(13) Cis/trans ratio for benzene-sensitized isomerization of 2-butene is 1: M. A. Golub, C. L. Stevens, and J. L. Brash, *J. Chem. Phys.*, **45**, 1503 (1966); S. Sato, K. K. Kuchi, and M. Tanaka, *J. Chem. Phys.*, **39**, 239 (1963).

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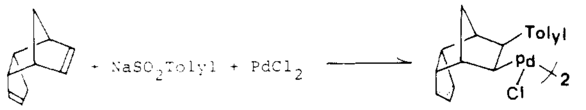
Reaction of Palladium Chloride and Sodium Alkylsulfinates with Diolefins

Summary: trans-Sulfonyl palladation products **2** and **3**, obtained by the reaction of $PdCl_2$ and sodium alkylsulfinates with diolefins, have been reduced selectively to give either saturated or unsaturated sulfones. Dicarbonylation of **2** provided the pentacyclic compound **6**.

Sir: Recently we have reported that sodium toluenesulfinate in the presence of $PdCl_2$ undergoes sulfur dioxide extrusion to form a Pd–tolyl intermediate,[1] which reacts with diolefins to give the cis addition products[2] (e.g., complex **1**, eq 1). In marked contrast to toluenesulfinate, alkylsulfinates react with diolefins as S-nucleophiles[3] to give the *trans*-sulfonyl-palladated complexes **2** and **3** in high yields[4] (eq 2). Into a homogeneous red solution of $PdCl_2$ (1 mmol) and sodium *tert*-butylsulfinate[5] (2 mmol) in 4 mL of H_2O and 6 mL of ethanol was added *endo*-dicyclopentadiene (1.3 mmol) and the reaction mixture was stirred at ambient temperature for 3–4 days. Dilution of the reaction mixture with H_2O, extraction with EtOAc, drying of the extracts over $MgSO_4$, and subsequent evaporation of the solvent gave yellow tarry residue, which was subjected to column chromatography (silica gel, hexane–acetone gradient) to give di-μ-chloro-bis[*exo*-6-(*tert*-butylsulfonyl)-3a,4,5,6,7,7a-hexahydro-*endo*-4,7-methanoindene-*endo*-5σ,2π]dipalladium(II) (**2**)[6] (R = *tert*-butyl or neophyl in 82 or 85% yields, respectively). Similarly di-μ-chloro-bis[1-(*tert*-butylsulfonyl)cyclooct-4-ene-8σ,4π]dipalladium(II) (**3**) was obtained in 87% yield by reaction with 1,5-cyclooctadiene.



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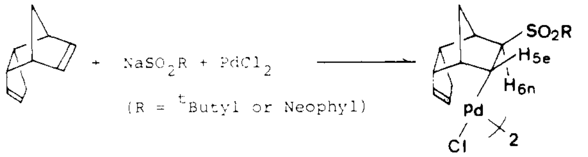
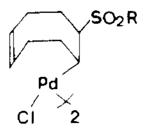
(1)



2

(2)



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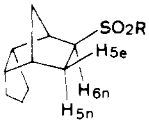

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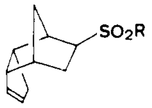
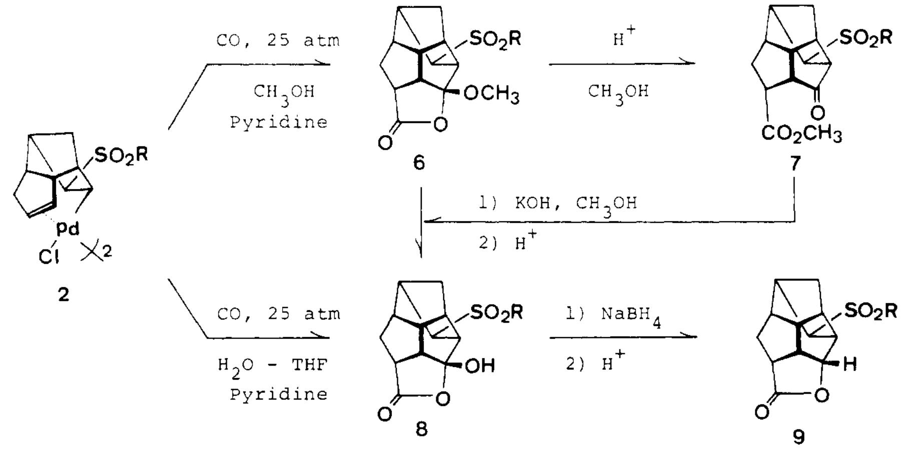


5

The structure of complex **2**, with trans orientation of the sulfonyl group and palladium and the remaining double bond positioned close to palladium, was determined unequivocally by selective hydrogenation and carbonylation reactions. Hydrogenation of **2** (R = *tert*-butyl, in acetone, atmospheric pressure for 2 h) provided saturated sulfone **4** quantitatively. In the presence of 5–6 equiv of pyridine, selective hydrogenation of the Pd–C bond took place, leaving the C_2–C_3 double bond intact, to give unsaturated sulfone **5** in 92% yield (>98% selectivity from VPC analysis; SiDC 550, He, 240 °C). Complex **2** (R = neophyl) was also hydrogenated selectively to give either saturated (**4**) or unsaturated sulfones (**5**) in 93 or 91% yields, respectively.[7] In the ^1H NMR spectrum of complex **2** (R = *tert*-butyl, acac complex) the H_{6n} proton on the sulfonyl-bearing carbon appeared as a doublet of quartets (δ 3.45; $J_{H_{6n},H_{5e}} = 5.0$ and $J = 1.5$ Hz in $CDCl_3$). The H_{6n} proton of **4** was split into a ddd (δ 3.11; $J_{H_{6n},H_{5n}} = 7.5$, $J_{H_{6n},H_{5e}} = 5.5$, and $J_{H_{6n},H_7} = 1.5$ Hz in $CDCl_3$). These observations, judging from the NMR spectra of norbornane systems,[8] clearly indicate the exo configuration of the sulfonyl group and trans relationship between sulfonyl group and palladium.

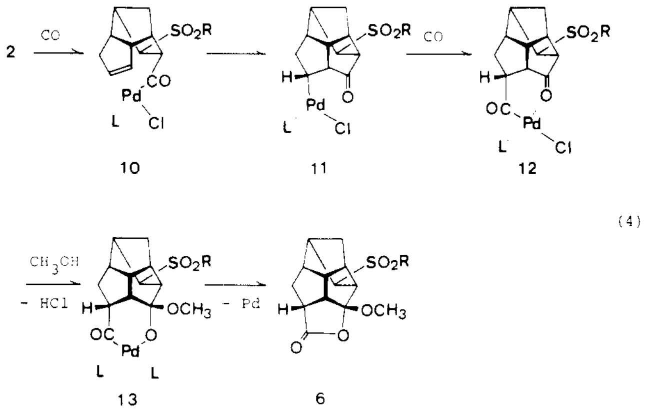
Carbonylation (CO, 25 atm at 100 °C for 4 h in methanol with or without 5–6 equiv of pyridine) gave a mixture of doubly carbonylated products[9] **6**[10] and **7**[11] in quantitative yield, the ratio depending on reaction conditions (eq 3). Under controlled conditions (CO, 25 atm, at 85 °C for 4 h in benzene–methanol 1:5 (v/v), 10 equiv of pyridine), **6** was produced selectively (together with **7** in <5%). Although **6** was thermally stable (160 °C for 3 h under arong), **6** isomerized completely to **7** when exposed to a catalytic amount of H_2SO_4 in refluxing methanol. Carbonylation of **2** in H_2O–THF (CO, 25 atm, at 100 °C for 4 h in the presence of 10 equiv of pyridine) gave **8** quantitatively, whose spectra and melting point were identical with those of the products obtained by alkaline hydrolyses of **6** and **7**. Reduction of **8** (in H_2O with 6 equiv of $NaBH_4$ and 1.1 equiv of KOH at ambient temperature for 2 h and acidic workup[12]) gave the five-membered lactone **9** in quantitative yield. The presence of five-membered lactone groups in **6**, **8**, and **9** and a five-membered ketone in **7**[13] is apparent from the IR spectra of these compounds (1765, 1765, 1770, and 1735



(3)

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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(4) For the reactions of PdCl$_2$ and sodium alkylsulfinates with 1,3-dienes, see Y. Tamaru, M. Kogotani, and Z. Yoshida, *J. Chem. Soc., Chem. Commun.*, 368 (1978).

(5) *tert*-Butyl- and neophylsulfinates were prepared according to the method reported by Allen; P. Allen, Jr., *J. Org. Chem.*, **7**, 23 (1942). For the details for the preparation of *tert*-butylsulfinate, see Y. Tamaru, M. Kagotani, R. Suzuki, and Z. Yoshida, *Chem. Lett.*, 1329 (1978).

(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$_4$Si standard) 56.9 (**C**HSO$_2$), 61.4 (SO$_2$**C**Me$_3$), 120.6 (**C**(OMe)OC=O), 178.0 (C=O).

(11) ^{13}C NMR of **7** (ethyl ester): δ (in CDCl$_3$, Me$_4$Si standard) 56.7 (**C**HSO$_2$), 61.5 (SO$_2$**C**Me$_3$), 172.9 (**C**O$_2$Et), 217.0 (C=O).

(12) S. Danishefsky, M. Hirama, K. Gombatz, T. Harayama, E. Berman, and P. Schuda, *J. Am. Chem. Soc.*, **100**, 6536 (1978).

(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$_2$R): 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$_4$Si standard) 119.5 (**C**(OMe)OC=O), 177.8 (C=O); IR (KBr disk) 1780 cm^{-1}.

(15) (a) J. Chatt, L. M. Vallarino, and L. M. Venanzi, *J. Chem. Soc.*, 2496, 3413 (1957); (b) J. K. Stille and R. A. Morgan, *J. Am. Chem. Soc.* **88**, 5135 (1966).

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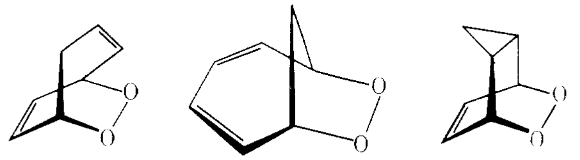
endo- and *exo*-7-Cyanonorcaradiene Endoperoxides: Synthesis, Characterization, and Transformations[1]

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$_2$Cl$_2$–pentane (2:1), afforded **3a**, mp 194–195 °C (from MeOH), in 33% yield and **3b**, mp 107–108 °C (from 1:1 CH$_2$Cl$_2$/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