of two methyls at C_7. The *syn*-methyl, which has a geometrical relationship to the carbonyl group not unlike that of an axial C_3 methyl in a chair cyclohexanone, is probably the critical influence here, although this point needs to be checked.

Thus, it appears that methyl substitution at a carbon adjacent to the carbonyl results in variable substituent shifts depending on the dihedral angle such that the shift is largest when the methyl group is eclipsed with the carbonyl and decreases with increasing dihedral angle, ultimately changing sign somewhere between 60 and 120°. The opposite trends observed for the ^{17}O and ^{13}C chemical shifts of most of these carbonyl compounds may be a result of an important contribution from carbonyl group polarization by the substituents.

The large deshielding ^{17}O shift induced by an axial C_3 methyl is more difficult to understand. A through-space interaction seems most reasonable, but this must surely take place through the intermediacy of the intervening carbonyl carbon, a center which is itself not affected very much by the substituent. Nonetheless, it should be noted that the substituent carbon–carbon bond in such compounds is reasonably proximate and roughly parallel to the axis of the carbon orbital involved in the π system of the carbonyl group, a situation which also obtains for an axial C_2 methyl and for the C_2-substituted series of Scheme III. Whether such interactions are a common source of the deshielding substituent effects in these diverse situations, however, remains to be established.

We are currently applying the information obtained in this study to the utilization of ^{17}O data in the conformational analysis of acyclic systems.[10]

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(10) Support of this work by a research grant from the National Science Foundation is gratefully acknowledged. Manual A. Centeno was the recipient of a fellowship from Universidad de Oriente, Venezuela. We thank Norsk Hydro for a generous gift of ^{17}O-labeled H_2O.

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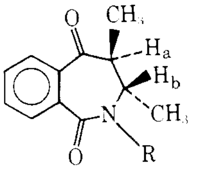
Photochemical Addition of Alkenes to N-Methylphthalimide. Stereochemistry of the Addition

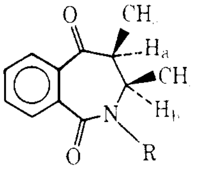
Summary: Irradiation of *N*-methylphthalimide in the presence of *cis*- and *trans*-2-butene gave *cis*-1,6,7-trimethyl- and *trans*-1,6,7-trimethyl-3,4-benzo-6,7-dihydroazepine-2,5-dione, respectively, with greater than 95% stereospecificity, suggesting that the addition proceeds via a concerted $_{\pi}2 + {}_{\sigma}2$ addition.

Sir: We recently reported the photochemical addition of dienes,[1] alkenes,[2] and vinyl ethers[3] to *N*-methylphthalimide to give 3,4-benzo-6,7-dihydroazepine-2,5-diones and have shown that the remarkable sensitivity of the addition process to alkene ionization potential[2] is due to competitive electron transfer quenching of the phthalimide excited state by the alkene.[4] Similar results have been found by Maruyama's group,[5] but the mechanism of the photochemical addition reaction is still open to question. Our initial suggestion on the gross mechanistic features of the reaction included either a two-step process involving a biradical intermediate (**2**) which could close to **3**[7] and subsequently open to the observed product, or a $_{\pi}2 + {}_{\sigma}2$ addition of the alkene to the C(=O)N bond of the imide to give **3** directly as outlined in Scheme I.

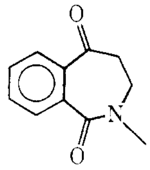
These mechanistic alternatives are amenable to a simple test; the direct $_{\pi}2 + {}_{\sigma}2$ process must be stereospecific, whereas the biradical intermediate **2** could result in loss of stereochemistry on the alkene moiety. Our substrate of choice for this investigation was 2-butene and irradiation of a mixture of *cis*- and *trans*-2-butene provided a mixture of **4a** and **4b.**



4a, R = CH3
5a, R = H



4b, R = CH3
5b, R = H



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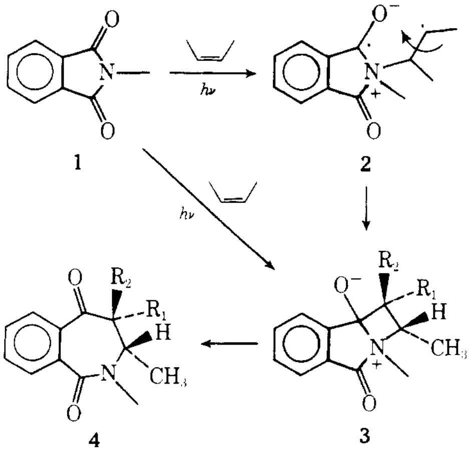
The determination of the stereochemistry of **4a** and **4b** is crucial to the study and should follow from analysis of the couplings observed for H_b in the two isomers. The spectrum of the mixture shows two doublets of quartets at δ 4.46 (J = 2.3, 7 Hz) and 3.96 (J = 9.9, 7 Hz). Stereochemical assignments for **5a** and **5b** have been made on the basis of equilibration results[8] in which the most stable isomer, with $J_{H_aH_b}$ = 2.3 Hz, was assigned the trans geometry (**5a**) and the isomer with

Scheme I



a, $R_1 = H; R_2 = CH_3$
b, $R_1 = CH_3; R_2 = H$

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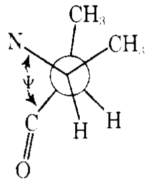
$J_{H_aH_b}$ = 10.1 Hz the cis geometry (**5b**). This assignment can only be correct if the seven-member ring, or at least the C(O)CCN portion of the ring in **4b** and **5b,** is nearly planar, i.e., the H_a–C–C–H_b dihedral angle is essentially 0°. Our approach was to demonstrate that the seven-membered ring in the unsubstituted analogue **6** is not planar and we investigated this point by computer simulating the A_2B_2 portion of the spectrum of **6**, which gives values of $J_{gem} = -20$ Hz, $J_{cis} = 6.8$ Hz, $J_{trans} = 4.2$ Hz (if $J_{cis} > J_{trans}$) or $J_{gem} = -20$ Hz, $J_{cis} = 4.2$ Hz, $J_{trans} = 6.8$ Hz (if $J_{trans} > J_{cis}$). This approach using the equation developed by Buys and Lambert,[10] where R =

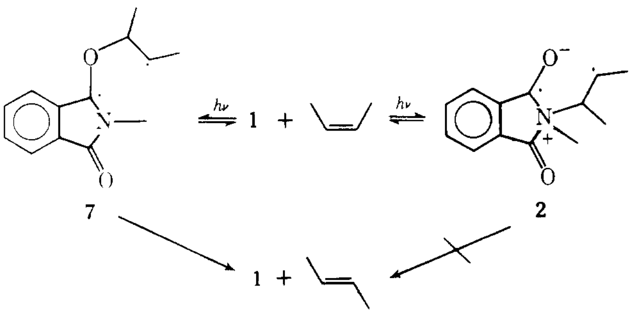
$$\cos \Psi = \left(\frac{3}{2 + 4R}\right)^{1/2} \tag{1}$$

J_{trans}/J_{cis}, is known to give accurate assessments of the angle Ψ for five- and six-membered rings, and thus the degree of pucker in the ring. Application of this equation to the coupling constants noted above gives Ψ values of 35° for the former case ($J_{cis} > J_{trans}$) and 54° for the latter case ($J_{trans} > J_{cis}$). Clearly the unsubstituted compound **6** is not planar and it is difficult to rationalize how the addition of *cis*-methyl substituents could cause the seven-membered ring to become more planar. We are forced to assign the material with the 9.9 Hz coupling to the trans isomer **4a** and that with the 2.3 Hz coupling to the cis isomer **4b.**



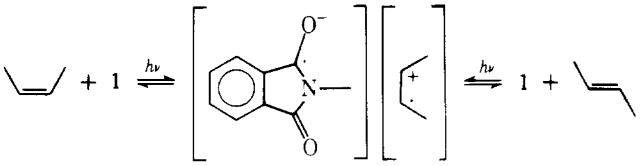
Irradiation of an excess of either *cis*- or *trans*-2-butene with **1** in acetonitrile resulted in the slow cis ⇌ trans isomerization of the alkene to a photoequilibration ratio of trans/cis = 4:1. Examination of the reaction mixture by NMR at low conversion, after careful solvent evaporation, indicated that the reaction is stereospecific.[11] Irradiation of **1** with an excess of *trans*-2-butene gave >99% **4a** and **1** with *cis*-2-butene gave >95% **4b.** These facts indicate that the reaction is either a concerted ${}_{\pi}2 + {}_{\sigma}2$ process or that the intermediate biradical **2** undergoes ring closure to **3** at a rate significantly faster than rotation around the $-CHCH_3-\dot{C}HCH_3$ bond.

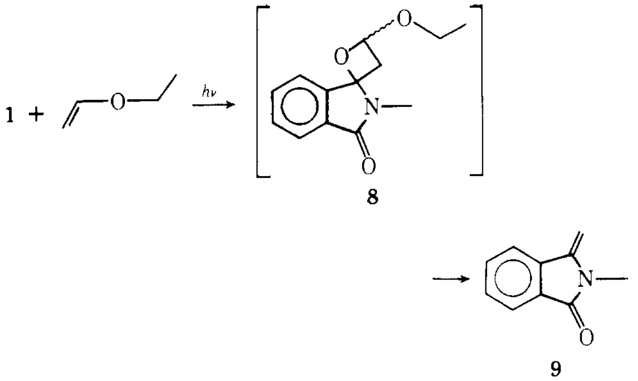
The mechanism of the cis ⇌ trans isomerization process is also of interest. The trans/cis ratio of 4:1 is consistent with isomerization via a Schenck type mechanism[12] rather than direct energy transfer[13] and this suggests that decay of a biradical intermediate such as **2** or **7** might be responsible.



However, decay of **2** as a cis ⇌ trans isomerization mechanism is inconsistent with stereospecific addition. An alternative mechanism is one involving initial electron transfer and isomerization of the alkene radical cation. Since we have shown that 2-methyl-2-butene undergoes exclusive electron transfer at the expense of the ${}_{\pi}2 + {}_{\sigma}2$ addition,[4] we investigated the possible intermediacy of the radical cation in the isomerization process by looking for cis ⇌ trans isomerization in 3-methyl-2-pentene which *must* electron transfer to **1** to form a radical cation. Irradiation of **1** in the presence of either *cis*- or *trans*-3-methyl-2-pentene in acetonitrile resulted in no ${}_{\pi}2 + {}_{\sigma}2$ product formation and *no alkene isomerization,* ruling out the radical cation as a possible intermediate.

We are left with a single mechanistic candidate, i.e., that cis ⇌ trans isomerization is an independent process which probably occurs via collapse of a Paterno–Büchi biradical intermediate like **7**. Although no Paterno–Büchi products have been isolated in the present system, there is some precedent in that we have observed the azaindanone, **9**, which arises from decomposition of the initially formed oxetane **8** from photolysis of **1** in the presence of ethyl vinyl ether.[3] We are now trying to obtain experimental evidence to substantiate this hypothesis.





We are continuing work on these and related systems and our future investigations will center on the quantitative and kinetic aspects of the addition reaction.

Acknowledgment. We thank Dr. Herman Ziffer for his help in operating the 220-MHz NMR at NIH. This work was partially supported by grants from the National Institutes of Health and the National Science Foundation.

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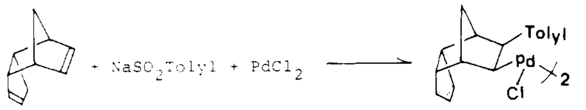
Reaction of Palladium Chloride and Sodium Alkylsulfinates with Diolefins

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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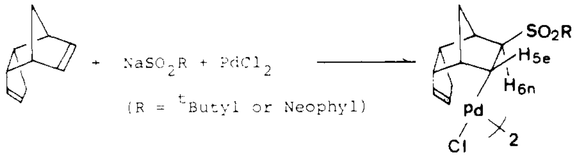

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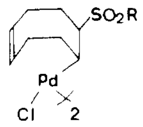

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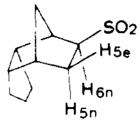

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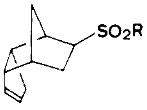

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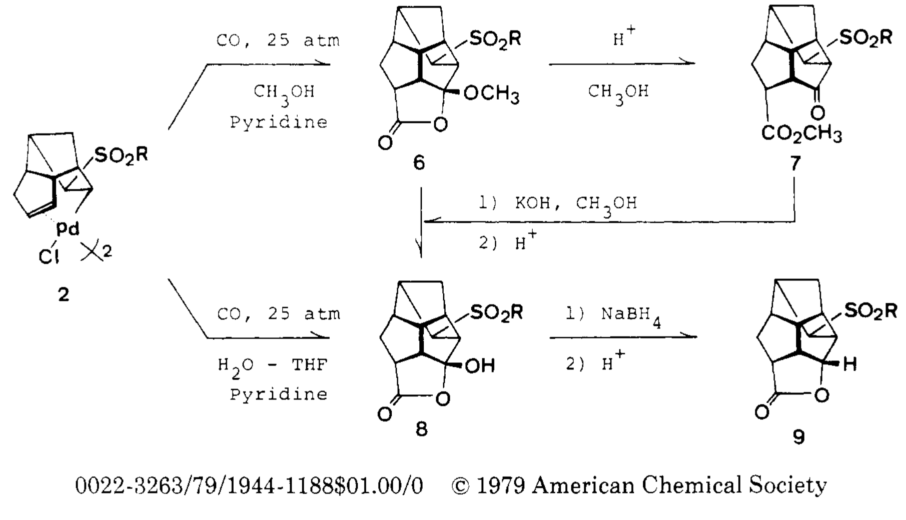
The structure of complex **2**, with trans orientation of the sulfonyl group and palladium and the remaining double bond positioned close to palladium, was determined unequivocally by selective hydrogenation and carbonylation reactions. Hydrogenation of **2** (R = *tert*-butyl, in acetone, atmospheric 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 ^{1}H 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)