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Nitrobenzene Valence Bond Structures: Evidence in Support of "Through-Resonance" from ^{17}O Shieldings

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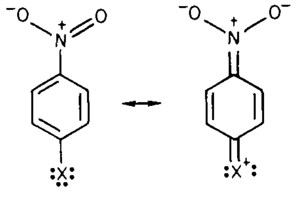
Very recently, Lipkowitz[1] presented ^{17}O NMR data from which he concluded that the electron distribution in a para-substituted nitrobenzene whose substituent possesses an unshared electron pair (e.g., Cl, OCH_3) is adequately described by structure **1** and


1 1a

that structure **1a** "is only a minor contributor to the total molecular wave function of para-substituted nitrobenzenes". Such a conclusion, if correct, would have far-reaching consequences because it refutes current concepts of the valence bond theory of resonance[2] and would require a complete revision of all standard textbooks of organic chemistry.

The direct resonance interaction of X with the nitro group is an example of the phenomenon that is now termed "through-resonance",[5] as defined by Clark and Perrin.[6] This is also the interaction whose presence requires the use of the σ^+ parameter for Hammett equation correlations.[5,7] Since Lipkowitz based his conclusion on limited experimental evidence,[8] we have reexamined the ^{17}O spectra of three of the para-substituted nitrobenzenes that he studied together with six additional derivatives whose electron-donating or attracting groups cover a 3-fold larger range of σ values. We report that our investigation reveals the ^{17}O shieldings to be strongly influenced by the nature of the para substituent and in a manner *completely consistent* with existing valence bond theory.

Table I. ^{17}O Shieldings Data[a] for Some Para-Substituted Nitrobenzenes ($4\text{-}X\text{-}C_6H_4NO_2$)

X	δ	X	δ
NEt_2	−33.4	Cl	0.7
NH_2	−25.8	COMe	3.3
OMe	−9.2	COOMe	7.2
Me	−3.7	CHO	8.6
H	0.0	CN	7.7

[a] In ppm measured relative to nitrobenzene for solutions in acetonitrile (300 mg in 2.5 mL) with 10-mm sample tubes. ^{17}O spectra were obtained at 27.12 MHz with a Varian XL-200 instrument; operating conditions were as follows: 200–400K transients, 90° pulse, 0.01-s repetition rate, and 32K transforms. Estimated precision ±1 ppm; negative values represent shifts to higher field (increased shielding).

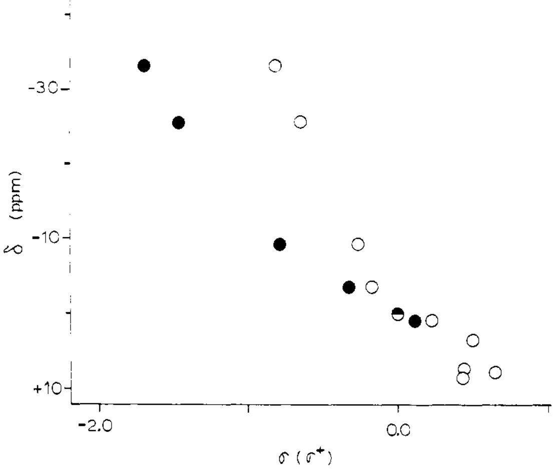


Figure 1. Plot of ^{17}O shieldings for nitrobenzenes (Table I) against σ (open circles) and σ^+ (closed circles) values.

The ^{17}O shieldings for the nitro group of the compounds examined are listed in Table I. All ^{17}O spectra were obtained with solutions that were sufficiently dilute (12% w/v) to have viscosities close to that of the solvent (acetonitrile) giving sufficiently narrow lines[9] to provide reasonably precise shieldings. Although ^{17}O signals are inherently broad owing to quadrupolar relaxation, our conditions afforded lines having half-widths of ~300 Hz. A plot of our ^{17}O data against σ (taken from ref 7) and σ^+ (taken from ref 10) values is presented in Figure 1, from which a correlation between δ and σ is apparent and a somewhat more linear relation exists between δ and σ^+. The trend is in the expected direction with the most electron-donating substituent ($X = NEt_2$) causing the ^{17}O signal to appear at highest field just as the greater charge on oxygen in **1a** would suggest. The fact that the correlation is improved with the σ^+ parameter is strong evidence for resonance interaction of the type shown in **1a**, which is precisely the "direct resonance interactions" for which the σ^+ values were created.[5,7] While the correlation between δ and the electronic properties of the substituents could undoubtedly be improved by using a multiparameter approach,[11] the crude δ vs. σ^+ correlation is itself sufficient evidence for the "through-resonance" interaction depicted by **1a**.

The reason for the stark contrast between our results and those of Lipkowitz[8] is not completely clear. Our use of acetonitrile, which proved to be the best solvent for nitrobenzene derivatives, may be a contributing factor. However, the importance of this factor cannot be assessed since Lipkowitz[1] provided no specific details on his use of solvents. It is evident that the greater precision of our data (±1 vs. ±5 ppm) coupled with our choice of substituents having a wider range of σ values (1.5 vs. 0.5 units) has clearly revealed the presence of substantial substituent effects on ^{17}O shifts.

It is interesting that the ^{17}O shielding changes observed in these nitrobenzenes are similar in magnitude and direction to those found previously for a series of para-substituted acetophenones.[12] These are also consistent with the very large increase in ^{17}O shielding (407 ppm) observed for the deprotonation of nitromethane,[9] much of which can be ascribed to the increased electron density on oxygen. For example, the exaltation in dipole moment (1.34 D)[13]

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(1) Lipkowitz, K. B. *J. Am. Chem. Soc.* **1982**, *104*, 2647.

(2) The earliest evidence for the importance of **1a** comes from dipole moment data showing exalted moments in such compounds, yet no such effects in sterically hindered 2,3,5,6-tetramethyl derivatives.[3-5]

(3) Ingraham, L. L. "Steric Effects in Organic Chemistry"; Newman, M. S., Ed.; Wiley: New York, 1956; p 479.

(4) Ferguson, L. N. "The Modern Structural Theory of Organic Chemistry"; Prentice-Hall: New York, 1964; p 344.

(5) Hammett, L. P. "Physical Organic Chemistry", 2nd ed.; McGraw-Hill: New York, 1970; p 358.

(6) Clark, J.; Perrin, D. D. *Q. Rev. Chem. Soc.* **1964**, *18*, 295.

(7) Hine, J. "Structural Effects on Equilibria in Organic Chemistry"; Wiley: New York, 1974; Chapter 3.

(8) The test for sensitivity in shielding to changes in X was limited by (a) choosing only three substituents ($X = CH_3$, Cl, OCH_3) whose σ values cover only a 0.5σ unit range, (b) the use of three different media (neat, benzene, or chloroform), and (c) less precise ^{17}O data (±5 ppm).

(9) In a recent review, Klemperer (Klemperer, W. G. *Angew. Chem., Int. Ed. Engl.* **1978**, *17*, 246) discusses the ways in which line widths due to short T_2 values may be decreased, i.e., by using low viscosity media or higher temperatures.

(10) Hoefnagel, A. J.; Wepster, B. M. *J. Am. Chem. Soc.* **1973**, *95*, 5357.

(11) Swain, C. G.; Lupton, E. C. *J. Am. Chem. Soc.* **1968**, *90*, 4328.

(12) Sardella, D. J.; Stothers, J. B. *Can. J. Chem.* **1969**, *47*, 3089.

0002-7863/82/1504-6475$01.25/0

J. Am. Chem. Soc. 1982, 104, 6476–6477

for *p*-(dimethylamino)nitrobenzene indicates the through-resonance effect to increase the electron density at the nitro group by 0.2 e (or 0.1 e per oxygen atom). The resulting increase of ~30 ppm in ^{17}O shielding ($X = NEt_2$ vs. H) suggests the effect to be ~300 ppm per electron. This is significantly larger than the generally accepted values for ^{13}C and ^{1}H, which are 160[14] and 10 ppm/electron, respectively.

In conclusion, ^{17}O shieldings in nitrobenzenes have been found to be sensitive to the electronic character of para substituents precisely in the manner anticipated from consideration of valence bond structure **1a**. Furthermore, the large sensitivity to electron density changes indicates ^{17}O to be an attractive probe of electron distributions.

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Registry No. 4-NEt_2-$C_6H_4NO_2$, 2216-15-1; 4-NH_2-$C_6H_4NO_2$, 100-01-6; 4-OMe-$C_6H_4NO_2$, 100-17-4; 4-Me-$C_6H_4NO_2$, 99-99-0; $C_6H_5NO_2$, 98-95-3; 4-Cl-$C_6H_4NO_2$, 100-00-5; 4-COMe-$C_6H_4NO_2$, 100-19-6; 4-COOMe-$C_6H_4NO_2$, 619-50-1; 4-CHO-$C_6H_4NO_2$, 555-16-8; 4-CN-C_6H_4-NO_2, 619-72-7.

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(13) Reference 3, p 508.

(14) Lammertsma, K.; Cerfontain, H. *J. Am. Chem. Soc.* **1979**, *101*, 3618.

Intramolecular Type II "Metallo-Ene" Reactions of (2-Alkenylallyl)magnesium Chlorides: Regio- and Stereochemical Studies

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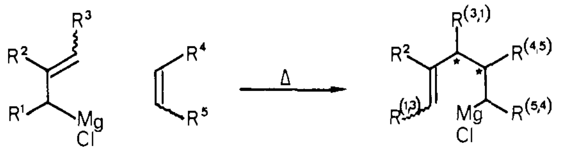
Despite the extensive pioneering work of Lehmkuhl[1], the formal ene addition of allylic Grignard reagents to olefins (eq 1) has not yet been applied to strategically devised organic synthesis. Also the more selective intramolecular type-I reaction[2] of 2,7-octadienylmagnesium halide[3] (eq 1, $R^3 = R^4 = (CH_2)_3$, $R^1 = R^2 = R^5 = H$) is virtually unexploited.[4]



(1)

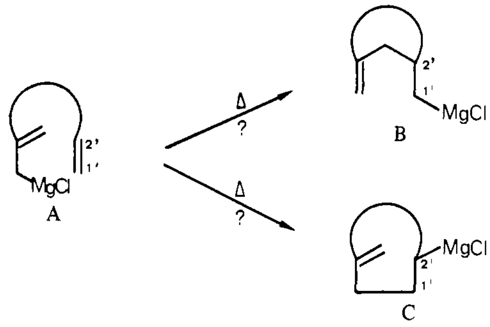
In conjunction with our interest in intramolecular ene reactions[2,5] we have examined the unprecedented "type-II metallo-ene" reaction (eq 1, $R^2 = R^4 = (CH_2)_n$). Our results showing the highly regio- and stereocontrolled formation of seven-, six-, and even five-membered methylene-substituted carbocycles are summarized in eq 2 and Table I.

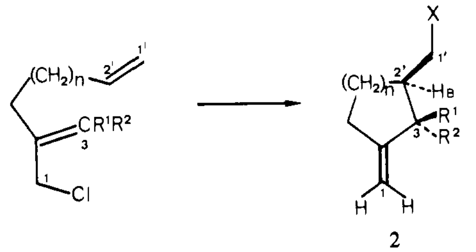
Table I. Thermal Cyclization of (2-Alkenylallyl)magnesium Chlorides Prepared from 1 and Subsequent Trapping

entry	*n*	R^1	R^2	Δ, temp, °C (time, h)	yield of *2*,[a,b] %	X
a	3	H	H	80 (17)	71	$CONHC_6H_5$[c]
b	2	H	H	80 (17)	72	$CONHC_6H_5$[c]
c	1	H	H	130 (23)	71	$CONHC_6H_5$[c]
d	3	CH_3	H	90 (60)	40[d]	$CONHC_6H_5$[c]
e	2	CH_3	H	80 (17)	86	$CONHC_6H_5$[c]
f	2	*n*-C_6H_{13}	H	80 (17)	81	H[e,f]
g	2	CH_3	CH_3	80 (17)	80	$CONHC_6H_5$[c]
h	2	CH_3	CH_3	80 (17)	*g*	H[e]

[a] Overall yield based on 1. [b] The products 2 were also characterized by ^{13}C NMR (90.561 MHz) and by melting point (ether-pentane, °C): 2a, 89–90; 2b, 131–132; 2c, 98–100.5; 2d, 115–116; 2e, 123–125; 2g, 121–123; 2f and 2h are oils. [c] Crude 2, X = MgCl was trapped with $C_6H_5N{=}C{=}O$ (1.2 equiv), −10 °C → room temperature 1 h, and the resulting mixture was heated in boiling bromobenzene for 12 min. [d] Noncyclized allylmagnesium chloride was trapped in 20% yield. [e] Crude 2, X = MgCl, was trapped with aqueous NH_4Cl, 0 °C. [f] The configuration of the single product 2f has not yet been determined. [g] Yield not determined.

Scheme I





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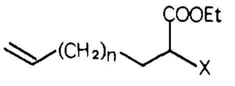
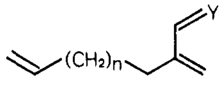
(2)

The allyl chlorides **1**[6] were readily prepared either from the malonates **3**[6] (**1a** to **1f**) or from the phosphonate **6**, *n* = 2[6] (**1g**).[7]



3, X = COOEt
6, X = $PO(OEt)_2$



4, Y = H, OH
1a–c, Y = H, Cl
5, Y = O

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(1) (a) For a recent review on additions of allylmagnesium halides and bis(2-alkenyl)zinc to olefins see: Lehmkuhl, H. *Bull. Soc. Chim. Fr.* **1981**, *part II*, 87. (b) See also: Shepherd, L. H., Jr. U.S. Patent 3 597 488, 1971; *Chem. Abstr.* **1971**, *75*, 88751c. Barbot, F.; Miginiac, P. *J. Organomet. Chem.* **1978**, *145*, 269.

(2) For a review on intramolecular ene reactions and their classification according to the mode by which the enophilic chain is attached at the olefinic terminal (type I), at the central atom (type II), or at the allylic terminal (type III) of the ene unit see: Oppolzer, W.; Snieckus, V. *Angew. Chem.* **1978**, *90*, 506; *Angew. Chem., Int. Ed. Engl.* **1978**, *17*, 476.

(3) Felkin, H.; Kwart, L. D.; Swierczewski, G.; Umpleby, J. D. *J. Chem. Soc., Chem. Commun.* **1975**, 242. Felkin, H.; Umpleby, J. D.; Hagaman, E.; Wenkert, E. *Tetrahedron Lett.* **1972**, 2285. Fukutani, H.; Takizawa, M.; Okada, H. *Japan Patent* 7 239 034 1972; *Chem. Abstr.* **1973**, *78*, 111498y.

(4) For a few isolated examples see ref 1 and the following: Courtois, G.; Masson, A.; Miginiac, L. *C. R. Hebd. Seances Acad. Sci. Paris, Ser. C*, **1978**, *286*, 265.

(5) Oppolzer, W.; Andres, H. *Tetrahedron Lett.* **1978**, 3397; *Helv. Chim. Acta* **1979**, *62*, 2282. Oppolzer, W.; Robbiani, C. *Ibid.* **1980**, *63*, 2010. Oppolzer, W.; Robbiani, C.; Bättig, K. *Ibid.* **1980**, *63*, 2015; Oppolzer, W.; Marazza, F. *Ibid.* **1981**, *64*, 1575. Oppolzer, W.; Bättig, K. *Ibid.* **1981**, *64*, 2489. Oppolzer, W.; Bättig, K.; Hudlicky, T. *Tetrahedron* **1981**, *37*, 4359.

(6) All new compounds were characterized by IR, ^{1}H NMR (360 MHz), and mass spectroscopy.

(7) **3** and **6** are easily accessible by alkylation of diethyl malonate (2 equiv, NaOEt (1.1 equiv), EtOH, reflux, 2 h) or of triethyl phosphonoacetate, respectively, with alkenyl bromides. Treatment of **3** with (i) NaH, DME; (ii) $LiAlH_4$;[8] (iii) $SOCl_2$, Et_2O gave **1a**[6] (51%) and **1b**[6] (45%). **1c**[6] (32%) was prepared by reaction of **4**, *n* = 1,[6] with NCS and DMS.[9] The 3-alkylallyl chlorides **1d–f**[6] were obtained (41–68%) from **4**[6] by treatment with (i) $COCl_2$, Me_2SO;[10] (ii) RMgBr, Et_2O; (iii) $SOCl_2$, Et_2O, 0 °C. For preparation of **1g**[6] (39%), **6**, *n* = 2,[6] was treated successively with (i) NaH, DME; (ii) acetone, 80 °C, 3 h;[11] (iii) $LiAlH_4$, Et_2O; (iv) MsCl, pyridine, -10 → 0 °C; (v) 1 N aqueous HCl, 0 °C, 5 min.[12]

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