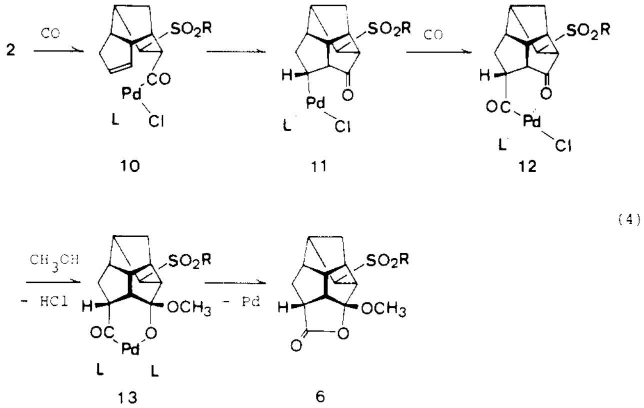
cm^{-1}, respectively).

The structure of **6** reflects stereospecific carbonylation with retention of configuration and stereospecific *cis* addition of Pd–acyl to the coordinated double bond (eq 4). That is, after the first carbonylation with retention of configuration, cis addition of Pd–acyl to the double bond coordinated to Pd seems to take place to give intermediate **11**. The formation of **6** as a primary product might be explained as a result of a second carbonylation with retention of configuration followed by nucleophilic displacement of Pd(0) by the carbonyl oxygen atom, probably via intermediate **13**. A similar carbonylation was observed[14] for the alkoxyl counterparts[15] of **2** (with alkoxyl group in place of sulfonyl group). The present dicarbonylation is expected to serve as another methodology for triquinacene and dodecahedrane chemistry.[16]



(4)

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(6) All new compounds reported here gave sharp melting points and satisfactory elemental analyses within ±0.3% for C, H, and O. Yields refer to isolated, spectrally and chromatographically homogeneous materials.

(7) *tert*-Butyl 4-cyclooctenyl sulfone was obtained in rather low yield (~45%) owing to the decomposition of **3** in the presence of pyridine.

(8) For determination of the configurations of substituents on the norbornane system by NMR spectroscopy, see A. Gaudemer, "Stereochemistry", Vol. 1, H. B. Kagan, Ed., Georg Thieme, Stuttgart, 1977.

(9) For related work, see S. Brewis and P. R. Hughes, *Chem. Commun.*, 489 (1965); 6 (1966); 71 (1967).

(10) ^{13}C NMR of **6**: δ (in $CDCl_3$, Me_4Si standard) 56.9 ($\mathbf{C}HSO_2$), 61.4 ($SO_2\mathbf{C}Me_3$), 120.6 ($\mathbf{C}(OMe)OC{=}O$), 178.0 ($C{=}O$).

(11) ^{13}C NMR of **7** (ethyl ester): δ (in $CDCl_3$, Me_4Si standard) 56.7 ($\mathbf{C}HSO_2$), 61.5 ($SO_2\mathbf{C}Me_3$), 172.9 ($\mathbf{C}O_2Et$), 217.0 ($C{=}O$).

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(13) While **7** (methyl ester) showed a sharp single absorption at 1735 cm^{-1} in the IR spectrum, **7** (ethyl ester) showed a couple of absorptions at 1740 and 1730 cm^{-1} due to two carbonyl groups.

(14) **6** (with -OMe in place of $-SO_2R$): mp 133.0–133.5 °C (from benzene-*n*-hexane); bp 150 °C (0.03 mmHg) (Kugelrohr); ^{13}C NMR δ (in $CDCl_3$, Me_4Si standard) 119.5 ($\mathbf{C}(OMe)OC{=}O$), 177.8 ($C{=}O$); IR (KBr disk) 1780 cm^{-1}.

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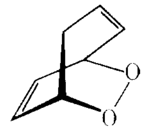
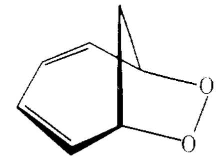
endo- and *exo*-7-Cyanonorcaradiene Endoperoxides: Synthesis, Characterization, and Transformations[1]

Summary: The title compounds, **3a** and **3b**, were prepared by singlet oxygenation of the corresponding norcaradiene derivatives **2a** and **2b**, characterized by diimide reduction as the respective norcarane endoperoxides **4a** and **4b**, and transformed into their respective diepoxides **5a** and **5b** on heating and ene epoxides **6a** and **6b** on deoxygenation with triphenylphosphine.

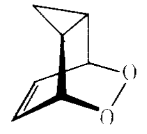
Sir: Recent publications[2] on the photooxidation of cycloheptatriene, providing evidence for the formation of the (2 + 4) and (2 + 6) adducts A and B, prompt us to communicate our preliminary results that the singlet oxygenation of 7-cyanocycloheptatriene (**1**) affords the (2 + 4) adduct C, possessing the norcaradiene endoperoxide structure. Since electron-withdrawing substituents at the 7 position in cycloheptatriene favor the norcaradiene valence tautomer,[3] a search for the norcaradiene endoperoxide skeleton C was warranted in the singlet oxygenation of 7-cyanocycloheptatriene (**1**).



A



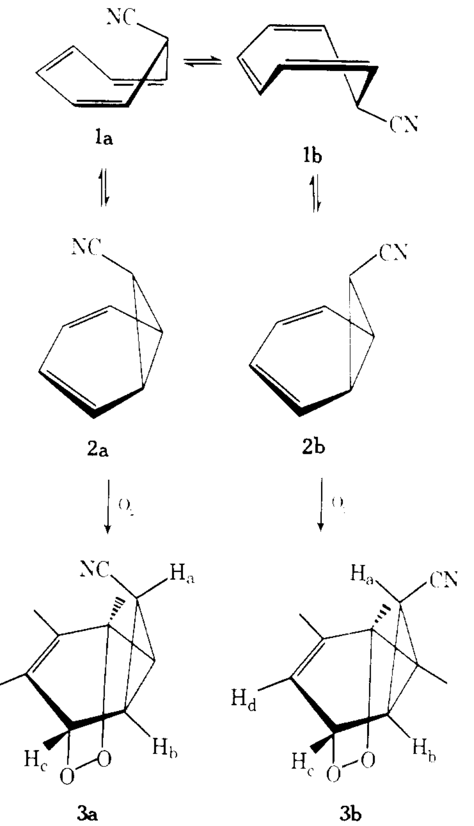
B



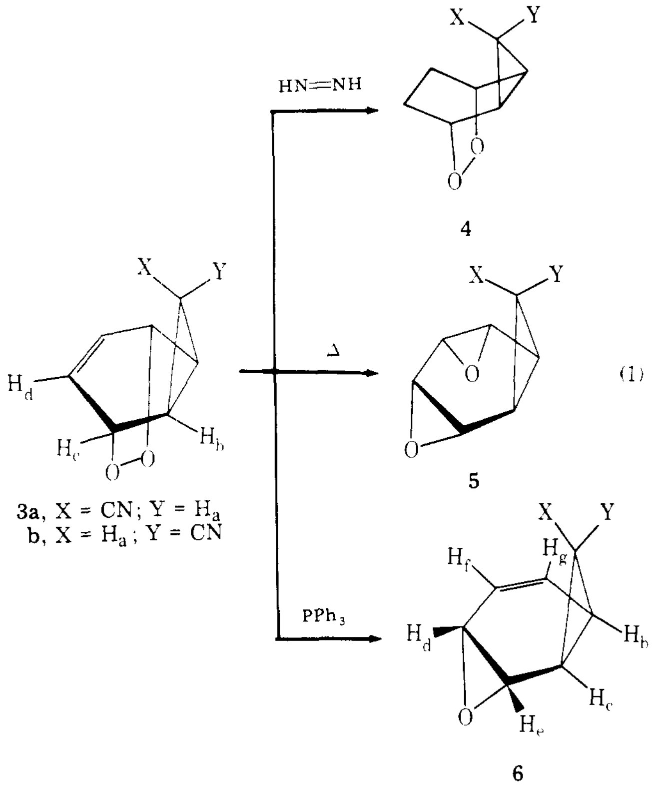
C

The tetraphenylporphyrin-sensitized photooxygenation of **1** in CCl_4 at 0 °C, using a General Electric 400-W sodium lamp, followed by low temperature (−30 °C) silica gel chromatography eluting with CH_2Cl_2–pentane (2:1), afforded **3a**, mp 194–195 °C (from MeOH), in 33% yield and **3b**, mp 107–108 °C (from 1:1 CH_2Cl_2/CCl_4), in 42% yield. As side product (5% yield) the known[4] endoperoxide of tropone was also obtained, matching the physical constants and spectral data of the authentic material.

Scheme I



The structural assignment of the *endo*- and *exo*-cyanonorcaradiene endoperoxides rests on correct C, H, and N elemental analysis and the following spectral data: the endo isomer **3a** shows proton resonances[5] (60 MHz, $CDCl_3$, Me_4Si) at δ_a 1.45 (t, J = 7.9 Hz, 1 H), δ_b 2.0–2.3 (m, 2 H), δ_c 4.8–5.2 (m, 2 H), and δ_d 6.2–6.5 (AA′ part of AA′XX′ system, 2 H) and IR (Nujol, cm^{-1}) bands at 3030 (olefinic C–H) and 2230 (aliphatic $C\equiv N$); the exo isomer **3b** shows proton resonances (60 MHz, $CDCl_3$, Me_4Si) at δ_a 0.98 (t, J = 3.28 Hz, 1 H), δ_b 2.22 (m, 2 H), δ_c 4.7–5.1 (m, 2 H), and δ_d 6.10 (AA′ part of AA′XX′ system, 2 H), and IR ($CHCl_3$ and KBr, cm^{-1}) at 3030 (olefinic C–H) and 2240 (aliphatic $C\equiv N$).



Chemical confirmation of this structural assignment was obtained through diimide reduction (eq 1) in CH_2Cl_2 at 0 °C,[6] affording the norcarane endoperoxides **4a** from **3a** in 87% yield, mp 140 °C dec (from 1:1 CH_2Cl_2-pentane), and **4b** from **3b** in 59% yield, mp 152–154 °C dec (from 1:1 CH_2Cl_2-pentane). The structural assignments of the *endo*- and *exo*-7-cyanonorcarane endoperoxides rests on correct C, H, and N elemental analysis and the following spectral data: the endo isomer **4a** shows proton resonances (60 MHz, $CDCl_3$, Me_4Si) at δ 1.55–2.4 (m, methylene and cyclopropyl, 7 H) and 4.3–4.6 (m, bridgehead, 2 H), and IR ($CDCl_3$ and KBr, cm^{-1}) bands at 2960 (aliphatic C–H) and 2245 (aliphatic $C\equiv N$); the exo isomer **4b** shows proton resonances (60 MHz, $CDCl_3$, Me_4Si) at δ 1.2–1.8 (m, cyclopropyl, 3 H), 1.8–2.5 (m, methylene, 4 H), and 4.2–4.5 (m, bridgehead, 2 H), and IR ($CDCl_3$ and KBr, cm^{-1}) bands at 2980 and 2960 (aliphatic C–H) and 2250 (aliphatic $C\equiv N$).

On heating in toluene (sealed tube) at 120 °C for 1 h the norcaradiene endoperoxides **3a,b** were transformed (eq 1) quantitatively into the diepoxides **5a**, mp 199–200 °C (from 1:1 CH_2Cl_2-pentane), and **5b**, mp 159–160 °C[7] (from 1:1 CH_2Cl_2–pentane). Their structures were confirmed by correct C, H, and N elemental analysis and the following spectral data: the endo isomer **5a** shows proton resonances (60 MHz, $CDCl_3$, Me_4Si) at δ 1.88 (s, cyclopropyl, 3 H) and 4.2–4.5 (m, epoxy, 4 H), and IR ($CHCl_3$ and KBr, cm^{-1}) bands at 2980 and 2900 (aliphatic C–H) and 2245 (aliphatic $C\equiv N$); the exo isomer **5b** shows proton resonances (60 MHz, $CDCl_3$, Me_4Si) at δ_a 1.45 (t, J = 4.6 Hz, 1 H), δ_b 2.08 (d, J = 4.6 Hz, 2 H), and δ_c 3.2 (s, 4 H), and IR ($CHCl_3$ and KBr, cm^{-1}) bands at 2990 and 2960 (aliphatic C–H) and 2245 (aliphatic $C\equiv N$).

Deoxygenation with triphenylphosphine in $CHCl_3$ at 0 °C of the norcaradiene endoperoxides **3a,b**, followed by silica gel column chromatography and eluting with CH_2Cl_2–pentane (1:1), gave (eq 1) the ene epoxides **6a**, mp 98 °C (needles from 1:1 CH_2Cl_2–pentane) in 85% yield, and **6b**, colorless oil (n_D^{25} 1.5045) in 95% yield. Their structures were assigned on the basis of correct elemental analysis and the following spectral data: the endo isomer **6a** shows proton resonances (60 MHz, $CDCl_3$, Me_4Si) at δ_a 1.6–2.4 (m, 3 H), δ_b 2.85–3.1 (m, 1 H), δ_c 3.45–3.65 (d of d, J = 3.96 and 1.74 Hz, 1 H), and δ_d 5.79–5.9 (m, 2 H), and IR ($CHCl_3$ and KBr, cm^{-1}) bands at 3050 (olefinic C–H), 2980 (aliphatic C–H), 2245 (aliphatic $C\equiv N$), and 1650 (C=C); the exo isomer **6b** shows proton resonances[8] (60 MHz, $CDCl_3$, Me_4Si) at δ_a 1.45–1.60 (t, 1 H), δ_b 1.65–2.00 (d of d, 1 H), δ_c 2.15–2.45 (m, 1 H), δ_d 2.7–2.9 (m, 1 H), δ_e 3.4–3.6 (d of d, 1 H), and δ_f and δ_g 5.4–6.0 (m, 2 H), and IR ($CHCl_3$ and KBr, cm^{-1}) bands at 3020 (olefinic C–H), 2940 (aliphatic C–H), 2220 (aliphatic $C\equiv N$), and 1650 (C=C).

The results of the singlet oxygenation of **1** leading to the novel bicyclic peroxides **3a,b** are rationalized in Scheme I. In view of the established[3] ring inversion **1a** $\rightleftharpoons$ **1b** and the valence tautomerism **1** $\rightleftharpoons$ **2**, the endo adduct **3a** should be derived from **2a** and the exo adduct **3b** from **2b**. Consequently, the dienophilic reactivity of singlet oxygen toward cycloheptatriene substrates provides a convenient and versatile synthetic entry into unusual and hitherto unknown bicyclic peroxides.

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(8) With the help of double resonance experiments the following coupling constants could be determined: $J_{d,g}$ = 1.49, $J_{c,e}$ = 1.76, $J_{b,g}$ = 3.49, $J_{d,e}$ = 3.99, $J_{d,f}$ = 3.99, $J_{a,b}$ = $J_{a,c}$ = 4.33, $J_{b,c}$ = 6.66, and $J_{f,g}$ = 9.33 Hz. The small $J_{c,e}$ = 1.76 Hz coupling suggests an anti configuration for the cyclopropyl and epoxy rings; the large $J_{f,g}$ = 9.33 Hz indicates an undistorted C=C bond and $J_{b,g}$ = 3.49 Hz and $J_{d,f}$ = 3.99 Hz couplings imply the expected dihedral angles between the respective protons. Dreiding models confirm that the cyclohexene ring is essentially planar. An X-ray crystallographic analysis of this unusual structure should be of interest to corroborate the above structural conclusions.
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