order kinetics were obtained by following the disappearance of the absorption due to the nitrogen–nitrogen bond.[43] Infinity readings were taken after a minimum of ten half-lives. Within experimental error 100% decomposition was observed; no residual absorption between 355 and 450 mμ was observed. Approximately 80–100 points were taken during a run and these were computer processed to obtain the nonlinear least-squares solution of the first-order rate constant. Isotope effects were determined by simultaneously measuring the rates of decomposition of the protium and deuterium compounds in the same cell carriage.

Deuterium Content and Correction of Isotope Effects. The deuterium content of *meso*- and *dl*-II was determined by both combustion and nmr. The nmr measurements involved a minimum of two independent determinations of the proton ratios for labeled and unlabeled compounds by integration following repetitive scanning with a Varian C-1024. Spectra of the *meso* compounds taken in chloroform-*d* were corrected for the contribution by protium in the solvent to the area under the phenyl absorption. Spectra of the *dl* compounds were taken in carbon tetrachloride. Comparison of the proton ratios in the deuterated compounds, assuming no deuteration in the phenyls, to the corresponding ratios in the protium analogs gave the atom fraction of deuterium.

Chauvenet's criterion[44a] was used to test the validity of each measured isotope effect. On this basis one of the five determinations for *meso*-II and none of the four for *dl*-II were rejected.

The isotope effects were corrected to 2 atoms of D by use of the equation

$$V \pm \sigma_V = (X \pm \sigma_X)^{2.000/(Y \pm \sigma_Y)}$$

where V is the corrected effect, X is the observed effect, Y refers to the atoms of α-deuterium, and σ represents the associated standard deviations. The equation used to calculate the error in V, σ_V, was derived from the expression $\sigma_V = \pm[(\varphi V/\varphi X)^2\sigma_X{}^2 + (\varphi V/\varphi Y)^2\sigma_Y{}^2]^{1/2}$.[44b]

Thermocouple Calibration. The thermocouple was calibrated against a NBS-calibrated thermometer over the temperature range of the kinetic experiments using a modified Cottrell pump.[45] Solvents and corrected thermometer and thermocouple readings were: methylcyclohexane, 101.26_6°, 5.335; toluene, 110.46_5°, 5.842; 1,1,2-trichloroethane, 113.58_0°, 6.014; 2,3-dimethylhexane, 115.80_6°, 6.135. The slope, intercept, and standard deviations of the slope, intercept, and y axis obtained from a linear least-squares fit of $T°$ *vs.* emf were 18.160, 4.378, 0.024, 0.140, and 0.0146, respectively.

Bath temperatures in terms of voltage ($\bar{X}_i$) and the associated deviations (ΔX_i) were: 5.076 ± 0.001, 5.622 ± 0.001, 6.107 ± 0.002. The average bath temperature ($\bar{T}_i$) corresponding to each $\bar{X}_i$ was calculated using the previous regression line. Deviations in each $\bar{T}_i$ arise from fluctuations (ΔX_i) in the bath temperature ($\bar{X}_i$) and errors in the thermocouple calibration. The effect resulting from the former was obtained by calculating $T_i \pm \Delta T_i$ for each $\bar{X}_i \pm \Delta X_i$. The latter was obtained by calculating $\sigma_{(T_i \pm \Delta T_i)}$ for each $\bar{X}_i \pm \Delta X_i$.[46] The deviation in each T_i is then one-half of the calculated range.

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