Tetrahedron Letters No. 50, pp 4817 - 4820.
©Pergamon Press Ltd. 1979. Printed in Great Britain.

0040-4039/79/1208-4817$02.00/0

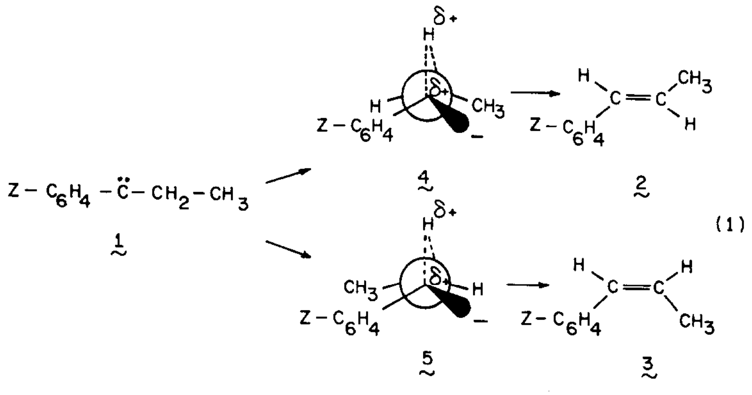
Orbital and Conformational Preferences in Rearrangements of 1-Phenyl-1-Propylidenes

B. A. Dellacoletta and H. Shechter*

Department of Chemistry, The Ohio State University, Columbus, Ohio 43210

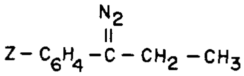
Summary: The stereochemistry of rearrangement of substituted 1-phenyl-1-propylidenes to trans and cis-propenylbenzenes is substituent dependent.

A fascinating aspect of carbenes is the possible discrimination in the interactions of their non-bonded orbitals with substituents.[1] It has been suggested that electron-donor para substituents favor a planar conformation for a singlet phenylcarbene in order to stabilize its electron-deficient, carbene p orbital.[1] Conversely, electron-withdrawing para substituents are presumed to enhance twisting of the phenyl group to a perpendicular conformation in which the electron-rich, carbene σ orbital is favorably delocalized.[1] A study is now reported of orbital and conformational effects in rearrangements of substituted 1-phenyl-1-propylidenes (1) to trans (2) and cis (3)-propenylbenzenes (Eq 1). The research design is to determine whether the preference for transition state 4[2] over 5 is controlled by the electrical and steric demands of the substituents attached to the phenyl ring.



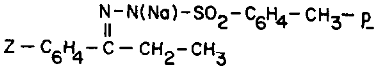
(1)

The present investigation has involved decomposition of ortho, meta, and para-substituted 1-diazo-1-phenylpropanes (6) as generated from sodium salts (7)[3a] of propiophenone p-tosylhydrazones[3b] at 180-300°C (Table 1). Hydrogen migration in 1 to give 2[3c] and 3[3c] is the only carbenic process observed. Temperature, the pyrolysis period, and the type and amount of excess base have no significant effect on the ratios (2/3) of the propenylbenzenes formed. A propenylbenzene (2 and 3) produced is not altered after formation. The standard deviations for all ratios of 2 and 3 are less than ± 1% except where Z = p-OCH_3 (1.1%).



$Z-C_6H_4-C(=N_2)-CH_2-CH_3$

6



$Z-C_6H_4-C(=N-N(Na)-SO_2-C_6H_4-CH_3\text{-}p)-CH_2-CH_3$

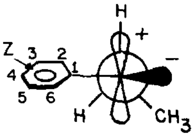
7

TABLE 1

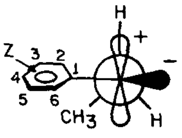
Thermolysis of Sodium Salts (**7**) of Z-Substituted Propiophenone *p*-Tosylhydrazones[3]

Z	**2**(*trans*) %	**3**(*cis*) %	**2**/**3** (*trans*/*cis*)	Z	**2**(*trans*) %	**3**(*cis*) %	**2**/**3** (*trans*/*cis*)
p-OCH$_3$	85.7±1.1	14.3±1.1	6.0(5.6-6.5)	*m*-CH$_3$	76.4±0.8	23.6±0.8	3.2(3.1-3.4)
p-C(CH$_3$)$_3$	80.5±0.3	19.5±0.3	4.1(4.0-4.2)	*m*-OCH$_3$	75.7±0.6	24.3±0.6	3.1(3.0-3.2)
p-CH$_3$	75.4±0.9	24.6±0.9	3.1(2.9-3.2)	*m*-CN	72.3±0.7	27.7±0.7	2.6(2.5-2.7)
p-Br	75.9±0.8	24.1±0.8	3.1(3.0-3.3)				
p-Cl	75.5±0.4	24.5±0.4	3.1(3.0-3.2)	*o*-OCH$_3$	62.0±1.5	38.0±1.5	1.6(1.5-1.7)
H	71.7±0.5	28.3±0.5	2.5(2.4-2.6)	*o*-CH$_3$	71.9±0.5	28.1±0.5	2.6(2.5-2.6)
p-CO$_2$C$_2$H$_5$	69.9±0.5	30.1±0.5	2.3(2.2-2.4)	*o*-C$_2$H$_5$	75.2±1.6	24.8±1.6	3.0(2.8-3.2)
p-CN	63.5±0.7	36.5±0.7	1.7(1.7-1.8)	*o*-Br	70.6±0.7	29.4±0.7	2.4(2.3-2.5)

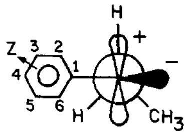
Para-substituted 1-phenyl-1-propylidenes (**1**, Z*p*) convert to *para*-substituted propenylbenzenes (**2** and **3**, Z*p*) in *trans*/*cis* ratios (**2**/**3**) ranging from 6.0 to 1.7/1 (Table 1). Electron-donation in groups increase the conversions to *trans*-propenylbenzenes (**2**, Z*p*) in the order: *p*-OCH$_3$ > *p*-C(CH$_3$)$_3$ > *p*-CH$_3$, *p*-Br, and *p*-Cl > H > *p*-CO$_2$-C$_2$H$_5$ > *p*-CN. Of further note is that the relative effects on **2**/**3** are greater with electron-donating than with electron-withdrawing substituents.[4] The effects of *para*-substituents on the conversions of **1** to **2** and **3** are interpretable on the basis of orbital-preference factors[1] in **4** and **5**. When Z*p* in **1** is electron-donating, the phenyl ring may be relatively perpendicular to the vacant carbene orbital as in **8** and **9**. On the basis that **8** and **9** are structurally similar to transition states **4** (Z*p*) and **5** (Z*p*), conversions to *trans*-propenylbenzenes (**2**, Z*p*) should be favored over their *cis*-isomers (**3**, Z*p*) because the steric interaction between the (relatively coplanar) phenyl and methyl groups in **5** (Z*p*) is greater than for the phenyl groups and hydrogen in **4** (Z*p*). When Z*p* in **1** is electron-withdrawing, the phenyl ring may twist from the vacant orbital and overlap significantly with the filled carbenic orbital as in **10** and **11**. Thus in **5** (Z*p*), as now structurally similar to **10**, the steric repulsion of the phenyl and methyl groups will be relatively small and conversion to *trans*-propenylbenzenes (**2**, Z*p*) is less predominant. From the sizes of the *trans*/*cis* ratios (**2**, Z*p*/**3**, Z*p*) observed (Table 1) and the orbital preference rationalization, resonance effects appear to be of greater significance than inductive effects in establishing the stereochemistries which allow hydrogen



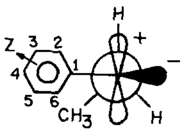
8, Z at C-4
12, Z at C-3 or C-5
16, Z at C-2 or C-6



9, Z at C-4
13, Z at C-3 or C-5
17, Z at C-2 or C-6



10, Z at C-4
14, Z at C-3 or C-5
18, Z at C-2 or C-6



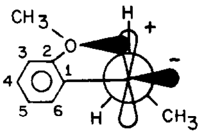
11, Z at C-4
15, Z at C-3 or C-5
19, Z at C-2 or C-6

migration in the above systems.[4]

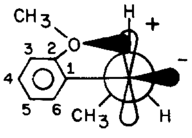
Support for the conclusions that orbital effects and, in particular, resonance factors are important in establishing 4 and 5 arises in the rearrangements of *meta*-substituted 1-phenyl-1-propylidenes[5a] (1, Z*m*) to *meta*-substituted propenylbenzenes (2 and 3, Z*m*) in that the *trans*/*cis* ratio range is only from 3.3 to 2.6/1 (Table 1) in the order: *m*-CH_3 = *m*-OCH_3 > *m*-CN. Conversion of 1 (Z*m*) to *trans*-propenes 2 (Z*m*) is therefore enhanced by electron-donating and diminished by electron-withdrawing *meta* substituents. The effects, however, are small. Resonance effects involving *meta* substituents and the orbitals of the carbenic center should not be as large as when the substituents are *para*. Thus the steric differences between 4 and 5 are presumed not to be as great when the substituents are *meta* compared to *para*. The effects of *para* over *meta* substituents are revealed farther by rearrangement of 1-(3,4-dimethoxyphenyl)-1-propylidene to 1-(3,4-dimethoxyphenyl)-1-propenes in *trans*/*cis* ratio of 5.9 (5.5-6.4) whereas 1-(3,5-dimethoxyphenyl)-1-propylidene isomerizes to give a *trans*/*cis* ratio of 1-(3,5-dimethoxyphenyl)-1-propenes of only 2.7 (2.6-2.7).

Study has been extended to rearrangement of *ortho*-substituted 1-phenyl-1-propylidenes (1, Z*o*). On the basis of traditional steric effects in reaction products, hydrogen migration in 1 (Z*o*) would be expected to give larger *trans*/*cis* ratios (2, Z*o*/3, Z*o*) for conversions to propenylbenzenes than do *para*-substituted 1-phenyl-1-propylidenes (1, Z*p*). The facts are otherwise, however, in that the ratios range from 2.6 to 1.6/1 (Table 1) in the order: *o*-CH_3 > *o*-Br > *o*-OCH_3. Even for 1-(*o*-ethylphenyl)-1-propylidene (1, Z = *o*-C_2H_5), the ratio is only 3.0/1. The results may be interpreted to indicate that *ortho* substituents lead to twisting (18 and 19) of the phenyl group away from positions relatively perpendicular to the vacant orbitals of 16 and 17. Thus the transition states for rearrangement are close to reactants rather than products, the steric differences in transition states 4 (Z*o*) and 5 (Z*o*) are not great, and the resulting *trans*/*cis* ratios for 2 (Z*o*) to 3 (Z*o*) are not large.

Of particular interest is that 1-(*o*-methoxyphenyl)-1-propylidene (1, Z = *o*-OCH_3) gives the smallest product ratio, 2 (Z = *o*-OCH_3)/3 (Z = *o*-OCH_3) = 1.6, of the present study even though the methoxy group is a strong electron donor of considerable volume and the ratio, 2 (Z = *p*-OCH_3)/3 (Z = *p*-OCH_3) = 6.0, from the *para* analog (1, Z = *p*-OCH_3) is so large. The fact that the *trans*/*cis* ratio of propenylbenzenes from 1 (Z = *o*-OCH_3) is so small implies that the *o*-methoxyphenyl group is highly turned and rearrangement occurs from transition states related to 18 (Z = OCH_3) and 19 (Z = OCH_3). Further, the influence of the *o*-methoxy group is so great in the present system that compounding electronic effects may be operational. Thus, transition states related to 16 (Z = *o*-OCH_3 at C-6) and 17 (Z = *o*-OCH_3 at C-6) are in part unfavorable because of repulsion between the p electrons of methoxy oxygen and the filled, carbene σ orbital, whereas when the transition states are near 18 (Z = o-OCH_3) and 19 (Z = o-OCH_3), an electron pair from oxygen may penetrate the vacant p-orbital of the carbenic center (such as in 20 and 21),[5b] therefore "locking" the systems, and lowering the energy dfferences into rearrangement.



20



21

The effects of the orbital and conformational preferences on various intra- and intermolecular reactions of carbenes are being studied further.[1]

Acknowledgement. Support of this research by the National Science Foundation and the State of Ohio is gratefully acknowledged.

References

(1) R. J. Miller, L. S. Yang, and H. Shechter, J. Am. Chem. Soc., 99, 938 (1977); R. J. Miller and H. Shechter, ibid., 100, 7920 (1978).

(2) (a) The rearrangements to 2 and 3 are assumed to involve preferential migration of hydrogen from positions parallel to the vacant p orbitals of the carbenic centers of phenylcarbenes by singlet processes in which the rearrangement transition states are close in structure to the reactant carbenes. (b) For development of the theory of the stereochemistry of carbenic rearrangements, see (c) V. W. Powell, and M. C. Whiting, Tetrahedron, 12, 168 (1961); (d) R. Hoffmann, G. D. Zeiss, and G. W. Van Dine, J. Am. Chem. Soc., 90, 1485 (1968); (e) N. Bodor and M. J. S. Dewar, ibid., 94, 9103 (1972); (f) H. E. Zimmerman, Acc. Chem. Res., 5, 393 (1972); (g) A. Nickon, F-C. Huang, R. Weglein, K. Matsuo, and H. Yagi, J. Am. Chem. Soc., 96, 5264 (1974); (h) J. A. Altmann, O. S. Tee, and K. Yates, ibid., 98, 7132 (1976); (i) P. K. Freeman, T. A. Hardy, J. R. Balyeat, and L. D. Wescott, J. Org. Chem., 42, 3356 (1977); (j) E. P. Kyba, J. Am. Chem. Soc., 99, 8330 (1977); (k) L. S. Press and H. Shechter, ibid., 101, 509 (1980); and (l) the references therein.

(3) (a) Sodium salts 7, prepared from propiophenone p-tosylhydrazones[3b] in methylene chloride and sodium hydride (1.0-1.1 equiv) or sodium methoxide (1.1 equiv) and solvent removal, were pyrolyzed dry at 180°-300° (1.0-0.02 mm) for ~ 5 min and gave 2 and 3 in 50-80% isolated yields. Minor products of 6 are corresponding azines. (b) All new compounds of this research are of proper analysis. (c) Propenylbenzenes 2 and 3 were identified and analyzed by GC methods.

(4) Such effects may be rationalized on the basis that a p-orbital can be better delocalized than a sp^2-orbital at a carbenic center.[1]

(5) (a) Structures 12-15 with Z at C-3 or C-5 and 16-19 with Z at C-2 or C-6 illustrate the different conformers when the unsymmetrically-substituted phenyl groups are parallel or perpendicular to the unfilled carbenic orbitals. (b) Conformers of 20 and 21 with methoxy groups at C-6 are presumed to be of higher energies than those illustrated above because of greater steric interactions.

(Received in USA 27 August 1979)