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The Stereochemistry of Rearrangements of Aryl and Hetaryl Groups to Primary Carbenic Centers

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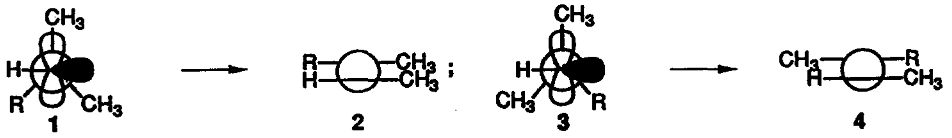
Abstract: The products and stereochemistries of carbenic decompositions of varied 2-aryl-1-diazoalkanes and 1-diazo-2-(2-hetaryl)propanes have been determined.

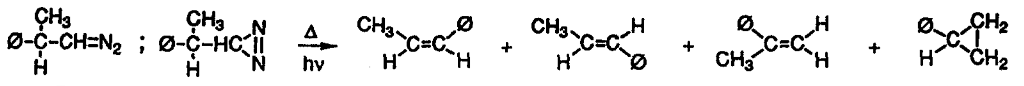
The stereochemistry of carbon-skeleton rearrangements of carbenes has not been well-established.[1a-e] In the only examples which reveal overall stereochemical differences in carbon skeletal rearrangements of alkyl carbenes (expressed as conformers 1 and 3) to olefins, methyl migrations in 2,2-dimethyl-1-butylidene (R = C_2H_5), 2,2,3-trimethyl-1-butylidene [R = $CH(CH_3)_2$], 2-cyclopropyl-2-methylpropylidene (R = c-C_3H_5), and 2-methyl-2-phenylpropylidene (R = C_6H_5) yield (E)-olefins 2 in preference to their more strained (Z)-isomers 4.[1f,g] It is not clear however whether the overall stereochemistries of the above methyl rearrangements are controlled in transition states (Eq 1) which reflect steric and electronic differences in initial conformers (1 and 3) or their developing subsequent olefins (2 and 4). Of note also are that migrations of the phenyl groups in *cis*- and *trans*-5-*t*-butyl-2-phenylcyclohexylidenes give 4-*t*-butyl-2-phenylcyclohexene preferentially by axial processes[1h] and thermolysis of 1-diazo-2,2-diphenylpropane yields (Z)- rather than (E)-1,2-diphenyl-1-propene.[1i] The overall stereochemistries of rearrangements of varied aryl and hetaryl groups to primary singlet carbenes are now reported. These studies define more clearly the effects of conformation, bridging, and reorganization in carbenic carbon-skeleton rearrangements to olefins.



(1)

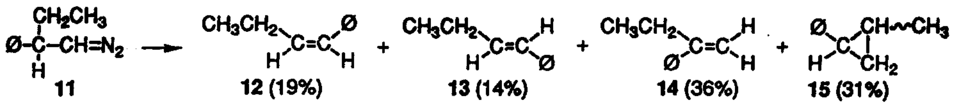
Thermolyses of 1-diazo-2-phenylpropane (5, Eq 2) generated *in situ* from 2-phenylpropanal *p*-tosylhydrazone and sodium hydride (1.0-1.1 equiv) or sodium methoxide (12 equiv) in diglyme at 115-160°C are now found to yield (Z)-1-phenyl-1-propene (7) and (E)-1-phenyl-1-propene (8) by phenyl migrations,[2] 2-phenylpropene (9) by hydrogen rearrangement, and phenylcyclopropane (10) by *beta* C-H insertion. These results are essentially identical to those for photolysis (25°C) of sodium 2-phenylpropanal *p*-tosylhydrazonate and thermolysis (100°C) or photolysis (25°C) of 3-(1-phenylethyl)diazirine (6, Eq 2) in benzene. The facts of present interest are that the ratios of 7:8 range from 1.80-

1.36:1.0 in all experiments and thus the more sterically strained (Z)-1-phenyl-1-propene 7 is produced more extensively than is its (E)-isomer 8.

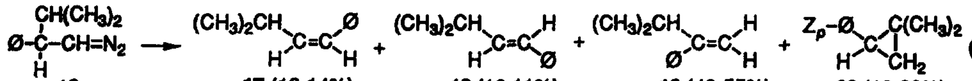


5 6 7 (18-13%) 8 (10-12%) 9 (38-41%) 10 (33-24%) (2)

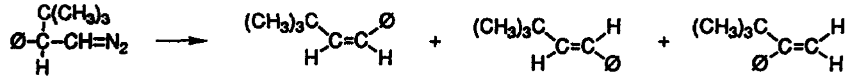
Phenyl migrations to give (Z)- rather than their isomeric less strained (E)-olefins also occur in carbenic decompositions of 1-diazo-2-phenylbutane (11, Eq 3) and 1-diazo-3-methyl-2-phenylbutane (16, Eq 4). At 160°C 11 converts to (Z)(12)- and (E)(13)-1-phenyl-1-butenes in 1.36:1.0 ratio and the ratios of (Z)(17)- to (E)(18)-3-methyl-1-phenyl-1-butenes from 15 at 160-250°C range from 1.39-1.13:1.0. Of particular difference then are that thermolyses of 1-diazo-3,3-dimethyl-2-phenylbutane (21, Eq 5) at 195-250°C yield (E)(23)-, the more stable isomer, in preference (2.0-1.5:1) to (Z)(22)-3,3-dimethyl-1-phenyl-1-butene by phenyl migrations along with 3,3-dimethyl-2-phenyl-1-butene (24). In none of the above experiments is there significant isomerization of the reaction products after formation.



11 12 (19%) 13 (14%) 14 (36%) 15 (31%) (3)



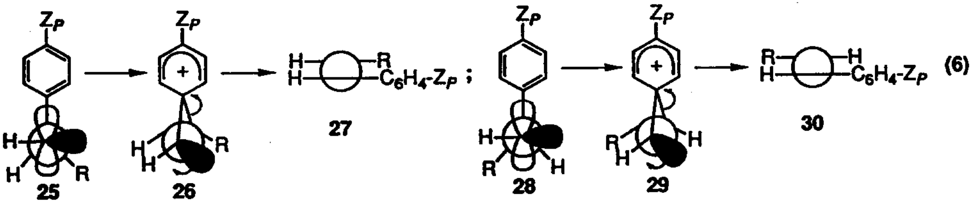
16 17 (18-14%) 18 (16-11%) 19 (49-55%) 20 (18-20%) (4)



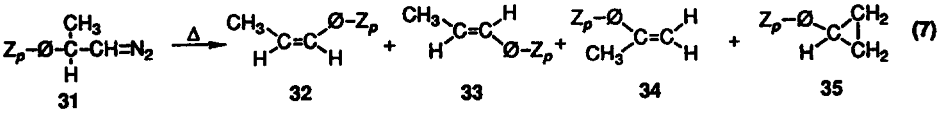
21 22 (11-9%) 23 (20-15%) 24 (67-76%) (5)

Phenyl migrations in conversions of 5, 6, 11, and 16 to (Z)-olefins (7, 12, and 17) in preference to their thermodynamically more stable (E)-isomers (8, 13, and 18) are revealing. Such rearrangements are interpretable upon electron-donor bridging of the phenyl groups in singlets 25 and 28 (Eq 6) to form 26 and 29 [Z = H and R = CH_3, C_2H_5, and $(CH_3)_2CH$] in which the eclipsed substituents on C-2 suffer greater repulsions from the hydrogen atom than from the non-bonded electron pair on C-1.[3a,b] On the basis that eclipsing repulsion by hydrogen on C-1 is dominant and thence less with hydrogen than for methyl, ethyl, and 2-propyl on C-2, 26 [Z_p = H, R = CH_3, C_2H_5, and $(CH_3)_2CH$] will be of lower energy than 29, closer in structure to 25 than is 29 to 28, and formed more extensively than 29 [Z_p = H, R = CH_3, C_2H_5, and $(CH_3)_2CH$]. Transfer of the phenyl groups to

C-1 with twisting and minimal orbital reorganization in formation of the carbon-carbon double bonds then leads to 27 in preference to 30 [Z_p = H, R = CH_3, C_2H_5, and $(CH_3)_2CH$]. Of significance then is that varied 1-diazo-2-(*p*-substituted-phenyl)propanes (31, Eq 7) convert at 160°C to (1) (Z)(32)- and (E)(33)-1-(*p*-substituted-phenyl)-1-propenes by *p*-substituted-phenyl rearrangements in which the ratios of 32:33 formed decrease with Z_p- in the order: *p*-CH_3, 1.95 > *p*-CH_3O, 1.85 > *p*-Cl, 1.46 > *p*-CN, 1.21,[3c] (2) 2-(*p*-substituted-phenyl)propenes (34, 29-38%), and (3) (*p*-substituted-phenyl)cyclopropanes (35, 27-45%). The increases in the ratios of 32:33 when the *para*-substituents (Z_p) are electron-donating may then be rationalized (Eq 6) on the basis that the substituted phenyl groups participate relatively early and tightly such that, because of increased differences in repulsion, rearrangements via 26 (R = CH_3) are facilitated relative to 29 (R = CH_3). Finally, it appears that 21 converts to the more stable (E)-1-butene 23 [30; Z_p = H, R = $(CH_3)_3C$] rather than 22 [27; Z_p = H, R = $(CH_3)_3C$] in order to minimize eventual repulsions between the *t*-butyl and the phenyl groups in rearrangements of 26 [Z_p = H, R = $C(CH_3)_3$] and 28 [Z_p = H, R = $C(CH_3)_3$] which are loosely bridged.



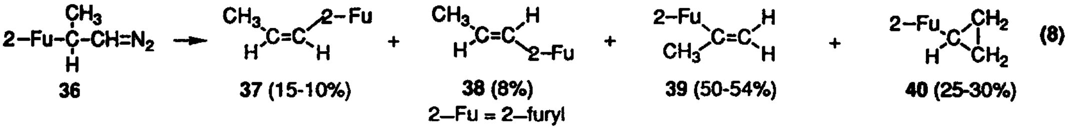
(6)



(7)

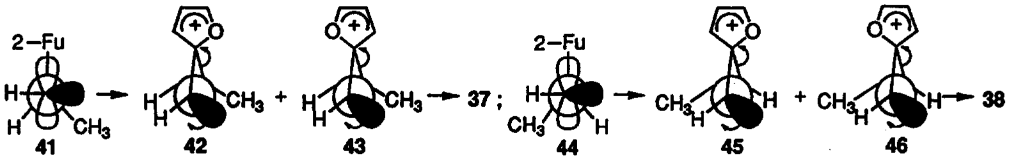
ted-phenyl)propenes (34, 29-38%), and (3) (*p*-substituted-phenyl)cyclopropanes (35, 27-45%). The increases in the ratios of 32:33 when the *para*-substituents (Z_p) are electron-donating may then be rationalized (Eq 6) on the basis that the substituted phenyl groups participate relatively early and tightly such that, because of increased differences in repulsion, rearrangements via 26 (R = CH_3) are facilitated relative to 29 (R = CH_3). Finally, it appears that 21 converts to the more stable (E)-1-butene 23 [30; Z_p = H, R = $(CH_3)_3C$] rather than 22 [27; Z_p = H, R = $(CH_3)_3C$] in order to minimize eventual repulsions between the *t*-butyl and the phenyl groups in rearrangements of 26 [Z_p = H, R = $C(CH_3)_3$] and 28 [Z_p = H, R = $C(CH_3)_3$] which are loosely bridged.

The stereochemistries of rearrangements of the 2-furyl group to a primary carbenic center have been studied. 1-Diazo-2-(2-furyl)propane (36, 2-Fu = 2-furyl), prepared by aprotic decomposition of sodium 2-(2-furyl)propanal *p*-tosylhydrazonate, thermolyzes at 150-250°C (Eq 8) to (Z)(37)- and (E)(38)-1-(2-furyl)-1-propenes in 1.88-1.25:1 ratios, 2-(2-furyl)propene (39), and 2-cyclopropylfuran (40). Propenes 37 and 38 are apparently formed by 1,2-migrations of the 2-furyl group. Though less stable thermodynamically, 37 is produced more extensively than 38 and thus the overall rearrangement behavior of 36 is similar to that of 5, 6, 11, 16, and 25. Therefore 41 is presumed to be more populated



(8)

than **44** (Eq 9), participative bridging of the 2-furyl group to give **42** and/or **43** rather than **45** and/or **46** is sterically advantageous, and rearrangements to **37** and **38** reflect the compositions of their bridged precursors.^{4}



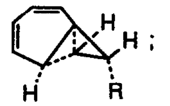
(9)

Study is now being made of (1) the stereochemistries of carbenic migration of varied unsaturated, electron-donor, hetaryl and aryl groups and (2) vicinal substituent attraction and negative hyperconjugation^{1c,d} in carbenic rearrangements.

__Acknowledgement__. This research was supported by the National Science Foundation.

References and Notes

1. For summaries of and references to 1,2-rearrangements to divalent carbon, see (a) Nickon, A. *Acc. Chem. Res.* **1993**, *26*, 84; (b) Garcia-Garibay, M.A. J. Am. Chem. Soc. 1993, *115*,7011; (c) Tomioka, H.; Sugiura, T.; Masumoto, Y.; Izawa, Y.; Inagaki, S.; Iwase, K. *Chem. Comm.* 1986, *693*; (d) Tomioka, H.; Hayashi, N.; Inoue, N.; Izawa, Y. *Tetrahedron Lett.* 1985, *26*, 1651, and (e) Schaffer, II, H. F. *Acc. Chem. Res.* **1979**, *12*, 288. (f) Kraska, A. R.; Cherney, L. I.; Shechter, H. *Tetrahedron Lett.* **1982**, *23*, 2163. (g) Kraska, A. R.; Chang, K. T.; Chang, S-J.; Moseley, C. G.; Shechter, H. *Tetrahedron Lett.* 1982, *23*, 1627. (h) Seghers, L.; Shechter, H. *Tetrahedron Lett.* 1976, *17*, 1943. (i) Slack, W. E.; Moseley, C. G.; Gould, K. A.; Shechter, H. *J. Am. Chem. Soc.* 1974, *96*, 7596.
2. Propenes **7** and **8** are concluded to be formed by phenyl rather than methyl migrations because (1) methyl rearrangement in decompositions of 1-diazo-2,2-diphenylpropane to give 1,1-diphenyl-1-propene is < 1%^{1i} and (2) the phenyl:methyl migratory aptitudes in thermolyses of 1-diazo-2-methyl-2-phenylpropane at 120-200°C average 16.4:1.
3. (a) Eclipsing effects on C-1 and C-2 in **26** and **29** should be attenuated by the hydrogen atoms at the 2- and 6-positions of the bridging phenyl groups. (b) Factors which also may play roles in formation of **26** in preference to **29** include: (1) electron attraction of the non-bonded electron pair on C-1 with alkyl (or aryl) groups on C-2 is more extensive in **25** than with hydrogen on C-2 in **28**, (2) negative hyperconjugation of the non-bonded electron pair on C-1 with alkyl (or aryl) groups on C-2 is more prevalent in **25** than with hydrogen on C-2 in **28**,^{1c,d} and (3) bridging as in **A** rather than as in **B**. (c) The migratory aptitudes for the various phenyl groups and the corresponding σ_o substituent constants give a linear free energy correlation of $\rho = -0.42 \pm 0.02$ with a correlation coefficient of 0.99.

A =


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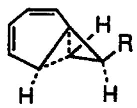

4. The overall stereochemistries of migration of the methyl groups as in Eq 1 are now presumed to be determined primarily in early transition states which reflect steric and electronic differences in conformers **1** and **3**. Conversion of 1-diazo-2,2-diphenylpropane to (Z)- rather than (E)-1,2-diphenyl-1-propene may also be interpreted similarly.^{1i}

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