π-Facial Selectivities in Cycloadditions to Norbornyl- and Norbornenyl-Fused *p*-Benzoquinones

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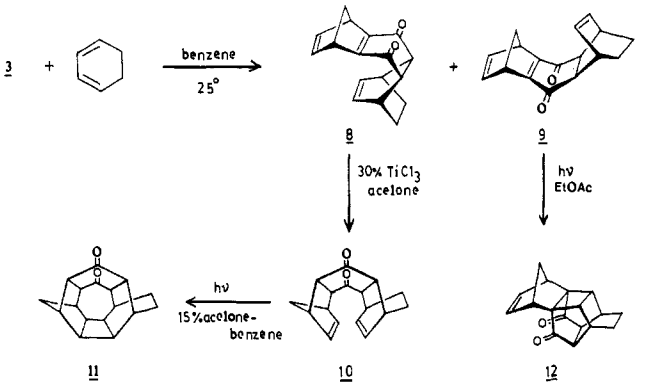
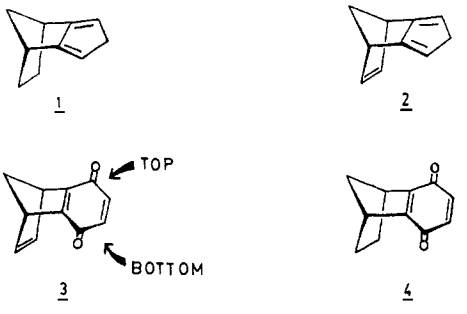
Abstract: The stereochemistry of the Diels–Alder cycloaddition of several dienes to the facially perturbed dienophiles 2,3-norbornenobenzoquinone (**3**) and 2,3-norbornanobenzoquinone (**4**) has been examined. Unambiguous structural proof for the adducts formed has been obtained from complementary ^1H and ^{13}C NMR spectral data and in two cases through X-ray crystal structure determination. While 1,3-cyclopentadiene, 1,3-cyclohexadiene, and cyclooctatetraene exhibit preference for addition to **3** from the bottom side, the stereochemical outcome is reversed in their response to **4**. 1,3-Diphenylisobenzofuran and 1,2,3,4-tetrachloro-5,5-dimethoxycyclopentadiene engaged **3** from the top side with marked selectivity, which is further enhanced in their reaction with **4**. The observed stereoselectivities seem to be essentially controlled by steric interactons at the transition state. Model calculations provide support for this interpretation.

The issue of stereoselectivities exhibited by facially perturbed dienes in Diels–Alder reactions has been subjected to considerable theoretical and experimental scrutiny in recent years.[3] In particular, the stereoselectivity of Diels–Alder additions to norbornyl- and norbornenyl-fused diene systems, e.g., isodicyclopentadiene **1** (ICPD) and isodicyclopentatriene **2** (ICPT), has been extensively investigated by several groups[4-8] and a variety of models based on simple steric effects, product stability,[8] various orbital interactions,[6a,k,9,10] and torsional effects[11] have been proposed to rationalize the observations. However, complementary investigations involving the response of a facially perturbed dienophile to various dienes has not received matching attention.[12] In this context, our attention was drawn to 2,3-norbornenobenzoquinone (**3**);

Scheme I





NPBQ)[13] and 2,3-norbornanobenzoquinone (**4**; dihydro **3**, DNPBQ),[13] dienophiles incorporating a bicyclo[2.2.1]heptyl moiety and having their two faces differentiated through the presence of methano and etheno (ethano in **4**) bridges. It was anticipated that a study of stereochemical outcome (top vs bottom) of cycloadditions to **3** and **4** would shed light on the operation of some of the stereoelectronic influences inherent in the norbornyl and norbornenyl frameworks.

(1) (a) Hyderabad. (b) Madras. (c) Bangalore.
(2) Author to whom enquiries about X-ray crystallographic studies should be addressed.
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(12) For example, see: Mazzocchi, P. H.; Stahly, B.; Dodd, J.; Rondan, N. G.; Domelsmith, L. N.; Rozeboom, M. D.; Caramella, P.; Houk, K. N. *J. Am. Chem. Soc.* **1980**, *102*, 6482.
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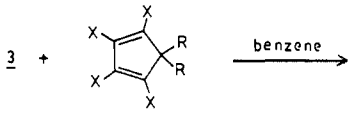
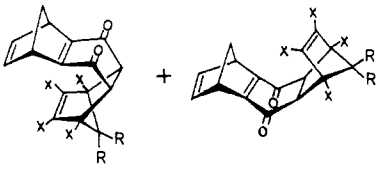
Our initial observations[14,15] with **3**, made in another context, fully supported this expectation. We found that addition of 1,3-cyclopentadiene (**5a**) to **3** furnished 1:1 adducts **6a** and **7a**



5a. R=X=H
5b. R=OCH_3, X=Cl



6a. R=X=H
6b. R=OCH_3, X=Cl

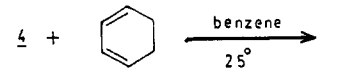
7a. R=X=H
7b. R=OCH_3, X=Cl

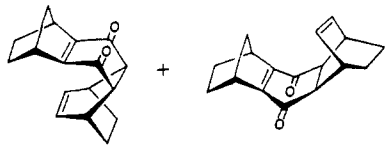
in a ratio of 35:65 (top to bottom). However, addition of 5,5-dimethoxytetrachloro-1,3-cyclopentadiene (**5b**) to **3** furnished **6b** and **7b** in a ratio of 77:23 (top to bottom).[15] This reversal of stereoselectivity could not be readily rationalized and provided the impetus for a detailed study. In this report, we describe the results of cycloaddition of several dienes, viz., 1,3-cyclohexadiene, cyclooctatetraene (COT), 1,3-diphenylisobenzofuran (**17**) and isodicyclopentatriene (**2**), to dienophiles **3** and **4** and provide a rationale for the observations on the basis of theoretical considerations.

Results

Cycloaddition with 1,3-Cyclohexadiene and COT. 1,3-Cyclohexadiene was added to NPBQ **3** at room temperature in benzene solution to furnish two 1:1 endo adducts **8** and **9** (62 bottom:38 top) in 95% yield. The endo configuration and stereostructures of **8** and **9** were secured on the basis of incisive analyses of ^1H NMR and ^{13}C NMR data (Table I) and chemical transformations indicated in Scheme I. A distinguishing ^1H NMR feature of the "bottom-side" adduct **8** and the "top-side" adduct **9** is the relative shielding of the cyclohexene olefinic protons in the former (δ 5.98) compared to the latter (δ 6.13). We have consistently observed this shielding effect in other pairs of adducts also and it has proved valuable in stereochemical assignments.

Reduction of the ene–dione moiety in **8** with aqueous $TiCl_3$[16] furnished the dione **10** via stereoselective reduction from the exo face.[14] Photochemical intramolecular 2 + 2 cycloaddition in **10** furnished the heptacyclic caged dione **11** and established the stereostructure of **8**. On irradiation **9** furnished **12** through intramolecular 2 + 2 cycloaddition. Addition of 1,3-cyclohexadiene to DNPBQ **4** furnished two cycloadducts **13** and **14** (20:80) in 80% yield, corresponding to bottom-side and top-side cycloaddition products, respectively.

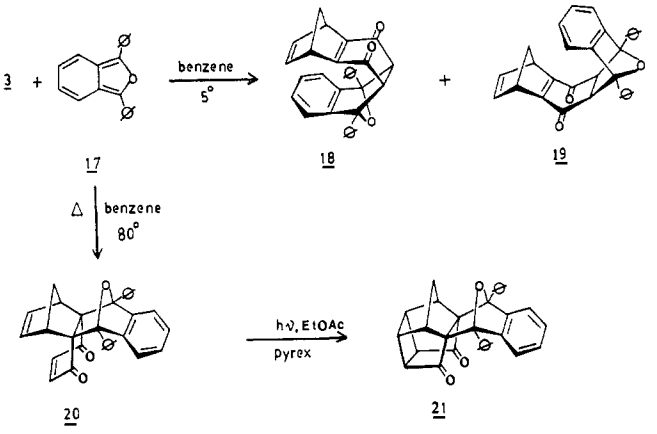




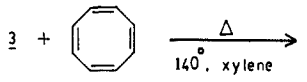
13 **14**

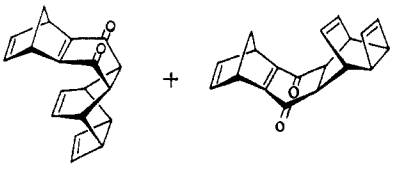
COT exhibited sluggishness in reactivity toward **3** and only under stringent conditions (xylene, reflux) was it possible to isolate two 1:1 endo adducts **15** and **16** (55:45) in 70% yield. Once again the relative shielding of cyclohexene olefinic protons in **15** (δ 5.73) as compared to **16** (δ 5.87) made the distinction between the two isomers possible (Table I). However, to place our assignments beyond reproach, a confirmatory, X-ray crystal structure determinaton was carried out on **16**.

Scheme II



17 **18** **19** **20** **21**

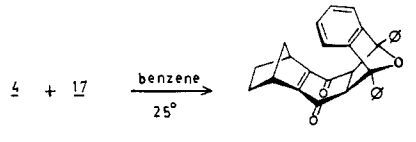




15 **16**

Cycloadditions with Diphenylisobenzofuran 17. Diphenylisobenzofuran **17** is a reactive and interesting diene and readily reacted with NPBQ in benzene at 5 °C to furnish two endo adducts **18** and **19** (19:81) in 95% yield. ^1H NMR and ^{13}C NMR spectral data presented in Table I enabled unambiguous structural assignments to **18** and **19**. In particular, strong shielding of the norbornadiene methylene protons (δ 1.04 and 1.81; cf. δ 2.28 in the precursor **3**) and olefinic protons (δ 6.2; cf. δ 6.84 in **2**) in **19** and **18**, respectively, by the aromatic ring were of significant diagnostic value. In contrast to the response of cyclopentadiene, cyclohexadiene, and COT to **3**, diphenylisobenzofuran exhibits preference for addition from the top, a behavior reminiscent of addition of **5b** to **3**. When the reaction of **17** with **3** was carried out in refluxing benzene, a new 4 + 2 cycloaddition product **20** was isolated. The thermodynamically more stable exo adduct **20** was also obtained when either of the adducts **18** and **19** were equilibrated in refluxing benzene. The spectral characteristics of **20**, particularly the deshielding of the norbornene methylene syn proton (δ 3.01) and shielding of the anti proton (δ 1.15), exhibited very close resemblance to the exo Diels–Alder adduct of norbornadiene and diphenylisobenzofuran.[17] On exposure to UV irradiation, **20** underwent smooth 2 + 2 photocycloaddition in a predictable manner to furnish **21** (Scheme II). This firmly established the exo formulation **20**.

Lastly, the reaction between **17** and DNPBQ **4** was investigated and this furnished a single endo adduct **22** in quantitative yield, through exclusive addition from the top side.



22

Cycloadditions with Isodicyclopentatriene (2, ICPT). The diene **2** offered intriguing possibilities in view of its known propensity

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Table I. ^1H and ^{13}C NMR Chemical Shifts of Diels–Alder Adducts of NPBQ and DNPBQ with Various Dienes

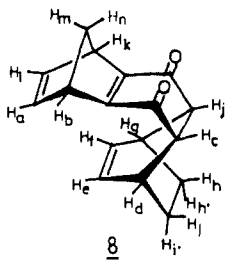
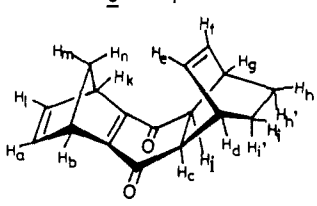
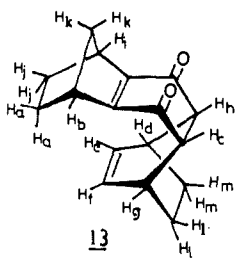
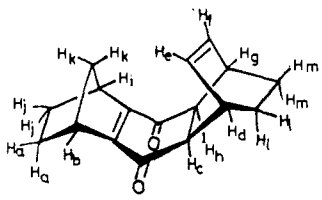
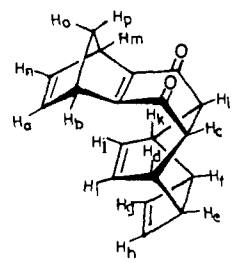
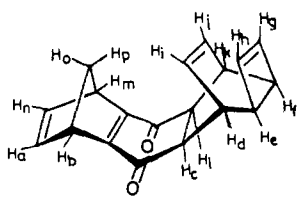
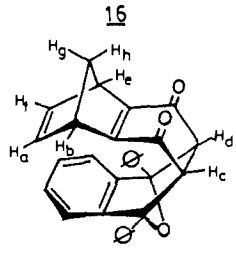
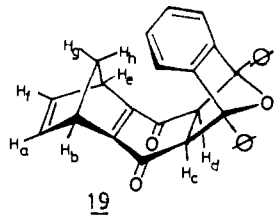
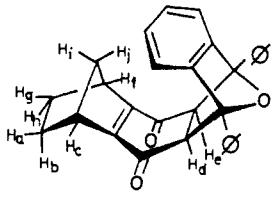
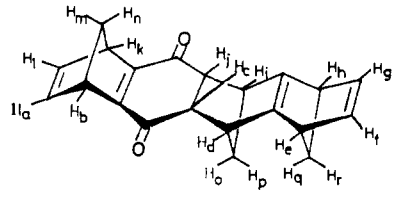
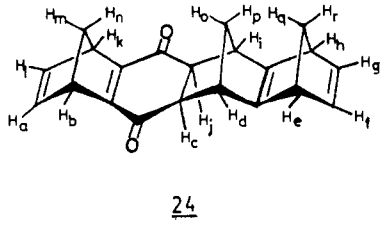
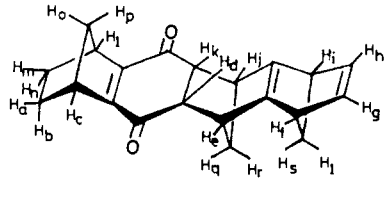
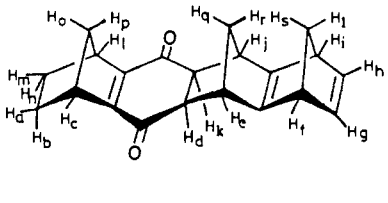
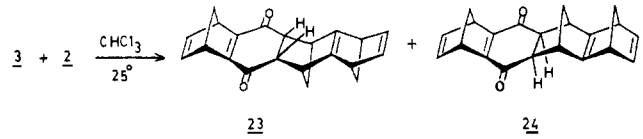
compound	^1H NMR	^{13}C NMR
 8	δ 6.74 (2 H, dd, $J_1 = J_2 = 2$ Hz, $H_{a,l}$), 5.98 (2 H, dd, $J_1 = 6$ Hz, $J_2 = 4$ Hz, $H_{e,f}$), 3.96 (2 H, m, $H_{b,k}$), 3.14 (2 H, br s, $H_{d,g}$), 2.96 (2 H, s, $H_{c,j}$), 2.14 (2 H, m, $H_{m,n}$), 1.46 (4 H, AB q, with st. $J_1 = 8$ Hz, $J_2 = 9$ Hz, $H_{h,h',i,i'}$)	δ 195.8, 166.7, 142.7, 133.1, 72.8, 51.5, 48.6, 35.3, 24.9
 9	δ 6.74 (2 H, dd, $J_1 = J_2 = 2$ Hz, $H_{a,l}$), 6.13 (2 H, dd, $J_1 = 5$ Hz, $J_2 = 4$ Hz, $H_{e,f}$), 3.92 (2 H, m, $H_{b,k}$), 3.12 (2 H, br s, $H_{d,g}$), 2.86 (2 H, s, $H_{c,j}$), 2.08 (2 H, AB q, $J_1 = J_2 = 6$ Hz, $H_{m,n}$), 1.48 (4 H, Ab q, with st. $J_1 = J_2 = 9$ Hz, $H_{h,h',i,i'}$)	δ 195.9, 166.6, 142.4, 133.1, 72.8, 51.8, 48.6, 36.1, 25.1
 13	δ 6.06 (2 H, dd, $J_1 = 6$ Hz, $J_2 = 4$ Hz, $H_{e,f}$), 3.36 (2 H, br s, $H_{b,i}$), 3.24 (2 H, m, $H_{d,g}$), 2.92 (2 H, s with st., $H_{c,h}$), 2.0–1.0 (10 H, series of m, $H_{a,j,k,l,m}$)	
 14	δ6.14 (2 H, dd, $J_1 = 6$ Hz, $J_2 = 4$ Hz, $H_{e,f}$), 3.34 (2 H, br s, $H_{b,i}$), 3.04 (2 H, br s, $H_{d,g}$), 2.88 (2 H, s, $H_{c,h}$), 2.0–0.9 (10 H, series of m, $H_{a,j,k,l,m}$)	
 15	δ 6.8 (2 H, dd, $J_1 = J_2 = 2$ Hz, $H_{a,n}$), 5.84 (2 H, s, $H_{g,h}$), 5.73 (2 H, dd, $J_1 = 6$ Hz, $J_2 = 4$ Hz, $H_{i,j}$), 4.02 (2 H, br s, $H_{b,m}$), 3.2 (2 H, br s, $H_{d,k}$), 2.88 (4 H, s, $H_{c,e,f,l}$), 2.2 (2 H, m, $H_{o,p}$)	δ 195.6, 166.5, 142.8, 138.1, 129.1, 72.8, 50.1, 48.7, 44.8, 40.2
 16	δ 6.76 (2 H, dd, $J_1 = J_2 = 2$Hz, $H_{a,n}$), 5.87 (2 H, dd, $J_1 = 6$ Hz, $J_2 = 4$ Hz, $H_{i,j}$), 5.84 (2 H, s, $H_{g,h}$), 3.96 (2 H, br s, $H_{b,m}$), 3.14 (2 H, br s, $H_{d,k}$), 2.84 (2 H, br s, $H_{c,l}$), 2.76 (2 H, s, $H_{e,f}$), 2.13 (2 H, AB q, $J_1 = J_2 = 8$ Hz, $H_{o,p}$)	δ 195.7, 166.5, 142.5, 138.1, 129.1, 72.9, 50.5, 48.7, 45.1, 41.0
 18	δ 8.0–7.7 (4 H, m), 7.6–7.28 (6 H, m), 7.2–6.72 (4 H, m), 6.2 (2 H, dd, $J_1 = J_2 = 2$ Hz, $H_{a,f}$), 4.26 (2 H, s, $H_{c,d}$), 3.76 (2 H, m, $H_{b,e}$), 2.04 (2 H, m, $H_{g,h}$)	δ 191.6, 164.8, 145.2, 141.6, 135.6, 129.0, 128.4, 127.9, 121.0, 91.6, 73.8, 56.2, 47.9

Table I (Continued)

compound	^{1}H NMR	^{13}C NMR
 **19**	δ 8.0–7.7 (4 H, m), 7.6–7.32 (6 H, m), 7.28–6.9 (4 H, m), 6.64 (2 H, dd, $J_1 = J_2 = 1.5$, Hz, $H_{a,f}$), 4.14 (2 H, s, $H_{c,d}$), 3.52 (2 H, m, $H_{b,e}$), 1.81 (1 H, $^1/_2$ AB q, $J = 6$ Hz, H_g), 1.04 (1 H, $^1/_2$ AB q, $J = 6$ Hz, H_h)	δ 191.7, 164.6, 145.3, 142.1, 135.5, 129.1, 128.8, 128.4, 128.0, 121.4, 91.7, 70.5, 56.2, 48.1
 **22**	δ 8.04–7.8 (4 H, m), 7.64–7.36 (6 H, m), 7.28–6.92 (4 H, m), 4.10 (2 H, s, $H_{d,e}$), 2.94 (2 H, br s, $H_{e,f}$), 1.70 (2 H, $^1/_2$ AB q, $J_1 = J_2 = 10$ Hz, $H_{a,g}$), 0.92 (2 H, $^1/_2$ AB q, $J = 10$ Hz, $H_{b,h}$), 0.88 (1 H, $^1/_2$ AB q, $J_1 = J_2 = 8$ Hz, H_i), 0.52 (1 H, $^1/_2$ AB q, $J = 8$ Hz, H_j)	δ 192.6, 155.6, 145.3, 135.5, 129.0, 128.6, 128.3, 128.0, 121.3, 91.6, 56.8, 45.2, 41.0, 25.5
 **23**	δ 6.87 (2 H, dd, $J_1 = J_2 = 2$ Hz, $H_{a,l}$), 6.53 (2 H, dd, $J_1 = J_2 = 2$ Hz, $H_{f,g}$), 4.06 (2 H, dd, $J_1 = J_2 = 2$ Hz, $H_{b,k}$), 3.46 (2 H, s, $H_{e,h}$), 3.28 (2 H, s, $H_{d,i}$), 2.29 (1 H, $^1/_2$ AB q, $J = 7$ Hz, H_r), 2.19–2.20 (2 H, m, $H_{m,n}$), 2.04 (1 H, $^1/_2$ AB q, $J = 7$ Hz, H_q), 1.97 (2 H, d, $J = 0.9$ Hz, $H_{c,j}$), 1.36 (1 H, $^1/_2$ AB q, $J = 9$ Hz, H_o), 1.00 (1 H, $^1/_2$ AB q, $J = 9$ Hz, H_p)[a]	
 **24**	δ 6.81 (2 H, dd, $J_1 = J_2 = 2$ Hz, $H_{a',l}$), 6.49 (2 H, dd, $J_1 = J_2 = 2$ Hz, $H_{f,g}$), 4.02 (2 H, dd, $J_1 = J_2 = 2$ Hz, $H_{f,g}$), 3.45 (2 H, s, $H_{e,h}$), 3.27 (2 H, s, $H_{d,i}$), 2.29 (1 H, $^1/_2$ AB q, $J = 7$ Hz, H_r), 2.19 (2 H, d with st. $J = 6$ Hz, $H_{m,n}$), 2.03 (1 H, $^1/_2$ Ab q, $J = 7$ Hz, H_q), 1.90 (2 H, s, $H_{c,j}$), 1.50 (1 H, $^1/_2$ AB q, J = 9 Hz, H_o), 1.43 (1 H, $^1/_2$ AB q, $J = 9$ Hz, H_p)[a]	
 **25**	δ 6.51 (2 H, dd, $J_1 = J_2 = 2$ Hz, $H_{g,h}$), 3.46 (4 H, s, $H_{c,f,i,l}$), 3.38 (2 H, s, $H_{e,j}$), 2.20 (1 H, $^1/_2$ AB q, $J = 6$ Hz, H_t), 2.05 (1 H, $^1/_2$ AB q, $J = 6$ Hz, H_s), 1.93 (2 H, $^1/_2$ AB q, $J = 7.5$ Hz, $H_{a,m}$), 1.92 (2 H, d, $J = 1$ Hz, $H_{d,k}$), 1.57 (1 H, $^1/_2$ AB q, $J = 11$ Hz, H_o), 1.40 (1 H, $^1/_2$ AB q, $J = 11$ Hz, H_p), 1.36 (1 H, $^1/_2$ AB q, $J = 9.3$ Hz, H_q), 1.10 (2 H, $^1/_2$ AB q, $J = 7.5$ Hz, $H_{b,n}$), 0.99 (1 H, $^1/_2$ AB q, $J = 9.3$ Hz, H_r)[a]	δ 197.0, 160.0, 157.6, 138.4, 70.0, 49.0, 48.7, 47.3, 46.3, 43.4, 41.0, 25.2
 **26**	δ 6.50 (2 H, dd, $J_1 = J_2 = 2$ Hz, $H_{g,h}$), 3.44 (2 H, s, $H_{f,i}$), 3.42 (2 H, s, $H_{c,l}$), 3.20 (2 H, s, $H_{e,j}$), 2.18 (1 H, $^1/_2$ AB q, $J = 6$ Hz, H_t), 2.02 (1 H, $^1/_2$ AB q, $J = 6$ Hz, H_s), 1.90 (2 H, $^1/_2$ AB q, $J = 7.5$ Hz, $H_{a,m}$), 1.88 (2 H, s, $H_{d,k}$), 1.58 (1 H, $^1/_2$ AB q, $J = 6$ Hz, H_o), 1.53 (1 H, $^1/_2$ AB q, $J = 9.6$ Hz, H_q), 1.47 (1 H, $^1/_2$ AB q, $J = 9.6$ Hz, H_r), 1.37 (1 H, $^1/_2$ AB q, $J = 6$ Hz, H_p), 1.11 (2 H, $^1/_2$ AB q, $J = 7.5$ Hz, $H_{b,n}$)[a]	δ 196.8, 160.0, 158.1, 138.2, 70.0, 49.6, 48.7, 47.7, 46.9, 43.2, 41.2, 25.3

[a] Spectra recorded at 300 MHz.

toward stereoselective additions from its bottom side.[6] An interesting point of enquiry, therefore, was whether there would be concordance or discordance between the stereoelectronic preferences operative in **2** and **3** during the cycloaddition process. In principle, eight diastereomeric adducts are possible in the reaction between **2** and **3**. However, when equimolar quantities of **2** and **3** were stirred in chloroform solution (25 °C), only two 1:1 adducts **23** and **24** were formed in exactly equal amounts. That both **23**



23 **24**

and **24** were exo adducts became apparent from the shielded ^{1}H NMR resonances of the endo hydrogens α to the carbonyl groups at δ 1.97 (in **23**) and δ 1.90 (in **24**) (Table I). Such shielding of the endo protons by the distal norbornadiene double bonds is well documented[6b] and has been employed for stereochemical assignments in the cycloaddition chemistry of **2**.[6] However, a distinction between the two exo adducts **23** and **24** could not be achieved on the strength of the spectral data alone, and therefore, recourse was taken to X-ray crystallography to unambiguously pin down one of the adduct structures. In the event, the structure of **23** was solved and shown to be the product arising through the addition of ICPT to NPBQ from the bottom side.

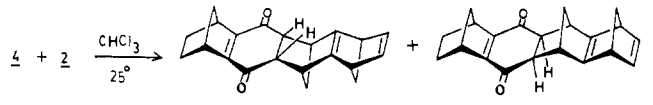
Next, the reaction of DNPBQ **4** was investigated. As in the case with NPBQ **3**, once again only two exo adducts **25** and **26**

Table II. Cycloaddition Selectivity and Reaction Conditions

		cycloaddn cond			stereoselectivy	
dienophile	Diene	solv	temp, °C	% yield	top, %	bottom, %
NPBQ	**5a**	benzene	25	100	35	65[a]
DNPBQ	**5a**	benzene	25	100	78	22[a]
NPBQ	**5b**	toluene	110	90	77	23[a]
DNPBQ	**5b**	toluene	110	95	100	
NPBQ	Ch[c]	benzene	25	95	38	62[a]
DNPBQ	Ch[c]	benzene	25	80	80	20[a,b]
NPBQ	COT	xylene	140	70	45	55[b]
NPBQ	**17**	benzene	5	95	81	19[a]
DNPBQ	**17**	benzene	25	100	100	
NPBQ	**2**	chloroform	25	95	50	50[b]
DNPBQ	**2**	chloroform	25	90	60	40[b]

[a] Determined by ^{1}H NMR. [b] Determined by HPLC. [c] 1,3-Cyclohexadiene.

were formed in 90% yield but in a 4:6 ratio, respectively. Structures to **25** and **26** were assigned on the basis of spectral characteristics displayed in Table I. As compared to **3**, **4** exhibits a small preference for addition from the top side. A notable feature of this cycloaddition is that ICPT maintains its integrity toward cycloadditions from its bottom side when engaged by **3** and **4**.



25 **26**

Table II summarizes the stereoselectivities observed in the cycloaddition reactions examined in the present study. Several experiments were performed to ensure whether or not the product ratio indicated here represents the kinetic cycloaddition stereoselectivities. In most cases, control experiments employing purified products established that there was no equilibration at room temperature in the solvents employed for preparative-scale experiments. To complete the entries in Table II, we have also studied the cycloaddition of DNPBQ **4** with cyclopentadienes **5a** and **5b** (vide Experimental Section).

Discussion

The observed π-facial selectivities of NPBQ and DNPBQ presented in Table II exhibit two significant features. Compared to NPBQ **3**, DNPBQ **4** has a uniformly greater preference for cycloaddition to the top face. For example, the top/bottom product ratio changes from 35:65 to 78:22 in the reaction with cyclopentadiene **5a** on going from NPBQ to DNPBQ. The stereoselectivities with diphenylisobenzofuran **17** as well as with the tetrachlorocyclopentadiene derivative **5b** follow the same trend. The second interesting feature of the observed results is the dependence of product distribution on the choice of the diene. While cyclopentadiene, cyclohexadiene, and cyclooctatetraene fall into one group, dienes **17** and **5b** yield a different set of product ratios. The cycloaddition products resulting from ICPT **2** belong to yet another category: these are the only products resulting from exo addition with respect to the diene.

The diene dependence of stereoselectivities rules out any important role for ground-state structural or electronic effects involving NPBQ and DNPBQ alone. In line with this expectation, the geometries of the two dienophiles optimized at the MNDO level[18] show no unusual distortions. The reactive olefinic centers are essentially planar,[19] unlike facially perturbed systems such as methylenenorbornyl derivatives.[20] Further, the calculated wave functions show no orbital tilting[6k] or related distortions.[10] So σ/π mixing effects, such as those held responsible for determining the facial selectivity in ICPD **1**,[6a,k,10] can be ruled out in the present systems.

The variation in product distribution with the diene as well as the greater preference for cycloaddition to the top face of DNPBQ can be understood in terms of steric interactions.[21] The endo hydrogens in DNPBQ may be expected to encumber the bottom face endo cycloaddition transition state. Further, the steric requirements of **17** and **5b** are clearly different from those of **5a** or cyclohexadiene. The observed variations in top/bottom ratios are thus not unreasonable.

Model calculations were carried out to confirm the dominant role of steric interactions at the transition state in determining product ratios. An approach quite similar to that employed by Brown and Houk[11,22] to successfuly rationalize the π-facial selectivity of ICPD with a variety of dienophiles, but with a few additional simplifications, was used. The transition-state geometries were constructed from MNDO calculations on appropriate model systems (see Computational Details). The nonbonded interactions between the diene and the dienophile in these structures were computed by using MM2 parameters.[23] The energies were obtained for the top and the bottom face cycloaddition transition states involving NPBQ and DNPBQ as the dienophile and 1,3-butadiene, *o*-quinodimethane, and 2,3-dichlorobutadiene as model dienes. These models include the critical steric interactions expected in the experimentally studied systems. Thus, butadiene is the model for **5a** and cyclohexadiene, as well as the valence isomer of cyclooctatetraene, *o*-quinodimethane for **17**, and 2,3-dichlorobutadiene for **5b**.[24]

Product ratios at 25 °C were calculated from the computed differences in steric energies by using the standard Boltzmann factors. The results are compared with experimental data in Table III. Although the agreement between the calculated and observed ratios is not quantitative, the performance of the simple model is quite reasonable. The major success of the model is that a mixture of products is obtained experimentally whenever it is predicted. Thus, products from both the top and the bottom face attack are predicted for the additions of the three model dienophiles with NPBQ. Experimentally product mixtures are obtained with **5a**, cyclohexadiene, cyclooctatetraene, and **17**, as well as with **5b**. The computational model also correctly predicts the total preference for the top face attack at DNPBQ by both the isobenzofuran **17** and the chlorodiene **5b**. Although there is a general underestimation of nonbonded repulsions for the bottom face attack, leading to incorrect predictions of the major product in a few cases, the concordance between the model and experiment

(18) Dewar, M. J. S.; Thiel, W. *J. Am. Chem. Soc.* **1977**, *99*, 4907.
(19) Optimized geometries and calculated heats of formation are included as supplementary material.
(20) (a) Houk, K. N.; Paddon-Row, M. N.; Caramella, P.; Rondan, N. G. *J. Am. Chem. Soc.* **1981**, *103*, 2436. (b) Houk, K. N.; Rondan, N. G.; Paddon-Row, M. N.; Caramella, P.; Mareda, J.; Mueller, P. H. *Ibid.* **1982**, *104*, 4947. (c) Angel, E. C.; Fringuelli, F.; Pizzo, F.; Porter, B.; Taticchi, A.; Wenkert, E. *J. Org. Chem.* **1986**, *51*, 2642.
(21) The slight preference for the bottom face cycloaddition in NPBQ compared to DNPBQ may be due to a favorable secondary orbital interaction involving the remote 5–6 π bond of NPBQ and a diene orbital of appropriate symmetry. However, both EHT and MNDO calculations do not support this hypothesis. The orbital energies as well as the coefficients of the LUMO of NPBQ and DNPBQ are virtually identical. There is no contribution from the p orbitals on the etheno bridge of NPBQ in this key frontier orbital. The calculations do indicate the presence of a relatively low lying LUMO+1 as well as a high HOMO in NPBQ with significant contributions from the three C=C units in the molecule. However, the phase relationships involving the remote double bond are not suitable for favorable interactions in the NPBQ-(LUMO+1) – diene(HOMO) pair as well as in the dienophile (HOMO) – diene(LUMO) pair. Therefore, the observed results cannot be attributed to stabilizing secondary orbital interactions favoring the bottom face attack at NPBQ.
(22) For recent reviews and other applications of the MO/MM2 transition-state modeling approach, see: (a) Houk, K. N.; Paddon-Row, M. N.; Rondon, N. G.; Wu, Y.-D.; Brown, K. F.; Spellmeyer, D. C.; Metz, J. T.; Li, Y.; Loncharich, R. J. *Science (Washington, D.C.)* **1986**, *231*, 1108. (b) Houk, K. N. *Pure Appl. Chem.* **1989**, *61*, 643. (c) De Amici, M.; De Micheli, C.; Ortisi, A.; Gatti, G.; Gandolfi, R.; Toma, L. *J. Org. Chem.* **1989**, *54*, 793. For a molecular mechanics study of diastereoselectivity in Diels–Alder additions based on the "product-oriented" approach, see: Marshall, J. A.; Grote, J.; Audia, J. E. *J. Am. Chem. Soc.* **1987**, *109*, 1186.
(23) Allinger, N. L. *J. Am. Chem. Soc.* **1977**, *99*, 8127.
(24) The use of three small dienes stripped of most substituents to model the various dienes studied experimentally is indeed a simplification. However, the neglected portions of the dienes are well beyond the range of significant nonbonded interactions with the norbornyl unit in all the systems.

Table III. Calculated Energy Differences [E = E(Top) − E(Bottom) in kcal/mol] and Predicted Product Ratios (T/B = Top/Bottom at 25 °C) for Model Dienes and Observed Product Ratios in Corresponding Experimental Systems

dienophile	model diene	E	T/B theory	T/B exptl	exptl diene
NPBQ	butadiene	0.1	46:54	35:65	cyclopentadiene **5a**
				38:62	cyclohexadiene
				45:55	cyclooctatetraene
DNPBQ	butadiene	0.4	34:66	78:22	cyclopentadiene **5a**
NPBQ	*o*-quinodimethane	0.4	34:66	81:19	isobenzofuran **17**
DNPBQ	*o*-quinodimethane	−4.4	100:0	100:0	isobenzofuran **17**
NPBQ	2,3-dichlorobutadiene	0.1	46:54	77:23	tetrachlorocyclopentadiene **5b**
DNPBQ	2,3-dichlorobutadiene	−3.7	100:0	100:0	tetrachlorocyclopentadiene **5b**

is nearly as good as that obtained by Brown and Houk.[11] It is reasonable to conclude that steric interactions essentially determine the π-facial selectivity in the cycloadditions of NPBQ and DNPBQ. Interestingly, a similar conclusion was arrived at recently concerning the π-facial selectivity in cycloadditions to hydroxymethyl-substituted cyclopentadienes.[25]

The model calculations reveal a structural feature in the transition state of critical importance in determining the relative steric energies, especially for the two cases in which total preference for the top face attack is predicted. In the Diels–Alder transition state, the hydrogens attached to C_2 and C_3 of the diene are bent significantly toward the dienophile to maximize favorable frontier orbital interactions. The out-of-plane bending is more than 10° for both MNDO and ab initio STO-3G transition structures.[11,26] As a result, benzo fusion, as well as chloro substitution at the diene, causes increased steric repulsion with the endo hydrogens at the C_5 and C_6 atoms of DNPBQ. Exclusive attack at the top face results in these systems. If the diene is assumed to remain planar, a mixture of products is predicted even in these cases. Interestingly, the significance of the pyramidalization at the C_2 and C_3 positions of the diene in the Diels–Alder transition state has been noted in other contexts as well.[11,26]

The observed product distribution (only two out of eight possible adducts in a 50:50 ratio) in the cycloaddition of ICPT to NPBQ can also be understood in terms of the present analysis. As in previous studies,[6k] the diene ICPT imposes its preference for the bottom face attack. However, an endo approach with respect to the diene is not feasible due to the resulting steric crowding. For an exo addition, both the methano and the etheno bridges are quite removed from the diene. There is no steric preference and hence additions to the top as well as the bottom faces of NPBQ are equally feasible. Thus, the formation of exclusively two products in equal quantities in this reaction is entirely consistent with steric considerations. However, with DNPBQ steric effect of the ethano bridge is felt even in the exo mode of addition and a small preference for top addition is observed.

Conclusions

Facially perturbed dienophiles **3** and **4** have been shown to exhibit a range of stereoselectivities in their reaction with various cyclic dienes. Compared to **3**, **4** consistently prefers the top face cycloaddition to a greater extent. The product distribution is also sensitive to the choice of the diene. Molecular orital calculations rule out any favorable secondary orbital interactions for the bottom face endo attack of a diene at NPBQ. Model calculations, exclusively taking into account nonbonded forces between the diene and the dienophile at the transition state, account for the observed product distributions. The π-facial selectivity in the cycloadditions of NPBQ and DNPBQ are thus essentially determined by steric interactions.

Experimental Section

All melting points are uncorrected and were determined on a Büchi SMP 20 apparatus. The spectra and analytical data were recorded on the following instruments: Perkin-Elmer Model 297 spectrophotometer (IR), JEOL FX 100 spectrometer (^{1}H and ^{13}C NMR), JEOL JMS DX-303 (mass spectra), Perkin-Elmer 240C (CHN analysis), Water Associates Model 440 (HPLC, μ-Porosil column and dichloromethane as eluent). Column chromatography was performed with Acme's silica gel (100–200 mesh). All nonhalogenated solvents were dried over sodium wire. Chloroform was distilled over P_2O_5.

Starting Materials. The starting materials norbornenobenzoquinone **3**,[13] dihydronorbornenobenzoquinone **4**,[13] 1,2,3,4-tetrachloro-5,5-dimethoxycyclopentadiene (**5b**),[27a] cyclohexadiene,[27b] and isodicyclopentatriene **2**[6b] were prepared according to the literature procedures. Commercial samples of cyclooctatetraene and isobenzofuran **17** were used for the reactions.

Reaction of 2,3-Norbornenobenzoquinone (3) with 1,3-Cyclohexadiene. To a solution of norbornenobenzoquinone **3** (100 mg, 0.58 mmol) in 5 mL of benzene was added excess of freshly prepared cyclohexadiene, and the reaction mixture was stirred at room temperature (25 °C) for 5 h. Removal of solvent furnished in quantitative yield a mixture of the two products **8** and **9** in a ratio of 62:38 (as estimated by ^{1}H NMR). The product mixture was charged on a silica gel (25 g) column. Elution with 5% ethyl acetate–hexane first furnished the minor adduct **9**, which was recrystallized from dichloromethane–hexane: mp 150 °C; IR (KBr) ν_{max} 1650, 1600, 1285, 695 cm^{-1}. Anal. Calcd for $C_{17}H_{16}O_2$: C, 80.92; H, 6.39. Found: C, 80.95; H, 6.38.

Further elution of the column with the same solvent furnished the major adduct **8**, which was recrystallized from hexane: mp 107–108 °C; IR (KBr) ν_{max} 1650, 1600, 1280, 700 cm^{-1}. Anal. Calcd for $C_{17}H_{16}O_2$: C, 80.92; H, 6.39. Found: C, 80.92; H, 6.40.

Reduction of Enedione 8 with Aqueous $TiCl_3$. To a stirred solution of compound **8** (10 mg, 0.04 mmol) in acetone was added 15% aqueous $TiCl_3$ solution dropwise until a pale purple color persisted. The reaction mixture was poured into water and extracted with ether (3 × 10 mL). The combined ethereal layer was washed with $NaHCO_3$ and brine and dried over sodium sulfate. Removal of solvent furnished a crude material, which was filtered through a silica gel (5 g) column. Elution with 15% ethyl acetate–hexane gave pure **10** (10 mg, 100%), which was recrystallized from dichloromethane–hexane: mp 191–3 °C dec; IR (KBr) ν_{max} 1700, 1240, 700 cm^{-1}; ^{1}H NMR (100 MHz, $CDCl_3$) δ 6.11 (2 H, dd, J_1 = 5 Hz, J_2 = 4 Hz), 6.0 (2 H, dd, J_1 = J_2 = 2 Hz), 3.4 (2 H, s), 3.3–2.96 (6 H, m), 1.56–1.0 (6 H, series of m). Anal. Calcd for $C_{17}H_{18}O_2$: C, 80.28; H, 7.13. Found: C, 80.20; H, 7.09.

Photolysis of 10. A solution of compound **10** (10 mg, 0.04 mmol) in 5 mL of 15% acetone–benzene was irradiated for 1.5 h with a 450-W Hanovia medium-pressure mercury vapor lamp using Vycor filter. The residue after removal of solvent was charged on a silica gel (5 g) column. Elution with 20% ethyl acetate–hexane furnished **11** (8 mg, 80%), which was recrystallized from hexane: mp 71–75 °C; IR (KBr) ν_{max} 2900, 1680, 1460, 720 cm^{-1}; ^{1}H NMR (100 MHz, $CDCl_3$) δ 3.04 (2 H, br s), 2.90 (4 H, br s), 2.72 (6 H, m), 1.84 (2 H, br s), 1.53 (4 H, AB q, J_1 = J_2 = 10 Hz); ^{13}C NMR (25.0 MHz, $CDCl_3$) δ 212.3, 54.3, 52.4, 47.2, 44.8, 42.4, 36.0, 30.4, 25.8. Anal. Calcd for $C_{17}H_{18}O_2$: C, 80.28; H, 7.13. Found: C, 80.54, H, 7.25.

Photolysis of 9. A solution of **9** (10 mg, 0.039 mmol) in 5 mL of ethyl acetate was purged with a slow stream of nitrogen and irradiated with a 450-W Hanovia medium-pressure mercury vapor lamp for 5 h. The solvent was evaporated off and the residue charged on a silica gel (5 g) column. Elution with 10% ethyl acetate–hexane furnished the photolyzed adduct **12** (6 mg, 60%), which was recrystallized from dichloromethane–hexane: mp 199–200 °C; IR (KBr) ν_{max} 2950, 1725, 1070, 745 cm^{-1}; ^{1}H NMR (100 MHz, $CDCl_3$) δ 6.24 (2 H, m), 2.88 (2 H, m), 2.56 (2 H, m), 2.36 (2 H, br s), 2.22 (2 H, m), 1.96–1.18 (6 H, m); Mass spectrum, (M^+) calcd for $C_{17}H_{16}O_2$ 252, found 252.

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Reaction of Dihydronorbornenobenzoquinone 4 with Cyclohexadiene. To a solution of dihydronorbornenobenzoquinone **4** (100 mg, 0.574 mmol) in 5 mL of benzene was added excess cyclohexadiene, and the reaction mixture was stirred overnight at room temperature. Removal of solvent gave a mixture of the two adducts **13** and **14** in a ratio of 20:80 (as estimated by ^{1}H NMR and HPLC). The product mixture was charged on a silica gel (25 g) column. Elution with 5% ethyl acetate–hexane furnished first the minor adduct **13**, which was recrystallized from hexane: mp 114–115 °C; IR (KBr) ν_{max} 1650, 1600, 1000, 690 cm^{-1}. Anal. Calcd for $C_{17}H_{18}O_2$: C, 80.28; H, 7.13. Found: C, 79.84; H, 7.11.

Further elution of the column with the same solvent furnished the major adduct **14**, which was recrystallized from hexane: mp 131–133 °C; IR (KBr) ν_{max} 1655, 1600, 1250, 1000, 700 cm^{-1}. Anal. Calcd for $C_{17}H_{18}O_2$: C, 80.28; H, 7.13. Found: C, 80.34; H, 7.14.

Reaction of 2,3-Norbornenobenzoquinone (3) with Cyclooctatetraene. To a solution of norbornenobenzoquinone **3** (172 mg, 1.0 mmol) in 5 mL of xylene was added excess cyclooctatetraene (208 mg, 2.0 mmol), and the reaction mixture refluxed overnight. Removal of solvent in vacuo gave some unreacted starting material and a mixture of products **15** and **16** in a ratio of 55:45 (as estimated by HPLC). This crude material was charged on a long silica gel (50 g) column. Slow elution with 3% ethyl acetate–hexane first gave the unreacted starting material. Further elution gave product **16**, which was recrystallized from hexane: mp 205 °C; IR (KBr) ν_{max} 1645, 1290, 790, 690 cm^{-1}. Anal. Calcd for $C_{19}H_{16}O_2$: C, 82.58, H, 5.84. Found: C, 82.68; H, 5.88.

Further elution of the column with the same solvent gave **15**, which was recrystallized from hexane: mp 176–177 °C; IR (KBr) ν_{max} 1660, 1280, 700 cm^{-1}. Anal. Calcd: C, 82.58, H, 5.84. Found: C, 82.39; H, 5.82.

The overall yield of the reaction was 70% based on starting material recovery.

Reaction of 2,3-Norbornenobenzoquinone (3) with 1,3-Diphenylisobenzofuran 17. To a solution of norbornenobenzoquinone **3** (100 mg, 0.58 mmol) in 5 mL of benzene was added diphenylisobenzofuran **17** (157 mg, 0.58 mmol), and the reaction mixture was stirred at ~5 °C for 15 min. Removal of solvent under vacuum gave quantitative yield of a mixture of compounds **18** and **19** in a ratio of 19:81 (as estimated by ^{1}H NMR). The product mixture was chromatographed on a silica gel (30 g) column. Elution with 5% ethyl acetate–hexane gave first the major compound **19**, which was recrystallized from dichloromethane–hexane: mp 176–177 °C; IR (KBr) ν_{max} 1650, 1590, 985, 690 cm^{-1}. Anal. Calcd for $C_{31}H_{22}O_3$: C, 84.14; H, 5.01. Found: C, 83.90; H, 5.02.

Further elution of the column with the same solvent gave the minor compound **18**, which was recrystallized from dichloromethane–hexane: mp 171 °C; IR (KBr) ν_{max} 1650, 1600, 1290, 990, 690 cm^{-1}; HRMS (M^+) calcd for $C_{31}H_{22}O_3$ 442.1569, found 442.1580.

Reaction of 2,3-Norbornenobenzoquinone (3) with 1,3-Diphenylisobenzofuran (17) under Thermodynamic Conditions. A mixture of norbornenobenzoquinone **3** (200 mg, 1.16 mmol) and diphenylisobenzofuran **17** (315 mg, 1.16 mmol) in 15 mL of benzene was heated under reflux for 5 h. Removal of solvent and filtration through a silica gel column furnished 500 mg of material, which was a mixture of three products as indicated by TLC. Fractional crystallization of the material from dichloromethane–hexane furnished the thermodynamic product **20** (200 mg, 40%). ^{1}H NMR spectrum of the mother liquor revealed the presence of compounds **18** and **19**. Compound **20**: mp 198–199 °C; IR (KBr) ν_{max} 1660, 1610, 1280, 1010, 745, 700 cm^{-1}; ^{1}H NMR (100 MHz, $CDCl_3$) δ 8.0–7.76 (4 H, m), 7.66–7.30 (6 H, m), 7.28–6.96 (4 H, m), 6.10 (2 H, m), 5.84 (2 H, s), 3.08 (2 H, m), 3.01 (1 H, $^1/_2$ AB q, J = 10 Hz), 1.15 (1 H, $^1/_2$ AB q, J = 10 Hz); ^{13}C NMR (25.0 MHz, $CDCl_3$) δ 200.5, 147.6, 141.9, 137.6, 135.3, 128.5, 128.1, 126.8, 120.6, 90.1, 72.6, 47.6, 43.1. Anal. Calcd for $C_{31}H_{22}O_3$: C, 84.14; H, 5.01. Found: C, 84.00; H, 5.05.

Photolysis of 20. A solution of enedione **20** (50 mg, 0.113 mmol) in ethyl acetate (125 mL) was irradiated for 2 h with a Hanovia medium-pressure mercury vapor lamp using a Pyrex filter. The solvent was removed under vacuum and the residue filtered through a small silica gel (5 g) column. Elution with 25% ethyl acetate–hexane gave the photolysed product **21** (45 mg, 90%), which was recrystallized from dichloromethane–hexane: mp >270 °C; IR (KBr) ν_{max} 1750, 1600, 750, 710 cm^{-1}; ^{1}H NMR (100 MHz, $CDCl_3$) δ 7.88–7.66 (4 H, m), 7.64–7.28 (6 H, m), 7.24–7.0 (4 H, m), 3.12–2.9 (2 H, m), 2.8 (1 H, $^1/_2$ AB q, J = 10 Hz), 2.8–2.56 (4 H, m), 1.48 (1 H, $^1/_2$ AB q, J = 10 Hz); ^{13}C NMR (25 MHz, $CDCl_3$) δ 210.6, 146.1, 136.4, 128.6, 127.9, 126.3 (2 C), 122.0, 88.2, 74.9, 45.8, 42.9, 40.5, 37.0. Anal. Calcd for $C_{31}H_{22}O_3$: C, 84.14; H, 5.01. Found: C, 84.25; H, 5.04.

Reaction of Dihydronorbornenobenzoquinone 4 with 1,3-Diphenylisobenzofuran (17). To a solution of dihydronorbornenobenzoquinone **4** (50 mg, 0.287 mmol) in 5 mL of benzene was added diphenylisobenzofuran **17** (78 mg, 0.288 mmol), and the reaction mixture was stirred at room temperature for 30 min. Removal of solvent gave the product **22** in quantitative yield, which was recrystallized from dichloromethane–hexane: mp 213–214 °C; IR (KBr) ν_{max} 1660, 1590, 700 cm^{-1}. Anal. Calcd for $C_{31}H_{24}O_3$: C, 83.76; H, 5.44. Found: C, 83.57; H, 5.49.

Reaction of 2,3-Norbornenobenzoquinone (3) with Isodicyclopentatriene 2. To a solution of isodicyclopentatriene **2** (130 mg, 1.0 mmol) in 5 mL of chloroform, cooled to 0 °C, was added norbornenobenzoquinone (170 mg, 0.98 mmol), and the reaction mixture was stirred at room temperature for 4 h. Removal of solvent under vacuum gave a mixture of two products, *exo,anti*-**23**, and *exo,syn*-**24** in a ratio of 50:50 (as estimated by HPLC). The product mixture was charged on a long silica gel (50 g) column. Slow elution with 2% ethyl acetate–hexane first furnished the pure exo,syn adduct **24**, which was recrystallized from dichloromethane–hexane: mp 152–153 °C; IR (KBr) ν_{max} 3000, 1655, 1290, 740 cm^{-1}; HRMS (M^+) calcd for $C_{21}H_{18}O_2$ 302.1307, found 302.1335.

Further elution of the column with the same solvent gave a mixture of **24** and **23** and the last few fractions were pure in **23**, which was recrystallized from dichloromethane–hexane: mp 150 °C; IR (KBr) ν_{max} 3000, 1650, 1290, 720 cm^{-1}; ^{13}C NMR of mixture (25.0 MHz, $CDCl_3$) δ 195.8, 195.6, 183.7, 166.8, 166.7, 160.0, 159.9, 142.6, 142.4, 142.2, 138.1, 138.0, 135.5, 73.5, 72.7, 69.6, 49.1, 48.2, 46.6, 46.2, 42.9, 42.8. The overall yield of the reaction was 95%. HRMS (M^+) calcd for $C_{21}H_{18}O_2$ 302.1307, found 302.1308.

Reaction of Dihydronorbornenobenzoquinone 4 with Isodicyclopentatriene 2. To a solution of excess isodicyclopentatriene **2** (70 mg, 0.538 mmol) in chloroform was added dihydronorbornenobenzoquinone **4** (50 mg, 0.287 mmol), and the reaction mixture was stirred overnight at room temperature. Removal of solvent under vacuum gave a mixture of two products *exo,anti*-**25** and *exo,syn*-**26** in a ratio of 40:60 (as estimated by HPLC) in an overall yield of 90%. The product mixture was charged on a long silica gel (20 g) column. Slow elution with 3% ethyl acetate–hexane furnished first the *exo,anti*-**25** adduct, which was recrystallized from hexane: mp 152.5–153.5 °C; IR (KBr) ν_{max} 3000, 1660, 1605, 730 cm^{-1}.

Further elution of the column with the same solvent furnished the *exo,syn*-**26** adduct, whih was recrystallized from hexane: mp 148 °C; IR (KBr) ν_{max} 3000, 1650, 1600, 740 cm^{-1}. Anal. Calcd for $C_{21}H_{20}O_2$: C, 82.86; H, 6.62. Found: C, 82.76; H, 6.64.

Reaction of Dihydronorborenobenzoquinone 4 with Cyclopentadiene. To a solution of dihydronorbornenobenzoquinone **4** (100 mg, 0.574 mmol) in 10 mL of benzene was added excess of freshly cracked cyclopentadiene at 0 °C, and the reaction mixture was stirred at room temperature for 1 h. Removal of solvent furnished in quantitative yield a mixture of two products in a ratio of 78 (top side):22 (bottom side) (as estimated by ^{1}H NMR). The product mixture was charged on a silica gel (25 g) column. Elution with 5% ethyl acetate–hexane first, furnished the minor bottom-side addition product: mp 133 °C; IR (KBr) ν_{max} 2950, 1650, 1600, 1320, 700 cm^{-1}; ^{1}H NMR (100 MHz, $CDCl_3$) δ 5.88 (2 H, dd, J_1 = J_2 = 2 Hz), 3.48 (2 H, br s), 3.35 (2 H, s with st.), 3.2–3.04 (2 H, m), 1.96–0.8 (8 H, series of m); ^{13}C NMR (25.0 MHz, $CDCl_3$) δ 196.3, 157.6, 134.9, 50.3, 48.4, 48.2, 46.7, 40.8, 25.1. Anal. Calcd for $C_{16}H_{16}O_2$: C, 79.97; H, 6.71. Found: C, 79.85; H, 6.78.

Further elution of the column with the same solvent furnished the major top-side addition product: mp 128 °C; IR (KBr) ν_{max} 2925, 1650, 1595, 1320, 700 cm^{-1}; ^{1}H NMR (100 MHz, $CDCl_3$) δ 6.0 (2 H, dd, J_1 = J_2 = 2 Hz), 3.44 (2 H, br s), 3.32 (2 H, br s), 3.16 (2 H, m), 2.0–0.96 (8 H, series of m); ^{13}C NMR (25.0 MHz, $CDCl_3$) δ 195.9, 157.9, 134.5, 50.7, 49.4, 49.0, 47.7, 40.4, 24.7. Anal. Calcd for $C_{16}H_{16}O_2$: C, 79.97; H, 6.71. Found: C, 79.73; H, 6.73.

Reaction of Dihydronorbornenoquinone 4 with 1,2,3,4-Tetrachloro-5,5-dimethoxycyclopentadiene (5b). To a solution of dihydrononorbornenobenzoquinone **4** (100 mg, 0.575 mmol) in 10 mL of toluene was added **5b** (160 mg, 0.6 mmol) and the mixture refluxed for 12 h. Removal of solvent and crystallization of the residue from dichloromethane–hexane furnished a single adduct (235 mg, 95%): mp 200 °C; IR (KBr) ν_{max} 2960, 1680, 1600, 990 cm^{-1}; ^{1}NMR (100 MHz, $CDCl_3$) δ 3.66 (3 H, s), 3.6 (3 H, s), 3.58 (2 H, s), 3.36 (2 H, br s), 1.92 (2 H, $^1/_2$AB q, J = 8 Hz), 1.64 (1 H, $^1/_2$ AB q, J = 10 Hz), 1.34 (1 H, $^1/_2$ AB q, J = 10 Hz), 1.1 (2 H, $^1/_2$ AB q, J = 8 Hz); ^{13}C NMR (25.0 MHz, $CDCl_3$) δ 188.8, 158.6, 129.8, 111.1, 77.8, 57.3, 53.0, 52.0, 45.9, 41.7, 25.3. Anal. Calcd for $C_{18}H_{16}Cl_4O_4$: C, 49.34; H, 3.68. Found: C, 49.19; H, 3.69.

X-ray Crystal Structure Determination of 16 and 23. Crystal data for **16**: $C_{19}H_{16}O_2$; a = 6.293 (1), b = 28.348 (1), c = 7.856 (1) Å; 2406 reflections measured, 2143 with $I > 2.5\sigma(I)$. Crystal data for **23**: $C_{21}H_{18}O_2$; a = 7.925 (1), b = 9.281 (2), c = 20.918 (3) Å; space group $P2_12_12_1$; Z = 4; D_{calcd} = 1.30 g cm^{-3}; 1752 reflections measured, 1567 with $I > 2.5\sigma(I)$. The three-dimensional intensities were recorded on an Enrauf-Nonius CAD-4 automatic diffractometer employing Cu Kα (λ

= 1.5418 Å) radiation in W-2θ scan mode with $\Delta\omega = (1.0 + 0.14 \tan \theta)$ and aperture width of $(3 + 0.42 \tan \theta)$. Structures were solved by employing direct methods and calculations were performed on a VAX 11/730 computing system using the SDP package.[28] The packing of both the molecules **16** and **23** is stabilized by van der Waals interactions.

Computational Details

The constrained-synchronous transition-state structure for the ethylene + butadiene cycloaddition computed at the MNDO level was chosen as the basic model.[26] The optimized MNDO geometries of NPBQ and DNPBQ were then grafted onto this structure by appropriate replacement of the hydrogen atoms in the ethylene unit. The different dienes studied experimentally were represented by the following three models: 1,3-butadiene, *o*-quinodimethane, and 2,3-dichlorobutadiene. The geometrical modifications to the diene part of the transition-state model was carried out as for the diene with MNDO or standard geometries. The steric interactions between the diene and the norbornyl skeleton of the dienophile were computed by using MM2 parameters.[23] Since torsional effects were not likely to be important in the present systems, only the van der Waals interactions were considered. Therefore, unlike the earlier study,[11] no partial geometry optimization was carried out. There was also no need to add new parameters to the MM2 force field. The various transition-state model geometries for the top and the bottom face attack in each case as well as the computed nonbonded interaction energies are included as supplementary material.

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Supplementary Material Available: Tables of optimized MNDO geometries and heats of formation of **3** and **4**, the transition-state model geometries with **3** and **4** as the dienophile and butadiene, *o*-quinodimethane, and 2,3-dichlorobutadiene as the diene for both the top and the bottom face cycloadditions, along with the computed nonbonded interaction energies (14 pages). Ordering information is given on any current masthead page.

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π-Bonding in Four-Coordinate Aluminum Aryloxide Compounds

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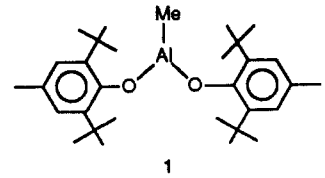
Abstract: The interaction of $AlMe_3$ with the substituted phenols 2,6-di-*tert*-butyl-4-methylphenol (BHT-H), 2,6-diisopropylphenol (DIP-H), and 2,4,6-trimethylphenol (MesOH) in the presence of pyridine (py) or 3,5-dimethylpyridine (3,5-Me_2py) leads to the formation of mono, bis, and tris aryloxide compounds. The molecular structures of $AlMe_2$(BHT)(py) (**3a**), $AlMe(OMes)_2$(3,5-Me_2py) (**8b**), and $Al(DIP)_3$(py) (**7a**) have been determined by X-ray crystallography. The Al–O distances are shorter and Al–O–C angles larger than usually found for aluminum alkoxides. The presence of a π-type interaction between the aryloxide ligands and the four-coordinate aluminum centers is proposed to account for the structural results. Compound **3a**: monoclinic $P2_1/n$, $a = 10.193$ (7) Å, $b = 17.989$ (10) Å, $c = 12.249$ (11) Å, $\beta = 96.44$ (6)°, $Z = 4$, $R = 0.076$, $R_w = 0.078$. Compound **8b**: monoclinic $P2_1/n$, $a = 11.767$ (2) Å, $b = 10.232$ (2) Å, $c = 21.562$ (5) Å, $\beta = 105.43$ (2)°, $Z = 4$, $R = 0.076$, $R_w = 0.091$. Compound **7a**: monoclinic $P2_1/n$, $a = 13.032$ (2) Å, $b = 21.308$ (3) Å, $c = 14.605$ (2) Å, $\beta = 107.99$ (1), $Z = 4$, $R = 0.068$, $R_w = 0.068$.

The tendency of aluminum alkoxide and aryloxide compounds to maximize their coordination number by associating to give aggregates containing tetrahedral and octahedral centers is well-documented.[1] The use, however, of the sterically hindered aryloxide derived from 2,6-di-*tert*-butyl-4-methylphenol (BHT-H, from the trivial name butylated hydroxytoluene) results in the isolation of monomeric aryloxide compounds of aluminum.[2,3] The X-ray structural determination of $AlMe(BHT)_2$ (**1**) has been reported,[4] and it confirms the monomeric nature of this compound. The short Al–O distances [average 1.686 (2) Å] and large Al–O–C angles [average 143.6 (2)°] in **1** are consistent with the presence of π-bonding between the aryloxide oxygens and the vacant aluminum p_z orbital (*z* perpendicular to the AlO_2C plane). This bonding scheme is compatible with the commonly accepted concept that the presence of π-bonding to a group III element requires a trigonal planar coordinatively unsaturated metal center. We have recently reported, however, that π-bonding may also be present between oxygen and aluminum in four-coordinate complexes.[5]



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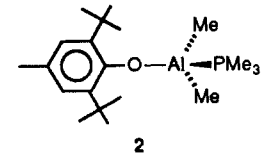

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The presence of a short Al–O distance [1.736 (5) Å] and a large Al–O–C angle [164.5 (4)°] in the X-ray structure of $AlMe_2$-

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