as indicated by the appearance of the CdCl spectrum in absorption.

The marked trend in the rates and activation energies of the olefins points to the electrophilic nature of the triplet cadmium atom by analogy with the behavior of the triplet mercury atom.[9] The generally lower rate constants with cadmium reflect the nonvertical nature of triplet energy transfer, $Cd(^3P)$ + olefin → olefin (nonvertical triplet). The activation energies are probably due to the presence of an energy barrier at the cross-over point of the potential energy surfaces correlating with the $Cd(^3P)$ + olefin and Cd + olefin (triplet) states.

The quenching by methylsilane is *via* hydrogen abstraction from the silicon moiety

$$CH_3SiH_3 + Cd(^3P) \longrightarrow CH_3SiH_2 + CdH$$

Silicon hydrides are excellent hydrogen donors, but the high value of the rate constant is somewhat surprising since it is considerably higher than the rate constant for hydrogen abstraction by hydrogen atoms,[10] $3.1 \times 10^8$ l. mol$^{-1}$ sec$^{-1}$, while the enthalpy changes of the two reactions are approximately equal.

Further studies are in progress.

**Acknowledgments.** The authors are indebted to the National Research Council of Canada for financial assistance and Mr. R. Kadlecz for helpful assistance in the construction of the apparatus.

[9] Y. Rousseau, O. P. Strausz, and H. E. Gunning, *J. Chem. Phys.*, **39**, 962 (1963).

[10] K. Obi, H. S. Sandhu, H. E. Gunning, and O. P. Strausz, *J. Phys. Chem.*, **76**, 3911 (1972).

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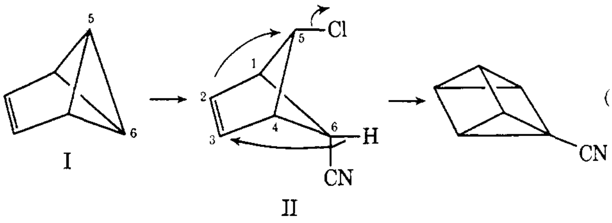
## Additions of Chlorosulfonyl Isocyanate and Sulfenyl Halides to Benzvalene

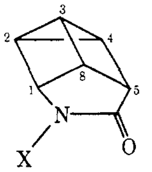
*Sir:*

Benzvalene (I) has suddenly become so readily available[1] that if we knew how it behaved, it could become a very useful molecule in synthesis.[2] The reactions of benzvalene with two kinds of reagents, sulfenyl halides[3] and chlorosulfonyl isocyanate,[4] are reported here and result in syntheses of derivatives of benzvalene and of bicyclo[2.1.1]hexene, materials difficult to make otherwise. The study of sulfenyl halides and chlorosulfonyl isocyanate began with the idea that if benzvalene could be transformed into a material like II below and then further transformed as indicated in eq 1, a simple synthesis for prismanes would result. The first of these goals has been achieved but not the second.[5]

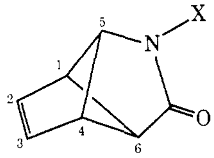


(1)

Chlorosulfonyl isocyanate (1.1 mol in $CH_2Cl_2$, initially −20°, then 5 hr at 25°) reacts with benzvalene in ether giving IIIa (6 parts), IVa (2 part), and another adduct (2 parts),[6] which were not isolated but, upon further reaction with dimethylformamide at room temperature for 48 hr,[7] give II and an isomeric chloronitrile and with 4 *N* NaOH in acetone–water[4d] at 0° IIIb and IVb.[8] Both nitriles and lactams were isolated by chromatography on silica gel[9] and then crystallized.[10,11]



III



IV

a, X = $SO_2Cl$
b, X = H

The proton nmr spectra provide the primary evidence for the structures: for II the similarity to the spectrum of the analogous dibromobicyclo[2.1.1]hexane;[2a,12] for IIIb the five chemical shifts[14] in the spectrum of the

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[1] T. J. Katz, E. J. Wang, and N. Acton, *J. Amer. Chem. Soc.*, **93**, 3782 (1971).

[2] Two uses are reported in (a) R. J. Roth and T. J. Katz, *J. Amer. Chem. Soc.*, **94**, 4770 (1972) and (b) T. J. Katz and N. Acton, *ibid.*, **95**, 2738 (1973).

[3] (a) W. H. Mueller, *Angew. Chem., Int. Ed. Engl.*, **8**, 482 (1969); (b) I. B. Douglass and N. Kharasch in "Organic Sulfur Compounds," Vol. 1, N. Kharasch, Ed., Pergamon Press, New York, N. Y., 1961.

[4] (a) H. Ulrich, *Chem. Rev.*, **65**, 369 (1965); (b) R. Graf, *Angew. Chem., Int. Ed. Engl.*, **7**, 172 (1968); (c) E. J. Moriconi, *Mech. React. Sulfur Compounds*, **3**, 131 (1968); (d) L. A. Paquette, J. R. Malpass, and T. J. Barton, *J. Amer. Chem. Soc.*, **91**, 4714 (1969); (e) L. A. Paquette, S. Kirschner, and J. R. Malpass, *ibid.*, **92**, 4330 (1970); (f) L. A. Paquette and G. R. Krow, *ibid.*, **91**, 6107 (1969); (g) L. A. Paquette, M. J. Broadhurst, C. Lee, and J. Clardy, *ibid.*, **95**, 4647 (1973).

[5] Reagents tried: $KOC(CH_3)_3$ in THF, $MN[Si(CH_3)_3]_2$ (M = Li, Na, K) in $(C_2H_5)_2O$, $LiN(i\text{-}C_3H_7)_2$ in $(C_2H_5)_2O$, KH in $(C_2H_5)_2O$, $KNH_2$ in $NH_3$.

[6] The three adducts were isolated by Dr. Nancy Acton, and their ratio in the reaction product analyzed by proton nmr. The third is incompletely characterized.

[7] The reaction is patterned on the conversion of *N*-chlorosulfonyl-β-lactams into unsaturated nitriles: (a) K. Matterstock and G. Lohaus, DAS 1,253,704 (1964) mentioned in R. Graf, *Angew. Chem., Int. Ed. Engl.*, **7**, 172 (1968); (b) E. J. Moriconi and C. C. Jalandoni, *J. Org. Chem.*, **35**, 3796 (1970).

[8] The expected third lactam has not yet been isolated.

[9] Using *n*-pentane–ether for the nitriles and $CH_2Cl_2$–$CH_3OH$ for the lactams.

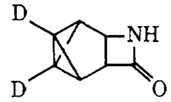
[10] For each new compound the analyses for all elements except oxygen were determined satisfactorily and the mass spectra exhibit the required parent peaks. Infrared absorptions characteristic of all functional groups were observed.

[11] Yields and melting points: II, 31%, 26–27° (from pentane); the isomer of II, 10%, 40–41° (from ether–pentane); IIIb, 21%, 86–87° (from $CHCl_3$–pentane); IVb, 5%, 80–81° (from ether–pentane).

[12] In $CDCl_3$: $\tau$ 3.07 (t, 1.97 H, $H_2$, $|J_{12}|$ = 2 Hz), 5.51 (t, 1.03 H, $H_6$, $|J_{16}|$ = 2 Hz), 5.68 (s, 0.99 H, $H_5$), 6.92 (q 2.08 H, $H_1$). The difference in the chemical shifts in the dibromo derivative and in II is larger for the triplets than for the singlets, indicating the location of Cl and and CN.[13]

[13] (a) L. M. Jackman and S. J. Sternhell, "Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry," 2nd ed, Pergamon Press, New York, N. Y., 1969, table 3-2-10; (b) ref 2a, footnotes 12 and 13.

[14] If the structure had been *i* there would have been only four.



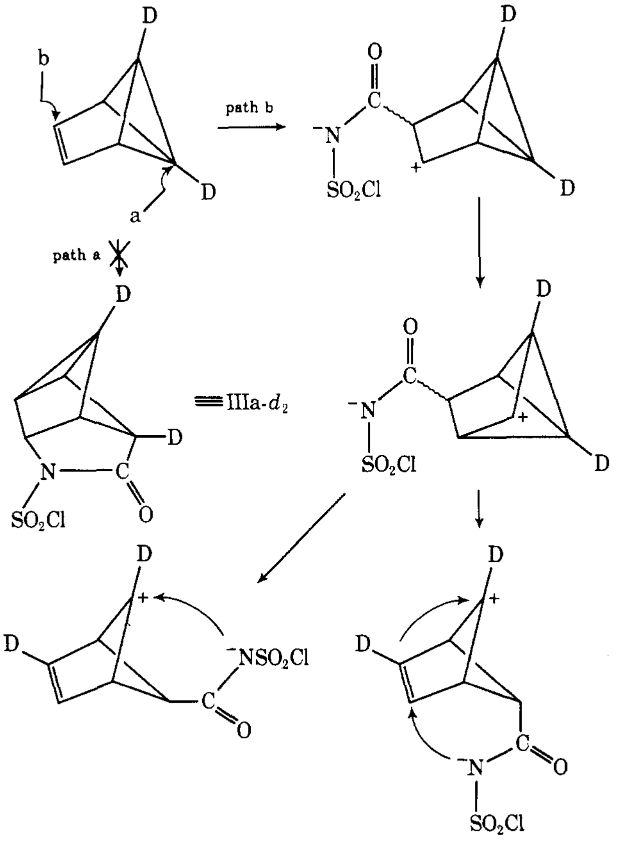
i

IIIb's resonances in $CDCl_3$ are $\tau$ 2.73 (NH) and multiplets 5.62 ($H_1$, $|J_{18}|$ = 5.5 Hz, $|J_{1NH}|$ = $|J_{12}|$ = 2 Hz), 6.54 ($H_5$), 7.17 ($H_3$ and $H_8$), 7.60 ($H_2$), 7.83 ($H_4$). $H_5$ is split by NH into 1 Hz doublets.

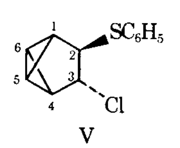
material prepared from 5,6-dideuterated I,[2,15] for IVb the absence of more than four resonances even when Eu(fod)$_3$[16] was added.[17]

Although IVa might seem to arise by chlorosulfonyl isocyanate adding to the central bond of the bicyclo[1.1.0]butane, and IIIa similarly, path a in Scheme I, the actual path followed is b. The intensities of the proton nmr resonances in the IIIb, IVb, and II produced from 5,6-dideuterated I[15] prove this.[18]

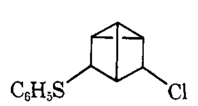
**Scheme I**



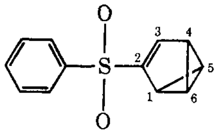
Benzenesulfenyl chloride[19] in $CH_2Cl_2$ adds quickly to benzvalene in ether at −78° giving a liquid adduct in seemingly quantitative yield, which after oxidation with *m*-chloroperbenzoic acid in chloroform (0°, then ambient temperature) gives the corresponding sulfone a crystalline solid, mp 99–100°, in 92% yield. The structure of the adduct is V and not VI the analog of IIIa. This fact was deduced by preparing it from 5,6-dideuterated benzvalene and comparing the intensities of the proton nmr resonances[20] with the mechanistic spectrum of possibilities. That the sulfur and chlorine are trans is shown by $|J_{23}|$ = 1.4 Hz in V and 2.3 in the sulfone.[21] Sodium bistrimethylsilylamide[22] in ether at ambient temperature dehydrohalogenates the sulfone giving the crossed diphenyl sulfone VII, a colorless crystalline solid, mp 95–96°, in 80% yield.[23] This is the first simply substituted benzvalene to be prepared and one of very few benzvalene derivatives of any kind.[24,25]



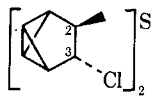
V



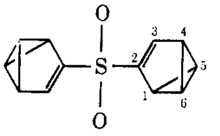
VI



VII



VIII



IX

Similarly, sulfur dichloride (0.5 mol) yields VIII, a faintly yellow liquid obtained in almost quantitative yield,[26] presumably a mixture of diastereomers.[27] *m*-Chloroperbenzoic acid gives the corresponding sulfones (82% yield, mp 132–136°)[28] and then sodium bistrimethylsilylamide the doubly crossed diphenylsulfone IX,[29,30] a colorless solid, mp 90° dec, that explodes when struck.

The essential distinction between the chlorosulfonyl isocyanate and the sulfenyl halide additions is not that the former reagent attacks the bicyclo[1.1.0]butane (at (a) in Scheme I) and the other the double bond (at (b)) but that episulfonium ions do not undergo the Wagner–Meerwein rearrangement.[31–34]

**Acknowledgments.** We are grateful to the National Institutes of Health (GM 19173) for its support.

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(15) ≥99% deuterated (pmr).

(16) R. E. Rondeau and R. E. Sievers, *J. Amer. Chem. Soc.*, **93**, 1522 (1971).

(17) $CDCl_3$: $\tau$ 3.67 ($H_2$, t, $|J_{12}|$ = 2 Hz, 3.77 (NH, broad s), 5.16 ($H_5$, d, $|J_{56}|$ = 8 Hz, 6.18 ($H_6$, d), 6.64 ($H_1$, t). The $H_5$ and $H_6$ resonances are split into 2 Hz doublets by the NH.

(18) The intensities of the resonances of protons 1, 2, 4, 5, and 3 + 8 combined in IIIb were 0.51, 0.63, 0.98, 0.94, and 0.98; of protons 1, 2, 5, and 6 in IVb 2.00, 0.97, <0.02, and 1.02; and of protons 1, 2, 5, and 6 in II 2.00, 0.98, ≤0.02, and 1.01.

(19) From thiophenol [F. Runge, A. Jumar, and F. Koechler, *J. Prakt. Chem.*, **21**, 39 (1963)] using the procedure of W. H. Mueller and P. E. Butler, *J. Amer. Chem. Soc.*, **90**, 2075 (1968).

(20) For the 5,6-dideuterated sulfide V in $CCl_4$: $\tau$ 2.76 (m, phenyl, 4.95 H), 6.09 (m, $H_3$, 0.99 H), 6.64 (m, $H_2$, 1.01 H), a symmetrical AB quartet $\tau$ 7.69 and 7.82, $|J|$ = 5 Hz, ($H_1$ and $H_4$, 1.02 H, 1.02 H). $H_5$ and $H_6$ if present would have appeared at $\tau$ 7.61, under the $\tau$ 7.69 peaks. For the 5,6-dideuterated sulfone ($CDCl_3$) $\tau$ 2.27 (m, phenyl, 5.04 H), 5.62 (m, $H_2$, 0.97 H), 6.59 (m, $H_3$, 1.00 H), 7.45 (m, $H_5$ and $H_6$, ≤0.06 H), 7.61 (m, $H_1$ and $H_4$, 1.99 H).

(21) (a) A. A. Bothner-by, *Advan. Magn. Resonance*, **1**, 195 (1965). (b) In cis adducts of benzvalene $|J|$ = 7.5–9.1 Hz: N. Acton, unpublished work in this laboratory; von M. Christl, *Angew. Chem.*, **85**, 666 (1973).

(22) U. Wannegat and H. Niederprüm, *Chem. Ber.*, **94**, 1540 (1971).

(23) Pmr ($CDCl_3$): $\tau$ 2.44 (m, phenyl, 5.44 H), 3.19 ($H_3$, 0.94 H, dd 2, 1.5 Hz), 5.82 ($H_5$, 1.78 H, t, 1.5 Hz), 7.59 ($H_1$, 0.94 H, $|J_{14}|$ = 6.3, $|J_{13}|$ = 2, $|J_{15}|$ = 1.5 Hz), 7.80 ($H_4$, 0.94 H, $|J_{43}|$ = $|J_{45}|$ = 1.5 Hz). Eu(fod)$_3$ shifts $H_1$ more than $H_4$.

(24) Reference 1, footnotes 1 and 2.

(25) We call this crossed diphenyl sulfone, phenyl staurophenyl sulfone. σταυροσ, cross.

(26) Proton nmr ($CCl_4$): $\tau$ 6.16 (m, ≈ $W_{1/2}$ 3.5 Hz, $H_3$), 6.98 (m, $W_{1/2}$ = 3.5 Hz, $H_2$), 7.66 (broad m).

(27) For the corresponding sulfone the melting range is wide, and in the presence of Eu(fod)$_3$ the $H_2$ and $H_3$ resonances are each resolved into two components.

(28) Proton nmr ($CDCl_3$): $\tau$ 5.53 (m, $H_2$, 0.96 H), 6.66 (m, $H_3$, 0.99 H), 7.37 (broad m, 4.05 H).

(29) Distaurophenyl sulfone.[25] Proton nmr ($CDCl_3$): $\tau$ 3.25 ($H_3$, 0.98 H, dd, 2, 1.5 Hz), 5.87 ($H_5$, 2.06 H, t 1.5 Hz), 7.56 ($H_1$, 0.98 H, ddt, 6.3, 2, 1.5 Hz), 7.76 ($H_4$, 1.03H, dq, 6.3, 1.5 Hz).

(30) $\lambda_{max}$ (nm, $C_2H_5OH$) 227 sh ($\epsilon$ 2580), 270 (5000).

(31) Chlorosulfonyl isocyanate does add to bicyclo[1.1.0]butanes.[32] Both reagents add to norbornene,[33,34] and the Wagner–Meerwein rearrangement occurs in neither case.

(32) L. A. Paquette, G. R. Allen, Jr., and M. J. Broadhurst, *J. Amer. Chem. Soc.*, **93**, 4503 (1971).

(33) E. J. Moriconi and W. C. Crawford, *J. Org. Chem.*, **33**, 370 (1968).

(34) (a) W. H. Mueller and P. E. Butler, ref 19; (b) H. C. Brown, J. H. Kwakami, and K.-T. Liu, *J. Amer. Chem. Soc.*, **95**, 2209 (1973).

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