Secondary α-Deuterium Isotope Effects in the Thermal Decomposition of 2,2′-Dimethoxy-1,1′-diphenylazoethane and 1,1′-Diphenylazobutane

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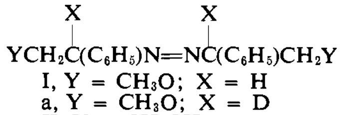
Abstract: α-Secondary deuterium isotope effects are reported for the pyrolysis of 2,2′-dimethoxy-1,1′-diphenylazoethane (I) and 1,1′-diphenylazobutane (II). As for *meso*- and *dl*-1,1′,2,2′-tetraphenylazoethane (III), α effects for I and II are lower than the one for 1,1′-diphenylazoethane (IV). The α effect for II is similar to the ones for the diastereoisomers of III. Thus the reduction in isotope effects for *meso*- and *dl*-III can reasonably be ascribed to steric effects in the reactant rather than anchimeric assistance to bond homolysis by β-phenyl. The abnormal α effect for I is discussed in terms of (1) participation by neighboring oxygen, (2) decomposition *via* a "classical" transition state in which the methoxy group is in a bisected conformation, or (3) a two-step mechanism. Calculations indicate that nontransferability of the bending force constants associated with the α-benzylic hydrogens between members of a homologous series of compounds is of limited importance in producing variations in the α effect.

The thermal decomposition of symmetrically substituted azo compounds containing two α-benzylic carbons is known to involve simultaneous rupture of both carbon–nitrogen bonds.[2] The α-deuterium isotope effect in decomposition of *meso*- and *dl*-1,1′,2,2′-tetraphenylazoethane (III)[3] (1.22 and 1.20) and the primary nitrogen effect for *meso*-III[4] (1.0158) are smaller than the values for decomposition of 1,1′-diphenylazoethane (IV) (k_H/k_D = 1.27,[2c] k_{14}/k_{15} = 1.0229[5]). An increase in the reactant-like character of the transition state for III compared to IV was preferred to nontransferability of α-benzylic carbon–hydrogen bending force constants as an explanation for the alterations in the isotope effects.[3] Participation by β-phenyl or a more hindered reactant conformation was advanced as reasons for this shift in the reactantlikeness of the transition state.[3] The evidence seemed to favor participation as the more plausible explanation. The conclusion that the α effect for both diastereomeric forms of III ruled out formation of a bridged 1,2-diphenylethyl radical[3] is reinforced by an epr study which supports the classical structure for the 2-phenylethyl radical.[6]

In a further study of the relationship between the α effect and reactant structure, α effects in the pyrolysis of 2,2′-dimethoxy-1,1′-diphenylazoethane (I) and 1,1′-diphenylazobutane (II) have been measured. To assess the importance of nontransferability on the magnitude of k_H/k_D, the changes in reactant α carbon–hydrogen bending force constants required to produce a given variation in the isotope effect have been calculated.



$$YCH_2\overset{X}{\overset{|}{C}}(C_6H_5)N{=}N\overset{X}{\overset{|}{C}}(C_6H_5)CH_2Y$$

I, Y = CH_3O; X = H

a, Y = CH_3O; X = D

II, Y = CH_3CH_2; X = H

a, Y = CH_3CH_2; X = D

Results and Discussion

Excellent first-order kinetics were observed for decomposition of all compounds. Experimental rate constants and associated per cent deviations for I and II as a function of temperature are tabulated in Table I. Within the precision of the measurements (columns 5 and 6) of the k's for I the plot of log k *vs.* $1/T$ is linear. For II the per cent deviations in k_{calcd} from the best least-squares line are generally somewhat greater than those for k_{exp}, which do not exceed 2%. The discrepancies are small and probably attributable to imprecision in the measured specific rate constants and temperature.

The rate constant for I is independent of a *ca.* fivefold variation in initial concentration (Table II), which rules out induced decomposition as a contributing mechanism in the pyrolysis of I.

Table III presents the observed and corrected (2 atoms of α-D) isotope effects and the deuterium content of each compound determined by both nmr (proton ratios determined by integration following repetitive scanning with a Varian C-1024) and combustion. Excellent agreement in the deuterium contents measured by the two methods was obtained except for the first sample of Ia (made by reduction of the azine in ethanol-*O-d*) in which total atoms of D per molecule were found to be 2.10 (1.726 atoms of α- and 0.3778 atoms of β-D) and 2.41 by nmr and combustion, respectively. This discrepancy was removed (see Experimental Section). The larger standard deviation in $(k_H/k_D)_{cor}$ for sample 2 of IIa resulted from fluctuations in bath temperature. However, the agreement in the α effect for both samples is excellent.

Isotope effects extrapolated to 105.28° and activation parameters for the four azo compounds are tabulated in Table IV. Since the β substituents have different steric, electronic, and participatory characters, it is clear from the data in Table IV that the magnitude of

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[1] (a) NDEA Fellow 1968–1969, deceased 1969; (b) NSF–URP Summer 1967; (c) NSF–URP Summer 1968.

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

[3] S. E. Scheppele and S. Seltzer, *ibid.*, 90, 358 (1968).

[4] Unpublished results of S. Mylonakis, S. E. Scheppele, and S. Seltzer.

[5] S. Seltzer and S. Mylonakis, *J. Amer. Chem. Soc.*, 89, 6584 (1967).

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Table I. Comparison of Observed and Calculated Rate Constants for Decomposition of I and II

Compd	Temp, °C[b]	$k_{obsd} \times 10^3$, min^{-1} [a]	% dev, k_{obsd}	$k_{calcd} \times 10^3$, min^{-1}	% dev, k_{calcd}
I	106.06 ± 0.13	1.372 ± 0.024	±1.80	1.352	0.01
	113.81 ± 0.04	3.313 ± 0.030	0.09	3.340	−0.81
	118.09 ± 0.05	5.306 ± 0.028[c]	0.53	5.420	−0.02
	122.19 ± 0.06	8.621 ± 0.051	0.59	8.535	1.00
	126.54 ± 0.05	13.616 ± 0.125	0.29	13.676	−0.44
	133.66 ± 0.10	29.240 ± 0.300	1.20	28.953	1.00
II	93.88 ± 0.10	1.001 ± 0.004[d]	0.41	0.989	1.26
	105.68 ± 0.07	4.175 ± 0.004[e]	0.10	4.141	0.82
	106.86 ± 0.03	4.638 ± 0.029[c]	0.64	4.756	−2.54
	107.35 ± 0.15	4.888 ± 0.096[c]	1.96	5.036	−3.02
	119.55 ± 0.07	20.348 ± 0.340[d]	1.67	19.973	1.84

[a] Not rounded for computational purposes. Deviations are standard deviations. [b] Imprecision in thermocouple calibration contributes *ca.* ±0.02° to uncertainties in temperature. [c] Average of rate constants from isotope studies. [d] Average of three determinations. [e] Average of two determinations.

Table II. Rate Constants for Decomposition of I as a Function of Initial Concentration of I at 120.59°

Concn, *M*	$k \times 10^3$, min^{-1}	$k_{av} \times 10^3$, min^{-1}
0.012	6.92	7.01 ± 0.08
0.011	7.09	
0.026	7.00	6.96 ± 0.04
0.021	6.93	
0.050	7.08	7.07 ± 0.01
0.051	7.06	

Table III. Isotope Effects in the Decomposition of 2,2′-Dimethoxy-1,1′-diphenylazoethane-*1,1′*-d_2 and 1,1′-Diphenylazobutane-*1,1′*-d_2 in Ethylbenzene[a,b]

Compd	Temp, °C	Atoms of α-d[c]	$(k_H/k_D)_{obsd}$[d]	$(k_H/k_D)_{cor}$[e]
I-d_2	118.09	1.726 ± 0.013	1.1602 ± 0.0029[f,g]	1.188 ± 0.004
	118.09	1.781 ± 0.003[h]	1.1650 ± 0.0009[g,i]	1.187 ± 0.001
II-d_2	106.68	1.688 ± 0.004	1.1618 ± 0.0063[j]	1.194 ± 0.008
	107.35	1.728 ± 0.006	1.1759 ± 0.0115[k]	1.206 ± 0.014

[a] Columns three and four are not rounded for computational purposes; the last one is. [b] All deviations are standard deviations. [c] Determined by nmr; duplicate combustion analysis gives in order of entry 2.407 ± 0.004, 1.816 ± 0.003, 1.676 ± 0.004, 1.726 ± 0.004. [d] Measured simultaneously. [e] k_H/k_D observed corrected to 2.0 atoms of D. [f] Measured k_H/k_D = 1.1681 ± 0.0029; corrected for presence of 0.3778 ± 0.0153 atom of β-D (nmr) assuming $(k_H/k_D)_\beta$ = 1.0175/D; see S. Seltzer and E. J. Hamilton, Jr., *J. Amer. Chem. Soc.*, **86**, 3775 (1966). [g] Average of three determinations. [h] Total atoms of D by nmr = 1.80_3 ± 0.014, 1.781 atoms of α-, and 0.022 ± 0.014 atom of β-D. [i] Not corrected for 0.022 atom of β-D. [j] Average of five determinations. [k] Average of four determinations.

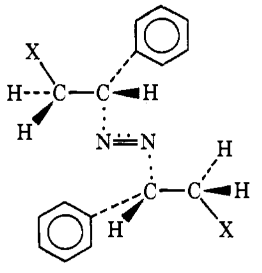
Table IV. Isotope Effects and Rate Constants at 105.28° and Activation Parameters

Compd	k_H/k_D	$k \times 10^3$, min^{-1}	E_a, kcal/mol	$\Delta S^{\ddagger}$, eu
I	1.194[a]	1.24[e]	34.0 ± 0.1	7.4 ± 0.6
II	1.201[a,b]	3.95[e]	33.5 ± 0.4	8.5 ± 1.0
meso-III	1.225[a,c]	4.66[e]	33.1[c] ± 0.2	7.6 ± 0.5
dl-III	1.207[a,c]	5.47[e]	33.2[c] ± 0.2	8.2[c] ± 0.4
IV	1.27[d]	5.41[d]	32.6[f]	7.0[f]

[a] Extrapolated from data at other temperatures assuming A_H/A_D = 1; R. R. Johnson and E. S. Lewis, *Proc. Chem. Soc.*, 52 (1958). [b] Average of two extrapolated values, 1.195 and 1.208; see Table III. [c] See ref 3. [d] See ref 2c. [e] Extrapolated from data at other temperatures. [f] See ref 9e.

the isotope effect is not determined solely by one of these factors.

Two possible general transition states for decomposition of these azo compounds are V, classical, and VI, involving anchimerically assisted C–N bond homolysis. The reactantlike–productlike character of V should depend on: (1) possible steric hindrance in the reactant state resulting from interaction of the ends of the azo compound,[7] and (2) the polar character of the β substituent. An increase in the reactantlikeness of V could arise from replacement of the methyl groups in IV by the larger groups XCH_2.[7] Symmetry considerations make it unlikely that transition- and ground-state polarization are much different, and indicate that transition-state charge development should be delimiting.[8] Nevertheless an inductive effect seems reasonable since (a) symmetrically substituting a pair of methyl groups for hydrogens in either azomethane or 1,1′-diphenylazomethane results in a *ca.* 3 kcal/mol reduction in $\Delta H^{\ddagger}$,[9] and (b) although the situation is not exactly



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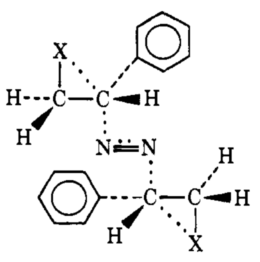

VI

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[9] (a) C. Steel and A. F. Trotman-Dickenson, *J. Chem. Soc.*, 975 (1959); (b) C. Steel and K. J. Laidler, *J. Chem. Phys.*, **34**, 1827 (1961), quoting from W. D. Clark, Ph.D. Dissertation, University of Oregon, Eugene, Ore., June 1958; (c) A. V. Blackham and N. L. Eatough, *J. Amer. Chem. Soc.*, **84**, 2922 (1962); (d) G. Williams and A. S. Lawrence, *Proc. Roy. Soc. London, Ser. A*, **156**, 455 (1936); (e) S. G. Cohen and C. H. Wang, *J. Amer. Chem. Soc.*, 77, 2457 (1955).

analogous, both inductive and resonance effects are important in determining the pyrolysis rates of 1,1′-dimethyl-1,1′-(3,3′- and 4,4-′disubstituted)diarylazoethanes[10] and 1,1′-(4,4′-disubstituted)diarylazoethanes.[11] If inductive effects parallel those for electrophilic radicals the degree of bond breaking in V should decrease for electron-donating substituents and increase for electron-withdrawing ones. The magnitude of k_H/k_D depends upon the reduction in the α H–C–N bending force constants upon passing from the reactant state to the transition state.[12] Consequently, k_H/k_D should (a) decrease with increasing reactantlikeness and (b) increase with increasing radicallikeness of V. Participation, decomposition *via* VI, should also cause a reduction in k_H/k_D[12,13] (interaction between β-phenyl and C-α partially compensating for the reduction of the α H–C–N bending force constant).

If decomposition proceeds *via* V, the α effect for *meso*- and *dl*-III ($X = C_6H_5$) reflects increased reactantlikeness of the transition state induced by the increase in reactant strain upon replacing a pair of β-hydrogens in IV with phenyls. In view of the E_s values in Table V, II and both diastereomeric forms of III[14] are judged to possess comparable strain energy. Compound II decomposes *via* V. Thus the above hypothesis requires similar α effects for II and *meso*- and *dl*-III. Alternatively, if the reduced α effect for the diastereoisomers of III reflects phenyl participation (decomposition *via* VI), strain energy in II should be negligible and k_H/k_D for II should be larger than the values for III and similar to the value for IV. Clearly the α effects for II (1.201) and *meso*- and *dl*-III (1.225 and 1.207) support the hindered reactant concept and cast doubt upon the anchimerically assisted mechanism for III. Although the differences in α effects approach the level of experimental uncertainty, the average value of k_H/k_D for II is *ca.* 1 and 2% lower than the average values for *dl*- and *meso*-III, respectively. If real, these differences would be consistent, other factors being equal, with some perturbation of the reactantlike–productlike character of V resulting from the opposite inductive effects of β-ethyl and β-phenyl as measured by their σ^* values (Table V).

Table V. Values of σ^* and E_s for R of $(RCH_2CH(C_6H_5)N{=})_2$[a]

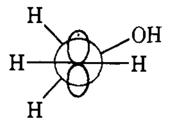
R	Compd	σ^* [b]	E_s[b]
H	IV	0.0	0.0
CH_3CH_2	II	−0.115	−0.36
CH_3O	I	0.52	−0.19
C_6H_5	*meso*- and *dl*-III	0.215	−0.38

[a] Based upon R in RCH_2X. [b] R. W. Taft, Jr., in "Steric Effects in Organic Chemistry," M. S. Newman, Ed., Wiley, New York, N. Y., 1956, Chapter 13.

Assume I decomposes *via* simple two-bond rupture, *i.e.*, *via* transition state V, with X being CH_3O. The E_s values predict that I should be intermediate between IV and II or III in strain energy. The σ^* values indicate that the inductive destabilization of V should be considerably larger for CH_3O than for C_6H_5. For decomposition of I steric and electronic effects place opposite demands upon the reactantlike–productlike character of the transition state. The net result will depend quantitatively upon the relative importance of each effect. Qualitatively, we might reason that the effects should approximately cancel and so yield a value of k_H/k_D for I similar to the value for IV, 1.27. Clearly the observed effect (1.194) is inconsistent with this prediction.

A detailed understanding of the "abnormal" α effect for I is desirable in view of the magnitude of the reduction in the isotope effect compared to IV, *ca.* 29%. Three explanations involving structure–reactivity effects can be advanced. The transition state could be stabilized by interaction of the incipient odd electron on C-α with an unoccupied orbital on neighboring oxygen, *i.e.*, decomposition *via* VI. Electron promotion on oxygen appears to be important in stabilizing α-oxyalkyl radicals.[15] α-Isotope effects (first two[3] temperatures corrected to 106.47° and the latter two to 105.28° for 2 atoms of D) consistent with neighboring aryl participation have been reported for the formolysis of 2-phenylethyl[16] (1.17) and 2-anisylethyl tosylates[17] (1.17) and 2,4-dimethoxyphenylethyl[18] (1.19) and 3,5-dimethoxyphenylethyl brosylates[18] (1.17). If participation is assumed, the α effect for I argues against a σ-bonded bridged intermediate radical.[3]

A cogent argument against participation by neighboring oxygen, other factors being equal, is the observation that the 2-hydroxyethyl radical exists in a bisected conformation, VII.[19] Decomposition of I could conceivably proceed *via* a transition-state V in which each methoxy group is similarly in an approximately bisected conformation(s). Such a transition state, if more reactantlike than in the decomposition of IV, would be consistent with the α effect for I. For it to be less reactantlike would require an increase in one or more of the force constants associated with the α-benzylic hydrogen in passing from the reactant to the transition state to compensate for the reduction in the α H–C–N bending force constant. Precedent does not appear to exist for this intriguing possibility.



VII

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(14) Although the E_s value does not differentiate between the diastereomeric forms of III, Dreiding models indicate the *dl* isomer to be more strained than the meso.[3]

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A crossover in mechanism from symmetrical to two-step cleavage is a possible but seemingly implausible explanation for the α effect for I.[2c,20]

Since the α effect alone does not permit a decision among explanations, detailed studies of the bonding in the transition state of I and of the nature of the 2-methoxy-1-phenylethyl radical are in progress.

Interestingly the α effect in the gas-phase decomposition of 3,3′-azo-1-propene (VIII) (k_H/k_D = 1.33/4α-D at 161.75°) presents similar interpretative problems.[21] Two alternatives considered were (a) simultaneous C–N bond rupture with little radicallike character of the transition state or (b) stepwise cleavage with considerable allylic radical character in the transition state. Extrapolation of the data for the hypothetical α,α'-d_2 reactant, *i.e.*, $k_H/k_D = (1.33)^{1/2}$, to 105.28° yields $k_H/k_D = 1.18$. Thus the magnitude of the α effect for VIII, like I, is either unusually small (simultaneous mechanism) or large (two-step mechanism[20a,b]).

A direct relationship between the magnitude of the α effect and reactivity (mechanism) demands transferability of bending force constants associated with the α-hydrogen in the reactant state. For a series of homologous compounds undergoing a given reaction, nontransferability would produce variations in k_H/k_D even though the transition-state bonding might not change with molecular structure. The maintenance of force constant values in the alkanes[22] *a priori* might suggest transferability of α C–H force constants between II and IV. However, I and III do not differ in structure from IV simply by the presence of α-alkyl groups. For these compounds the expected constancy in the force constants is more difficult to establish, even qualitatively. Calculations, *vide post*, indicate that a reduction of about 3–7, 4.5–11, or 9–22% averaged over all three, any two, or one of the α carbon–hydrogen reactant-state bending force constants would be required to reduce the α effect from 1.27 for IV to 1.225 for *meso*-III (*ca.* an 18% reduction) and to 1.194 for I (*ca.* a 29% reduction). Clearly, the required changes of 9–25% in bending force constants are not negligible and militate against nontransferability as an acceptable explanation for the changes observed in k_H/k_D upon replacement of pairs of β-hydrogens in IV by methoxy, phenyl, or ethyl groups. The absence of a correlation between (a) the steric and electronic effects of the substitutent and (b) the direction of change in the force constants, and the transferability of carbon–hydrogen force constants in the *tert*-butyl halides[23] and from 1,2-ethanedithiol[24] to the 2-bromo- and 2-chloroethanethiols[25] provides supporting evidence. Wolfsberg's and Stern's conclusion[12,26] that the variation in the isotope effect results from variation in the transition-state force fields at the isotopically substituted position is thus reinforced.

Model Calculations. Various experimental[27] and theoretical studies[12] have confirmed that the difference in loss of zero-point energy between protio and deuterio compounds in the ground states and transition states is principally responsible for the α effect.[13] The net reduction in the zero-point vibrational frequencies per α C–H bond upon passing from the reactant state to the transition state for the protio compound is related to the α effect per D by eq 1, where $\nu_{H,i}/\nu_{D,i}$ and $\nu_{H,i}^{\ddagger}/$

$$k_H/k_D = \exp[(1 - 1/\bar{r})(hc/2kT)\sum_i(\nu_{H,i} - \nu_{H,i}^{\ddagger})] \quad (1)$$

$\nu_{D,i}^{\ddagger}$ have been assumed equal to $\bar{r}$.[13,27a,b] A mean value for $\bar{r}$ equal to 1.31[27a,b] appears preferable to a value of 1.35.[13] The net frequency decreases calculated per α-H(D) for I through IV from eq 1 are seen to depend upon the value of $\bar{r}$ (Table VI).

Table VI. Frequency Decreases of α C–H Modes Required to Produce α Effects at 105.28° [a]

	$\bar{r}$ = 1.35		$\bar{r}$ = 1.31		$\bar{r}$ = 1.20	
Compd	$\Delta\nu$, cm^{-1} [b]	$-\Delta\Delta\nu$, cm^{-1} [c]	$\Delta\nu$, cm^{-1} [b]	$-\Delta\Delta\nu$, cm^{-1} [c]	$\Delta\nu$, cm^{-1} [b]	$-\Delta\Delta\nu$, cm^{-1} [c]
IV	242	0	266	0	377	0
meso-III	206	36	226	40	320	57
dl-III	191	51	209	57	297	80
I	180	62	197	69	279	98
II	186	56	204	62	289	88

[a] Calculated per α-D. [b] $\Delta\nu = \Sigma_i(\nu_{H,i} - \nu_{H,i}^{\ddagger})$. [c] Relative to IV, *i.e.*, $\Delta\Delta\nu = \Delta\nu_{subs} - \Delta\nu_{IV}$.

The reaction coordinate for decomposition of IV is the symmetrical stretching frequency of the C–N=N–C group.[5,28] To calculate the reduction in the reactant-state α C–H bending force constants required to reduce the α effect for IV to the value observed for each β,β'-disubstituted IV, we assume: (1) all decompositions occur *via* V, (2) the transition-state force fields involving the isotopically substituted positions are identical for I through IV (identical with the force field deduced for decomposition of IV[5]) and (3) the reactant-state α C–H stretching force constants are either independent of β substitution or do not contribute to the isotope effect.[12,29] An assumption other than (2) requires alteration in transition-state bonding with a change in reactant structure. The difference in loss of zero-point energy between substituted IV (I, II, and diastereomeric III) and IV is related to the ratio of the α effects by eq 2,

$$(k_H/k_D)_{subs}/(k_H/k_D)_{IV} = \exp\{(1 - 1/\bar{r})(hc/2kT)\sum_i[(\nu_{H,i,subs} - \nu_{H,i,IV}) - (\nu_{H,i,subs}^{\ddagger} - \nu_{H,i,IV}^{\ddagger})]\} \quad (2)$$

where subs refers to a substituted reactant. From assumption 2 the term in eq 2 involving the transition-state frequencies vanishes and eq 2 reduces to eq 3.

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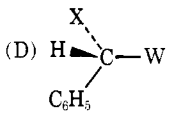
(27) (a) S. Seltzer, *J. Amer. Chem. Soc.*, **83**, 1861 (1961); (b) A. A. Zavitsas and S. Seltzer, *ibid.*, **86**, 3836 (1964); (c) C. Y. Wu and P. E. Robertson, *Chem. Ind.* (*London*), 195 (1966).

(28) See Seltzer and Hamilton, Jr., Table III, footnote *f*.

(29) (a) A. V. Willi, *Z. Naturforsch. A*, **21**, 1377 (1966); *A*, **21**, 1385 (1966); (b) A. V. Willi and C. M. Won, *J. Amer. Chem. Soc.*, **90**, 5999 (1968).

$$(k_H/k_D)_{subs}/(k_H/k_D)_{IV} = \exp[(1 - 1/\bar{r})(hc/2kT)\sum_i(\nu_{H,i,subs} - \nu_{H,i,IV})] \quad (3)$$

The problem reduces to calculating the reduction in the α-benzylic hydrogen force constants required to reproduce the value of the frequency difference term in eq 3 for various values of $\bar{r}$ (see Table VI, columns 3, 5, and 7). With the force constants and bond lengths given by Seltzer and Mylonakis for IV,[5] normal mode frequencies were calculated for the tetrahedral pseudoreactant molecule IX in which C_6H_5, X (CH_3 or CH_3OCH_2), and W (α-phenylethylazo group) were assigned point masses 77, 15 or 45, and 133, respectively. Vibrational frequencies were calculated for masses of X equal to 15 and 45 and in each case for α-protium and deuterium. The frequencies are seen (Table VII) to be reasonable. In harmony with changes in potential energy, these data lead to the following frequency assignments: ν_1 is a pure CH stretch, ν_7, ν_8, and ν_9 involve $CXW(C_6H_5)$ bending motions, the pseudosymmetric $CXW(C_6H_5)$ stretch is ν_6, and, although there is coupling of the internal coordinates in the normal modes, ν_2 and ν_3 can be assigned principally to the hydrogen bending frequencies and ν_4 and ν_5 to the $CXW(C_6H_5)$ asymmetric stretching motions. The assignments for IX, $HCXW(C_6H_5)$, are analogous to those of the structurally related compound chloroform, $HCCl_3$.[30] Total bending force constant reductions of 15 (results presented in Table VIII) and 25% produce total frequency decreases of *ca.* 70 and 115 cm^{-1}, apparently independently of whether the change is assigned to one motion or equally divided over all three. Approximately 90% of the total frequency changes (Table VIII) are seen to reside in ν_2–ν_5, in harmony with the frequency assignments.



IX

Table VII. Frequencies for Pseudomolecule IX

	Frequencies, cm^{-1}, for X					
	CH_3, mass 15			CH_3OCH_2, mass 45		
	α-H	α-D	ν_H/ν_D	α-H	α-D	ν_H/ν_D
ν_1	2923	2159	1.35	2923	2158	1.35
ν_2	1385	1275	1.09	1361	1219	1.12
ν_3	1339	1216	1.10	1335	1208	1.11
ν_4	1033	834	1.24	949	758	1.25
ν_5	940	740	1.27	933	735	1.27
ν_6	761	711		730	700	
ν_7	385	382		269	268	
ν_8	294	294		206	206	
ν_9	195	194		188	188	

The model, simplified force field analysis with its neglect of off-diagonal force constants, and absence of ir analysis of this class of compounds warrant only tentative conclusions concerning nontransferability of force constants as an explanation for reductions in the α effect. A total decrease of *ca.* 9 and 22% (by interpolation) in the CH bending force constants is required to account for the smallest and the largest $\Delta\Delta\nu$ in Table VI. Force constant nontransferability as an acceptable explanation for the reductions in the α effect appears to depend upon the number of bending constants affected and upon the magnitude of $\bar{r}$. Evidence has been presented that an $\bar{r}$ value of 1.31 is more realistic than one of 1.35.[27a,b] For IX five frequencies, ν_1–ν_5, are associated with the CH motion. The related r_i values (Table VII), computed from the corresponding frequencies from IX-H and IX-D, when averaged indicate the even smaller $\bar{r}$ value of 1.21. The observed reductions in the α effects (Table VI) would then require about 3–7, 4.5–11, or 9–22% reduction averaged over all three, any two, or one of the bending force constants. For $\bar{r} \geq 1.35$, which seems unreasonable, transferability of reactant force constants is perhaps an acceptable explanation for *meso*-III, but for $\bar{r} \leq 1.31$, a reasonable expectation, it becomes very tenuous for all four compounds.

Table VIII. Reactant Frequencies as a Function of Changes in C–H Bending Force Constants in IX

ν_1	Frequencies, cm^{-1} IV[a]	$\Delta\nu$, cm^{-1} for % reduction in 15% HCN	15% HCC_6H_5	15% $HCCH_3$	5% in each
ν_1	2923	0	0	0	0
ν_2	1385	−2	−11	−34	−21
ν_3	1339	−38	−33	−7	−22
ν_4	1033	−4	−5	−26	−11
ν_5	940	−14	−14	−1	−9
ν_6	761	−5	−4	−1	−3
ν_7	385	−2	−2	−2	−2
ν_8	294	0	0	0	0
ν_9	195	−1	−1	−1	−1
Total $\Delta\nu$		−66	−70	−72	−69

[a] For Y = CH_3 (mass 15) and force constants from ref 5.

To alter the α effect by a given percentage, we conclude, would require in general a similar percentage alteration in the force field associated with the α C–H bond in the reactant. Thus nontransferability would appear to be an acceptable qualitative explanation only for small variations in the α effect.

Experimental Section[31]

α,α-Dimethoxyacetophenone Azine. α-Methoxyacetophenone[32] (36.6 g, 0.234 mol) and anhydrous hydrazine (4.1 g, 0.128 mol) were refluxed for 1 hr in absolute ethanol (35 ml) containing 10 drops of glacial acetic acid. The crude product obtained from evaporation of the ethanol under reduced pressure was taken up in ether, washed with a saturated solution of sodium bicarbonate and with water, and dried over magnesium sulfate. Recrystallization three times from methanol yielded 24.6 g (71%) of product, mp 58–59°.

Anal. Calcd for $C_{18}H_{20}N_2O_2$: C, 72.95; H, 6.80; N, 9.45. Found: C, 73.08; H, 6.67; N, 9.57.

n-Butyrophenone Azine. n-Butyrophenone (Aldrich Chemical) (54.6 g, 0.37 mol) and 6.2 g (0.18 mol) of anhydrous hydrazine dissolved in 70 ml of absolute ethanol were converted to the azine by the above procedure. Recrystallization from methanol yielded 46 g (86%) of product, mp 40–41°.

Anal. Calcd for $C_{20}H_{24}N_2$: C, 82.15; H, 8.27; N, 9.58. Found: C, 82.21; H, 8.30; N, 9.58.

2,2'-Dimethoxy-1,1'-diphenylazoethane (I). Method a. Palladium on charcoal (5%), 2.0 g, suspended in 70 ml of tetrahydrofuran

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(30) C. Herzberg, "Infrared and Raman Spectra," Van Nostrand, Princeton, N. J., 1945, pp 316, 317.

(31) (a) All melting points are uncorrected. (b) Elemental analyses performed by Galbraith Laboratories, Inc. (c) Deuterium analysis by combustion performed by Mr. Josef Nemeth, Urbana, Ill.

(32) R. B. Moffett and R. L. Shriner, "Organic Syntheses," Collect. Vol. III, Wiley, New York, N. Y., 1955, p 562.

was equilibrated with hydrogen gas, and 6.02 g of the methoxy azine was then reduced at atmospheric pressure. Two to three hours were required for uptake of 2 mol of hydrogen. The hydrazine obtained from the reaction mixture was oxidized in benzene with yellow mercuric oxide.[3] Crude I was repeatedly recrystallized from *n*-hexane: mp 83.8–84.8°; $\lambda_{\max}$ 361 mμ (ϵ (benzene) 41.4); nmr (CCl_4) δ 3.1 (6 H, $-OCH_3$); δ_{av} 3.8 (4 H, β-CH_2) d of quartets, AB portion of ABX ($|J_{AB}| = 10.1$ Hz, $|J_{AX} + J_{BX}| = 13.2$ Hz); 4.7 (2 H, α-CH) four lines, X portion of ABX ($|J_{AX} + J_{BX}| = 13.2$ Hz); 7.2 (10 H, C_6H_5) m.

Anal. Calcd for $C_{18}H_{22}N_2O_2$: C, 72.46; H, 7.43; N, 9.39. Found: C, 73.06; H, 6.99; N, 9.51.

Method b. The same procedure was followed except that the reduction was carried out in benzene which had been repeatedly washed with sulfuric acid, aqueous sodium hydroxide, and water, dried over magnesium sulfate, and distilled from sodium metal.

2,2′-Dimethoxy-1,1′-diphenylazoethane-*1,1′-d*$_2$ (Ia). Method a. Palladium on charcoal (5%), 1.0 g, suspended in 55 ml of ethanol-*O-d* was equilibrated with deuterium gas; 5.4 g of the methoxy azine was then reduced at atmospheric pressure. After the requisite volume of gas had been taken up, the reaction mixture was worked up by the usual procedure. Crude Ia was repeatedly recrystallized from *n*-hexane: mp 84.5–85.2°; $\lambda_{\max}$ 361 mμ; (ϵ (benzene) 41.8); nmr (CCl_4) δ_{av} 3.9 (β-CH_2), AB($|J_{AB}| = 10.1$ Hz).

Method b. Purified benzene was used as solvent as in method b for I.

1,1′-Diphenylazobutane (II). *n*-Butyrophenone azine, 9.0 g, was reduced by method b for I in 75 ml of purified benzene containing 3 g of 5% Pd/C. Crude II was repeatedly recrystallized from methanol: mp 57.5–58.5°; $\lambda_{\max}$ 361 mμ (ϵ (benzene) 43.2); nmr (CCl_4) δ_{av} 1.1 (10 H, 4γ-CH_2 + 6CH_3) m; 2.0(4 H, β-CH_2) m; δ 4.4 (2 H, α-CH) t; δ_{av} 7.2 (10 H, C_6H_5) m.

Anal. Calcd for $C_{20}H_{26}N_2$: C, 81.16; H, 8.90; N, 9.51. Found: C, 81.17; H, 9.32; N, 9.63.

1,1′-Diphenylazoethane-*1,1′-d*$_2$ (IIa). *n*-Butyrophenone azine, 12 g, was reduced by method b for IIa using *ca.* 100 ml of purified benzene and 4 g of 5% Pd/C. Crude IIa was repeatedly recrystallized from methanol: mp 57.5–58.5°; $\lambda_{\max}$ 361 mμ (ϵ (benzene) 43.2).

Kinetics. The isotope effects were determined by simultaneously measuring the rates of decomposition of the protium and deuterium compounds as previously described.[3]

Deuterium Content and Correction of Isotope Effects. The nmr measurement of deuterium content involved at least two independent determinations of the proton ratios for the labeled and unlabeled compounds by integration following repetitive scanning with a Varian C-1024. All spectra were taken in carbon tetrachloride. For Ia, made by reduction of the azine in ethanol-*O-d*, measurements were independently made by two of us. The wiggle-beat pattern on the high-field side of the methyl absorption in the spectra of I and Ia prevented accurate and reproducible determinations of the methyl proton ratios. Since precedent[33] exists for expecting essentially no excess deuterium in the phenyl rings, an assumption implicit in the nmr analysis, the discrepancy then most reasonably results from deuterium in the methyl groups of Ia.

The difference in deuterium content for sample 1 of Ia between combustion and nmr was resolved by repetitively integrating single-scan nmr spectra of solutions of I and Ia in chloroform-*d* (100 atom % D) containing methylene chloride (X). Chloroform-*d* was chosen because of increased compound solubility. The mole ratios of I:X and Ia:X were chosen to be *ca.* 1:5 so as to yield nearly identical areas under the proton absorption peaks of interest due to the azo compound (aromatic and methylene plus methyl) and X. To achieve maximum accuracy the areas under the methylene and methyl absorptions were taken together and the atoms of deuterium total in the methylene plus methyl groups were calculated. The analysis yielded 0.65 ± 0.03 atom of D in the methylene plus methyl groups of sample 1 of Ia. The atoms of deuterium in the methyl groups of Ia are calculated to be 0.37. No excess deuterium was observed in the phenyl groups, *i.e.*, ±0.1 atom of D (±1.0 atom % D). The agreement in total atoms of deuterium between combustion, 2.41, and nmr, 2.38 ± 0.04 is quite satisfactory. Including the maximum atoms of aromatic D results in less than a 3% difference in total atoms of D, *i.e.*, 2.41 *vs.* 2.47. Since no kinetic isotope effect is expected from methyl deuterium, the observed isotope effect was corrected for the atoms of α protium and β deuterium as determined by nmr (Table III). The magnitude of the β effect was evaluated on the assumption that it equals that for decomposition of IV per D.[28,35] The value of $(k_H/k_D)_{cor}$ so obtained is in excellent agreement with the value for sample 2 of Ia, assuming, 0.65 atom of β-D produces a negligible alteration in the corrected effect, *i.e.*, 1.182.

Duplicate analysis of the atom per cent excess D by combustion differed by ±0.03–0.04%.

The isotope effects were corrected to 2 atoms of α-D using the previously given equation.[3] The standard deviation in the corrected α effect was computed from the standard deviations associated with the average experimental isotope effect and with the atoms of α deuterium as previously described.[3] For sample 1 of Ia the error analysis incorporates the standard deviations associated with the β effect.

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(33) The reduction of acetophenone azine in dioxane with Pd/C results in ≦0.07 atom % D incorporation in the phenyl rings.[2c] Negligible, if any, exchange of aromatic ring protium for deuterium accompanies reduction (Pd/C) of the azine precursors to *meso*- and *dl*-III in tetrahydrofuran and to Ia and IIa in benzene (*vide supra*). The diphenylmethane-α,α-d_2 from catalytic reduction of benzophenone in glacial acetic acid-*O-d* has 99.9 atom % H in the phenyl rings.[34]

(34) S. E. Scheppele, R. K. Mitchum, J. W. Burnham, and E. J. Eisenbraun, *J. Catal.*, **19**, 89 (1970).

(35) Very similar β isotope effects have been observed in perester decompositions[36] and chlorination of isobutane,[37] both free-radical reactions.

(36) (a) T. Koenig and W. Brewer, *Tetrahedron Lett.*, 2773 (1965); (b) T. Koenig and R. Wolf, *J. Amer. Chem. Soc.*, **89**, 2948 (1967); (c) T. Koenig and R. Wolf, *ibid.*, **91**, 2574 (1969).

(37) E. M. Hodnett and P. S. Juneja, *J. Org. Chem.*, **33**, 1233 (1968).