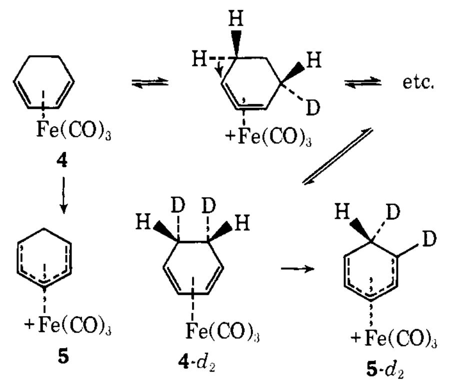
of the nmr solution led to recovery of the diene complex in about 85% yield. Use of trifluoroacetic-*O-d* acid led to the complete disappearance of the anti methyl signal within 1 min (the time necessary to run the spectrum). Thus, protonation is readily reversible under these conditions.[5]

The nmr spectrum of a solution of cyclohexadiene-iron tricarbonyl (**4**) in CF_3CO_2H was essentially the same as that in benzene. Protonation of this compound nonetheless occurs, since a solution in CF_3CO_2D led to rapid incorporation of two atoms of deuterium into the methylene groups,[6] *via* the mechanism shown in Scheme II. That two, and only two, deuterium atoms are incorporated implies a *stereospecific*, reversible protonation.[7]

Scheme II



While it has been assumed[2,8] that protonation occurs on the side of the ligand near the metal (endo)[9] there is no direct proof of the stereochemistry of this process. We offer such proof. When **4** is treated with trityl fluoroborate in methylene chloride, the cyclohexadienyliron tricarbonyl cation **5** is formed.[8,12] The nmr spectrum of this compound is shown in Figure 1A; particularly noteworthy are the signals at δ 2.08 and 3.10, corresponding to the exo and endo methylene protons, respectively. This assignment is consistent with the coupling constants to the protons on C_1 and C_5; the coupling to the exo proton is close to 0 Hz, because the dihedral angle involved is approximately 90°,[13] while the endo coupling is larger (6.5 Hz). Similar hydride abstraction from **4**-d_2 gave **5**-d_2, whose spectrum is shown in Figure 1B. The endo proton at δ 3.10 is no longer visible, and the two-proton triplet at 4.35 has become a one-proton doublet, indicating, respectively, the presence of deuterium at C_1 and C_6 endo as indicated. The remaining changes in the spectrum are likewise consistent with this deuteration pattern. The spectrum demonstrates clearly that hydride abstraction and proton addition occur from opposite sides of the ligand, and that the protonation is endo. Confirmation of this conclusion comes from the work of Lewis and coworkers,[12b] who showed that hydride abstraction with Ph_3C^+ and hydride addition with BH_4^- occur on the same side of the ligand. Since there is ample evidence that nucleophilic attack on these systems occurs exo to the metal,[14] these results also imply endo protonation.

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[5] Diene complex recovered from this solution showed deuterium at C-4 and, to a lesser extent, C-1. No deuterium could be detected in the methyl group.

[6] Determined by nmr and mass spectroscopy of the reisolated diene complex.

[7] Isomerization of diene complexes in acid has been observed: A. J. Birch and M. Haas, *Tetrahedron Lett.*, 3705 (1968).

[8] M. A. Haas, *Organometal. Chem. Rev., Sect. A*, **4**, 307 (1969).

[9] Protonation of complexes containing *noncoordinated* double bonds has been shown to occur endo to the metal.[10,11]

[10] A. Davison, W. McFarlane, L. Pratt, and G. Wilkinson, *J. Chem. Soc.*, 4821 (1962).

[11] S. Winstein, H. D. Kaesz, C. G. Kreiter, and E. C. Friedrich, *J. Amer. Chem. Soc.*, **87**, 3267 (1965).

[12] (a) E. O. Fischer and R. D. Fischer, *Angew. Chem.*, **72**, 919 (1960); (b) A. J. Birch, P. E. Cross, J. Lewis, D. A. White, and S. B Wild, *J. Chem. Soc. A*, 332 (1968).

[13] (a) P. L. Pauson, G. H. Smith, and J. H. Valentine, *ibid., C*, 1061 (1967); (b) M. R. Churchill and R. Mason, *Proc. Roy. Soc.*, **279**, 191 (1964); (c) P. H. Bird and M. R. Churchill, *Chem. Commun.*, 777 (1967).

[14] See ref 8 for examples.

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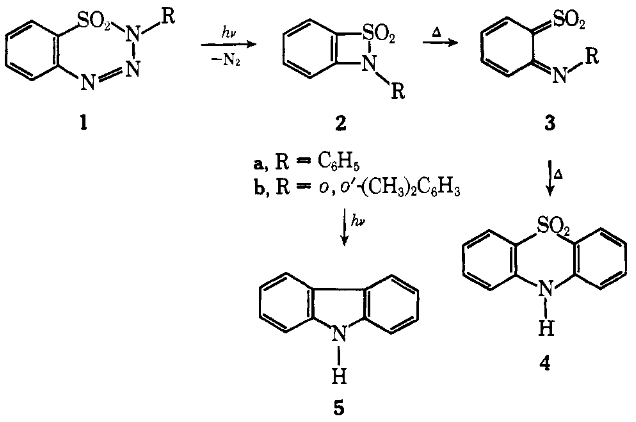
Benzothiazete 1,1-Dioxides

Sir:

Benzo-fused four-membered heterocycles containing two heteroatoms are currently unknown although a number of the monocyclic counterparts have been reported. However, the "ortho quinoid" valence isomers of such heterocycles are well-known stable organic reagents.[1] We wish to report the isolation and reactions of a derivative of the title structure as the first member of this new class of heterocycles.

2-Phenyl-2*H*-1,2,3,4-benzothiatriazine 1,1-dioxide (**1a**) derived from the nitrosation of *o*-amino-*N*-phenylbenzenesulfonamide[2] was irradiated[3] in toluene solution ($10^{-2}M$) at −78° and after the rapid evolution of nitrogen ceased a crude solid was isolated which resisted purification and spectroscopic analysis due to its thermal instability. Immediate reaction of this product at 30° with added nucleophiles such as water or aniline to give the conjugate addition products, *N*-phenyl-*o*-aminobenzenesulfonic acid and *N,N'*-diphenyl-*o*-aminoben-



a, R = C_6H_5
b, R = o,o'-$(CH_3)_2C_6H_3$

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[1] A benzodioxete structure which was assigned by Wilstatter to a colorless modification of *o*-quinone remains an intriguing but as yet unsupported proposal: R. Wilstatter and A. Pfannenstiel, *Ber.*, **41**, 2508 (1908); W. M. Horspool, *Quart. Rev., Chem. Soc.*, **23**, 204 (1969).

[2] F. Ullman and C. Gross, *Ber.*, **43**, 2694 (1910).

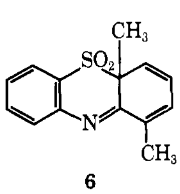
[3] Photolyses were conducted using a 450-W Hanovia lamp in a Pyrex probe.

zenesulfonamide, is consistent with a structural assignment such as **2a**.[4]

Subsequent irradiation[3] of crude **2a** at 30° in benzene solution ($10^{-2}M$) resulted in the formation of carbazole (**5**) by a process which formally represents the extrusion of sulfur dioxide and 1,5 cyclization of the intermediate syn diphenylamino diradical.[5] Since phenothiazine dioxide (**4**) is photochemically stable a possible route involving excitation of **2a** to the valence isomer **3a** with concomitant thermal cyclization to **4** may be excluded. However, **3a** is probably an intermediate in the rapid thermal conversion (30%) of **2a** to **4**[6] in *p*-xylene at 130°.

An increase in the conjugative stabilization of **2** relative to **3** should increase the endothermicity of the valence isomerization and thus permit purification and characterization of a benzothiazete 1,1-dioxide. Bulky ortho substituents carried by the *N*-phenyl group would cause a twisting about the C–N bond due to an ortho,ortho′ steric interaction and reduce the coplanarity of the π-electron system in **3** or the transition state from which it is derived. Such a hypothesis proved to be correct as evidenced by the following experiments.

Photolysis[3] of 2-(2,6-dimethylphenyl)-2*H*-1,2,3,4-benzothiatriazine 1,1-dioxide (**1b**)[4], mp 150–151° dec, in anhydrous benzene ($10^{-2}M$) at 30° afforded after crystallization from benzene 60% of **2b** as colorless prisms, mp 112–113° dec. The nmr spectrum ($CDCl_3$, 60 MHz) displayed a methyl singlet (6 H) at τ 7.68 and an aromatic proton multiplet (7 H) at 2.50–3.20, while the asymmetric and symmetric SO_2 stretching modes occurred at 1159 and 1345 cm^{-1} in the infrared. An exact mass determination gave 259.067 (calcd for $C_{14}H_{13}NO_2S$, 259.066) and prominent fragment ions occurred at $(M - SO_2)^+$ and $(M - SO_2N)^+$. The reactivity of **2b** toward nucleophiles paralleled **1a** but prolonged irradiation[3] in hexane solution failed to provide any monomeric products. Pyrolysis of **2b** in refluxing toluene afforded an isomer (exact mass of 259.066) as yellow needles, mp 83–84°. A structural assignment of **6** is consistent with the observed ir absorption at 1150 and 1305 cm^{-1} and nmr ($CDCl_3$, 60 MHz) signals centered at τ 2.38 (4 H) and 3.59 (3 H) as multiplets and 7.93 (3 H) and 8.40 (3 H) as singlets.



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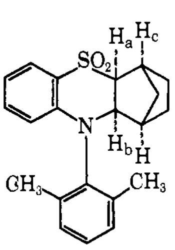

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In a closely related thermolysis, **1b** in mesitylene (150°) gave **6** along with a trace of **2b**. Such transformations are readily explicable in terms of the valence isomerization of **2b** to the syn isomer of **3b** followed by electrocyclic closure. Evidence for the thermal production of **3b** was provided by the exclusive formation of cycloadduct **7**, mp 173–174°, when **2b** was refluxed in norbornene solution.[4] The assigned exo structure is based on the appearance in the nmr spectra ($CDCl_3$, 60 MHz) of a quartet at τ 3.74 for H_a with $J_{ab} = 8$ Hz and $J_{ac} < 1$ Hz and H_b at τ 3.15.[7] The bridge and bridgehead protons were found as multiplets centered at τ 8.50, 6.72, and 6.88 while the aromatic protons at 2.0–3.0 and a methyl singlet (6 H) at 7.83 completed the spectrum.

Acknowledgment. We wish to thank the National Science Foundation (GP-9411) and the National Institutes of Health (GM-2672) for support.

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[4] Spectroscopic analysis including exact mass determination for all new compounds was consistent with the assigned structures.

[5] This intermediate has previously been invoked in a related study of benzotriazole photochemistry: E. M. Burgess, R. Carithers, and L. McCullagh, *J. Amer. Chem. Soc.*, **90**, 1923 (1968).

[6] Identified by mixture melting point comparison with an authentic sample.

[7] P. Laszzlo and P. von R. Schleyer, *J. Amer. Chem. Soc.*, **86**, 1171 (1964).

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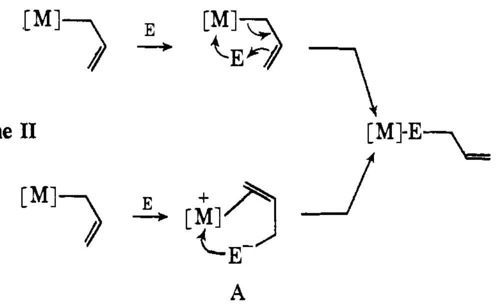
Metal-Assisted Cycloaddition Reactions

Sir:

The insertion of sulfur dioxide into metal–alkyl bonds to give alkyl-metal sulfones has been shown to be a rather general reaction for a number of transition metal complexes.[1] When these reactions are applied to metal–allyl complexes, they are often accompanied by an allylic rearrangement in which insertion occurs with 1,3 migration of the metal atom.[2] Although these rearrangements have been depicted as concerted processes[2] (Scheme I, E = SO_2), it is apparent that they may alternatively by pictured as proceeding stepwise through a dipolar intermediate A (Scheme II).

Scheme I[3]

Scheme II



In principle, this dipolar intermediate may alternatively collapse by addition of the anionic terminus to the coordinated double bond (Scheme III), but this

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[1] J. P. Bibler and A. Wojcicki, *J. Amer. Chem. Soc.*, **86**, 5051 (1964); A. Wojcicki and F. A. Hartman, *ibid.*, **88**, 844 (1966); J. P. Bibler and A. Wojcicki, *ibid.*, **88**, 4862 (1966); F. A. Hartman and A. Wojcicki, *Inorg. Chem.*, 7, 1504 (1968); S. E. Jacobson and A. Wojcicki, *J. Amer. Chem. Soc.*, **93**, 2535 (1971). A review of these reactions has recently been provided by W. Kitching and W. Fong, *Organometal. Chem. Rev.*, **5**, 315 (1970).

[2] F. A. Hartman, P. J. Pollick, R. L. Downs, and A. Wojcicki, *J. Amer. Chem. Soc.*, **89**, 2493 (1967); F. A. Hartman and A. Wojcicki, *Inorg. Chim. Acta*, **2**, 289 (1968); M. R. Churchill and J. Wormald, *Inorg. Chem.*, **10**, 573 (1971).

[3] The symbol [M] is used to denote a complex organometalic radical.