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Diels–Alder Reaction between Vinylcyclohexene and Benzoquinones. A Shortcoming of the FMO Approach

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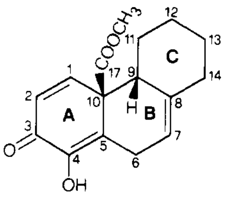
The cycloaddition of 1-vinylcyclohexene to in situ obtained 3- and 4-carbomethoxy-1,2-benzoquinone gives monoadducts; both crystal structures have been determined by X-ray diffraction. In the former reaction, the formation of a bis adduct is also observed. It is shown that the FMO approximation gives erroneous predictions of the regioselectivities. Moreover, the PMO predictions of chemo- and regioselectivities are strongly dependent on the level of approximation in the use of the PMO equation as well as on the distances between the reaction centers. It is suggested that these difficulties can be overcome if the interaction energies are calculated for the geometry corresponding to the minimum of the nonbonding energy of each possible adduct. These minima are considered as good descriptions of the early stages of the reaction. The obtained theoretical predictions are in good qualitative and semiquantitative agreement with the experimental results. The dominant term leading to endo selectivity is the polar term.

We recently investigated the efficacy of 2-carbomethoxy-1,4-benzoquinone (2CPBQ) in the cycloaddition with 1-vinylcyclohexene (VCH) in the building up of the hydrophenanthrene skeleton of 9,10-*syn*-podocarpane diterpenoids.[1a] To build up the same framework with different functionalities, 3-carbomethoxy-1,2-benzoquinone (3COBQ) and 4-carbomethoxy-1,2-benzoquinone (4COBQ) were submitted to cycloaddition with 1-vinylcyclohexene. To obtain the compounds useful to our synthetic proposal the "initial" bond formation in the cycloaddition had to occur between C-1′ of 3COBQ or 4COBQ and C-1 of VCH (adduct A in Figure 3). The aim of the synthesis was achieved because the useful compounds **1** and **2** were actually obtained; X-ray diffraction established their structures.



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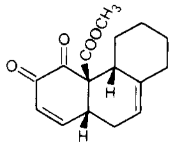

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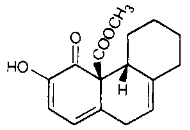

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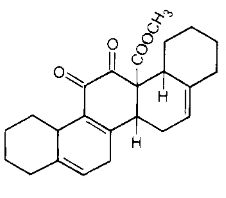

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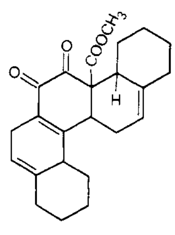

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Taking into account the present knowledge of pericyclic reactions,[2-6] we wondered if the significance of these results was obvious. We are persuaded that the entire set of results was neither predictable by analogic arguments nor could it be rationalized by the frontier molecular orbital (FMO) method.

In fact, the regioselectivity of the Diels–Alder reaction between an electron-poor dienophile and an electron-rich monosubstituted diene has been widely studied,[7-10] whereas there is little knowledge on the addition of dissymmetrical olefins to 1,2-disubstituted dienes.[2a,11] In those rare cases where a rigorous proof of structure is given, anti or syn products resulting from either predominant exo or endo cycloaddition can be found.[12-15] Moreover, the use of *o*-quinones as dienophiles has received little attention.[16] Ansell et al.[17] had shown that *o*-quinones bearing

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[§] Istituto di Chimica Fisica.

(1) (a) Orsini, F.; Pelizzoni, F.; Pitea, D.; Abbondanti, E.; Mugnoli, A. *J. Org. Chem.* **1983**, *48*, 2866–2870. (b) Pitea, D. *J. Mol. Struct. THEOCHEM* **1983**, *93*, 347–352.

(2) (a) Sauer, J. *Angew. Chem., Int. Ed. Engl.* **1967**, *6*, 16–33. (b) Sauer, J.; Sustmann, R. *Ibid.* **1980**, *19*, 779–807.

(3) (a) Houk, K. N. *J. Am. Chem. Soc.* **1973**, *95*, 4092–4094. (b) Houk, K. N.; Sims, J.; Watts, C. R.; Luskus, L. J. *Ibid.* **1973**, *95*, 7301–7315. (c) Houk, K. N. *Acc. Chem. Res.* **1975**, *8*, 361–369.

(4) Epiotis, N. D. *J. Am. Chem. Soc.* **1973**, *95*, 5624–5632.

(5) Fleming, I. "Frontier Orbitals and Organic Chemical Reactions"; J. Wiley: New York, 1982; pp 28–58.

(6) Eisenstein, O.; Lefour, J. M.; Anh, N. T.; Hudson, R. F. *Tetrahedron* **1977**, *33*, 523–531.

(7) Alder, V. K.; Vogt, W. *Liebigs Ann. Chem.* **1949**, *564*, 120–137.

(8) Ansell, M. F.; Clements, A. H. *J. Chem. Soc. C.* **1971**, 275–279.

(9) Cohen, T.; Mura, A. J., Jr.; Shull, D. W.; Fogel, E. R.; Ruffner, R. J.; Falck, J. R. *J. Org. Chem.* **1976**, *41*, 3218–3219.

(10) Overman, L. E.; Taylor, G. F.; Houk, K. N.; Domelsmith, L. N. *J. Am. Chem. Soc.* **1978**, *100*, 3182–3189.

(11) Jean, Y.; Salem, L. *J. Am. Chem. Soc.* **1978**, *100*, 5568–5569.

(12) Ansell, M. F.; Brooks, G. T. *J. Chem. Soc.* **1956**, *4518*–4524.

(13) Nazarov, I. N.; Kucherov, V. F.; Andreev, V. M.; Segal, G. M. *Croat. Chim. Acta* **1957**, *29*, 369–391.

(14) Winternitz, F.; Balmossiere, C. *Tetrahedron* **1958**, *2*, 100–115.

(15) Ireland, R. E.; Thompson, W. G.; Mandel, N. S.; Mandel, G. S. *J. Org. Chem.* **1979**, *44*, 3583–3585.

(16) Houben-Weyl "Methoden der Organischen Chemie"; Grundmann, C.; George Thieme Verlag: Stuttgart, 1979; pp 3–185.

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a 4-electron withdrawing substituent were sufficiently activated to react as dienophile with reactive acyclic dienes such as 2,3-dimethylbutadiene. Al-Hamdany et al.[18] reported the formation of a "normal" bis adduct in the reaction of 3-substituted catecholes with the same diene in the presence of an oxidizing agent. In these examples, the nature of the employed diene precludes any discussion on regio- and stereoselectivity. To the best of our knowledge the only previous example rigorously verified in terms of regiostereoselectivity and endo stereoselectivity is the condensation of 5-substituted-4-methoxy-1,2-benzoquinones with *trans*-1-methoxy-1,3-butadiene.[19]

We showed[1] that in the cycloaddition of VCH to 2CPBQ the FMO method predicts the formation of a product other than the one expected.[20-23] To explain the observed regioselectivity, some of the usual additional arguments (e.g., secondary orbital interactions[24] or corrections in the denominator of the $1/\Delta E$ equation to compensate for the proximity of the molecules[3,25,26]) have been tentatively introduced but without success. Analysis suggested the rather limited applicability of the generalized orbitals when the diene underwent multiple substitution. Similar examples may be found in the literature: a donor substituent enlarges the remote C-4 coefficient in the HOMO of a 1-phenyl substituted butadiene and the neighboring C-1 coefficient in the HOMO of a 2-methyl substituted butadiene, whereas, in a 1-phenyl-2-methyl disubstituted butadiene, the greatest coefficient is not at C-4 but at C-1.[27]

For the above reasons, the theoretical analysis presented here thoroughly explores the applicability of the complete Perturbational Molecular Orbital (PMO) theory[28] for rationalizing and predicting the regio-, stereo-, and chemoselectivities[29] observed in the reactions of *o*-benzoquinones. For comparison, the reaction of 2CPBQ with VCH will also be discussed.

Experimental Section

NMR spectra were taken on Varian XL 100, Varian XL 200, and Brucker WP 80 SY Spectrometers. IR spectra were recorded on a Perkin-Elmer 681 Spectrometer. UV spectra were recorded on a Perkin-Elmer 551 spectrometer. Mass spectra were recorded on a Varian MAT 112 apparatus. X-ray diffraction data were collected on a Nonius CAD 4 diffractometer.

Starting Materials. 1-Vinylcyclohexene and silver oxide were made by a previously reported procedure.[1a] Methyl 3,4-dihydroxybenzoate and Methyl 2,3-dihydroxybenzoate were prepared from acids with methanol and hydrochloric acid.

Methyl 4-Hydroxy-3-oxo-9*β*H-15,16-bisnorpodocarpa-1,4,7-trien-17-oate (1). A solution of 24 g (144 mmol) of methyl 3,4-dihydroxybenzoate and 17 g (160 mmol) of 1-vinylcyclohexene in 300 mL of benzene/ether was treated with 66 g (290 mmol) of silver oxide under nitrogen and in the dark. The mixture was stirred for 1 h and filtered through Celite. The filter pad was washed with ether and the combined filtrate was evaporated in vacuo to give 35 g of an orange solid. Recrystallization from diisopropyl ether gave 1 (11.4 g, 55%): mp 122–124 °C; IR ($CHCl_3$) 3350, 1735, 1650, 1610 cm^{-1}; UV max (EtOH) 245 nm (ϵ 5800), 315 nm (ϵ 5200); UV max (EtOH–0.1 N NaOH) 370 nm (ϵ 11 000); ^1H NMR ($CDCl_3$) δ 6.93 (d, 1 H, J = 10 Hz), 6.57 (d, 1 H, J = 10 Hz), 5.38 (m, 1 H), 3.77 (s, 3 H); ^{13}C NMR ($CDCl_3$) δ 180.3 s, 171.0 s, 149.4 d, 144.2 s, 140.6 s, 128.1 d, 125.2 s, 114.3 d, 55.9 s, 53.3 q, 48.5 d, 36.4 t, 29.9 t, 29.5 t, 26.5 t, 25.3 t. Anal. Calcd for $C_{16}H_{18}O_4$: C, 70.05; H, 6.61. Found: C, 70.12; H, 6.76. MS, m/z 274.

Cycloaddition of Methyl 2,3-Dihydroxybenzoate to 1-Vinylcyclohexene. A solution of 8.94 g (53.2 mmol) of methyl 2,3-dihydroxybenzoate and 7.55 g (70.0 mmol) of 1-vinylcyclohexene in 270 mL of benzene was treated with 54 g (380 mmol) of sodium sulfate and 25 g of silver oxide (108 mmol) under nitrogen and in the dark. The mixture was heated at reflux with rapid stirring for 1 h and filtered through Celite. The filter pad was washed with benzene and the combined filtrate was evapored in vacuo. Chromatography on silica gel (hexane/AcOEt = 8:3) gave **4** (4 g, 20%), **2** (2.6 g, 18%), and **3** (0.45 g, 3%). Recrystallization of **4** from ethyl acetate/hexane gave crystals: mp 165–167 °C; IR ($CHCl_3$) 1725, 1675, 1620 cm^{-1}; UV max (EtOH) 261 nm (ϵ 3410), 295 nm (sh); UV max (EtOH–0.1 N NaOH) 308 nm (ϵ 9600); ^1H NMR ($CDCl_3$) δ 5.3 (m, 2 H), 3.7 (s, 3 H); ^{13}C NMR ($CDCl_3$) δ 191.7 s, 183.5 s, 172.4 s, 163.1 s, 137.2 s, 136.8 s, 130.8 s, 116.0 d, 114.0 d, 65.8 s, 52.5 q, 43.4 d, 42.9 t, 42.1 d, 35.4 t, 34.3 t, 33.2 t, 32.3 t, 28.3 t, 27.2 t, 26.0 d, 25.8 t, 25.6 t, 23.8 t. Anal. Calcd for $C_{24}H_{28}O_4$: C, 75.76; H, 7.42. Found: C, 75.51; H, 7.59. Recrystallization of **2** from diisopropyl ether/ethyl acetate gave crystals: mp 78–80 °C; IR ($CHCl_3$) 1720, 1685, 1600 cm^{-1}; UV max (EtOH) 244 nm (ϵ 6042); ^1H NMR ($CDCl_3$) δ 7.46 (dd, 1 H, $J_{4,3}$ = 10 Hz, $J_{4.5}$ = 6 Hz), 6.38 (d, 1 H, $J_{3,4}$ = 10 Hz), 5.42 (m, 1 H), 3.8 (s, 3 H), 3.34 (ddd, 1 H, $J_{5,4}$ = 6 Hz, $J_{5,6\alpha}$ = 12 Hz, $J_{5,6\beta}$ = 6 Hz); ^{13}C NMR ($CDCl_3$) δ 191.6 s, 184.2 s, 172.2 s, 156.4 d, 136.9 s, 129.8 d, 115.8 d, 66.4 s, 52.8 q, 42.5 d, 42.4 d, 34.4 t, 31.5 t, 26.3 t, 26.1 t, 25.7 t. Anal. Calcd for $C_{16}H_{18}O_4$: C, 70.05; H, 6.61. Found: C, 70.27; H, 6.73. MS, m/z 274. Recrystallization of **3** from diisopropyl ether gave light yellow crystals: mp 145 °C; IR ($CHCl_3$) 3450, 1740, 1640, 1580 cm^{-1}; UV max (EtOH) 363 nm (ϵ 4610); UV max (EtOH–0.1 N NaOH) 412 nm (ϵ 4715), 270 nm (ϵ 3409); ^1H NMR ($CDCl_3$) δ 6.44 (d, 1 H, J = 7 Hz), 6.18 (bd, 1 H, J = 7 Hz), 5.32 (m, 1 H), 3.68 (s, 3 H); ^{13}C NMR ($CDCl_3$) δ 194.9 s, 168.3 s, 145.4 s, 141.2 s, 139.1 s, 117.2 d, 115.7 d, 115.4 d, 65.0 s, 53.1 q, 51.5 d, 35.9 t, 32.6 t, 29.6 t, 29.5 t, 26.4 t. Anal. Calcd for $C_{16}H_{18}O_4$: C, 70.05; H, 6.61. Found: C, 70.25; H, 6.69. MS, m/z 274.

Crystal Structure Determination of Compounds 1 and 2. After preliminary examination by means of Weissenberg photographs, a crystal of 1[30] was ground in a sphere (r = 0.17 mm) and mounted on a Nonius CAD 4 four-circle diffractometer equipped with a graphite monochromator. Twenty-five reflections were centered with Cu K_α radiation (λ = 1.54178 Å) to refine the lattice

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(17) Ansell, M. F.; Bignold, A. J.; Gosden, A. F.; Leslie, V. J.; Murray, R. A. *J. Chem. Soc. C.* **1971**, *1414*–1422.

(18) Al-Hamdany, R.; Ali, B. *J. Chem. Soc., Chem. Commun.* **1978**, 397–397.

(19) (a) Mazza, S.; Danishefsky, S.; McCurry, P. *J. Org. Chem.* **1974**, *39*, 3610–3611. (b) Danishefsky, S.; Schuda, P. F.; Mazza, S.; Kato, K. *Ibid.* **1976**, *41*, 3468–3473. (c) Danishefsky, S.; Schuda, P. F.; Caruthers, W. *Ibid.* **1977**, *42*, 2179–2180.

(20) Bohlmann, F.; Mathar, W.; Schwarz, H. *Chem. Ber.* **1977**, *110*, 2028–2045.

(21) (a) Houk, K. N.; Domelsmith, L. N.; Strozier, R. W.; Patterson, R. T. *J. Am. Chem. Soc.* **1978**, *100*, 6531–6533. (b) Tegmo-Larsson, I.-M.; Rozeboom, M. D.; Houk, K. N. *Tetrahedron. Lett.* **1981**, *22*, 2043–2046. (c) Tegmo-Larsson, I.-M.; Rozeboom, M. D.; Rondan, N. G.; Houk, K. N. *Ibid.* **1981**, *22*, 2047–2050.

(22) El-Enany, M.; Abd El-Fattah, A.; El-Basil, S. *Indian J. Chem. Sect. B* **1981**, *20B*, 592–594.

(23) Zhixing, C. *Theor. Chim. Acta (Berlin)* **1983**, *62*, 293–299.

(24) Ginsburg, D. *Tetrahedron* **1983**, *39*, 2095–2135.

(25) Fukui, K. "Theory of Orientation and Stereoselection"; Springer-Verlag: West Berlin, 1975.

(26) Houk, K. N. In Marchand, A. P.; Lehr, R. E. "Pericyclic Reactions"; Academic Press: New York, 1977; Vol. 2.

(27) Alston, P. V.; Ottenbrite, R. M. *J. Org. Chem.* **1975**, *40*, 1111–1115.

(28) (a) Salem, L. *J. Am. Chem. Soc.* **1968**, *90*, 542–552, 553–566. (b) Devaquet, A.; Salem, L. *Ibid.* **1969**, *91*, 3793–3800. (c) Devaquet, A. *Mol. Phys.* **1970**, *18*, 233–247.

(29) The following terminology will be used: regioselectivity = head-to-head and head-to-tail orientational choice involved when both diene and dienophile are unsymmetrically substituted (e.g., adducts A vs. B and C vs. D); stereoselectivity = endo/exo selection; chemoselectivity or side selectivity = discrimination between chemically nonequivalent double bonds (adducts A, B vs. C, D). With reference to the numbering of atoms given in Figure 2, adducts A, B, C, and D are identified by the bonds between atoms 1-1′ and 4-2′, 1-2′ and 4-1′, 1-4′ and 4-5′, 1-5′ and 4-4′, respectively.

(30) For compound 1, a preliminary account was reported by Mugnoli, A.; Moretto, A.; Orsini, F.; Pelizzoni, F. *Acta Crystallogr. Sect. A* **1981**, *A37S*, C84.

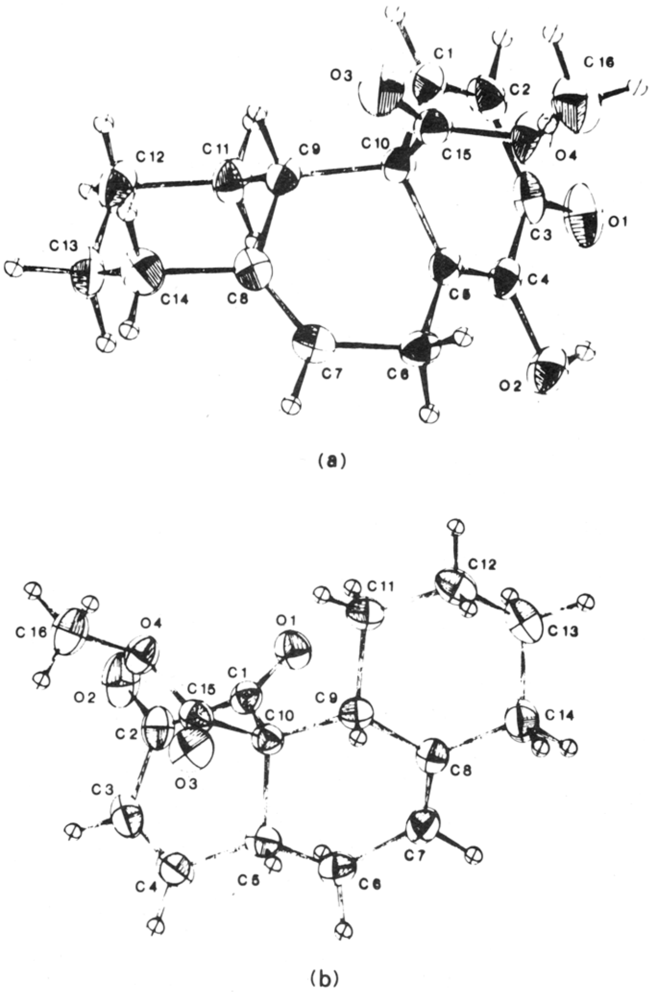

Figure 1. Thermal ellipsoid plots at 0.30 probability level: (a) compound **1**; (b) compound **2**. Hydrogen atoms, treated as isotropic, are on an arbitrary scale.

parameters, resulting in $a = 14.284$ (2) Å, $b = 8.624$ (1) Å, $c = 22.639$ (2) Å, $\beta = 93.07$ (1)°, monoclinic space group $C2/c$, $d_{\mathrm{obsd}} = 1.305$ (by flotation in a dilute K_2HgI_4 solution), $d_{\mathrm{calcd}} = 1.308$ g cm^{-3} for $Z = 8$ ($C_{16}H_{18}O_4$, M_r 274.32). Intensities were collected on the same diffractometer with Mo Kα radiation ($\lambda = 0.71069$ Å) with the ω scan mode (scan width = 1.20°, variable scan speed between 1.82° and 4° min^{-1}, θ range from 2° to 25°). One check reflection was monitored periodically to test the crystal stability, and three to test the crystal orientation. Lorentz and polarization factors were applied; absorption effects were neglected ($\mu = 0.55$ cm^{-1} for Mo Kα radiation). 2436 independent reflections were measured of which 1373 having $F \geqslant 2\sigma(F)$ were considered as observed.

A beautiful, transparent crystal of **2** was ground in a sphere ($r = 0.23$ mm) and mounted on the same diffractometer. Twenty-five reflections were centered with Mo Kα radiation ($\lambda = 0.71069$ Å) to refine the lattice parameters, resulting in $a = 9.344$ (1) Å, $b = 14.835$ (1) Å, $c = 10.179$ (1) Å, $\beta = 100.67$ (1)°, monoclinic space group $P2_1/n$, $d_{\mathrm{obsd}} = 1.310$ (by flotation in a dilute K_2HgI_4 solution), $d_{\mathrm{calcd}} = 1.314$ g cm^{-3} for $Z = 4$ ($C_{16}H_{18}O_4$, M$_r$ 274.32). Intensities were collected with Mo Kα radiation in the ω/θ scan mode (scan width = 0.8°, variable scan speed between 1.18 and 6.67° min^{-1}, θ range from 3° to 27.5°). One check reflection was monitored periodically to test the crystal stability, and three to test the crystal orientation. Lorentz and polarization factors were applied; absorption effects were neglected. 3159 independent reflections were measured of which 1841 having $F \geqslant 2\sigma(F)$ were considered as observed.

The two crystal structures were solved by direct methods with the system of programs SHELX 76.[31] For both compounds, all the non-hydrogen atoms were located on the corresponding "best" E map and all the hydrogen atoms were recognized subsequently via difference electron density syntheses during the refinement. This was performed by isotropic and then anisotroic full-matrix least-squares procedure on carbon and oxygen atoms, with a total number of 181 parameters in each structure; the contributions of the hydrogen atoms were included in the structure factor calculations with a thermal factor equal to the U (equivalent) value for the bonded atom. In the final cycle most shifts were less than 0.1σ, the maximum shift being less than 0.5σ; the discrepancy indexes over the observed reflections converged to $R = 0.039$ for compound **1** and to 0.038 for compound **2**. In both cases a final difference map showed no significant features, the electron density values ranging between ±0.19 e Å^{-3} (compound **1**) and ±0.16 e Å^{-3} (compound **2**).

The numbering of atoms is shown on the thermal ellipsoids plots[32] of Figure 1. The final coordinates of the heavier atoms as well as those of the hydrogen atoms and the anisotropic thermal parameters are included as supplementary material. The observed and calculated structure factors are available from the author (A.M.).

Computational Methods. With the use of the intermolecular orbital treatment of Salem and Devaquet,[28] the interaction energy (E_{int}) between the MOs of two conjugated molecules can be expressed as

$$E_{\mathrm{int}} = E_{\mathrm{rep}} + E_{\mathrm{mix}} + E_{\mathrm{pol}} \tag{1}$$

In this summation,[33] the closed-shell repulsion term (E_{rep}) and

$$E_{\mathrm{rep}} = \sum_{\mathrm{rr'}} (q_{\mathrm{r}} + q_{\mathrm{r'}})\eta_{\mathrm{rr'}} S_{\mathrm{rr'}} \tag{2}$$

the attractive term (E_{mix}) depend on the overlap between the interacting orbitals ($E_{\mathrm{over}} = E_{\mathrm{rep}} + E_{\mathrm{mix}}$). For the sake of simplicity, the terms of eq 3 have been simbolized as follows:

$$E_{\mathrm{mix}} = [E_\eta(\mathrm{j,k'}) + E_{\mathrm{s}}(\mathrm{j,k'})] + [E_\eta(\mathrm{k,j'}) + E_{\mathrm{s}}(\mathrm{k,j'})]$$

$$E_{\mathrm{mix}} = -2\sum_{\mathrm{j}}^{\mathrm{occ}}\sum_{\mathrm{k'}}^{\mathrm{vac}} \left[\frac{(\sum_{\mathrm{rr'}} c_{\mathrm{jr}} c_{\mathrm{k'r'}} \eta_{\mathrm{rr'}})^2}{E_{\mathrm{k'}} - E_{\mathrm{j}}} + 1/4(E_{\mathrm{k'}} - E_{\mathrm{j}}) \times (\sum_{\mathrm{rr'}} c_{\mathrm{jr}} c_{\mathrm{k'r'}} S_{\mathrm{rr'}})^2 \right] - 2\sum_{\mathrm{j'}}^{\mathrm{occ}}\sum_{\mathrm{k}}^{\mathrm{vac}} \left[\frac{(\sum_{\mathrm{rr'}} c_{\mathrm{kr}} c_{\mathrm{j'r'}} \eta_{\mathrm{rr'}})^2}{E_{\mathrm{k}} - E_{\mathrm{j'}}} + 1/4(E_{\mathrm{k}} - E_{\mathrm{j'}})(\sum_{\mathrm{rr'}} c_{\mathrm{kr}} c_{\mathrm{j'r'}} S_{\mathrm{rr'}})^2 \right] \tag{3}$$

The equation for the Coulombic term (E_{pol}), representing electrostatic interactions between net charges on the atoms, is ($\epsilon = 1$)

$$E_{\mathrm{pol}} = \sum_{\mathrm{ss'}} \Delta Q_{\mathrm{s}} \Delta Q_{\mathrm{s'}} / R_{\mathrm{ss'}} \tag{4}$$

Nonbonded interactions (E_{nb}) between all pairs of atoms s,s′ of the two addends were treated by using a Lennard–Jones "6–12" potential function:[34]

$$(E_{\mathrm{nb}})_{\mathrm{ss'}} = d_{\mathrm{ss'}} / R^{12}{}_{\mathrm{ss'}} - e_{\mathrm{ss'}} / R^{6}{}_{\mathrm{ss'}} \tag{5}$$

According to the PMO theoretical grounds, the analysis derived here concerns only those geometrical situations in which the two

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(31) Sheldrick, G. M. "SHELX 76, A Program for Crystal Structure Determination"; University of Cambridge: England, 1976.

(32) Johnson, C. K. "ORTEP, A Fortran Thermal-Ellipsoid Plot Program for Crystal Structure Illustrations"; U.S. Atomic Energy Commission Publication ORNL-3794, 1965.

(33) The following abbreviations apply: r,r′ and s,s′ = pairs of interacting atoms; $q_{\mathrm{r}},q_{\mathrm{r'}}$ = charge densities at centers r and r′; $\Delta Q_{\mathrm{s}},\Delta Q_{\mathrm{s'}}$ = net charges at centers s and s′; $c_{\mathrm{jr}},c_{\mathrm{kr}}$ = AO coefficients at center r in an occupied j or in a virtual k MO of the first molecule; $c_{\mathrm{j'r'}},c_{\mathrm{k'r'}}$ = AO coefficients of the second molecule; E_{j} = molecular orbital energy; $S_{\mathrm{rr'}}$ = overlap intergral; $\eta_{\mathrm{rr'}} = KS_{\mathrm{rr'}}$; $K = k(H_{\mathrm{rr}} + H_{\mathrm{r'r'}})$, $H_{\mathrm{CC}} = -11.4$ eV, $H_{\mathrm{OO}} = -14.8$ eV, $k = 1.75/2$; for further details, see ref 1a.

(34) Scott, R. A.; Scheraga, H. A. *J. Chem. Phys.* **1966**, *45*, 2091–2101.

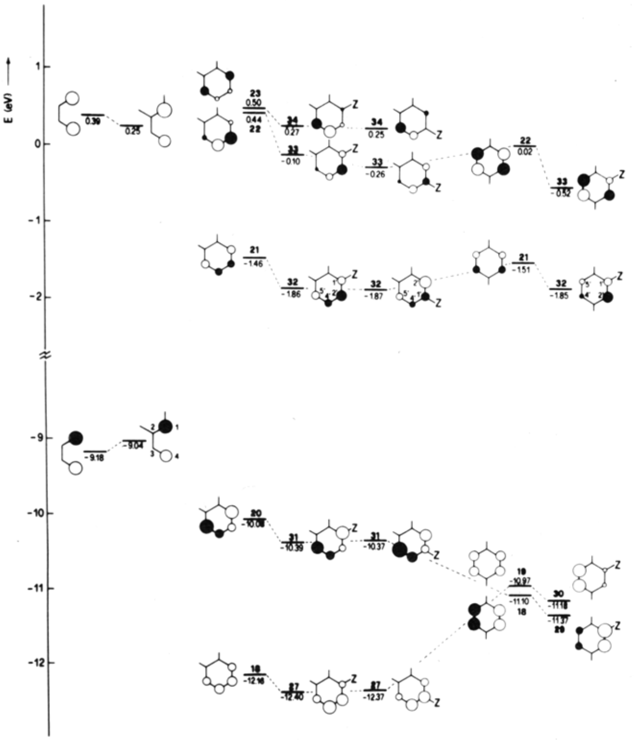

Figure 2. MNDO coefficients and energies of the most important π molecular orbitals of 1-vinylcyclohexene, 3- and 4-carbomethoxy-1,2-benzoquinone, 2-carbomethoxy-1,4-benzoquinone, and the parent compounds.

molecules interact in a four-center (or eight-center) approach with the molecular planes of diene and dienophile skeletons parallel to each other (see Figure 4 in ref 1a). Both symmetric and asymmetric configurations were studied.

Overlap integrals were calculated by standard formulas[35] taking into account the deviations of the overlapping orbitals from the alignment required for pure σ overlapping.[1a]

The geometries of the coplanar conformations of 3- and 4-carbomethoxy-1,2-benzoquinones were optimized by MNDO calculations.[36] The relative order of both coefficient magnitudes and energies of the MOs are shown in Figure 2. It was previously shown that these orders are substantially independent of the methods (both semiempirical or ab initio) of calculations.[1]

Results and Discussion

Products of Diels–Alder Reactions. 1-Vinylcyclohexene reacts with methyl 3,4-dihydroxybenzoate in the presence of silver oxide. A crystalline compound whose structure and relative stereochemistry correspond to structure **1** was isolated in good yield as the sole cycloaddition product. Clearly, **1** is the result of a Diels–Alder reaction followed by the enolization of the obtained α-diketone to tautomeric diosphenol.

The reaction of methyl 2,3-dihydroxybenzoate with 1-vinylcyclohexene was more complicated. Rapid chromatography gave a crystalline mono adduct, mp 79–80 °C (18%), whose structure **2** has been proved by X-ray diffraction, enol **3** (3%), which could arise by tautomerization of **2** during the workup,[37] and a third crystalline compound, mp 165–167 °C (20%), whose analytical properties and a comparison of spectral data with those of **2** suggest it to be a bis adduct **4**. The data reported in the Experimental Section do not allow for a choice between structures **4'** and **4''**. Both structures do involve a Diels–Alder addition to the C(4')–C(5') double bond of the quinone obtained in situ, oxidation and further addition. The whole process was carried out in the presence of silver oxide and no intermediates were isolated.[38]

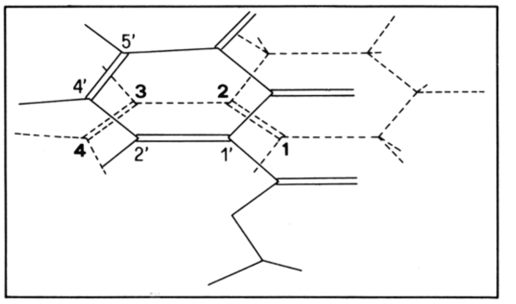

Figure 3. Transition-state model for the A-endo addition of 1-vinylcyclohexene to 3-carbomethoxy-1,2-benzoquinone as projection on the *xy* plane.

As the structures of compounds **1** and **2** were rigorously established by X-ray diffraction, the regiostereospecificity and endo stereospecificity of the cycloadditions of 3COBQ and 4COBQ to VCH were demonstrated.

Molecular Stereochemistry and Conformation in Crystals. The crystal structure determination of compounds **1** and **2** establishes the 9,10-*syn* junction for both substances and the 5,10-cis arrangement for compound **2**. The relevant torsion angles (see Figure 1) are as follows: C(15)–C(10)–C(9)–H(9) 41.6 (synclinal) for **1** and 49.9 (synclinal) for **2** and C(15)–C(10)–C(5)–H(5) −61.1 (synclinal) for **2**.

Owing to the different distribution of double bonds in the examined derivatives, ring A is remarkably puckered in compound **2**, whereas it is planar (within 0.014 Å) in compound **1**. In ring B corresponding torsion angles never differ by more than 7°. Ring C has essentially a chair conformation; however, some large deviations from the expected values of torsion angles are apparent. At least in part, they can be referred back to internal steric hindrance: e.g., for compound **2** the values of torsion angles C(14)–C(8)–C(9)–C(11) and C(8)–C(9)–C(11)–C(12) are only 38.6° and −42.8°, respectively, probably as a consequence of the repulsion exerted by the short intramolecular contact C(11)···O(1) (3.04 Å).

Bond distances and angles are in the normal range. Their values are included as supplementary material.

An intramolecular hydrogen contact is present in compound **1**, the O(2)···O(1) distance being 2.67 Å with an O–H···O angle of 129°. In the same compound, atom O(2) is involved even in a weak intermolecular hydrogen bond with atom O(3)' in $-^1/_2 + x$, $^1/_2 + y$, z, the O(2)···O(3)' distance being 3.14 Å and the O(2)–H···O(3)' angle 133°.

Besides this hydrogen linkage, there are some intermolecular contacts remarkably shorter than the sum of the involved van der Waals radii.[39] They are as follows: C(3)···C(16) in $-^1/_2 + x$, $-^1/_2 + y$, z (3.45 Å); C(6)···C(13) in $^1/_2 - x$, $^1/_2 - y$, $-z$ (3.68 Å); C(16)···C(16) in $1 - x$, y, $^1/_2 - z$ (3.77 Å) for compound **1**; C(12)···C(12) in $1 - x$, $-y$, $1 - z$ (3.69 Å) for compound **2**.

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[35] Mulliken, R. S.; Rieke, C. A.; Orloff, D.; Orloff, H. *J. Chem. Phys.* **1949**, *17*, 1248–1267.

[36] Dewar, M. J. S.; Thiel, W. *J. Am. Chem. Soc.* **1977**, *99*, 4899–4907. QCPE program 379.

[37] A quantitative enolization of **2** to **3** was carried out with Dabco in methanol at room temperature.

[38] We cannot account for all the material used in either the reaction of methyl 3,4-dihydroxybenzoate and methyl 2,3-dihydroxybenzoate with vinylcyclohexene. Although the analysis of the mother liquors shows several other unidentified spots, we believe that the major loss arises from a polimeric tar.

[39] Pauling, L. "The Nature of the Chemical Bond"; Cornell University Press: Ithaca, New York, 1960.

Table I. Contributions to the Attractive Energy Expressed As Percentages of the Energy E_η.[a] The Values Are for $R_{rr'} = R_{ss'} = 2$ Å[b]

		interacting MO's diene–dienophile[c]					
dienophile	adduct	HO-34	HO-33	HO-LU	LU-HO	LU-27[d]	ΔE_η[e]
3COBQ	A		17.3	25.5	21.5	15.2	5.9
	B		18.0	25.9	20.5	15.9	7.0
	C	23.9		20.4	19.9	18.2	8.5
	D	23.7		20.8	20.5	17.5	8.5
4COBQ	A		13.3	27.3	18.3	16.5	2.8
	B		13.4	27.9	19.0	15.9	3.3
	C	20.1	11.3	13.3	24.3	13.9	11.2
	D	20.2	10.6	13.4	25.1	13.3	10.6
2CPBQ	A		19.2	25.2	5.7	28.4	0.0
	B		19.6	25.7	5.7	28.3	0.9
	C		28.1	11.5	27.6	10.8	7.8
	D		28.2	11.3	27.6	10.8	7.6

[a] $E_\eta = E_\eta(j,k') + E_\eta(k,j')$. Energies are expressed in kJ mol^{-1}. [b] Except for the FMO's interactions, only contributions greater than 10% are reported. [c] For the numbering, see Figure 2. [d] For 2CPBQ, the MO's number of the dienophile is 29. [e] $E_\eta^\circ = -296.3$.

Perturbational Molecular Orbital Calculations. In each of the studied reactions, four possible chemo and regio adducts can be obtained.

An analysis of the frontier molecular orbitals (Figure 2) shows that the 1,2-disubstitution by the ring on the s–cis butadiene skeleton is the cause of the HOMO and LUMO energies and coefficients being somewhat different from the ones expected when there is monosubstitution by an electron donor group either at C-1 or at C-2.[5] The HOMO is raised in energy whereas the LUMO is lowered: the former effect is consistent whereas the latter is contrary to that expected. The polarizations of the HOMO and the LUMO correspond to those expected for 2-X substituted and 1-X substituted dienes, respectively; the coefficient of the HOMO at C-1 (0.56) is a little greater than the coefficient at C-4 (0.51). The effects of electron withdrawing group on the benzoquinones skeleton are those expected.[40] In the LUMOs, the coefficient magnitude is in the order C-2′ > C-1′ > C-5′ > C-4′, but the differences are strongly reduced in 3COBQ.[41] As Figure 2 shows, the smallest energy gaps are those between the HOMO of the diene and the LUMO of the dienophiles; hence, at the FMO level, this HOMO–LUMO interaction should give the largest contribution to the interaction energy (E_{int}, eq 1). It has been suggested[3a,42] that Diels–Alder reactions involving unsymmetrical components occur by a concerted but nonsynchronous mechanism[43,44] in which bond formation first occurs between reaction centers having the largest coefficients. So, bonding between carbons 1 and 2′ should precede the bonding between other centers and, in each case, the regio adduct B[29] should be the major product. This prediction is clearly at odds with experimental results. In any case, owing to the small difference in sizes of terminal HOMO coefficients in VCH, FMO theory could hardly be expected to be very reliable.

Another reason for the failure of the FMO approximation lies in the contributions of other orbital interactions to the stabilization energy (E_{mix}, eq 3). The most important contributions along the concerted synchronous pathways are reported in Table I. It can be clearly seen that the relative weight of each interaction changes for different adducts of the same dienophile as well as for the same adduct of different dienophiles. Moreover, $E_\eta(j,k')$ and $E_\eta(k,j')$ are of the same order of magnitude. Similar results have also been obtained from calculations at $R_{rr'} \neq R_{ss'}$.

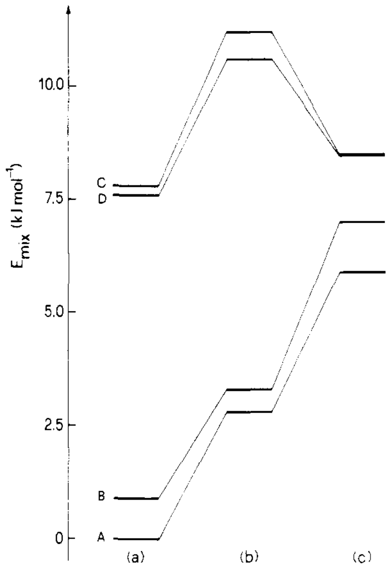

Figure 4. Distributions and relative attractive energies for the reactions of 1-vinylcyclohexene with: (a) 2-carbomethoxy-1,4-benzoquinone; (b) 4-carbomethoxy-1,2-benzoquinone; (c) 3-carbomethoxy-1,2-benzoquinone.

At a more advanced level of approximation, the stabilization energy can be used to study the change in energy which accompanies the interactions between orbitals in both reactants. Along the concerted synchronous paths, the preferred chemo adducts result in A and B (Figure 4); the major regio adduct should be A, in agreement with the experimental findings. The formation of the bis adduct 4 is an important piece of information in establishing the lack of chemoselectivity of dienophile 3COBQ; as Figure 4 shows, the energy difference between the adduct's pairs A,B and C,D[29] is strongly reduced when the dienophile is 3COBQ and so there is a qualitative agreement between experiment and calculation.

However, this level of analysis does not allow a theoretical interpretation of the stereoselectivity. To do this, closed-shell repulsion (E_{rep}, eq 2) and Coulombic (E_{pol}, eq 4) terms must be introduced. These calculations may be made taking into account the overlap between either two pairs or four pairs of atomic p orbitals.

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(40) Rozeboom, M. D.; Tegmo-Larsson, I.-M.; Houk, K. N. *J. Org. Chem.* **1981**, *46*, 2338–2345.

(41) It can be noticed that the symmetries of the HOMO and the subadjacent HOMO (SHOMO) in 2CPBQ are reversed with respect to COBQs.

(42) Boeckman, R. K., Jr.; Ko, S. S. *J. Am. Chem. Soc.* **1980**, *102*, 7146–7149.

(43) Salem, L. "Electrons in Chemical Reactions"; J. Wiley: New York, 1982; pp 28–58.

(44) Dewar, M. J. S.; Chantranupong, L. *J. Am. Chem. Soc.* **1983**, *105*, 7152–7161, 7161–7167.

Table II. Interaction Energies (in kJ mol^{-1}) for the Endo Mechanism as a Function of the Distance $R_{rr'} = R_{ss'} = R$

		R = 2 Å			R = 3.2 Å			R = 4.0 Å		
dienophile	adduct	ΔE_{over}	ΔE_{pol}	ΔE_{int}	ΔE_{over}	ΔE_{pol}	ΔE_{int}	ΔE_{over}	ΔE_{pol}	ΔE_{int}
3COBQ	A	8.7	0.3	9.0	0.35	−0.23	0.12	0.010	−0.162	−0.15
	B	9.9	2.5	12.4	0.39	0.22	0.61	0.013	0.018	0.03
	C	7.6	2.2	9.8	0.28	0.16	0.45	0.008	−0.052	−0.04
	D	7.7	1.5	9.2	0.28	−0.03	0.25	0.008	−0.162	−0.16
4COBQ	A	4.4	1.2	5.6	0.17	0.00	0.17	0.003	−0.072	−0.07
	B	5.0	0.1	5.1	0.20	−0.36	−0.17	0.004	−0.242	−0.23
	C	11.1	−0.6	10.5	0.42	0.00	0.42	0.014	−0.032	−0.02
	D	10.7	1.8	12.5	0.40	0.03	0.44	0.013	−0.112	−0.10
2CPBQ	A	0.0	0.0	0.0	0.0	0.00	0.00	0.000	0.000	0.00
	B	0.8	−0.1	0.7	0.03	−0.17	−0.14	0.002	−0.113	−0.11
	C	5.5	1.8	7.2	0.18	0.17	0.35	0.004	−0.029	−0.02
	D	5.3	2.0	7.3	0.18	0.23	0.41	0.012	−0.025	−0.02
$E°$		−71.3	−7.4	−78.7	−2.78	−2.27	−5.05	−0.121	−1.098	−1.22

In the former case, the difference between the endo and exo interaction energies is entirely due to the polar terms.[45] Calculations[46] show that endo isomers are favored at any pair of distances $R_{rr'}$ and $R_{ss'}$.

In the latter case, i.e., when the "secondary interactions" are introduced[24] the E_{over} becomes less negative (higher activation enthalpy) for the endo mechanism than for the exo.[46,47] The introduction of the remote orbital interactions indicate a preference for the exo mechanism, thereby disagreeing with Alder's endo rule. Others have already obtained similar results.[28,48,49]

In the light of these facts, the polar effects rather than the secondary orbital interactions seem to be the dominant factor in stereoselectivity for such reactions.

The contributions of the polar and repulsive energies to the interaction energy emphasize a further problem. As Table II shows, at shorter distances between the reaction centers the polar terms are negligible in comparison with the corresponding overlap terms while, with increase in distance, the polar terms become increasingly more important. So, the "order of stability" of the adducts changes with distance. The same occurs when concerted nonsynchronous paths are investigated.[50]

The observation that the order of stability depends on the distance between the reaction centers[3] as well as on the used energy criteria is not astonishing per se but is noteworthy especially in two contexts: (i) the use of the weakly interacting complexes in the early stages of the reaction as models for the corresponding transition states; (ii) the well-known sensitivity of the Diels–Alder reactions to steric factors.[2a] In other words, a basic question emerges: can the energy calculations be performed at any arbitrarily chosen pair of distances $R_{rr'}$ and $R_{ss'}$ for each possible approach or must these values reflect the "effective" possibility of approach of the two reagent molecules?

Table III. Values of the Interaction Energies (in kJ mol^{-1}) for the Endo Mechanism in the Minima of the Nonbonding Energy

dienophile	adduct	$R_{rr'}$, Å	$R_{ss'}$, Å	ΔE_{int}[a]
3COBQ	A	3.2	3.4	1.2
	B	3.2	3.2	0.4
	C	3.2	3.8	2.2
	D	3.6	3.4	2.1
4COBQ	A	3.2	3.2	0.2
	B	3.4	3.4	1.6
	C	3.8	3.4	3.4
	D	3.6	3.4	2.6
2CPBQ	A	3.0	3.4	0.0
	B	3.4	3.2	4.2
	C	3.0	3.6	1.6
	D	3.4	3.2	7.6

[a] $E_{int}° = -4.8$ kJ mol^{-1}.

We think that the interaction energy calculations cannot be performed at any arbitrary distance and that the effect of the proper volume of the molecules needs to be introduced as a fundamental component of the energetic criteria. We suggest here that the physical nonbonding interactions should be used to estimate the *effective* possibility of approach of the two reagent molecules and that a good picture of the weakly interacting complexes for the different geometries of approach should be given by the pair of distances rr′ and ss′ which minimize the nonbonding energy for the geometrical approach under examination.

Owing to the conformational characteristics of 1-vinylcyclohexene,[51] the validity of Hammond's postulate can be assumed[43] and the transition states should be reactant-like. Moreover, in going to the nonbonding energy minimum, the reagent molecules approach each other with an energy gain. To go on toward the products, the repulsive interactions must be overcome and bonds must be broken and formed. This requires deformations of the molecular skeletons, σ–π interactions, and so on, i.e., an energy cost. For the isomeric adducts formed from each pair of addends, we assume that the differences between these energies as well as between the entropies of activation are not significantly different; then, the relative energies of the transition states should be paralleled by the relative *interaction energies evaluated in the minima of the nonbonding energy.*

Table III shows the distances between the reaction centers in these minima (i.e., the localizations of the early stages of the reactions) as well as the corresponding interaction energies. The relative order of E_{int} is consistent

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(45) The distances between the four reaction centers in each pair of stereoisomers being the same at any fixed geometry, the $E_{over} = E_{mix} + E_{rep}$ terms are equal.

(46) These results are not reported here; they aree disposable upon request.

(47) The distances between the "remote" centers in the endo configurations are nearly equal to those between the "primary" centers whereas, in the exo configurations, they are significantly greater. As the consequence, when compared with the former case, the E_{rep} almost doubles in value and the E_{mix} has a lower percentage increment in the endo configuration whereas, in the exo isomers, the E_{rep} and E_{mix} values remain practically unchanged.

(48) Inukai, T.; Sato, H.; Kojima, T. *Bull. Chem. Soc. Jpn.* **1972**, *45*, 891–894.

(49) In simplified analyses, the E_{rep} term is frequently ignored as negligible and the undoubted stabilizing effect on E_{mix} of endo transition states determines a preference for the endo mechanism.

(50) If suitable geometrical conditions (e.g., quite small distances between the addends) are selected to study the early stages of the reactions, the attractive term prevails and a good agreement can be obtained between theory and experiments. However, this choice seems rather arbitrary with respect to the theoretical background of the PMO theory.

(51) Pitea, D.; Moro, G.; Tantardini, G. F.; Todeschini, R. *J. Mol. Struct.: THEOCHEM* **1983**, *105*, 291–306.

J. Org. Chem. 1985, 50, 1859-1863

with that of E_{mix} in Figure 4. The new information concerns the reaction pathways which should be rather unsymmetrical for the reactions of 2CPBQ and 3COBQ and symmetrical for 4COBQ.

In conclusion, the present work indicates that the predictions of the chemo- and regioselectivities in the vinylcyclohexene–benzoquinones cycloaddition are strongly dependent on the level of approximation in the use of the PMO equation as well as on the distances between the reaction centers. These difficulties can be overcome if the complete PMO equation is coupled to an "external" description of the early stages of the reactions. We suggest that this description should be provided by evaluating the minimum of the nonbonding energy.

The analysis of three reactions does not allow us to state a theory. The aim of the present work is to analyze the failure of the simplest theoretical approximation in these reactions and to search for an alternative theoretical approach. Further work on a larger set of examples is in course.

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Registry No. **1**, 95673-71-5; **2**, 95673-72-6; **3**, 95673-73-7; **4′**, 95673-74-8; **4″**, 95673-75-9; methyl 3,4-dihydroxybenzoate, 2150-43-8; methyl 2,3-dihydroxybenzoate, 2411-83-8; 1-vinylcyclohexene, 25168-07-4; 2-carbomethoxy-1,4-benzoquinone, 3958-79-0.

Supplementary Material Available: Final coordinates of the atoms and thermal parameters with their estimated standard deviations for the crystal structure determinations of compounds 1 and 2 (8 pages). Ordering information is given on any current masthead page.

Cationic Carbon-to-Nitrogen Rearrangements in *N*-(Arylsulfonoxy)amines[1]

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A series of *N*-alkyl-*O*-(arylsulfonyl)hydroxylamines was prepared by the reaction of amines with bis(arylsulfonyl) peroxides. In the absence of base, these amine derivatives underwent rearrangement involving the migration of groups from carbon to nitrogen. The migratory tendencies of the groups which rearranged were found to be in the order Ph > H > alkyl > Me. The migratory aptitudes Ph/Me > 72 and *n*-hexyl/Me = 4.2 suggest that these rearrangments are polar in nature and involve electron-deficient nitrogen species. Furthermore the migration of groups was found to be sensitive to the substitution pattern at the migration origin and subject to stereoelectronic control.

The reaction between amines and arylsulfonyl peroxides has been shown to be a convenient way to prepare *N*-(arylsulfonoxy)amines[2,3] (eq 1). These materials undergo

$$2RCH_2NH_2 + (ArSO_2O)_2 \xrightarrow[-78\ °C]{EtOAc} RCH_2NH\text{-}OSO_2Ar + RCH_2NH_3^+ArSO_3^- \quad (1)$$

facile biomolecular elimination to imines in the presence of bases.[4] In the absence of base, however, products resulting from carbon-to-nitrogen rearrangements have been observed.[5] The *N*-arylsulfonoxy derivatives of both tritylamines and benzhydrylamines decompose by ionization of the N–O bond that is accompanied by migration of an aromatic group from carbon to nitrogen (eq 2). These systems are highly prone to rearrangment because of the good migrating groups present in these compounds.

$$PhCArRNHOSO_2Ar' \rightarrow PhCR{=}NAr + ArCR{=}NPh \quad (2)$$

$$R = Ph,\ H$$

We wished to determine if carbon-to-nitrogen rearrangement is a general decomposition pathway of *N*-(arylsulfonoxy)amines—even those with poorer migrating groups present—and if so, what structural features influence the products. It was also pertinent to establish whether a polar mechanism is the general decomposition route for *N*-(arylsulfonoxy)amines. To address these issues we prepared a series of *N*-(arylsulfonoxy)amines and studied their decompositions. The results are reported herein.

Results

A series of amines were converted to their corresponding *N*-(*m*-(trifluoromethyl)phenylsulfonoxy) (OTFBs) derivatives by reaction with *m*-(trifluoromethyl)benzenesulfonyl peroxide in ethyl acetate solvent. They were purified by low-temperature silica gel chromatography. Adducts **1**, **4**, **6**, and **7** were sufficiently stable to be isolated whereas adducts **2**, **3**, **5**, and **8** could not be isolated in pure form. Consequently they were generated, purified, and used in situ.

Ethyl acetate or chloroform solutions of adducts **1–8** decomposed slowly at room temperature to give rearranged products (eq 3). The progress of the reaction was monitored by thin-layer chromatography and by testing for the presence of adduct, which gave a positive starch/iodine

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[1] Taken in part from the Ph.D. Thesis of A.K. submitted to the Graduate School of New Mexico State University, Decemter 1983.

[2] (a) Hoffman, R. V.; Belfoure, E. L. *Synthesis* **1983**, 34. (b) Hoffman, R. V.; Belfoure, E. L. *J. Am. Chem. Soc.* **1979**, *101*, 5687. (c) Hoffman, R. V.; Cadena, R. *Ibid.* **1977**, *99*, 8226.

[3] For other attempts to prepare these materials, see: (a) Berlin, A. Y.; Shchukina, M. N.; Sayanova, E. D. *Zh. Obshch. Khim.* **1944**, *14*, 249. (b) Gassman, P. G.; Hartman, G. D. *J. Am. Chem. Soc.* **1973**, *95*, 449. (c) Boche, G.; Mayer, N.; Bernheim, M.; Wagner, K. *Angew. Chem., Int. Ed. Engl.* **1978**, *17*, 687. (d) Gassman, P. G.; Granrud, J. E. *J. Am. Chem. Soc.* **1984**, *106*, 1498, 2448.

[4] (a) Hoffman, R. V.; Belfoure, E. L. *J. Am. Chem. Soc.* **1982**, *104*, 2183. (b) Hoffman, R. V.; Cadena, R. *Ibid.* **1977**, *99*, 8226. (c) Hoffman, R. V. *Ibid.* **1976**, *98*, 6702.

[5] (a) Hoffman, R. V.; Poelker, D. J. *J. Org. Chem.* **1979**, *44*, 2364. (b) Hoffman, R. V.; Cadena, R.; Poelker, D. J. *Tetrahedron Lett.* **1978**, 203.

0022-3263/85/1950-1859$01.50/0