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NUCLEOPHILIC CHARACTER IN DIMETHYLVINYLIDENE CARBENE CARBON-HYDROGEN INSERTION REACTIONS

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Nucleophilic character in singlet carbene addition to olefins is noted when the vacant p orbital of the carbene is stabilized by an adjacent electron donating substituent or by participation in an aromatic system[2]. Nucleophilic carbene character in carbon-hydrogen insertion reactions has not been reported. We have found that dimethylvinylidene carbene (**A**)[3] undergoes insertion into the methylene protons of benzyl alcohols (**1**) to yield 1-phenyl-4-methyl-2,3-pentadien-1-ols (**2**) in good yields. Satisfactory analytical data were obtained for all new compounds (Table I).

$$\underset{\textbf{A}}{(CH)_3C{=}C{=}C{:}} \quad + \underset{\textbf{1}}{X\text{-}PhCH_2OH} \longrightarrow \underset{\textbf{2}}{X\text{-}PhCH(OH)CH{=}C{=}C(CH_3)_2}$$

$$X = p\text{-}Br,\ p\text{-}Cl,\ H,\ p\text{-}CH_3,\ p\text{-}OCH_3$$

Electron attracting substituents accelerate the rate of **A** insertion into the benzylic C-H bond; electron releasing substituents retard the rate relative to X=H. A good linear Hammett correlation (20°) was observed with a rho value of +0.52 ± 0.04 (r = 0.997, 99% confidence, Table II). The small positive rho value is in agreement with a transition state involving concerted insertion and a small partial negative charge on the benzylic carbon atom.[4] The hydroxyl function apparently is responsible for this nucleophilic behavior of **A** since neither cumene nor benzyl methyl ether was found to undergo insertion.

Table I

Yields, Spectral Data, and Elemental Analysis of Products

$(CH_3)_2C{=}C{=}CHCH(OH)Ph{-}X$

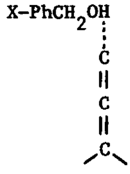
-X	Yield %	Ir cm^{-1} (neat)	Nmr (CCl_4), δ	
-H	72	3475 (OH) 3040, 3075, 3100 (aromatic) 1975 (allene) 700 (*mono*-substituted benzene)	7.2 (s, 5H, aromatic) 5.1 (s, 2H, C-H) 1.9 (broad, 1H, OH) 1.7 (d, 6H, CH_3, *J*=3Hz)	C H Calcd 82.7 8.1 Found 82.8 8.0
-Br	35	3350 (OH) 3025, 3050 (aromatic) 1950 (allene) 810 (*para*-disubstituted benzene)	7.1-7.6 (m, 4H, aromatic) 5.1 (s, 2H, C-H) 1.7 (d, 6H, CH_3,*J*=3Hz)	C H Br Calcd 56.9 5.2 31.6 Found 56.8 5.3 31.8
-Cl	56	3350 (OH) 3000 (aromatic) 1950 (allene) 810 (*para*-disubstituted benzene)	7.2 (s, 4H, aromatic) 5.1 (s, 2H, C-H) 1.7 (d, 6H, CH_3, *J*=3Hz)	C H Cl Calcd 69.1 6.3 17.0 Found 69.4 6.5 18.0
$-CH_3$	68	3400 (OH) 3000, 3050 (aromatic) 1950 (allene)	7.1 (m, 4H, aromatic) 2.4 (s, 3H, CH_3Ph- 1.7 (d, 6H, CH_3,*J*=3Hz)	C H Calcd 82.9 8.6 Found 81.5 8.6
$-OCH_3$	55	3350 (OH) 3050, 3025, 3000 (aromatic) 1950 (allene) 810 (*para*-disubstituted benzene)	5.0 (s, C-H) 1.7 (d, CH_3)	C H Calcd 76.4 7.9 Found 76.1 7.7

Table II

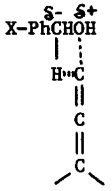
X	Relative Reactivity[a]
p-Br	1.2
p-Cl	1.1
H	1.0
p-CH_3	0.73
p-OCH_3	0.39

[a] Determined by glpc using competitive experiments. The values represent an average of three runs using benzyl alcohol standard, and three runs using para-methylbenzyl alcohol as a standard.

A mechanism which accomodates the observations is one in which the weakly electrophilic[5] singlet[6] **A** is attracted to the hydroxyl function through hydrogen bonding to give **B**[7] which then converts to ylide **C**. Ylide **C** then gives rise to the observed carbon-hydrogen insertion.



B



C

Thus hydrogen bonding facilitates the formation of the ylide. Precedence for similar behavior in other carbene reactions is found in reactions with 2-propanol which gives alpha carbon-hydrogen insertion whereas diethyl ether shows random insertion.[8]

Examination of Drieding molecular models for the carbon-hydrogen insertion reaction in ylide **C** reveals a slight preference (0.1 Å) for attack on the hydrogen atom[9] as opposed to attack on the electrons of carbon-hydrogen bond.[10] Substituents do not appreciably change the hybridization of benzylic carbon-hydrogen bonds in both toluene[11] and carbanion systems.[12] We feel that the substitutents in our system are exerting their influence on the negative charge only; effects on the carbon-hydrogen bond order are most likely negligible and do not influence the observed relative rates.

References

1. Taken from the Master's thesis of D. L. S., Southern Illinois University, 1974. Research support by the SIUE Office of Research and Projects is gratefully acknowledged.
2. R. Moss, "Carbenes," Vol. I, M. Jones, Jr. and R. Moss, Eds., John Wiley and Sons, New York, N. Y. 1973.
3. S. R. Landor and P. F. Whiter, *J. Chem. Soc.*, 5625 (1966).
4. A. Streitwieser, Jr. and H. F. Kock, (*J. Am. Chem. Soc.*, **86**, 404(1964) show that a full negative charge gives rise to a rho value of 4.0.
5. H. D. Hartzler, *J. Am. Chem. Soc.*, **96**, 7950 (1974).
6. T. B. Patrick, E. C. Haynie, and W. J. Probst, *J. Org. Chem.*, **37**, 1553 (1972).
7. J.C. Craig and C. D. Beard, *J. Am. Chem. Soc.*, **96**, 7950 (1974).
8. W. Kirmse, "Carbene Chemistry," 2nd Ed., Academic Press, New York, N. Y., 1971, pp. 230-231, 423-434.
9. R. C. Dobson, D. M. Hayes, and R. Hoffman, *J. Am. Chem. Soc.*, **93**, 6188 (1971); N. Bodor, M. J. S. Dewar, and J. S. Wasson, *ibid.*, **94**, 9095
10. C. D. Gutsche, G. L. Backman, W. Udell, and S. Bauerlein, *ibid.*, **93**, 5172 (1971).
11. C. H. Yoder, R. H. Tuck, and R. E. Hess, *ibid*, **91**, 539 (1969).
12. A. Streitwieser, Jr., M. R. Granger, F. Mares, and R. A. Wolf (*ibid.*, **95**, 4257 (1973) suggest that hybridization changes are negligible for carbon-hydrogen bonds in benzylic carbanions.