Carbon-13 NMR of Para-Substituted Hydrazones, Phenylhydrazones, Oximes, and Oxime Methyl Ethers: Substituent Effects on the Iminyl Carbon[1]

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Carbon-13 NMR spectroscopy has been a useful tool for the study of ground-state electronic environments of organic molecules. We have performed a systematic study of the carbon-13 NMR spectra of hydrazones, phenylhydrazones, oximes, and oxime ethers with a view toward trying to understand the electron distribution in these molecules.

The chemistry and nature of the carbon-nitrogen double bond has attracted many investigators because of the intriguing characteristics this simple atomic combination imparts to molecules.[2] Thus, depending upon the substituents on carbon and nitrogen, the molecule may display rotational freedom or exists as definite isomers. The mechanism of rotation around the carbon-nitrogen double bond still remains of interest.[3,4] A wide range of reactivity is possible which includes reactions at carbon or nitrogen, as well as, possibilities of hydrogen bonding and transfer. Throughout many studies, carbon-13 NMR spectroscopy has played a vital role.[5-15] More recently, nitrogen-15 NMR spectroscopy has been used to investigate the nature of the carbon-nitrogen double bond.[16-22] In this report we present a systematic carbon-13 NMR spectroscopic study of para-substituted hydrazones, phenylhydrazones, oximes, and oxime methyl ethers. The intention of this work was to more fully understand the nature of the carbon-nitrogen bond by assessing the substituent effects at the iminyl carbon.

Experimental Section

Samples were prepared and purified according to literature procedures.[23] Carbon-13 NMR spectra were obtained using a Varian XL-100/Nicolet TT-100 spectrometer operating at 25.15 MHz. A 45° pulse took 9 μs and the sweep width was 4000 Hz. Typically, 64 or less free-induction decays were collected over 8K computer points. Quadrature phase detection was used and the probe temperature was 28 °C. Sample concentration was carefully controlled (0.3 M) and the solvent was $CDCl_3$. In some cases, a few drops of Me_2SO-d_6 was added to enhance solubility. Proton coupled spectra were recorded when needed to assist signal assignment. Most of the carbon-13 chemical shifts were assigned by using known substituent effects and by internal consistency. Carbon-13 chemical shifts were measured relative to $CDCl_3$ and converted to the Me_4Si scale using the relationship $\delta\ Me_4Si = \delta\ CDCl_3 + 76.91$ ppm.

Results and Discussion

The carbon-13 chemical shifts for the hydrazones, phenylhydrazones, oximes, and oxime ethers are tabulated in Table I. The substituent effect on the ^{13}C chemical shift of the iminyl carbon atoms in these various classes was of primary interest. The ^{13}C chemical shifts of the aromatic carbons are well behaved and, in general, predictable according to known substituent effects in other aromatic systems.[24] The oximes and oxime methyl ethers exhibit *Z* and *E* forms at room temperature while the hydrazones and the phenylhydrazones show an average ^{13}C chemical shift for the iminyl carbon atoms most likely due to a rapid interconversion of the *Z* and *E* forms.

The iminyl carbons appeared in definite spectral regions depending upon the substituent attached to the trigonal nitrogen. Thus, this carbon appeared at 138-143 ppm for the hydrazones, 135-139 ppm for phenylhydrazones, 148-151 ppm for *E* oximes, 144-150 ppm for *Z* oximes, 147-149 ppm for *E* methyl ether oximes, and 143-146 ppm for *Z* methyl ether oximes. It is of interest to note the marked influence of the oxime configuration on the iminyl chemical shifts, the *Z* resonance being always higher than the *E*.

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[2] Patai, S. "The Chemistry of the Carbon-Nitrogen Double Bond"; Interscience: New York, 1970.

[3] Hwang, W. F.; Kuska, H. A. *J. Phys. Chem.* **1978**, *82*, 2126.

[4] Kerek, F.; Ostrogovich, G.; Simon, Z. *J. Chem. Soc. B* **1971**, 541.

[5] Fraser, R. R.; Dhawan, K. L.; Taymaz, K. *Org. Magn. Reson.* **1978**, *11*, 269.

[6] Vuik, C. P. J.; Hasan, M.; Holloway, C. E. *J. Chem. Soc. Perkin Trans. 2* **1978**, 1214.

[7] Buchanan, G. W.; Dawson, B. A. *Can. J. Chem.* **1978**, *56*, 2200.

[8] Solladie-Cavallo, A.; Golladie, G. *Org. Magn. Reson.* **1977**, *10*, 235.

[9] Bunnell, C. A.; Fuchs, P. L. *J. Org. Chem.* **1977**, *42*, 2614.

[10] Geneste, P.; Kamenka, J. M.; Brevard, C. *Org. Magn. Reson.* **1977**, *10*, 31.

[11] Naulet, N.; Filleux, M. L.; Martin, G. J.; Pornet, J. *Org. Magn. Reson.* **1975**, *7*, 326.

[12] Dondoni, A.; Lunazzi, L.; Giorgianni, P.; Maccantelli, D. *J. Org. Chem.* **1975**, *40*, 2979.

[13] Inamoto, N.; Kushida, K.; Masuda, S.; Ohta, H.; Satoh, S.; Famura, Y.; Tokumaru, K.; Tori, K.; Yoshida, M. *Tetrahedron Lett.* **1974**, 3617.

[14] Hawkes, G. E.; Herwig, K.; Roberts, J. D. *J. Org. Chem.* **1974**, *39*, 1017.

[15] Wolkowski, Z. W.; Vauthier, E.; Gonbeau, B.; Sauvaitre, H.; Musso, J. A. *Tetrahedron Lett.* **1972**, 565.

[16] Allen, M.; Roberts, J. D. *Can. J. Chem.* **1981**, *59*, 451.

[17] Batto, R. E.; Roberts, J. D. *J. Org. Chem.* **1979**, *44*, 140.

[18] Levy, G. C.; Godwin, A.; Holloway, C. E. *J. Magn. Reson.* **1979**, *34*, 327.

[19] Westerman, P. W.; Batto, R. E.; Roberts, J. D. *J. Org. Chem.* **1978**, *43*, 2590.

[20] Yavari, I.; Roberts, J. D. *J. Am. Chem. Soc.* **1978**, *100*, 4662.

[21] Batto, R. E.; Westerman, P. W.; Roberts, J. D. *Org. Magn. Reson.* **1978**, *11*, 510.

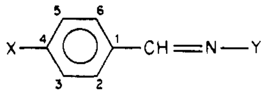
[22] Oatis, J. E.; Schultz, H. P. *Org. Magn. Reson.* **1978**, *11*, 40.

[23] Gordon, M. S.; Krause, J. G.; Linneman-Mohr, M. A.; Parchue, R. R. *Synthesis* **1980**, 244.

[24] Stothers, J. B. "Carbon-13 NMR Spectroscopy"; Academic Press: New York, 1972.

0022-3263/84/1949-0097$01.50/0

Table I. Carbon-13 Chemical Shifts for Hydrazones, Phenylhydrazones, Oximes, and Oxime Ethers

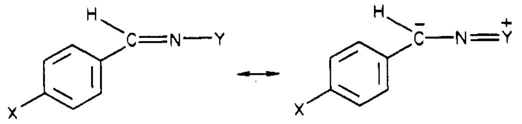


X	Y	C=N	C-1	C-2,6	C-3,5	C-4	X	C-1′	C-2′,6′	C-3′,5′	C-4′
H	NH_2	142.77	135.02	125.94	128.35	128.35					
Me	NH_2	143.26	132.34	126.02	129.18	138.54	Me, 21.13				
CO_2Me	NH_2	140.87	139.48	125.70	129.75	129.62	Me, 51.90; C=O, 166.69				
CN	NH_2	139.51	139.58	126.25	132.27	111.35	CN, 118.77				
OMe	NH_2	142.97	127.83	127.31	113.85	159.91	Me, 55.0				
NO_2	NH_2	138.55	141.61	126.13	123.75	147.05					
H	NPh	137.25	135.26	126.12	128.51	128.32		144.63	112.71	129.20	120.04
Me	NPh	137.59	132.54	126.12	129.22	138.41	Me, 21.23	149.78	112.73	129.22	119.92
CO_2Me	NPh	135.49	139.68	125.68	129.78	129.24	Me, 51.92, C=O, 166.81	144.05	112.83	129.24	120.49
NMe_2	NPh	138.64	123.60	127.43	112.17	150.70	Me, 40.45	145.34	112.54	129.12	119.33
OMe	NPh	137.39	128.07	127.49	114.05	159.97	Me, 55.20	144.92	112.60	129.18	119.74
Cl	NPh	135.78	133.80[a]	127.19	128.74	133.88[a]		144.68	112.73	129.24	120.23
NO_2	NPh	133.75	141.66	126.15	124.00	147.03		143.55	113.26	129.38	121.23
H	*cis*-OH	145.54	130.71	128.00	129.25	130.33					
CO_2Me	*cis*-OH	144.52	134.42	129.23	130.16	134.42	Me, 51.89				
OMe	*cis*-OH	145.28	123.77	132.36	113.38	160.13	Me, 54.93				
Cl	*cis*-OH	144.24	131.67	128.19	129.11	134.92					
H	*trans*-OH	150.33	131.87	127.00	128.43	130.24					
CH_3	*trans*-OH	150.25	130.97	126.90	129.38	140.19	Me, 21.27				
OMe	*trans*-OH	149.80	132.88	128.43	114.16	161.00	Me, 55.19				
Cl	*trans*-OH	149.30	132.21	128.14	129.01	135.75					
H	*trans*-OMe	148.26	132.44	126.77	128.42	129.72	Me, 61.67				
Me	*trans*-OMe	148.27	129.55	126.73	129.15	139.64	Me, 21.11; OMe, 61.54				
CO_2Me	*trans*-OMe	147.22	136.25	126.56	129.65	131.93	CO_2Me (Me, 51.87; CO, 166.25); Me, 61.95				
CN	*trans*-OMe	146.44	136.40	127.14	132.22	112.96	CN, 118.25; Me, 62.28				
NMe_2	*trans*-OMe	148.77	119.61	128.05	111.65	151.25	NMe, 39.86; Me, 61.29				
OMe	*trans*-OMe	147.98	124.72	128.29	113.54	160.80	Me, 55.04; NOMe, 61.55				
Cl	*trans*-OMe	147.05	130.60	127.97	128.75	135.64	Me, 61.85				
NO_2	*trans*-OMe	146.15	138.32	127.46	123.89	148.31	OMe, 62.50				
H	*cis*-OMe	145.51	131.86	130.57	128.16	129.52	Me, 62.28				
Me	*cis*-OMe	145.51	131.76	128.84	130.65	139.97	Me, 21.11; OMe, 61.99				
CO_2Me	*cis*-OMe	144.45	134.08	129.32	130.33	130.74	CO_2Me (Me, 51.87; CO, 166.25); Me, 62.54				
CN	*cis*-OMe	143.59	133.93	130.82	131.94	112.11	CN, 118.10; Me, 62.28				
NMe_2	*cis*-OMe	145.86	118.92	132.42	110.95	150.86	NMe, 39.70; Me, 61.92				
OMe	*cis*-OMe	145.15	123.71	132.57	114.00	160.51	NMe, 55.27; Me, 62.17				
Cl	*cis*-OMe	144.28		128.45	128.88	135.43	Me, 62.45				

[a] These assignments may be interchanged.

Hydrazones. Examination of Table I revealed that as the electron-withdrawing ability of the substituent increased, the ^{13}C chemical shift of the iminyl carbon atom moved upfield. This general trend was very well demonstrated by the Hammett plot shown in Figure 1 where the ^{13}C chemical shift was plotted vs. the Hammett σ_p value in this case. The rather substantial negative slope indicated the marked degree of sensitivity of this class to the substituent effect. One should also note that the σ_p values correlated better than the σ_I values. The σ_I values are a measure of the relative electron-donating or -withdrawing power of the substituent due to the inductive effect exclusive of resonance, while the σ_p values are a measure of the relative electron donater withdrawing power of the substituent due to mostly electronic effects, notably including resonance. So in the hydrazone system the greater correlation using the σ_p values indicated that resonance was of importance in the substituent effect on the ^{13}C chemical shift of the iminyl carbon atoms.

A rationalization for the general relationship between the ^{13}C chemical shifts and the Hammett σ constants is shown by resonance forms **1a** and **1b**. This type of res-



1a 1b

Y = NH_2, NHPh, OH, OMe

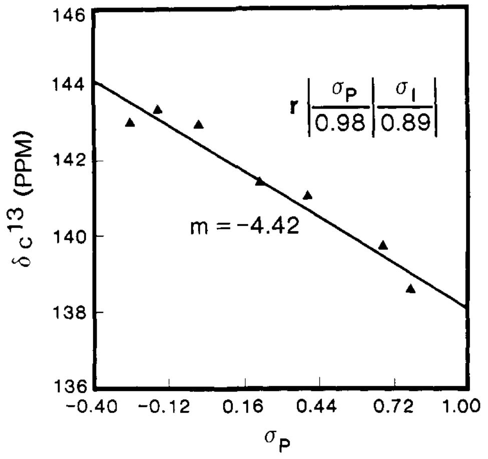


Figure 1. Plot of the iminyl carbon chemical shifts of hydrazones vs. the Hammett substituent constant, σ_p.

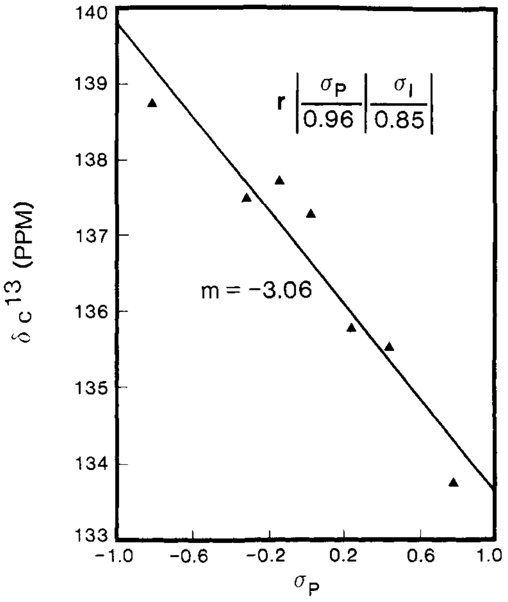


Figure 2. Plot of the iminyl carbon chemical shifts of phenylhydrazones vs. the Hammett substituent constant, σ_p.

onance is progressively stabilized as one increases the electron-withdrawing power of the substituent. Thus the iminyl carbon becomes increasingly shielded, and its ^{13}C chemical shift moves upfield. This type of resonance is consistent with several other phenomenon in the literature. For example, Roberts et al. has demonstrated that the ^{15}N chemical shift in iminyl nitrogen was less sensitive to a substituent effect compared to several other related compound classes, and that the non-iminyl nitrogen was rather sensitive to the substituent effect.[19] This is consistent with the resonance structures **1a** and **1b**, since the non-iminyl nitrogen would undergo a much greater change in charge distribution and bonding order than the iminyl nitrogen. Also consistent with this type of resonance is the fact that these benzaldehyde hydrazones cannot be resolved into *Z* and *E* forms at room temperature while the analogous alkyl hydrazones demonstrate two forms. This kind of resonance would allow free rotation around the C=N bond and thus would allow rapid interconversion between the two forms.

Phenylhydrazones. Examination of Table I again shows that as one increases the electron-withdrawing power of the substituent, the ^{13}C chemical shift of the iminyl carbon atom moves upfield. This was well demonstrated in the Hammett plot shown in Figure 2, however, the diminished slope in this phenylhydrazone case indicates that this class of compounds has a diminished sensitivity to the substituent effect compared to the hydrazones. Better correlation using the σ_p values was again observed indicating that resonance is of significance in this class of compounds as well. The diminished sensitivity of the phenylhydrazones relative to the hydrazones can also be demonstrated by directly plotting the ^{13}C chemical shifts of one class vs. the other (Figure 3). Any deviation of the slope from one is indicative of a differential sensitivity. In this case the slope of 0.8 reveals that the phenylhydrazones are less sensitive to the substituent effect than the hydrazones.

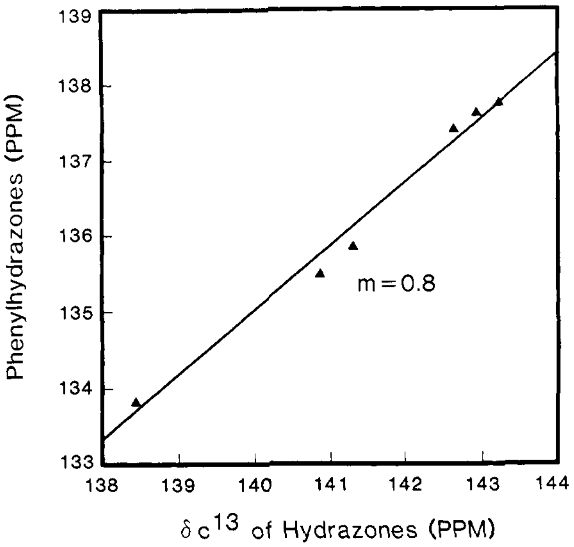


Figure 3. Plot of iminyl carbon chemical shifts of hydrazones vs. phenylhydrazones.

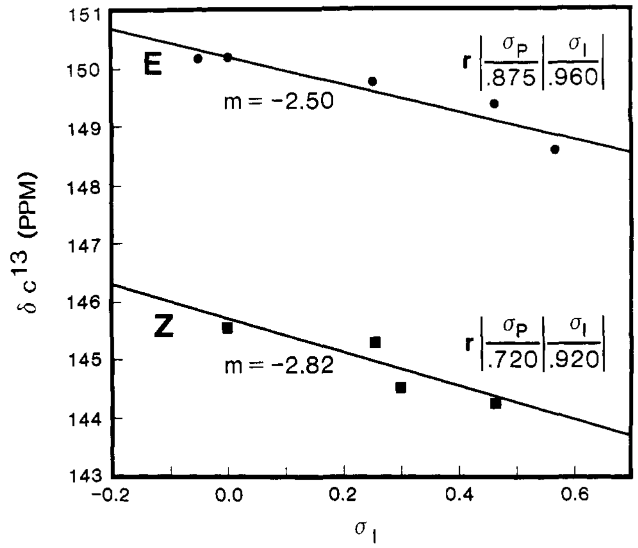


Figure 4. Plot of the iminyl carbon chemical shifts of *E* and *Z* isomers of oximes vs. the Hammett substituent constant, σ_I.

Oximes. For both the oxime *E* and *Z* isomers, as one increases the σ value or the electron-withdrawing power of the substituent, the chemical shift of the iminyl carbon atom moves upfield. However, the substituent effect was operative over a small range of chemical shifts, indicating a diminished sensitivity to the substituent effect. Figure 4 shows the much smaller negative slopes demonstrating the markedly diminished sensitivity of the oxime class to the substituent effect. In this case the σ_I value correlated much better than the σ_p value. This suggests that the inductive effect predominates in the oxime class, and

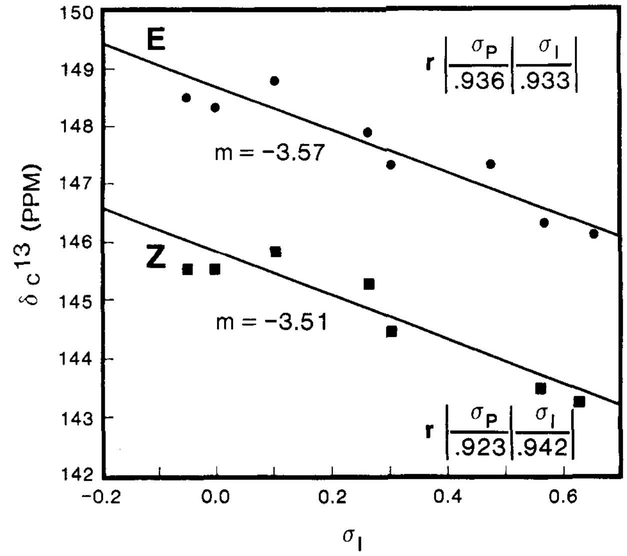


Figure 5. Plot of the iminyl carbon chemical shifts of *E* and *Z* isomers of oxime methyl ethers vs. the Hammett substituent constant, σ_I.

resonance is of reduced importance.

Oxime Methyl Ethers. One may note the same general trend as above with both *E* and *Z* isomers with respect to the chemical shifts. The *Z* isomers are consistently upfield from the *E* isomers. This is analogous to olefinic systems in which the ^{13}C chemical shifts of the cis isomers are consistently upfield from the trans isomers.[24] In the Hammett plot (Figure 5) one should note the intermediate magnitude of the slope revealing an intermediate sensitivity of the oxime methyl ethers as compared to the hydrazones and oximes. The σ_p and σ_I values correlated equally well. This suggests that resonance is of some importance when compared to the hydrazones and phenylhydrazones but of greater importance when compared to the oximes. This is consistent with the relative resonance-derived electron-donating abilities of the substituents on the iminyl nitrogen. The non-iminyl nitrogen of the hydrazones and phenylhydrazones are more able to donate electrons by resonance than the hydroxyl group of the oximes or the methoxy group of the oxime methyl ethers. Also, the methoxy group would be expected to be better able to donate electrons than the hydroxyl group (several hyperconjugated structures can be drawn for the methoxy moiety).

In summary, on one end of the scale the hydrazones have the greatest negative slope indicative of the greater sensitivity of this class to the substituent effect, and the ^{13}C chemical shifts correlate best using the σ_p values showing that resonance is of importance in this system. On the other end of the scale, the oximes have the smallest negative slope indicative of the low sensitivity of this class to the substituent effect, and the σ_I value correlates best demonstrating that the inductive effect predominates in this class of compounds. The phenylhydrazone and oxime methyl ether iminyl carbon displayed behavior intermediate between these two extremes.

Registry No. $PhCH{=}NNH_2$, 5281-18-5; 4-$CH_3C_6H_4CH{=}NNH_2$, 52693-87-5; 4-$MeO_2CC_6H_4CH{=}NNH_2$, 50466-15-4; 4-$NCC_6H_4CH{=}NNH_2$, 87829-00-3; 4-$CH_3OC_6H_4CH{=}NNH_2$, 5953-85-5; 4-$O_2NC_6H_4CH{=}NNH_2$, 6310-10-7; $PhCH{=}NNHPh$, 588-64-7; 4-$CH_3C_6H_4CH{=}NNHPh$, 2829-25-6; 4-$MeO_2CC_6H_4CH{=}NNHPh$, 87829-01-4; 4-$Me_2NC_6H_4CH{=}NNHPh$, 2829-28-9; 4-$MeOC_6H_4CH{=}NNHPh$, 622-73-1; 4-$ClC_6H_4CH{=}NNHPh$, 2829-26-7; 4-$O_2NC_6H_4CH{=}NNHPh$, 2829-27-8; (*Z*)-$PhCH{=}NOH$, 622-32-2; (*Z*)-4-$MeO_2CC_6H_4CH{=}NOH$, 87829-02-5; (*Z*)-4-$MeOC_6H_4CH{=}NOH$, 3717-22-4; (*Z*)-4-$ClC_6H_4CH{=}NOH$, 3717-23-5; (*E*)-$PhCH{=}NOH$, 622-31-1; (*E*)-4-$CH_3C_6H_4CH{=}NOH$, 3717-15-5; (*E*)-4-$MeOC_6H_4CH{=}NOH$, 3717-21-3; (*E*)-4-$ClC_6H_4CH{=}NOH$, 3717-24-6; (*E*)-$PhCH{=}NOMe$, 10229-53-5; (*E*)-4-$CH_3C_6H_4CH{=}NOMe$, 70286-36-1; (*E*)-4-$MeO_2CC_6H_4CH{=}NOMe$, 87829-03-6; (*E*)-4-$NCC_6H_4CH{=}NOMe$, 87861-01-6; (*E*)-4-$Me_2NC_6H_4CH{=}NOMe$, 87829-04-7; (*E*)-4-$MeOC_6H_4CH{=}NOMe$, 70286-37-2; (*E*)-4-$ClC_6H_4CH{=}NOMe$, 54615-09-7; (*E*)-4-$O_2NC_6H_4CH{=}NOMe$, 54615-10-0; (*Z*)-$PhCH{=}NOMe$, 10229-54-6; (*Z*)-4-$CH_3C_6H_4CH{=}NOMe$, 87861-02-7; (*Z*)-4-$MeO_2CC_6H_4CH{=}NOMe$, 87829-05-8; (*Z*)-4-$NCC_6H_4CH{=}NOMe$, 87861-03-8; (*Z*)-4-$Me_2NC_6H_4CH{=}NOMe$, 87829-06-9; (*Z*)-4-$MeOC_6H_4CH{=}NOMe$, 87861-04-9; (*Z*)-4-$ClC_6H_4CH{=}NOMe$, 87861-05-0.

Thermochemistry of Phenyl-Substituted Benzobicyclo[3.1.0]hex-2-enes. Evidence for Carbenes as Intermediates

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The thermal rearrangements of benzobicyclo[3.1.0]hex-2-ene (**21**) and its phenyl-substituted analogues **22–25** (Scheme V) as models of sterically constrained phenylcyclopropanes have been studied by means of flash vacuum pyrolysis. In most cases the major pathway was cleavage of the "internal" C(1)–C(5) cyclopropane bond followed by a 1,2-hydrogen or a 1,2-phenyl shift in the resulting biradical. For 6-phenylbenzobicyclo[3.1.0]hex-2-ene (**25**), substantial cleavage of the "external" C(1)–C(6) cyclopropane bond was observed, the phenyl substitution pattern being favorable for stabilization of the resulting biradical **62**. Phenyl-substituted 1,2-dihydronaphthalenes **44**, **47**, **51**, and **55** are among the major products. Comparison of the plots of the pyrolysis product composition of the 1,2-dihydronaphthalenes vs. pyrolysis temperature with similar plots of the title compounds (**22–25**) suggested that some of the minor products, viz., the 1,2-divinylbenzenes **31**, **42**, and **49**, are formed via carbenes **30**, **41**, **50**, **57**, and **61** rather than via biradicals. Especially at higher pyrolysis temperatures, a large amount of an oxidation product, viz., 1- or 2-phenylnaphthalene (**48** or **54**), is formed.

Thermal rearrangements of cyclopropanes have aroused considerable interest because of the intriguing theoretical problems involved.[1] At high temperatures cyclopropane (**1**) undergoes isomerization to propene (**3**), and the singlet