Gas chromatographic analyses were performed on a Varian 920 chromatograph equipped with a 6 ft × 0.25 in. stainless-steel column packed with 15% SE-30 on Chromosorb W. GC yields were obtained by using *n*-alkanes as internal standards.

Lithium bromide (aldrich Chemical Co., 99+%) was dried in an abderhalden flask over refluxing xylene at 0.3 torr.

Magnesium bromide was prepared from dibromoethane and magnesium and dried under vacuum at 150 °C.[6]

Zinc chloride (Aldrich Chemical Co., 98%) was dried with thionyl chloride followed by removal of excess $SOCl_2$ under high vacuum.[7]

Lithium chloride (Aldrich Chemical Co., 99%) was dried in an abderhalden flask over refluxing xylene at 0.3 torr.

The remaining metal salts were obtained as anhydrous materials from commercial sources. All metal salts were stored in a dessicator and transferred under argon in a glovebag. In several experiments, magnesium or lithium halides were transferred and weighed in the atmosphere without the protection of a glovebag or drybox, and triethylamine and solvents were taken directly from freshly opened bottles without prior purification. These modifications gave no significant change in yields compared to the general procedure below.

Triethyl phosphonoacetate was prepared from ethyl bromoacetate and triethylphosphite.[8]

HWE Reaction. General Procedure. The following procedure, with modification of scale, is representative of the procedure used to obtain the results in Tables I–III: a 50-mL flask with a septum inlet and magnetic stir bar was flame dried and flushed with argon. Anhydrous metal salt, 30 mmol, was weighed in a glovebag and transferred under a stream of argon to the flask. Solvent, 25 mL, and triethyl phosphonoacetate (25 mmol, 5.54 g) was added and the mixture stirred 5 min. Triethylamine (28 mmol, 3.9 mL) was added and the mixture stirred an additional 10 min. The carbonyl compound was then added dropwise (5 min), and the reaction mixture was stirred overnight. After being quenched with dilute aqueous HCl, the reaction mixture was extracted with ether (3 × 25 mL). The organic extracts were combined and dried over $MgSO_4$, and the solvent was removed under vacuum. Samples for GC or ^1H NMR analyses were taken, and the crude product was purified by short path distillation.

Ethyl cinnamate[1b] was prepared from 1 and benzaldehyde: bp 75 °C (0.2 mmHg); ^1H NMR ($CDCl_3$) δ 1.30 (t, 3 H), 4.18 (q, 2 H), 6.33 (d, 1 H), 6.7–7.7 (m, 6 H).

Ethyl 4-methyl-2-pentenoate[1b] was prepared from 1 and isobutyraldehyde: bp 60 °C (30 mmHg); ^1H NMR ($CDCl_3$) δ 0.96–2.48 (m, 9 H), 2.4 (septet, 1 H), 4.16 (q, 2 H), 5.75 (d, 1 H), 7.0 (d of d, 1 H).

Ethyl 2-nonenoate[9] was prepared from 1 and heptaldehyde: bp 72 °C (2 mmHg); ^1H NMR ($CDCl_3$) δ 0.8–1.1 (m, 3 H), 1.1–1.7 (m, 1 H), 1.9–2.5 (m, 2 H), 4.2 (q, 2 H), 5.75 (d, 1 H), 6.95 (m, 1 H).

Ethyl cyclohexylideneacetate[10] was prepared from 1 and cyclohexanone: bp 50 °C (0.2 mmHg); ^1H NMR ($CDCl_3$) δ 1.23 (t, 3 H), 1.4–1.8 (m, 6 H), 1.9–2.5 (m, 2 H), 2.7–3.1 (m, 2 H), 5.5 (s, 1 H).

Ethyl cyclopentylideneacetate[11] was prepared from 1 and cyclopentanone: bp 85 °C (10 mmHg), ^1H NMR ($CDCl_3$) δ 1.25 (t, 3 H), 1.8 (m, 6 H), 2.5 (m, 2 H), 4.2 (q, 2 H), 5.8 (m, 1 H).

Ethyl 5-phenyl-2,4-pentadienoate[10] was prepared from 1 and cinnamaldehyde: bp 90 °C (0.2 mmHg); ^1H NMR ($CDCl_3$) δ 1.33 (t, 3 H), 4.2 (q, 2 H), 5.95 (d, 1 H), 6.7–7.6 (m, 8 H).

Registry No. 1, 867-13-0; Et_3N, 121-44-8; LiBr, 7550-35-8; $MgCl_2$, 7786-30-3; $MgBr_2$, 7789-48-2; LiCl, 7447-41-8; PhCHO, 100-52-7; $PhCH{=}CHCO_2Et$, 103-36-6; $(CH_3)_2CHCHO$, 78-84-2; n-$C_6H_{13}CHO$, 111-71-7; PhCH=CHCHO, 104-55-2; $CH_3C(O)CH_3$, 67-64-1; $PhC(O)CH_3$, 98-86-2; $(CH_3)_2CHCH{=}CHCO_2Et$, 2351-97-5; n-$C_6H_{13}CH{=}CHCO_2Et$, 17463-01-3; $(CH_2)_4C{=}CHCO_2Et$, 1903-22-6; $PhCH{=}CHCH{=}CHCO_2Et$, 1552-95-0; ethyl cyclohexylideneacetate, 1552-92-7; cyclopentanone, 120-92-3; cyclohexanone, 108-94-1.

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Intramolecular Diels–Alder Reaction of 1-Nitrodeca-1,6,8-trienes

Mark J. Kurth,* Michael J. O'Brien, Håkon Hope, and Michael Yanuck

Department of Chemistry, University of California, Davis, California 95616

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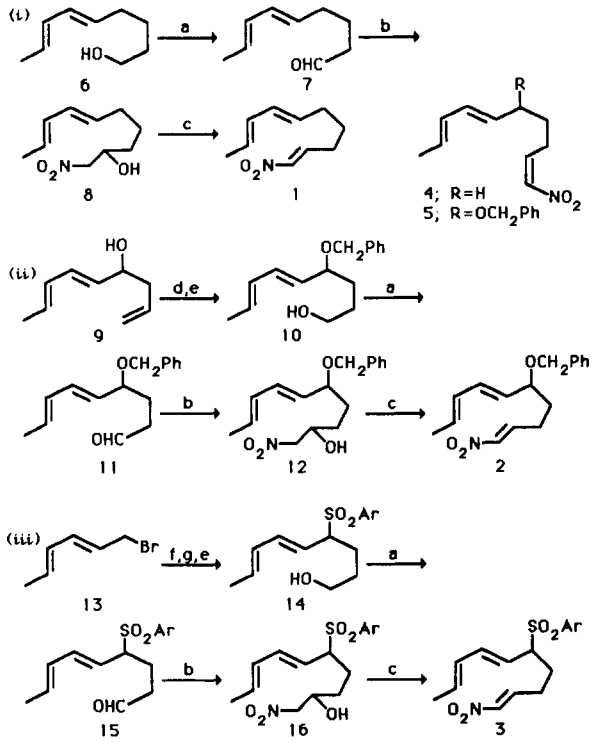
Nitro trienes **1**, **2**, and **3** are prepared from nona-5,7-dien-1-ols **6**, **10**, and **14**, respectively, via a three-step sequence involving PCC oxidation, nitro aldol condensation, and dehydration. Intramolecular Diels–Alder reaction of nitro trienes **1** and **2** preferentially affords endo cycloadducts possessing the trans ring fusion (9:1 trans/cis) while cyclization of **3** gives exclusively the trans-fused perhydroindene skeleton (**25c**/**25d**, 9:1). In contrast, (*Z*)-nitroolefins **4** and **5**, which are found to undergo cyclization at room temperature, produce a nearly 1:1 mixture of cis- and trans-fused cycloadducts.

Nitroaliphatic compounds have proven both versatile and unique as synthetic intermediates, particularly with regard to the extensive utility of the nitro group in organic functional group interconversions.[1] This utility is augmented by the many synthetic routes which access nitroaliphatics.[1,2] Of these routes, the intermolecular [4 + 2] cycloaddition of a nitroolefin and a 1,3-diene is the most reliable method for the stereoselective construction of

(1) For reviews, see: (a) Seebach, D.; Colvin, E. W.; Lehr, F.; Weller, T. *Quim. Ind.* (*Sao* Paula) **1979**, *33*, 1–18. (b) Schickh, O. V.; Apel. G.; Padeken, H. G.; Schwartz, H. H.; Segnitz, A. "Methoden der Organischen Chemies"; Georg Thieme Verlag: Stuttgart, 1971; Vol. X/1, pp 1–462. (c) Kornblum, N. *Org. React.* **1962**, *12*, 101–156.
(2) For recent examples, see: (a) Corey, E. J.; Samuelsson, B.; Luzzio, F. A. *J. Am. Chem. Soc.* **1984**, *106*, 3682–3. (b) Seebach, D.; Knochel. P. *Tetrahedron Lett.* **1982**, *23*, 3897–3900. (c) Corey, E. J.; Estreicher, H. *Tetrahedron Lett.* **1980**, *21*, 1117–20. (d) Seebach, D.; Henning, R.; Lehr, F.; Gonnerman, J. *Tetrahedron Lett.* 1977, 1161–4.

0022-3263/85/1950-2626$01.50/0

Scheme I[a]



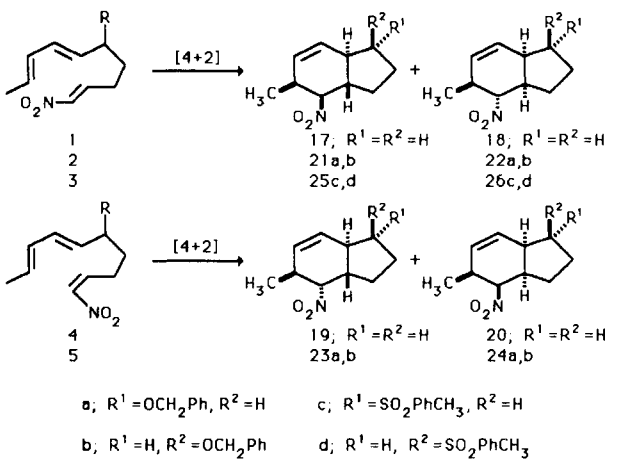
[a] (a) PCC–Celite. (b) CH_3NO_2, AGI-X10 resin (hydroxide form), EtOH. (c) DCC, CuCl, Et_2O. (d) (i) NaH; (ii) $PhCH_2Br$. (e) (i) 9-BBN, THF; (ii) H_2O_2, NaOH. (f) $C_7H_7SO_2Na\cdot 2H_2O$, DMF. (g) (i) *n*-BuLi, THF; (ii) allyl bromide.

six-membered ring nitroalicyclics.[3] Stereocontrolled access to complex nitrocarbocycles by the intramolecular variant of this reaction would, when coupled with the synthetic versatility of the nitro group, significantly extend the utility of this class of compounds in natural product total synthesis. However, for this intramolecularity to afford a synthetic advantage, there must be significant product selectivity in the cycloaddition.[4] Roush and co-workers have demonstrated that 1,6,8-trienes which bear a terminal carbomethoxy dienophile activating group exhibit poor secondary orbital control in uncatalyzed cycladditions, resulting in marginal product selectivity.[5] For example, thermal cyclization of methyl deca-2(*E*),7(*E*),9(*E*)-trienoate produced a 60:40 mixture of the trans- and cis-fused perhydroindenes, respectively. In contrast, Roush observed complete endo selectivity in the Lewis acid catalyzed variant of this reaction.[5] These results suggested to us that uncatalyzed perhydroindene product selectivity would afford an excellent test of nitro group activation in thermal intramolecular [4 + 2] cycloadditions. This, plus the potential utility of bicyclic nitro compounds in synthesis, prompted us to explore the Diels–Alder reaction of 1-nitrodeca-1,6,8-trienes.

Results and Discussion

Synthesis of Nitro Trienes. The all-trans trienes **1–3** were prepared in straightforward fashion as outlined in Scheme I. In each case, the chromatographed nona-5,7-dien-1-ol intermediate (**6**, **10**, and **14**) was judged by ^1H NMR to possess >95% *E,E* stereochemistry. Elaboration of the nitroolefin moiety was accomplished in a three-step sequence which began with PCC/Celite oxidation.[6] The resulting dienals were condensed with nitromethane in a polymer-supported quaternary ammonium hydroxide catalyzed nitroaldol.[7,8] At completion, the catalyst was removed by filtration, thus obviating a complicated work-up procedure. In order to assess nitroolefin stereochemistry, a mild β-hydroxynitroalkane dehydration protocol was required which would permit isolation of the reactive nitro triene. Seebach and Knochel's dicyclohexylcarbodiimide method,[9] which proceeds at 40 °C in the presence of catalytic amounts of copper(I) chloride, produced nitro trienes **1–3** in modest yield (~40%) and with good (*E*)-nitroolefin selectivity (~90:10 *E*/*Z*). These (*E*/*Z*)-nitroolefin mixtures were easily separated by silica gel chromatography. As expected, the ^1H resonance for C(2)-H is clearly indicative of nitroolefin geometry: this proton appearing at lower field in the (*E*)-nitroolefin.

Scheme II



Cycloadducts from 1 and 4. Cyclization of (*E*)-nitro triene **1** at 80 °C in toluene (0.06 M, sealed tube, 25 h) afforded an 89:11 mixture (500-MHz ^1H NMR) of two perhydroindenes which proved inseparable by silica gel MPLC (Scheme II). Structures **17** (major) and **18** (minor) were tentatively assigned on the basis of presumed endo selectively in the [4 + 2] cycloaddition.[3] In the interim, a chloroform-*d* solution of pure (*Z*)-nitroolefin **4**, isolated in 3% yield from the dehydration of **8**, underwent a Diels–Alder reaction at room temperature, giving a 53:47 mixture (500-MHz ^1H NMR) of two new perhydroindenes, **19** and **20**. It proved possible to make unambiguous stereochemical assignments for these four cycloadducts by comparing their ^1H NMR spectroscopic data with those reported by Roush et al. for the four cycloadducts of methyl 11-methyldodeca-2(*E*(and *Z*)),7(*E*),9(*E*)-trienoate.[5b] The ^1H NMR resonances for C(4)-H, the proton α to the W group, proved especially indicative of structure and are therefore tabulated for these eight perhydroindenes (Table I). In the trans-fused isomer i, this signal appears as a doublet of doublets, $J_{4,5}$ = 7.0–7.7 Hz and $J_{3a,4}$ = 10.9–11.4 Hz. These data require that C(3a)-H and C(4)-H occupy axial positions while C(5)-H occupies a pseudoequatorial

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(5) (a) Roush, W. R.; Ko, A. L.; Gillis, H. R. *J. Org. Chem.* **1980**, *45*, 4264–7. (b) Roush, W. R.; Gillis, H. R.; Ko, A. J. *J. Am. Chem. Soc.* **1982**, *104*, 2269–83.

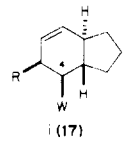
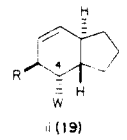
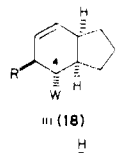
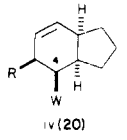
(6) Corey, E. J.; Suggs, J. W. *Tetrahedron Lett.* **1975**, 2647–50.

(7) Astle, M. J.; Abbott, F. P. *J. Org. Chem.* **1956**, *21*, 1228–31.

(8) For recent nitro aldol developments, see: (a) Rosini, G.; Ballini, R.; Sorrenti, P. *Synthesis* **1983**, 1014–6. (b) Seebach, D.; Beck, A. K.; Makhopadhyay, T.; Thomas, E. *Helv. Chim. Acta* **1982**, *65*, 1101–33.

(9) Seebach, D.; Knochel, P. *Synthesis* **1982**, 1017–8.

Table I. ^{1}H NMR Data for C(4)-H in 17–20 ($CDCl_3$)[a]

perhydroindene	NMR, δ: W = NO_2, R = CH_3	NMR, δ: W = CO_2CH_3, R = $CH(CH_3)_2$
 i (17)	4.68 (dd, J = 7.0, 10.9 Hz)	2.70 (dd, J = 7.7, 11.4 Hz)
 ii (19)	4.71 (d, J = 2.2 Hz)	2.81 (d, J = 4.9 Hz)
 iii (18)	3.97 (dd, J = 10.2, 11.2 Hz)	2.11 (dd, J = 10.8, 11.3 Hz)
 iv (20)	4.88 (t, J = 4.6 Hz)	2.93 (t, J = 4.9 Hz)

[a] This is a partial listing of the ^{1}H NMR data for 17–20. For a complete listing, see the Experimental Section.

position on the cyclohexenyl ring. In isomer ii, the C(4) epimer of i, the H_4–C–C–H_5 dihedral angle approaches 90°, and the C(4)-H signal simplifies to a doublet, $J_{3a,4}$ = 2.2–4.9 Hz (C(3a)-H axial and C(4)-H equatorial). Trans coupling constants of 10.2–10.8 and 11.2–11.3 Hz for C(4)-H in cis-fused isomer iii indicate that the C(3a), C(4), and C(5) cyclohexenyl protons all occupy axial positions. In contrast, C(4)-H in isomer iv appears as a triplet (doublet of doublets) with J = 4.9 Hz. This points to a gauche relationship between C(4)-H and its ^3J partners and implies conformational mobility in this cis-fused system. Inspection of the data in Table I reveals that in addition to the excellent correlations in peak multiplicity and coupling constants, there is remarkable covariation in chemical shift for C(4)-H in these two series [$\delta(NO_2) = \delta(CO_2CH_3) + 1.92 \pm 0.06$]. Hence, structure assignments for perhydroindenes **17–20** are secured and C(4)-H is shown to be a reliable stereochemical probe.

Cycloadducts from 2 and 5. On the basis of the product selectivity observed in the cyclization of **1**, the benzyloxy-modified (*E*)-nitro triene **2** was expected to yield four products: trans-fused cycloadducts **21a** and **21b** via endo addition and cis-fused cycloadducts **22a** and **22b** via exo addition. In fact, cyclization of **2** (0.06 M in toluene, 80 °C, 25 h) afforded three products in a 5:4:1 ratio and in 78% combined yield. These cycloadducts proved readily separable by medium-pressure liquid chromatography (MPLC) on silica gel. ^{1}H NMR analysis of the C(1)-H, C(4)-H, C(6)-H, and C(7)-H signals proved particularly useful in unraveling the stereochemistry of each cycloadduct. As illustrated in Table II, the major and median products, **21a** (39%) and **21b** (31%), respectively, display very similar resonances for C(4)-H, C(6)-H, and C(7)-H: The only significant difference occurs in the C(1)-H resonance. Furthermore, the C(4)-H signals in both **21a** and **21b** are essentially identical with those found in trans-fused perhydroindene **17** (Table I). Therefore, both major cycloadducts of **2** have the trans ring fusion and are only epimeric at C(1). The relative stereochemistry at this center could be tentatively assigned on the basis of the C(1) ^{1}H NMR data listed in Table II. Fortunately, **21b** crystallized and thus allowed a single-crystal X-ray diffraction analysis, the result of which is shown in Figure 1. This X-ray study verifies the trans ring fusion of these endo addition products and establishes the C(1) stereochemistry in both **21a** and **21b**. Inspection of the data in Table II reveals that the minor cycloadduct, **22a** (8.0%), is strikingly dissimilar from diastereomers **21a,b**. Again, the C(4)-H resonance provides symptomatic evidence of the perhydroindene stereochemistry: cis-fused adducts **18** (Table I) and **22a** displaying nearly identical C(4)-H signals. It is particularly noteworthy that **22a** is not simply a C(4) epimer of **21** [i.e., **23a,b**, cf. C(4)-H in **19** vs. **18** or **22a**]. This observation suggests that neither (*E*)/(*Z*)-nitroolefin or perhydroindene C(α)-nitro epimerization occurs under the conditions of the reaction.

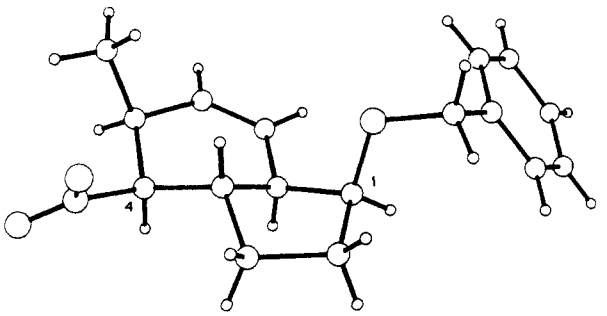


Figure 1. Stereoplot drawing of the X-ray structure of **21b**.

To verify this critical point, the Diels–Alder cycloaddition of (*Z*)-nitroolefin **5** (6% yield from **12**) was studied. Cyclization of **5** gave two products in a 54:46 ratio.[10] The signals for C(1)-H and C(4)-H in the major

Table II.[a] ^{1}H NMR Data for Cycloadducts from 2[b]

cycloadd	NMR, δ: C(1)-H	C(4)-H	C(6)-H	C(7)-H
21a	3.73 (ddd, 8.97, 5.82	4.71 (dd, 11.0, 7.04)	5.55 (ddd, 9.75, 3.00)	5.93 (d, 9.75)
21b	4.01 (dd, 5.0)	4.66 (dd, 11.9, 6.75)	5.62 (ddd, 9.76, 3.40)	5.91 (d, 9.76)
22a	3.64 (ddd, 6.23)	3.89 (dd, 10.6, 10.6)	5.44 (d, 9.91)	5.89 (ddd, 9.90, 2.70)

[a] Coupling constants in hertz are in parentheses. [b] This is a partial listing of the ^{1}H NMR Data. For a complete listing, see the Experimental Section.

Table III.[a] ^{1}H NMR Data for Cycloadducts from 3[b]

cycloadd	NMR, δ: C(1)-H	C(4)-H	C(6)-H	C(7)-H
25c	3.31 (ddd, 10.7, 6.5)	4.71 (dd, 11.0, 7.4)	5.54 (ddd, 9.9, 3.4, 3.4)	5.72 (d, 9.9)
25d	3.22 (m[c])	4.47 (dd, 10.3, 5.5)	5.53 (dd, 9.7, 1.4)	5.65 (ddd, 9.7, 4.9, 1.4)

[a] Coupling constants in hertz are in parentheses. [b] This is a partial listing of the ^{1}H NMR data. For a complete listing, see the Experimental Section. [c] The multiplicity of this proton was obscured because C(7a)-H resonates at the same frequency.

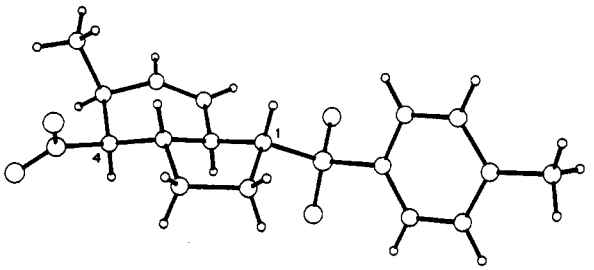


Figure 2. Stereoplot drawing of the X-ray structure of **25c**.

cycloadduct appeared as a doublet of doublets (δ 4.03, $J_{1,2} = J_{1,7a}$ = 5.1 Hz) and a doublet (δ 4.75, $J_{3a,4}$ = 3.5 Hz), respectively. the C(4)-H data are consistent with a trans ring fusion (cf. **19**). Drieding model analysis of trans-fused **23a** and **23b** suggests that the H_1–C–C–$H_{2\beta}$ dihedral angle approaches 90° when the benzyloxy substituent occupies the β-face. These data are consistent only with a structural assignment of **23b** to the major isomer. In contrast, the minor isomer displays a doublet of doublet of doublets for C(1)-H (δ 3.87, $J_{1,2} = J_{1,2\beta} = J_{1,7a}$ = 49 Hz) and a doublet of doublets for C(4)-H (δ 4.85, $J_{4,3a} = J_{4,5}$ = 4.9 Hz) which are congruent with assignment of structure **24a**.[11] These results with (*Z*)-nitroolefin **5** verify the structure assigned to **22a** and prove that neither nitroolefin or C(α)-nitro epimerization occur in these reactions.

Cycloadducts from 3. We next investigated the aryl sulfone modified (*E*)-nitrotriene **3**. Cyclization of **3** afforded essentially two products[12] in a 90:10 ratio (78% combined yield) which proved readily separable by silica gel MPLC. ^{1}H NMR data for the major product was entirely consistent with assignment of structure **25c**: both the C(1)-H and C(4)-H resonances were appropriate for this assignment (Table III). Indeed, this structure assignment was confirmed by single-crystal X-ray diffraction analysis, the result of which is indicated by the drawing of **25c** in Figure 2. A C(4)-H based structure assignment for the minor product suggested that it too was a trans-fused perhydroindene. The relative magnitudes of $J_{4,3a}$ and $J_{4,5}$ (10.3 and 5.5 Hz, respectively) are particularly informative. Drieding model analysis of the conformations available to cis isomers **26c,d** indicates that a large $J_{4,3a}$ and a small $J_{4,5}$ is highly unlikely. In contrast, analysis of **25d** suggests precisely this relative magnitude for these coupling constants. However, to verify structure **25d** for the minor isomer, we turned to the use of nuclear Overhauser enhancement difference (NOED) spectroscopy.[13]

Since **25c** was securely assigned, we first examined its difference NOE. Irradiation of C(4)-H_α proved particularly informative in that positive NOE's were observed for C(5)-H_α and C(7a)-H_α while no enhancement of C(3a)-H_β was detected. The consensus between our NOED and X-ray results, although anticipated on the basis of structure of **25c** (Figure 2), was, nonetheless, satisfying. We next undertook an analogous NOED study of the minor cycloadduct and were gratified to again observe positive NOE's for C(5)-H_α and C(7a)-H_α with no NOE for C-(3a)-H_β. Therefore the configuration of the minor cycloadduct **25d** is secured.

Compared to the carbomethoxy analogues reported by Roush and co-workers,[5,11,14] nitro-activated trienes **1–5** exhibit both increased reactivity and increased endo product selectivity in the uncatalyzed thermal cycloaddition reaction. The nearly complete endo selectivity realized in the cyclization of **3** was unexpected. Apparently the aryl sulfone moiety magnifies the strain and nonbonded interactions inherent in the exo transition state, thus further destabilizing it relative to the endo transition state. The high degree of internal asymmetric induction attained in this endo cyclization (**25c** vs. **25d**) is easily understood in terms of the steric requirements of the aryl sulfone moiety[15] and the dissimilar interactions afforded the two diastereotopic endo transition states.

The results described above establish the intramolecular Diels–Alder reaction of nitroolefins as a viable route to stereochemically complex nitrocarbocycles. The synthetic potential inherent in these results would appear to be considerable, and further studies and synthetic applications are currently underway.

Experimental Section

General Procedures. Proton magnetic resonance spectra were taken on a Varian EM 390, Nicolet NT-360, or Nicolet NM-500 instrument. Infrared spectra were recorded on a Beckman IR-8 spectrophotometer. Mass spectra were determined by Kei Miyano on a VG ZAB analytical instrument (electron impact, EI) through the Facility for Advanced Instrumentation, University of California, Davis. Elemental analyses were performed by the University of California, Berkeley, analytical laboratories. Medium-pressure liquid chromatography refers to chromatography done at 10–50 psi through EM Lobar columns packed with LiChroprep Si60 (40–65 μm) with hexane/EtOAc eluent and monitored by refractive index detection. Chromatotron refers to preparative, centrifugally accelerated, radial, thin-layer chromatography with silica gel 60 PF as stationary phase and with hexane/EtOAc as eluent.

(±)-4-(Phenylmethoxy)-5,7-nonadien-1-ol (10). To a solution of alcohol **9** (8.20 g, 59.5 mol) in DME (93 mL) was added NaH (3.43 g, 71.4 mmol), and the resulting mixture was stirred 10 min at room temperature. Benzyl bromide (8.50 mL, 71.4 mmol) was added, and the solution was heated to 85 °c for 3.5 h. Upon cooling to room temperature, the mixture was diluted with ether and washed with saturated NH_4Cl, 10% HCl, and brine. After the mixture was dried over Na_2SO_4, the solvent was removed and the resulting residue distilled to yield the benzyloxy triene as a colorless oil (12.7 g, 55.7 mmol, 96.6%) [bp 110–115 (0.2 torr; ^{1}H NMR (90 MHz, $CDCl_3$) δ 1.76 (d, J = 6.0 Hz, 3 H), 2.23 (m, 2 H), 3.79 (q, J = 7.0 Hz, 1 H), 4.30 (d, J = 12.0 Hz, 1 H), 4.60 (d, J = 12.0 Hz, 1 H), 4.9–6.3 (m, 7 H), 7.33 (m, 5 H); IR (CCl_4) 3080, 3040, 2940, 2870, 1640, 1450, 1085, 1070, 990, 915, 700 cm^{-1}; MS(EI), m/e (relative intensity) 187 ($M^+ - C_3H_5$, 100), 137 ($M^+ - CH_2Ph$, 5), 121 ($M^+ - OCH_2Ph$, 3); calcd for $C_{13}H_{15}O$ ($M^+ - C_3H_5$) 187.1123; found 187.1235].

To a ice-cold THF (25 mL) solution of this triene (11.3 g, 49.6 mmol) was added 9-BBN (143 mL, 0.38 M, 54.5 mmol) in THF over a period of 30 min. The resulting solution was warmed to room temperature and stirred overnight. Ethanol (50 mL) and 10% NaOH (35 mL) were added, the solution was cooled at 0 °C, and 30% H_2O_2 (40 mL) was added dropwise. The resulting mixture was heated to reflux for 2 h, cooled to room temperature, and saturated with anhydrous K_2CO_3, and the organic layer was separated. The aqueous layer was extracted once with ether, and the combined organics were dried (Na_2SO_4) and concentrated under reduced pressure. The crude product was purfied by filtration through a silica column (2:1 hexane/EtOAc), yielding **10** as a viscous oil (11.8 g, 47.9 mmol, 97%) [^{1}H NMR (90 MHz, $CDCl_3$) δ 1.4–1.7 (m, 4 H), 1.75 (d, J = 6.0 Hz, 3 H), 2.10 (s, 1 H), 3.55 (m, 2 H), 3.75 (q, J = 7.0 Hz, 1 H), 4.30 (d, J = 12.0 Hz, 1 H), 4.59 (d, J = 12.0 Hz, 1 H), 5.25–6.3 (m, 4 H), 7.3 (m, 5 H); IR (CCl_4) 3650–3150, 3050, 2950, 2890, 1450, 1060, 990, 700 cm^{-1};

(10) Two trace compounds (<2% combined yield) were observed in the 500-MHz ^{1}H NMR of **23b** and **24a**.
(11) Roush, W. R. *J. Org. Chem.* **1979**, *44*, 4008–10.
(12) In addition to the two major cycloadducts, two trace components (<1% combined yield) were observed in the 500-MHz ^{1}H NMR of the crude reaction mixture obtained from **3**.
(13) Hall, L. D.; Sanders, J. K. M. *J. Am. Chem. Soc.* **1980**, *102*, 5703–11.
(14) Roush, W. R.; Peseckis, S. M. *J. Am. Chem. Soc.* **1981**, *103*, 6696–704.
(15) Magnus, P. D. *Tetrahedron* **1977**, *33*, 2019–45.

MS(EI), m/e (relative intensity) 245 (M^+, 1), 228 ($M^+ - H_2O$, 1), 187 ($M^+ - (CH_2)_3OH$, 87), 155 ($M^+ - CH_2Ph$, 96), 144 (100), 137 (51), 119 (82); calcd for $C_{16}H_{20}O_2$ 246.1620; found 246.1646].

(±)-4-[(4-Methylphenyl)sulfonyl]-5,7-nonadien-1-ol (14). To a solution of bromohexadiene (**13**; 2.50 g, 15.5 mmol) in DMF (20 mL) was added $CH_3PhSO_2Na \cdot 2H_2O$ (3.65 g, 18.6 mmol) dissolved in 130 mL of DMF. The resulting solution was allowed to stir overnight, then diluted with water, and extracted three times with a 1:1 mixture of hexane/ether. The combined organics were washed with 10% HCl, H_2O, saturated $NaHCO_3$, and brine, then dried (Na_2SO_4), and concentrated under reduced pressure. The crude product was purified by medium-pressure liquid chromatography (2.5:1 hexane/ethyl acetate), yielding the diene sulfone as a light yellow oil (2.71 g, 11.5 mmol, 74%) [^{1}H NMR (90 MHz, $CDCl_3$) δ 1.70 (d, J = 6.0 Hz, 3 H), 2.44 (s, 3 H), 3.73 (d, J = 7.0 Hz, 2 H), 5.0–6.3 (m, 4 H), 7.30 (d, J = 7.0 Hz, 2 H), 7.75 (d, J = 7.0 Hz,2 H); IR (CCl_4) 3040, 2980, 2940, 2870, 1650, 1595, 1320, 1300, 1145, 1090, 985 cm^{-1}]. n-BuLi(1.55 M in hexane, 7.6 mL, 11.8 mmol) was added to a THF (45 mL) solution of this sulfone (2.65 g, 11.2 mmol) at −20 °C and stirred 5 min. After the solution cooled to −78 °C, allyl bromide (1.07 mL, 12.3 mmol) was added and the solution slowly warmed to 0 °C where it was quenched with water. The mixture was extracted with ether, and the combined organics were washed with water and brine and then dried (Na_2SO_4). After concentration under reduced pressure, the crude product was purified by medium-pressure liquid chromatography (3:1 hexane/ethyl acetate) to give the triene sulfone as a viscous oil (2.15 g, 7.78 mmol, 69%) [^{1}H NMR (90 MHz, $CDCl_3$) δ 1.72 (d, J = 7.0 Hz, 3 H), 2.43 (s, 3 H), 2.82 (m, 2 H), 3.52 (dt, J = 9.0, 4.0 Hz, 1 H), 5.92–6.23 (m, 6 H), 7.31 (d, J = 8.0 Hz, 2 H), 7.72 (d, J = 8.0 Hz, 2 H); IR (CCl_4) 3040, 2990, 2930, 2870, 1595, 1315, 1305, 1140, 1085, 985, 915 cm^{-1}]. This triene sulfone (1.0 g, 3.62 mmol) in THF (5 mL) was added dropwise to an ice-cold solution of 9-BBN in THF (11.9 mL, 0.38 M in THF, 4.52 mmol). The mixture was allowed to warm to room temperature where it was stirred an additional 2.5 h. Ethanol (4 mL) and 10% NaOH (3.2 mL) were added, the solution was cooled to 0 °C, and 30% H_2O_2 (2.6 mL) was added over 20 min. After addition was complete, the mixture was heated to reflux for 1 h and then cooled to room temperature. The aqueous phase was saturated with anhydrous K_2CO_3, and the layers were separated. The organic portion was dried (Na_2SO_4) and concentrated under reduced pressure, and the crude product was purified by medium-pressure liquid chromatography (1:1 hexane/ethyl acetate) to give **14** as a viscous oil (905 mg, 3.07 mmol, 85%) [^{1}H NMR (90 MHz, $CDCl_3$) δ 1.4–1.85 (m, 4 H), 1.71 (d, J = 7.0 Hz, 3 H), 2.1 (s, 1 H), 2.41 (s, 3 H), 3.50 (dt, J = 10.0, 4.0 Hz, 1 H), 3.60 (t, J = 6.0 Hz, 2 H), 5.0–6.2 (m, 4 H), 7.27 (d, J = 8.0 Hz, 2 H), 7.68 (d, J = 8.0 Hz, 2 H); IR ($CHCl_3$) 3630, 3600–3300, 3040, 3020, 2950, 2895, 1650, 1595, 1440, 1290, 1140, 1080, 990, 905 cm^{-1}; MS(EI), m/e (relative intensity) 294(2, M^+), 293(4, M^+ −H), 246(11), 153 (37), 139 (38, $M^+ - C_7H_7SO_2$), 123 (38), 91 (100); calcd for $C_{16}H_{22}O_3S$ 294.1289; found 294.1218].

5,7-Nonadienal (7). General PCC Oxidation Procedure. To a suspension of PCC (8.30 g, 38.5 mmol) and Celite (8.30 g) in CH_2Cl_2 (40 mL) was added **6** (770 mg, 5.50 mol) in CH_2Cl_2 (10 mL). The mixture was stirred for 1.75 h at room temperature, at which time it was diluted with ether and filtered through a short column of Florisil. Concentration of the filtrate under reduced pressure yielded **7** as a light yellow oil (459 mg, 3.33 mmol, 61%) which was used in the next step without further purification [^{1}H NMR (90 MHz, $CDCl_3$) δ 1.5–1.95 (m, 2 H), 1.70 (d, J = 7.0 Hz, 3 H), 2.08 (q, J = 7.0 Hz, 2 H), 2.41 (t, J = 7.0 Hz, 2 H), 5.25–6.1 (m, 4 H), 9.77 (s, 1 H); (CCl_4) 3035, 2950, 2830, 2725, 1730, 1445, 985, 910 cm^{-1}].

(±)-4-(Phenylmethoxy)-5,7-nonadienal (11). Oxidation of **10** (2.51 g, 10.2 mmol) with PCC (15.4 g, 71.3 mmol) as described above produced **11** as a light yellow oil (1.92 g, 7.86 mmol, 77%) [^{1}H NMR (90 MHz, $CDCl_3$) δ 1.77 (d, J = 6.0 Hz, 3 H), 1.90 (q, J = 7.0 Hz, 2 H), 2.45 (q, J = 7.0 Hz, 2 H), 3.80 (q, J = 7.0 Hz, 1 H), 4.29 (d, J = 12.0 Hz, 1 H), 4.56 (d, J = 12.0 Hz, 1 H), 5.25–6.3 (m, 4 H), 7.19 (m, 5 H), 9.78 (s, 1 H); IR (CCl_4) 3050, 2950, 2880, 2740, 1730, 1450, 1200, 1090, 1070, 990, 700 cm^{-1}].

(±)-4-[(4-Methylphenyl)sulfonyl]-5,7-nonadienal (15). Oxidation of **14** (830 mg, 2.82 mmol) with PCC (4.26 g, 19.7 mmol) as described above produced **15** as a light yellow oil (572 mg, 1.96 mmol, 69%) [^{1}H NMR (90 MHz, $CDCl_3$) δ 1.5–1.9 (m, 2 H), 1.75 (d, J = 6.0 Hz, 3 H), 2.42 (s, 3 H), 2.24–2.7 (m, 2 H), 3.63 (m, 1 H), 5.05–6.1 (m, 4 H), 7.30 (d, J = 8.0 Hz, 2 H), 7.68 (d, J = 8.0 Hz, 2 H), 9.75 (m, 1 H); IR (CCl_4) 3050, 2950, 2890, 2840, 2740, 1730, 1600, 1320, 1150, 1090, 995 cm^{-1}].

(±)-1-Nitro-6,8-decadien-2-ol (8). General Nitro Aldol Procedure. To a mixture of **7** (470 mg, 3.41 mmol), nitromethane (550 μL, 10.2 mmol), and ethanol (600 μL, 10.2 mmol) was added 280 mg of a resin-supported quaternary ammonium hydroxide catalyst which had previously been prepared by washing Bio-Rad AG1-X10 anion-exchange resin (chloride form, 100–200 mesh) with 5% NaOH (200 mL), water (200 mL), ethanol (100 mL), and ether (100 mL). The resulting mixture was stirred overnight at room temperature and then filtered and the solid residue was washed with ether. The combined organics were dried (Na_2SO_4) and concentrated under reduced pressure, and the resulting crude product was purified by chromatatron (3:1 hexane/ethyl acetate), yielding **8** as a light yellow oil (361 mg, 1.81 mmol, 53%) [^{1}H NMR (90 MHz, $CDCl_3$) δ 1.35–1.6 (m, 4 H), 1.72 (d, J = 6.0 Hz, 3 H), 1.9–2.3 (m, 2 H, 2.73 (s, 1 H), 4.24–4.52 (m, 3 H, 5.3–6.15 (m, 4 H); IR (CCl_4) 3680–3220, 3040, 2950, 2870, 1550, 1380, 1090, 990, 916 cm^{-1}; MS(EI), m/e (relative intensity) 199 (M^+, 4.0), 181 ($M^+ - H_2O$, 9.0), 169 ($M^+ - CH_2NO_2$, 12.0); calcd for $C_{10}H_{17}NO_3$ 199.1209; found 199.1226].

(±)-1-Nitro-5-(phenylmethoxy)-6,8-decadien-2-ol (12). Reaction of **11** (1.90 g, 7.78 mmol) with CH_3NO_2 (1.20 mL, 23.3 mmol) in the presence of ethanol (1.36 mL, 23.3 mmol) and resin-supported quaternary ammonium hydroxide (632 mg) produced **12** as a light yellow oil (2.16 g, 7.07 mmol, 91%) which was used in the next step without further purification [^{1}H NMR (90 MHz, $CDCl_3$) δ 1.4–1.7 (m, 4 H), 1.75 (d, J = 6.0 Hz, 3 H), 3.20 (s, 1 H), 3.80 (q, J = 7.0 Hz, 1 H), 4.25 (d, J = 12.0 Hz, 1 H), 4.30 (m, 3 H), 4.56 (d, J = 12.0 Hz, 1 H), 5.25–6.3 (m, 4 H), 7.30 (m, 5 H); IR (CCl_4) 3650–3250, 3040, 2940, 2870, 1550, 1450, 1380, 1060, 990, 700 cm^{-1}].

(±)-[5-[(4-Methylphenyl)sulfonyl]-1-nitro-6,8-decadien-2-ol (16). Reaction of **15** (546 mg, 1.87 mmol) with nitromethane (303 μL, 5.6 mmol) in the presence of ethanol (327 μL, 5.6 mmol) and resin-supported quaternary ammonium hydroxide (152 mg) produced **16** as a light yellow oil (616 mg, 1.74 mmol, 93%) which was used without further purification in the next step [^{1}H NMR (90 MHz, $CDCl_3$) δ 1.2–1.95 (m, 4 H), 1.69 (d, J = 7.0 Hz, 3 H), 2.42 (s, 3 H), 3.00 (s, 1 H), 3.48 (br t, J = 9.0 Hz, 1 H), 4.3 (m, 3 H), 5.0–6.2 (m, 4 H), 7.29 (d, J = 8.0 Hz, 2 H), 7.67 (d, J = 8.0 Hz, 2 H); IR ($CHCl_3$) 3600, 3580–3300, 3030, 2970, 2940, 2880, 1650, 1595, 1375, 1295, 1140, 1080, 990, cm^{-1}].

(1*E*,6*E*,8*E*)- and (1*Z*,6*E*,8*E*)-1-Nitro-1,6,8-decatriene (1 and 4). General Dehydration Procedure. Cuprous chloride (4 mg, 0.05 mmol) was added to an ether (5.8 mL) solution of dicyclohexylcarbodiimide (DCC; 450 mg, 2.17 mmol) and nitro aldol **8** (360 mg, 1.81 mmol). The resulting mixture was heated to 40 °C overnight in a resealable tube. After cooling to room temperature, it was diluted with hexane and filtered through Celite. The filtrate was washed with 5% HCl and brine, dried (Na_2SO_4), and concentrated under reduced pressure. Purification by medium-pressure liquid chromatography (95:5 hexane/EtOAc) gave, in order of elution, **1** (117 mg, 0.65 mmol, 36%) [^{1}H NMR (90 MHz, $CDCl_3$) δ 1.66–1.70 (m, 2 H), 1.71 (d, J = 6.0 Hz, 3 H), 1.9–2.4 (m, 4 H), 5.2–6.2 (m, 4 H), 6.94 (d, J = 14.0 Hz, 1 H), 7.28 (dt, J = 14.0, 7.0 Hz, 1 H); IR (CCl_4) 3040, 2980, 2880, 1650, 1530, 1440, 1355, 990, 960 cm^{-1}; MS(EI), m/e (relative intensity) 181 (M^+, 0.4), 151 (12), 135 (72), 79 (100); calcd for $C_{10}H_{15}NO_2$ 181.1103; found 181.1162 and **4** (11 mg, 0.06 mmol, 3.4%) [^{1}H NMR (60 MHz, $CDCl_3$) δ 1.4–1.7 (m, 2 H), 1.78 (d, J = 7.0 Hz, 3 H), 1.9–2.45 (m, 2 H), 2.5–3.0 (m, 2 H), 5.2–6.4 (m, 5 H), 6.90 (d, J = 8.0 Hz, 1 H); IR (CCl_4) 3040, 2960, 2890, 1650, 1525, 1440, 1350, 990, 740 cm^{-1}; MS(E/I), m/e (relative intensity) 181 (M^+, 0.6); calcd for $C_{10}H_{15}NO_2$ 181.1103; found 181.1135].

(±)-(1*E*,6*E*,8*E*)- and (1*Z*,6*E*,8*E*)-1-Nitro-5-(phenylmethoxy)-1,6,8-decatriene (2 and 5). Reaction of **12** (2.14 g, 7.01 mmol) with DCC (1.74 g, 8.41 mmol) and CuCl (17 mg, 0.18 mmol) as above gave, after purification (MPLC; 92:8 hexane/EtOAc), **2** (1.12 g, 3.90 mmol, 56%) [^{1}H NMR (90 MHz, $CDCl_3$) δ 1.6–1.8 (m, 2 H), 1.79 (d, J = 6.0 Hz, 3 H), 2.35 (q, J = 7.0 Hz, 2 H), 3.76 (q, J = 7.0 Hz, 1 H), 4.29 (d, J = 12.0 Hz, 1 H), 4.60 (d, J = 12.0 Hz, 1 H), 5.3–6.3 (m, 4 H), 6.89 (d, J = 13.0 Hz, 1 H), 7.27 (dt,

J = 13.0, 7.0 Hz, 1 H), 7.35 (m, 5 H); IR (CCl_4) 3040, 2950, 2880, 1550, 1530, 1350, 1080, 990, 700 cm^{-1}; MS(E/I), m/e (relative intensity) 196 (16, $M^+ - CH_2Ph$), 150 (2, $M^+ - CH_2Ph - NO_2$), 105 (78), 91 (100, $^+CH_2Ph$); calcd for $C_{10}H_{14}NO_3$ ($M^+ - CH_2Ph$) 196.0974, found 196.0968] and **5** (200 mg, 0.7 mmol, 9.9%) [^1H NMR (90 MHz, $CDCl_3$) δ 1.55–1.9 (m, 2 H), 1.76 (d, J = 6.0 Hz, 3 H), 2.80 (q, J = 7.0 Hz, 2 H), 3.77 (q, J = 7.0 Hz, 1 H), 4.28 (d, J = 12.0 Hz, 1 H), 4.60 (d, J = 12.0, 1 H), 5.3–6.3 (m, 5 H), 6.88 (d, J = 12.0 Hz, 1 H), 7.3 (m, 5 H); IR (CCl_4) 3040, 2940, 2880, 1525, 1350, 1090, 1070, 990, 700 cm^{-1}; MS(E/I), m/e (relative intensity) 196 (10 $M^+ - CH_2Ph$), 91 (100, $^+CH_2Ph$); calcd for $C_{10}H_{14}NO_3$ ($M^+ - CH_2Ph$) 196.0974, found 196.0958].

(±)-(1*E*,6*E*,8*E*)-5-[(4-Methylphenyl)sulfonyl]-1-nitro-1,6,8-decatriene (3). Reaction of alcohol **16** (53 mg, 1.52 mmol) with DCC (375 mg, 1.82 mmol) and CuCl (4 mg, 0.04 mmol) as above gave, after purification (MPLC; 2:1 hexane/EtOAc), **3** as a light yellow oil (220 mg, 0.66 mmol, 43%) [^1H NMR (90 MHz, $CDCl_3$) δ 1.5–1.65 (m, 2 H), 1.73 (d, J = 7.0 Hz, 3 H), 2.1–2.4 (m, 2 H), 2.46 (s, 3 H), 3.44 (dt, J = 10.0, 3.0 Hz, 1 H), 5.0–6.2 (m, 4 H), 6.94 (d, J = 15.0 Hz, 1 H), 7.0–7.4 (m, 1 H), 7.36 (d, J = 8.0 Hz, 2 H), 7.75 (d, J = 8.0 Hz, 2 H); IR ($CHCl_3$) 3045, 2980, 2950, 2980, 1650, 1595, 1545, 1350, 1325, 1300, 1290, 1140, 1085, 990 cm^{-1}. Anal. Calcd for $C_{17}H_{21}NO_4S$: C, 60.87; H, 6.32; N, 4.18. Found: C, 60.76, H, 6.34; N, 3.99].

(±)-5-Methyl-4-nitro-2,3,3aβ,4α,5α,7aα-hexahydro-1*H*-indene (17) and (±)-5-Methyl-4-nitro-2,3,3aα,4β,5α,7aα-hexahydro-1*H*-indene (18). (*E*)-Nitro triene **1** (65 mg, 0.36 mmol) was dissolved in benzene (6 mL) and heated to reflux for 30 h. After concentration under reduced pressure, the crude product was purified by medium-pressure liquid chromatography (98:2 hexane/EtOAc) to give an inseparable mixture of **17** and **18** (89:11) (42 mg, 0.23 mmol, 64%) [**17**, ^1H NMR (360 MHz, $CDCl_3$) δ 0.95 (d, J = 7.1 Hz, CH_3), 1.18–1.39 (m, H-1, H-3), 1.72–2,14 (m, H-3a, H-7a, 2 H-2's, H-1, H-3), 3.06 (ddq, $J_{4,5}$ = 7.0 Hz, $J_{5,6}$ = 3.8 Hz, $J_{5,}CH_3$ = 7.1 Hz, H-5α), 4.68 (dd, $J_{4,3}$a = 10.9 Hz, $J_{4,5}$ = 7.0 Hz, H-4α), 5.51 (ddd, $J_{6,7}$ = 9.6 Hz, $J_{5,6}$ = 3.8 Hz, $J_{6,7a}$ = 2.3 Hz, H-6), 5.80 (d, $J_{6,7}$ = 9.6 Hz, H-7); **18**, ^1H NMR (360 MHz, $CDCl_3$) δ 1.04 (d, J = 7.0 Hz, CH_3), 2.64 (ddq, $J_{5,6}$ = 3.0 Hz, J_{5,CH_3} = 7.0 Hz, H-5α), 3.97 (dd, J = 11.2, 10.2 Hz, H-4β), 5.39 (ddd, $J_{6,7}$ = 9.6 Hz, $J_{5,6}$ = 3.0 Hz, $J_{6,7a}$ = 3.0 Hz, H-6), 5.80 (d, $J_{6,7}$ = 9.6 Hz, H-7); **17** and **18**, IR (CCl_4) 3040, 2980, 2920, 2890, 1545, 1450, 1370, 720 cm^{-1}; MS(E/I), m/e (relative intensity) 181 (M^+, 4.1), 135 ($M^+ - NO_2$, 37), 119 (100); calcd for $C_{10}H_{15}NO_2$ 181.1103; found 181.0892].

(±)-5-Methyl-1α-(phenylmethoxy)-4-nitro-2,3,3aβ,4α,-5α,7aα-hexahydro-1*H*-indene (21a), (±)-5-Methyl-1β-(phenylmethoxy)-4-nitro-2,3,3aβ,4α,5α,7aα-hexahydro-1*H*-indene (21b), and (±)-5-Methyl-1α-(phenylmethoxy)-4-nitro-2,3,3aα,4β,5α,7aα-hexahydro-1*H*-indene (22a). (*E*)-Nitro triene **2** (127 mg, 0.44 mmol) was heated in the dark in degassed benzene at 80 °C for 23 h. The solvent was removed under reduced pressure and the resulting oil was purified by medium-pressure liquid chromatography (98:2 hexane/EtOAc) yielding, in order of elution, **21a** (49.8 mg, 0.173 mmol, 39%) [^1H NMR (500 MHz, $CDCl_3$) δ 0.92 (d, J = 6.6 Hz, CH_3), 1.50 (m, H-3α), 1.77 (m, H-2α), 2.06 (m, H-3β, H-3aβ), 2.20 (m, H-2β), 2.22 (m, $J_{1,7a}$ = 9.0 Hz, $J_{6,7a}$ = 3.0 Hz, H-7aα), 3.07 (ddq, $J_{4,5}$ = 7.0 Hz, $J_{5,6}$ = 3.0 Hz, J_{5,CH_3} = 7.1 Hz, H-5α), 3.73 (ddd, $J_{1,7a}$ = 9.0 Hz, $J_{1,2}$ = 9.0 Hz, $J_{1,2}$ = 5.8 Hz, H-1β), 4.48 (d, J = 11.8 Hz, CHHPh), 4.61 (d, J = 11.8 Hz, CH*H*Ph), 4.71 (dd, $J_{3a,4}$ = 11.0 Hz, $J_{4,5}$ = 7.0 Hz, H-4α), 5.55 (ddd, $J_{6,7}$ = 9.8 Hz, $J_{6,7a}$ = 3.0 Hz, $J_{5,6}$ = 3.0 Hz, H-6), 5.93 (d, $J_{6,7}$ = 9.8 Hz, H-7), 7,25–7.4 (m, Ar H); IR (CCl_4) 3040, 2980, 2950, 2880, 1545, 1350, 1110 cm^{-1}. Anal. Calcd for $C_{17}H_{21}NO_3$: C, 71.06; H, 7.37; N, 4.87. Found: C, 70.86; H, 7.41; N, 4.63], **21b** (39.6 mg, 0.138 mmol, 31%) as a solid [mp 118–119 °C from hexane; ^1H NMR (500 MHz, $CDCl_3$) δ 0.99 (d, J = 7.1 Hz, CH_3), 1.24 (m, H-3α), 1.95 (m, H-2α), 2.00 (ddd, $J_{1,7a}$ = 5.0 Hz, $J_{3a,7a}$ = 11.8 Hz, $J_{6,7a}$ = 3.4 Hz, H-7aα), 2.02 (m, H-2β), 2.19 (m, H-3β), 2.66 (dddd, $J_{3a,4}$ = 11.9 Hz, $J_{3a,3\alpha}$ = 11.8 Hz, $J_{3a,7a}$ = 11.8 Hz, $J_{3a,3\beta}$ = 6.4 Hz, H-3aβ), 3.08 (ddq, $J_{4,5}$ = 6.8 Hz, $J_{5,6}$ = 3.4 Hz, J_{5,CH_3} = 7.1 Hz, H-5α), 4.01 (dd, $J_{1,7a}$ = 5.0 Hz, $J_{1,2}$ = 5.0 Hz, H-1α), 4.45 (d, J = 12.4 Hz, *C*HHPh), 4.60 (d, J = 12.4 Hz, CH*H*Ph), 4.66 (dd, $J_{4,3a}$ = 11.9 Hz, $J_{4,5}$ = 6.8 Hz, H-4α), 5.62 (ddd, $J_{6,7}$ = 9.8 Hz, $J_{6,5}$ = 3.4 Hz, $J_{6,7a}$ = 3.4 Hz, H-6), 5.91 (d, $J_{6,7}$ = 9.8 Hz, H-7), 7.26–7.41 (m, Ar H); IR (CCl_4) 3040, 2990, 2880, 1550, 1365, 1160 cm^{-1}. Anal. Calcd for $C_{17}H_{21}NO_3$: C, 71.06; H, 7.37; N, 4.87. Found: C, 70.81; H, 7.50; N, 4.71], and **22a** (10.1 mg, 0.035 mmol, 8.0%) [^1H NMR (500 MHz, $CDCl_3$) δ 1.03 (d, J = 6.9 Hz, CH_3), 1.53 (m, H-3), 1.75 (m, H-2), 2.02 (m, H-2′, H-3′), 2.73 (m, H-5α), 2.79 (m, H-3aα), 3.64 (ddd, $J_{1,2}$ = 6.2 Hz, $J_{1,2}$ = 6.2 Hz, $J_{1,7a}$ = 6.2 Hz, H-1β), 3.89 (dd, $J_{4,5}$ = 10.6 Hz, $J_{4,3a}$ = 10.6 Hz, H-4β), (d, J = 10.8 Hz, C*H*HPh), 4.56 (d, J = 10.8 Hz, CH*H*Ph), 5.44 (d, $J_{6,7}$ = 9.9 Hz, H-6), 5.89 (ddd, $J_{6,7}$ = 9.9 Hz, $J_{7,7a}$ = 2.7 Hz, $J_{7,5}$ = 2.7 Hz, H-7), 7.27–7.4 (m, Ar H); IR (CCl_4) 3050, 2990, 2885, 1545, 1350, 1100 cm^{-1}; MS(EI), m/e (relative intensity) 196 (14, $M^+ - CH_2Ph$), 105 (40), 91 (100, $^+CH_2Ph$); calcd for $C_{10}H_{14}NO_3$ ($M^+ - CH_2Ph$) 196.0974, found 196.0962].

A recrystallized sample of **21b** was subjected to single-crystal X-ray diffraction analysis. Compound **21b** crystallizes from *n*-hexane in the monoclinic space group $P2_1/c$. The crystal data at 140 K are as follows: a = 11.766 (5) Å, b = 5.101 (3) Å, c = 24.18 (3) Å, β = 90.36 (5)°, ρ(calcd) = 1.31 g cm^{-3} for Z = 4; 2θ (max) = 50°; 1307 reflections with $F > 4\sigma(|F|)$ used, Mo K_α (graphite) (λ = 0.71069 Å), and ω scan, 58.6° min^{-1}; R = 0.092. SHELXTL programs on a DGC Eclipse S/230 computer were used.

(±)-5-Methyl-1β-(phenylmethoxy)-4-nitro-2,3,3aα,4α,-5α,7aα-hexahydro-1*H*-indene (23b) and (±)-5-Methyl-1α-(phenylmethoxy)-4-nitro-2,3,3aα,4α,5α,7aα-hexahydro-1*H*-indene (24a). (*Z*)-Nitro triene **5** (35 mg, 0.122 mmol) in benzene-d_6 (2 mL) was allowed to stand at room temperature and the progress of the cycloaddition monitored by ^1H NMR analysis. After 4 days the reaction was judged complete, and the solvent was removed under reduced pressure. Medium-pressure liquid chromatography (95:5 hexane/EtOAc) of the resulting mixture gave, in order of elution, **23b** (13 mg, 0.045 mmol, 37%) [^1H NMR (500 MHz, $CDCl_3$) δ 1.19 (d, J = 7.3 Hz, CH_3), 1.98 (m, $J_{1,2}$ = 5.2 Hz, H-2), 2.06 (m, $J_{1,7a}$ = 5.2 Hz, H-7a), 2.45 (m, $J_{3a,4}$ = 3.5 Hz, H-3aβ), 2.91 (dq, $J_{5,6}$ = 3.0 Hz, J_{5,CH_3} = 7.3 Hz, H-5α), 4.03 (dd, $J_{1,7a}$ = 5.2 Hz, $J_{1,2}$ = 5.2 Hz, H-1α), 4.46 (d, J = 12.4 Hz, C*H*HPh), 4.58 (d, J = 12.3 Hz, C*H*HPh), 4.75 (d, $J_{3a,4}$ = 3.5 Hz, H-4β), 5.64 (ddd, J = 10.4, 3.0, 3.0 Hz, H-6), 6.04 (d, J = 10.4 Hz, H-7), 7.28–7.4 (m, Ar H); IR (CCl_4) 3050, 2990, 2890, 1535, 1350, 1090, 1020, 700 cm^{-1}; MS(EI), m/e (relative intensity) 196 (6), $M^+ - CH_2Ph$), 91 (100, $^+CH_2Ph$); calcd for $C_{10}H_{14}NO_3$ ($M^+ - CH_2Ph$) 196.0974, found 196.0972] and **24a** (11 mg, 0.038 mmol, 31%) [^1H NMR (500 MHz, $CDCl_3$) δ 1.10 (d, J = 7.3 Hz, CH_3), 1.14 (m, H-3), 1.5–1.7 (m, H-2, H-2′, H-3′), 2.72 (m, $J_{1,7a}$ = 4.9 Hz, $J_{6,7a}$ = 3.2 Hz, $J_{7,7a}$ = 2.7 Hz, H-7aα), 2.87 (m, $J_{3a,4}$ = 5.4 Hz, H-3aα), 2.94 (dddq, $J_{4,5}$ = 5.4 Hz, $J_{5,6}$ = 3.2 Hz, $J_{5,7}$ = 2.7 Hz, J_{5,CH_3} = 7.3 Hz, H-5α), 3.87 (ddd, $J_{1,7a}$ = 4.9 Hz, $J_{1,2}$ = 4.9 Hz, $J_{1,2'}$ = 4.9 Hz, H-1β), 4.50 (d, J = 11.6 Hz, C*H*HPh), 4.54 (d, J = 11.6 Hz, CH*H*Ph), 4.85 (dd, $J_{4,5}$ = 5.4 Hz, $J_{4,3a}$ = 5.4 Hz, H-4α), 5.56 (ddd, $J_{6,7}$ = 10.3 Hz, $J_{5,6}$ = 3.2 Hz, $J_{6,7a}$ = 3.2 Hz, H-6), 5.72 (ddd, $J_{6,7}$ = 10.3 Hz, $J_{5,7}$ = 2.7 Hz, $J_{7,7a}$ = 2.7 Hz, H-7), 7.27–7.4 (m, Ar H); IR (CCl_4) 3045, 2985, 2890, 1545, 1350, 1260, 1090, 1020, 700 cm^{-1}; MS(EI), m/e (relative intensity) 196 (10, $M^+ - CH_2Ph$), 91 (100, $^+CH_2Ph$); calcd for $C_{10}H_{14}NO_3$ ($M^+ - CH_2Ph$) 196.0974, found 196.0974].

(±)-5-Methyl-1α-[(4-methylphenyl)sulfonyl]-4-nitro-2,3,3aβ,4α,5α,7aα-hexahydro-1*H*-indene (25c) and (±)-5-Methyl-1β-[(4-methylphenyl)sulfonyl]-4-nitro-2,3,3aβ,4α,5α,7aα-hexahydro-1*H*-indene (25d). (*E*)-Nitro triene **3** (144 mg, 0.429 mmol) was dissolved in degassed toluene (7.2 mL) and heated in the dark at 90 °C. After 25 h, the solvent was removed under reduced pressure. The resulting yellow oil was purified by medium-pressure liquid chromatography (3:1 hexane/EtOAc) and gave, in order of elution, **25c** (99 mg, 0.30 mmol, 69%) [^1H NMR (360 MHz, $CDCl_3$) δ 0.92 (d, J = 7.0 Hz, CH_3), 1.39 (m, H-3α), 1.99–2.26 (m, H-2, H-2′, H-3β, H-3aβ), 2.47 (s, Ar CH_3), 2.57 (ddd, $J_{3a,7a}$ = 11.0 Hz, $J_{1,7a}$ = 10.7 Hz, $J_{6,7a}$ = 3.4 Hz, H-7aα), 3.07 (ddq, $J_{4,5}$ = 7.0 Hz, $J_{5,6}$ = 3.4 Hz, J_{5,CH_3} = 7.1 Hz, H-5α), 3.31 (ddd, $J_{1,7a}$ = 10.7 Hz, $J_{1,7a}$ = 10.7 Hz, $J_{1,2\alpha}$ = 10.7 Hz, $J_{1,2\beta}$ = 6.5 Hz, H-1β), 4.74 (dd, $J_{3a,4}$ = 11.4 Hz, $J_{4,5}$ = 7.0 Hz, H-4α), 5.54 (ddd, $J_{6,7}$ = 9.9 Hz, $J_{5,6}$ = 3.4 Hz, $J_{6,7a}$ = 3.4 Hz, H-6), 5.72 (d, $J_{6,7}$ = 9.9 Hz, H-7) 7.37 (d, J = 8.1 Hz, Ar H), 7.77 (d, J = 8.1 Hz, Ar H); IR ($CHCl_3$) 3040, 2980, 2950, 2920, 2880, 1595, 1550, 1300, 1145, 1085 cm^{-1}. Anal. Calcd for $C_{17}H_{21}NO_4S$: C, 60.87; H, 6.31; N, 4.18. Found: C, 60.66; H, 6.31; N, 4.10] and **25d** (12 mg, 0.036 mmol, 8.3%) as a colorless oil [^1H NMR (360 MHz, $CDCl_3$) δ 0.96 (d, J = 4.1 Hz, CH_3), 1.49 (m, H-3α), 1.92 (m, H-2α), 2.08–2.16 (m, H-2β, H-3β), 2.46 (s, Ar CH_3), 2.83 (ddq, $J_{4,5}$ = 5.5 Hz, $J_{5,7}$ = 1.4 Hz, J_{5,CH_3} = 7.1 Hz, H-5α), 2.97 (m, $J_{3a,4}$ = 10.3 Hz, $J_{3a,3}$ = 7.9 Hz, $J_{3a,3'}$ = 4.9 Hz, H-3aβ), 3.23 (m, H-1α, H-7aα), 4.47

(dd, $J_{3a,4}$ = 10.3 Hz, $J_{4,5}$ = 5.5 Hz, H-4α), 5.53 (dd, $J_{6,7}$ = 9.7 Hz, $J_{6,7a}$ = 1.4 Hz, H-6), 5.65 (ddd, $J_{6,7}$ = 9.7 Hz, $J_{7,7a}$ = 4.9 Hz, $J_{5,7}$ = 1.4 Hz, H-7), 7.37 (d, J = 8.1 Hz, Ar H), 7.78 (d, J = 8.1 Hz, Ar H); IR (CCl_4) 3050, 2980, 2940, 2890, 1595, 1545, 1300, 1150, 1090 cm^{-1}; MS(EI), m/e (relative intensity) 179 (3, $M^+ - C_7H_7SO_2H$), 157 (100), 133 (73), 132 (96, $C_{10}H_{12}^+$); calcd for $C_{10}H_{13}NO_2$ ($M^+ - C_7H_7SO_2H$) 179.0946, found 179.0934].

A recrystallized sample of **25c** was subjected to single-crystal X-ray diffraction analysis. Compound **25c** crystallizes from hexane/ethyl acetate in the monoclinic space group $P2_1/c$. The crystal data at 140 K are as follows: a = 5.321 (2) Å, b = 14.057 (10) Å, c = 21.484 (9) Å, β = 91.65 (4)°; ρ(calcd) = 1.39 g cm^{-3} for Z = 4; 2θ(max) = 50°; 1129 reflections with $F > 6\sigma$ ($|F|$) used, Mo K_α (graphite) (λ = 0.71069 Å), and ω scan, 3° min^{-1}; R = 0.066. SHELXTL programs were used on a DGC Eclipse S/230 computer.

(±)-5-Methyl-4-nitro-2,3,3aβ,4β,5α,7aα-hexahydro-1*H*-indene (19) and (±)-5-Methyl-4-nitro-2,3,3aα,4α,5α,7aα-hexahydro-1*H*-indene (20). (*Z*)-Nitro triene 4 (11 mg, 0.061 mmol) in chloroform-*d* (0.5 mL) was allowed to stand at room temperature, and the progress of the cycloaddition was followed by ^1H NMR. After 3.5 days, the reaction was judged to be complete. The solvent was then removed under reduced pressure and the crude product was purified by medium-pressure liquid chromatography (95:5 hexane/EtOAc), yielding an inseparable mixture of **19** and **20** (53:47) (8.2 mg, 0.045 mmol, 74%) [**19**, ^1H NMR (360 MHz, $CDCl_3$) δ 1.15 (d, J = 7.5 Hz, 3 H, CH_3), 1.78 (m, $J_{3a,4}$ = 2.2 Hz, 1 H, H-3aβ), 2.92 (dq, $J_{5,6}$ = 3.0 Hz, J_{5,CH_3} = 7.5 Hz, 1 H, H-5α), 4.71 (d, $J_{3a,4}$ = 2.2 Hz, 1 H, H-4β), 5.54 (ddd, $J_{6,7}$ = 10.0 Hz, $J_{5,6}$ = 3.0 Hz, $J_{6,7a}$ = 3.0 Hz, 1 H, H-6), 5.90 (d, $J_{6,7}$ = 10.0 Hz, 1 H, H-7); **20**, ^1H NMR (360 MHz, $CDCl_3$) δ 1.11 (d, J = 7.1 Hz, 3 H, CH_3), 2.68 (m, $J_{6,7a}$ = 3.0 Hz, $J_{7,7a}$ = 3.0 Hz, 1 H, H-7aα), 2.74 (m, $J_{3a,5}$ = 4.9 Hz, 1 H, H-3aα), 2.93 (ddq, $J_{5,6}$ = 3.0 Hz, $J_{5,7a}$ = 3.0 Hz, J_{5,CH_3} = 7.1 Hz, 1 H, H-5α), 4.88 (dd, $J_{4,5}$ = 4.9 Hz, $J_{3a,4}$ = 4.9 Hz, 1 H, H-4α), 5.51 (ddd, $J_{6,7}$ = 10.0 Hz, $J_{6,7a}$ = 3.0 Hz, $J_{5,6}$ = 3.0 Hz, 1 H, H-6), 5.66 (ddd, $J_{6,7}$ = 10.0 Hz, $J_{5,}$ = 3.0 Hz, $J_{7,7a}$ = 3.0 Hz, 1 H, H-7); IR (CCl_4) 3040, 2980, 2900, 1530, 1540, 1350 cm^{-1}; MS(E/I), m/e (relative intensity 181 (2, M^+), 135 (23, $M^+ - NO_2$); calcd for $C_{10}H_{15}NO_2$ 181.1103, found, 181.1092].

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Registry No. 1, 96575-21-2; (±)-2, 96556-47-7; (±)-3, 96556-48-8; 4, 96556-49-9; (±)-5, 96575-22-3; 6, 64275-80-5; 7, 96556-50-2; (±)-8, 96556-51-3; (±)-9, 96556-52-4; (±)-9 (benzyloxy triene), 96556-69-3; (±)-10, 96556-53-5; (±)-11, 96556-54-6; 12, 96556-55-7; 13, 50999-04-7; 13 (diene sulfone), 96556-70-6; (±)-14, 96556-56-8; (±)-14 (triene sulfone), 96556-71-7; (±)-15, 96556-57-9; 16, 96556-58-0; (±)-17, 96556-59-1; (±)-18, 96556-60-4; (±)-19, 96556-61-5; (±)-20, 96556-62-6; (±)-21a, 96556-63-7; (±)-21b, 96556-64-8; (±)-22a, 96556-65-9; (±)-23b, 96575-45-0; (±)-24a, 96556-66-0; (±)-25c, 96556-67-1; (±)-25d, 96556-68-2; $PhCH_2Br$, 100-39-0; *p*-$MeC_6H_4SO_2Na$, 657-84-1; CH_2=$CHCH_2Br$, 106-95-6; NO_2Me, 75-52-5.

Supplementary Material Available: Listings of atom and hydrogen atom coordinates, bond distances, bond angles, isotropic and anisotropic thermal parameters for **21b** and **25c** (10 pages). Ordering information is given on any current masthead page.

Hybridization of the Lone Pair Electrons in Carbanions

Suk Ping So,* Ming Hau Wong, and Tien-Yau Luh*

Department of Chemistry, The Chinese University of Hong Kong, Shatin, N.T., Hong Kong

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The hybridization of the orbitals for the lone pair electrons of twelve acyclic, monocyclic, and polycyclic bridgehead carbanions has been calculated by the INDO-LMO method. Significant enhancement in s character has been found in methyl and all bridgehead carbanions. For other acyclic and cyclobutyl anions, rehybridization occurs in the opposite direction, presumably, due to the relief of B strain, while cyclopropyl anion retains the hybridization of its conjugate acid. The trend is discussed.

It is generally accepted that the percent s character contributed to the carbon–hydrogen bond by carbon adequately accounts for ranking of carbon acids in the absence of strongly acidifying substituents.[1] The intrinsic idea underlying this relationship is to assume that there is a negligible difference between the carbanion R^- and the carbon acid (RH) in (a) strain, (b) hybridization, and (c) solvation energy. It was, however, found that carbanions might, at most, be weakly solvated.[2] In 1956 Hammond suggested that the unshared pair of electrons in a carbanion should occupy an orbital having a considerable amount of s character.[3] If this were pure s orbital, the "natural" R–C–R bond angle in a carbanion would be 90°. B strain[4] would open this bond angle because of repulsion between the R groups and, thus, would increase the basicity of the anions. This view point has been tested by comparing the kinetic acidity of cubane with that of cyclopropane.[5] Despite the same formal C–H hybridization, cubane is 10^3 times as acidic as cyclopropane. Such an enhancement of acid strength for cubane was proposed to originate from the altered hybridization at the anionic carbon atom to an orbital with significantly enhanced s character.[5] Alternatively, one may argue that the steric environment for the lone pair in cubyl anion would be different from that in cyclopropyl anion.[1c] Ab initio molecular orbital calculations have been performed to show

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