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Pull-Push Mechanism for the 1,2-Hydrogen Rearrangement of Carbenes. Substituent and Deuterium Isotope Effects for Thermal Decomposition of 1-Phenyl-2-diazopropanes[1]

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Abstract: Intramolecular and intermolecular deuterium isotope effects have been measured for the thermal carbene H rearrangements of three substituted 1-phenyl-2-diazopropanes-*1-d* in hexane at 25 °C. The isotope effects, k_H/k_D, vary from ca. 1.2 to 1.5, increasing with electron-withdrawing substituents, for the formation of both *cis*- and *trans*-β-methylstyrenes. Product ratios were determined for these compounds as well as the corresponding undeuterated ones, permitting calculation of intermolecular primary and secondary isotope effects. In addition, the competition among the cis and trans products and the product of H migration from the terminal methyl group permitted determination of Hammett ρ values of ca. -1 for the competition between benzylic and terminal migration. The results strongly indicate a "pull-push" mechanism, which can be pictured roughly as electrophilic attack on the C-H bond by the phantom p orbital of the carbene along with backside nucleophilic attack by the carbene unshared electron pair to push the H away and form the π bond. The data are believed to be consistent only with a nonzero barrier for the carbene hydrogen rearrangement.

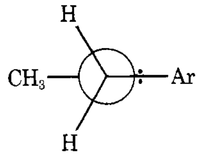
We have determined product ratios and competitive isotope effects for the hydrogen shift rearrangement in the thermal decomposition of substituted 1-phenyl-2-diazopropanes-*1-d* (eq 1) and the corresponding undeuterated compounds,

$$\mathrm{ArCHD{-}C(N_2)CH_3 \rightarrow ArCD{=}CHCH_3 + ArCH{=}CDCH_3 + ArCHDCH{=}CH_2} \quad (1)$$

in hexane at 25 °C. Both cis and trans isomers of β-methylstyrene are produced. The reactions are believed to proceed through an intermediate singlet carbene.[2] Primary diazo compounds have been reported to undergo self-catalyzed, cationic decompositions in competition with the production of carbenes,[3] but the secondary diazo compounds we have studied do not have an acidic hydrogen attached to the diazo carbon. Since our diazo compounds were generated under basic conditions and were allowed to decompose in the nonpolar solvent hexane, we believe that the reactions proceed exclusively by the carbene mechanism. Additional evidence includes the absence of appreciable deuterium loss during the reaction, ruling out significant proton intrusion from the glass surface, as discussed in the Experimental Section. It has also been found that 2-diazopropane is thermally unstable, with a half-life of 3 h at 0 °C in ether.[4] Although we have studied product competition and not rates, our compounds decomposed at rates of the same order of magnitude as that for 2-diazopropane.

MO-following considerations suggest ready rearrangement through gauche hydrogen migration,[5] and experiment indicates that an approximately perpendicular hydrogen (resembling gauche) rearranges more readily than an antiplanar one.[6] MO calculations favor a gauche migration in the case of methylcarbene,[7,8] but barriers to rearrangement of 0 and 21 kcal mol^{-1}, respectively, have been reported. The barrier for H rearrangement of the triplet carbene was calculated as 88 kcal mol^{-1}.[8]

An experimental study of the mechanism of rearrangement seemed particularly desirable in view of the question about barrier height. The mechanism indicated to be favorable[5-8] is quite interesting, since it involves a migration of H in a sort of spiral path and can be thought of as involving an electrophilic pull of hydride through the phantom p orbital of the carbene and concerted π-bond formation via backside attack of the carbene unshared electron pair to push the hydride off the carbon to which it was originally attached (*pull-push* mechanism), starting from approximate carbene conformations t, c, and T for formation of trans, cis, and terminal olefin.



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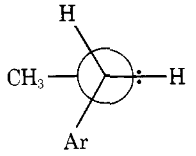

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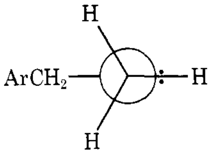

T

Cyclic electron reorganizations cannot rigorously be described as hydride transfers—in fact, there is significant delocalization so that the unshared pair is not really distinguishable in the transition state[5]—but the electron density at the benzylic carbon and the polarization of the C-H bond being broken can be probed with substituent and isotope effects, giving the following information.

(1) Isotope effects, k_H/k_D, for hydrogen migration are near 1.4, similar to those reported in a few other carbene rearrangements,[6,9-11] near the classical limit of $2^{1/2}$ and thus consistent with a very low or zero barrier.[12] (2) Hammett ρ values are approximately -1, some curvature being observed,

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Table I. Product Fractions from Thermal 1,2-H Rearrangement of $p\text{-ZC}_6\text{H}_4\text{CH}_2\ddot{\text{C}}\text{CH}_3$ and $p\text{-ZC}_6\text{H}_4\text{CHD}\ddot{\text{C}}\text{CH}_3$ in *n*-Hexane at 25 °C[a]

	Undeuterated series products			Deuterated series products		
Z	Trans (x_t)	Cis (x_c)	Term. (x_T)	Trans (x_t^D)	Cis (x_c^D)	Term. (x_T^D)
CH$_3$	0.734 ± 0.015	0.188 ± 0.011	0.078 ± 0.004	0.729 ± 0.015	0.184 ± 0.004	0.088 ± 0.004
H	0.688 ± 0.014	0.206 ± 0.012	0.106 ± 0.004	0.681 ± 0.006	0.195 ± 0.003	0.124 ± 0.003
Cl	0.607 ± 0.007	0.129 ± 0.005	0.264 ± 0.012	0.592 ± 0.014	0.119 ± 0.002	0.287 ± 0.010

[a] Product ratios are uncorrected GLC peak area ratios. Deuterated ratios are those experimentally observed, so that a certain amount of undeuterated products is also included. Actual fractions of deuterated product determined from ^{1}H NMR integrations can be calculated from Table III. Average deviations are listed for two separate, complete reactions.

Table II. Deuterium Kinetic Isotope Effects for Carbene 1,2-H Rearrangement of $p\text{-ZC}_6\text{H}_4\text{CHD}\ddot{\text{C}}\text{CH}_3$ in *n*-Hexane at 25 °C

Z	$(k_H/k_D)_{intra}$[a]	$(k_H/k_D)_{inter}$[b]	$(k_H/k_D)_{sec}$[c]
	Trans Series		
CH$_3$	1.18 ± 0.03	1.19 ± 0.01	1.01
H	1.34 ± 0.01	1.40 ± 0.01	1.05
Cl	1.46 ± 0.03	1.34 ± 0.02	0.92
	Cis Series		
CH$_3$	1.36 ± 0.02	1.39 ± 0.02	1.02
H	1.47 ± 0.02	1.51 ± 0.08	1.04
Cl	1.56 ± 0.03	1.49 ± 0.00	0.96

[a] The ratio of H migration to D migration gives the intramolecular isotope effect, $= f^{\alpha D}/f^{\beta D}$, where the f's are atom fractions of deuterium α and β to the phenyl group. [b] Calculated as $(1/2)(x_t/x_T)(x_T^D/x_t^D)(f_T^{HD}/f_t^{\beta D}) = (k_t/2k_t^D)/(k_T/k_T^{HD})$ where f_T^{HD} is the atom fraction D in terminal olefin product and the statistical factor of 2 arises from the presence of two benzylic H in the undeuterated diazo compound. Assuming that the secondary isotope effect for terminal H migration, k_T/k_T^{HD}, is small, this equals the intermolecular isotope effect, $k_t/2k_t^D$, with a corresponding expression for cis product. [c] Given by the ratio of inter- to intramolecular primary isotope effects.

for the competition between benzylic and terminal H migration. The effect of substituents on terminal migration must be small, and therefore the ρ values demonstrate a significant electron deficiency at the benzylic carbon. (3) Both the selectivity favoring benzylic over terminal migration and the sizable ρ values demonstrate that there is a significant barrier for both the terminal and the benzylic migrations. (4) A polarization $C^{\delta+}$---$H^{\delta-}$ for the bond being broken is indicated by isotope effects which increase with more electron-withdrawing substituents. These results strongly indicate a pull-push type transition state in which "hydride-like" H transfer leads π-bond formation.

The results are difficult to rationalize in terms of nonclassical carbene structures suggested by INDO MO calculations,[13] which ought to have larger isotope effects since the hydrogen is bridged between carbons.

Results

The deuterated and undeuterated diazo compounds were prepared by high-vacuum pyrolysis of the lithium tosylhydrazone salts from the corresponding ketones. Diazo compounds of >85% purity (<15% rearrangement product present) were produced, as shown by ^{1}H NMR at −20 °C, sufficient to ensure accuracy of intramolecular isotope effects (rather temperature insensitive) and product compositions after complete reaction at 25 °C in hexane. Product fractions are given in Table I, and isotope effects derived by calculation of atom fractions of deuterium at carbons α and β to the substituted phenyl groups through precise ^{1}H NMR integrations on the products isolated by GLC, which corrects for the presence of undeuterated diazo compound, are given in Table II. Atom fractions of deuterium found are given in Table III. The range of substituents investigated was limited by the requirement of obtaining significant yields of both conjugated and terminal olefins so that product fractions could be accurately determined.

Discussion

Several points emerge from the data. (1) The very low isotope effects imply a highly reactant-like or product-like transition state for the hydrogen rearrangement according to the Westheimer effect.[14] The equilibrium isotope effect would be about 1.4 (conversion of sp^3 to sp^2 carbon–hydrogen bonding[15]), so that it is difficult to rationalize the small observed isotope effects with a product-like transition state.[16] (2) The secondary isotope effects probably have significant errors, since their calculation depends on the product ratios as shown in Table II, footnote *b*. However, they appear to be so small as to preclude product-like transition states, since the equilibrium isotope effect for this position also involves sp^3 → sp^2 and would be about 1.4.[15] Instead, they suggest very reactant-like transition states. (3) The fact that significant amounts of terminal olefin are formed indicates a low selectivity characteristic of a low barrier and a reactant-like (with respect to H migration) transition state for the carbene rearrangement. The high cis/trans selectivity could result from steric factors in the transition states similar to those determining the populations of the reactant carbene conformations (c and t) and is thus consistent with a low barrier and reactant-like transition states. (4) Plots of log (k_t/k_T) and log (k_c/k_T), where the rate constant ratios are, for competitive rearrangement, equal to the product ratios (Table I), vs. Hammett σ values for the substituents will have slopes of $(\rho_t - \rho_T)$ and $(\rho_c - \rho_T)$, respectively. Since terminal rearrangement involves processes far from the phenyl ring, ρ_T will be small and the slopes of these plots will be nearly equal to ρ_t and ρ_c. The slopes are near negative unity for both trans and cis. Some negative curvature is also found in both plots (as well as in plots vs. σ^+), which might indicate a variable transition state with respect to charge development at the benzylic carbon, although one cannot take the curvature seriously at present, with only three substituents. These slopes do, however, demonstrate significant electron deficiency at the benzylic carbons in the transition states for H rearrangement. (5) Since it has been established by the above points that the transition state is reactant-like with respect to H migration, the trend of intramolecular isotope effects with substituent (Table II) can be interpreted in terms of the Westheimer effect.[14] There is a small but significant trend toward larger isotope effects with more electron-withdrawing substituents for the intramolecular case;[17] the intermolecular primary and secondary effects do not show so clear a trend, but their inherent errors are larger and may be systematic, since they (but not the intramolecular isotope effects) depend on observed product ratios (Table II, footnotes).[18] On the reactant-like side of the Westheimer-effect maximum, isotope effects increase as the hydrogen becomes more completely transferred, and this should occur for the slower ($\rho < 0$), more electron-withdrawing substituents according to Hammond-postulate considerations,[19] as well as being predicted for $C^{\delta+}$---$H^{\delta-}$ polarization of the bond being broken in the transition state, since electron withdrawal would

Table III. Deuterium Fraction in Products from Thermal 1,2-H Rearrangement of p-$ZC_6H_4CHD\ddot{C}CH_3$ in n-Hexane at 25 °C[a]

	Trans product				Cis product				Terminal product[b]
	Phenyl[b]		Methyl[c]		Phenyl[b]		Methyl[c]		
	$f_t^{\alpha D}$	$f_t^{\beta D}$	$f_t^{\alpha D}$	$f_t^{\beta D}$	$f_c^{\alpha D}$	$f_c^{\beta D}$	$f_c^{\alpha D}$	$f_c^{\beta D}$	f_T^{HD}
CH_3[d]	0.396	0.328	0.411	0.343	0.391	0.281	0.409	0.303	0.687
e	0.375	0.326	0.380	0.328	0.392	0.290	0.396	0.295	0.687
H[d]	0.361	0.270	0.352	0.259	0.395	0.274	0.383	0.259	0.636
e	0.349	0.264	0.345	0.258	0.358	0.243	0.354	0.238	0.630
Cl[d]	0.294	0.206	0.284	0.194	0.305	0.200	0.299	0.192	0.504
e	0.307	0.207	0.305	0.205	0.306	0.194	0.300	0.189	0.490

[a] Carbene not completely deuterated; therefore, total f^D for each product $\neq$ 1.0. These totals are not necessarily equal for the three different products, since the presence or absence of D will influence the fraction of carbene traversing each of the three product-forming pathways. Fractions f were in each case calculated from the formula $f = n -$ (integration of H at carbon being calculated)/(std), where std is the standard integration based on phenyl or methyl protons, as defined in footnotes *b* and *c*, and n is the number of chemically equivalent positions in question (= 1 for trans and cis, = 2 for terminal). Integration curves were repeatedly scanned until stable, then three to five curves were averaged. Isotope effects were calculated from each set of data and averaged to give the results shown in Table II. [b] Based on phenyl protons = 5 for Z = H; = 4 for Z = CH_3, Cl. [c] Based on methyl protons = 3 for Z = H, Cl; = 6 for Z = CH_3 (total of two methyl groups). [d] Reaction 1. [e] Reaction 2.

exert a force along the reaction coordinate opposing H migration, thus shifting the transition state geometry in the direction opposite to the force, i.e., to increased degree of H migration.[20] (6) These changes of isotope effect with substituent, as well as the larger isotope effects for the cis series than for the trans, also indicate that a barrier to H migration exists. The slower cis migration[19] and the predicted steric force effect opposing formation of cis product[20] both predict that H migration should be more complete for cis. The larger effects for cis are inconsistent with a hyperconjugative effect in the carbene as controlling the isotope effects, since conformation c would be, if anything, misaligned and therefore would have a smaller hyperconjugative interaction. (7) To the extent that the negative curvature in the $\rho\sigma$ plots is significant, it is also consistent with more extensive H migration with electron-withdrawing substituents, ρ becoming more negative.

The data presented provide multiple evidence favoring the existence of a barrier to H migration in carbenes, the pull-push mechanism, and the hydride-like nature of the migration.

Experimental Section[1b]

Melting points were determined with a Thomas-Hoover apparatus. Elemental analyses were performed by Micro-Analysis, Inc., Marshallton, Wilmington, Del. GLC was carried out on a Perkin-Elmer Model F-21, using a 6.7 mm × 12 m column packed with 20% Carbowax 20M on 60/80 mesh Chromosorb P, with N_2 as carrier gas. ^1H NMR spectra were determined on Varian A-60 and HA-100 NMR spectrometers; the latter was used for integration and decoupling studies. All samples were 10% carbon tetrachloride (spectrophotometry grade) solutions, using tetramethylsilane (Me_4Si) as internal standard. Chemical shifts are reported in δ units (parts per million downfield from Me_4Si). Infrared spectra were determined on Perkin-Elmer Model 137 and 521 spectrophotometers.

Benzaldehydes-*α-d*. Stephen reaction of benzonitrile, *p*-tolunitrile, and *p*-chlorobenzonitrile (all from Aldrich) with $SnCl_2$ and DCl, followed by hydrolysis, gave the benzaldehydes-*α-d*, in a manner similar to the reaction with HCl.[21] Properties for the deuterated aldehydes and literature values for undeuterated aldehydes were as follows: *p*-H, bp 76 °C (20 mm) [lit.[22a] 179 °C (751 mm)]; *p*-CH_3, bp 73 °C (10 mm) (lit.[22b] 204-205 °C); *p*-Cl, mp 46 °C (lit.[22c] 47 °C). They were also characterized by ^1H NMR, showing 0.899, 0.959, and 0.905 atom D per molecule, respectively. The C-D stretching infrared frequencies of benzaldehyde-*α-d* were identical with those previously reported.[23]

Benzyl-*α-d* Alcohols. The benzaldehydes were each reduced by $LiAlH_4$.[24] Properties for the deuterated alcohols and literature values for undeuterated alcohols were as follows: *p*-H, bp 70-71 °C (2 mm) [lit.[25a] 93 °C (10 mm)]; *p*-CH_3, mp 61 °C (lit.[25b] 61-62 °C); *p*-Cl, mp 74 °C (lit.[25c] 75 °C). They were also characterized by ^1H NMR, showing 0.896, 0.958, and 0.896 atom D per molecule, respectively.

Benzyl-*α-d* Bromides. The bromides were prepared by reaction of the alcohols with PBr_3 in ether.[26] Properties for deuterated bromides and literature values for undeuterated bromides were as follows: *p*-H, bp 61-62 °C (2 mm) [lit.[27a] 127 °C (80 mm)]; *p*-CH_3, mp 35 °C (lit.[27b] 35 °C); *p*-Cl, mp 49-51 °C (lit.[27c] 51 °C). They were also characterized by ^1H NMR, showing 0.893, 0.915, and 0.869 atom D per molecule, respectively.

Phenyl- and *p*-Tolylacetic-*α-d* Acids. This procedure did not work satisfactorily for the *p*-Cl compound, so an alternative route, described below, was adopted. The Grignard reagents of the *p*-H and *p*-CH_3 bromides were formed and carboxylated.[28] Properties for deuterated acids and literature values for undeuterated acids were as follows: *p*-H, mp 75-76 °C (lit.[29] 76-76.5 °C); *p*-CH_3, mp 93-94 °C (lit.[30] 91-92 °C). They were also characterized by ^1H NMR, showing 0.778 and 0.843 atom D per molecule, respectively.

1-Phenyl- and 1-(*p*-Tolyl)acetone-*1-d*. The acid chlorides were prepared from the above acids by reaction with $SOCl_2$,[31] and the purified acid chlorides were allowed to react with zinc-methyl iodide to give the corresponding acetone derivatives,[32] the key point in the success of this procedure in our hands being simply to ensure that the zinc-methyl iodide reagent was fully formed before addition of the acyl chloride. Commercial zinc-copper couple was activated at 150 °C in a dry nitrogen atmosphere, then refluxed at the same temperature with excess methyl iodide until a black solution formed. Properties for deuterated ketones and literature values for undeuterated ketones were as follows: *p*-H, bp 64-65 °C (2 mm) [lit.[33a] 86-87 °C (6 mm)]; *p*-CH_3, bp 75 °C (2 mm) (lit.[33b] 232-233 °C). They were also characterized by ^1H NMR, showing 0.637 and 0.713 atom D per molecule, respectively.

1-(*p*-Chlorophenyl)acetone-*1-d*. 1-(*p*-Chlorophenyl)-2-propanol-*1-d* was prepared by Grignard reaction of *p*-chlorobenzyl-*α-d* bromide with acetaldehyde,[34] and the crude alcohol was oxidized by CrO_3 in pyridine,[35] giving 1-(*p*-chlorophenyl)acetone-*1-d*, bp 95-96 °C (2 mm) [lit.[36] for undeuterated compound 100-101 °C (3 mm)]. The ^1H NMR showed 0.519 atom D per molecule.

1-Phenyl-, 1-(*p*-Tolyl)-, and 1-*p*-Chlorophenylacetone-*1-d* *p*-Toluenesulfonylhydrazones. The deuterated tosylhydrazones were prepared from the ketones by reaction with tosylhydrazine,[37] and undeuterated tosylhydrazones were also prepared in exactly the same way. Data for deuterated, followed by undeuterated, tosylhydrazones were as follows: *p*-H, mp 136-138, 136-137 °C (lit.[37] 134-135 °C for undeuterated); *p*-CH_3, mp 148-150, 149-150 °C; *p*-Cl, mp 140, 140-141 °C. Analytical data were obtained for undeuterated tosylhydrazones.

p-CH_3 Anal. ($C_{17}H_{20}N_2O_2S$) C, 64.73; H, 6.42.

p-Cl Anal. ($C_{16}H_{17}N_2O_2SCl$) C, 56.82; H, 4.94; O, 9.57.

1-Phenyl-2-diazopropanes. The lithium salts of the deuterated and undeuterated tosylhydrazones were prepared by reaction with butyllithium in tetrahydrofuran at 0 °C. Solvent was removed using a rotary evaporator, leaving the dry lithium salt on the inside walls of the flask. This flask was attached to a receiving flask cooled in a dry ice-acetone bath, and the system was evacuated. The lithium salt was heated at 160-170 °C at 0.01-0.1 mm (0.05-0.01 mm for *p*-Cl compounds) for 1 h. It was necessary to keep the pressure this low in order to obtain >85% pure diazo compounds. Wine-red or orange product condensed in the receiving flask. Integration of phenyl and vinyl protons in ^1H NMR spectra below −20 °C showed <15% rearrangement products.

Thermal Decomposition of Diazo Compounds. Decomposition of the diazo compounds was allowed to take place at 25 °C in hexane solutions of concentration 10–15% (w/v). Solvent was evaporated after complete decomposition and the products were analyzed and isolated by GLC. In each case, only the three olefinic rearrangement products as listed in Table I could be found on the GLC. From the data in Tables I and III, the calculated atoms of D per molecule in the mixed olefin product of rearrangement are 0.619 ± 0.015, 0.713 ± 0.019, and 0.498 ± 0.008 for *p*-H, *p*-CH_3, and *p*-Cl, respectively. These values are essentially equal to the corresponding ones for the ketones from which the tosylhydrazones were prepared, as given above, and they rule out the possibility of proton-exchanging processes involving any significant proton pool during the preparation and decomposition of the diazo compounds. In particular, protonation of diazo compounds by significant numbers of protons from the glass flask surface, leading to diazonium ions and elimination to olefin, is ruled out, since even in the presence of a reasonable isotope effect, significant deuterium depletion in the olefin products would result. A catalyzed process involving a small pool of glass protons would require absorption of the organic ions on the glass surface in association with Si–O^- counterions, with the glass sites acting to relay protons and deuterons eliminated onto another molecule of diazo compound. Since our diazo compounds were studied in hexane solution rather than neat[3] and cannot undergo autocatalyzed protonic decomposition[3] because they are secondary, we believe that we have studied completely carbenic, and not cationic, processes. 2-Diazopropane is considerably more thermally labile[4] than diazoethane, which is reported to be stable in ether at 20 °C for over 12 h.[38] It therefore seems probable that secondary diazo compounds lose nitrogen more readily than primary in general, and this factor would make carbenic decomposition compete more effectively with cationic decomposition in the secondary case, as in our experiments.

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(18) It should be emphasized that the intramolecular isotope effects are very precise and, we believe, accurate, so that their trend is significant, but that the intermolecular primary and secondary effects are considered valid only in order of magnitude, so that only their orders of magnitude are interpreted. These intermolecular effects are subject to errors of perhaps ±5% from the product ratios used in their calculation; the standard deviations given in Table II reflect only the reproducibility of the isotope effect calculations and do not include this extra error from product ratios (Table I).

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