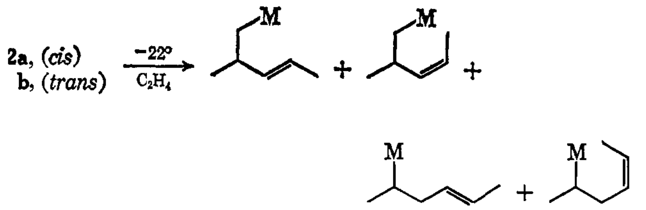
Table I. Rearrangement of *cis*-1,4-Hexadiene and *trans*- and *cis*-2-Methylvinylcyclopropanes[a]

Alkene	Time, min	Conditions[b]	Conversion, %	Yield of isomers, %	% of isomer mixture: 2-Me-1,3-Pd's *trans*	2-Me-1,3-Pd's *cis*	2,4-HD's[c] *t,t*	2,4-HD's[c] *t,c*	2,4-HD's[c] *c,c*
cis-1,4-HD	120	A	78	78	79.0			16.4	4.6
cis-1,4-HD + C_2H_4	20	B	67	99	5.7		4.2	64.0	26.1
3	120	A	58	68	79.0		13.4	7.6	
3 + C_2H_4	30	B	64	96	87.0	9.2	1.9	1.9	
4	120	A	68	53	63.4		24.0	12.6	
4 + C_2H_4	4	C	89	90	37.0	36.0	16.0	11.0	
4 + C_2H_4	5	B	51	99	20.3	65.4	4.7	8.6	1.0

[a] Conversions are based on per cent of starting material reacted. Yields are per cent of reacted starting material converted into C-6 isomers. [b] Conditions: A, 25°, 2.4 mmol of Ni in 35 ml of toluene, olefin:Al:Ni, 18:4.5:1; B, −22°, 0.02 mmol of Ni in 35 ml of toluene, olefin:Al:Ni, 211:14:1; C, same as B but at 25°. [c] *t,t*, *t,c*, and *c,c* refer to *trans,trans*, *trans,cis*, and *cis,cis*, respectively.

In order to monitor the formation of products with time, the concentration of the nickel component was decreased tenfold and a 211:14:1 olefin:Al:Ni ratio was used.[8] Under these conditions, 64% of **3** was converted into *trans*- and *cis*-2-methyl-1,3-pentadienes and *trans,trans*- and *trans,cis*-2,4-hexadienes in nearly quantitative yield within 30 min. Particularly noteworthy are the formation of *cis*-2-methyl-1,3-pentadiene and the pronounced change in the methylpentadiene:2,4-hexadiene ratio (Table I). The 2-methyl-1,3-pentadienes composed *ca.* 96% of the product mixture. Introduction of ethylene into toluene solutions of **4** under these same conditions at −22° resulted in the rapid formation of the same four products plus a small amount (1%) of *cis,cis*-2,4-hexadiene, *cis*-2-methyl-1,3-pentadiene composing 65% of the mixture. Control experiments demonstrated that the formation of *cis*-2-methyl-1,3-pentadiene is not a consequence of the higher olefin:Al:Ni ratio used.

The isomeric hydrocarbons formed in these reactions possess carbon skeletons that could be generated from rearrangement of organometallic products **2a** and **2b**, derived from the additive transfer of nickel hydride to the methylvinylcyclopropane double bond.[9] Any speculation regarding the mechanistic relevance of the methylvinylcyclopropane reactions to the *cis*-1,4- hexadiene rearrangement is unwarranted until a number of questions can be answered. Although *cis*-1,4-hexadiene, **3**, and **4** all afford *trans*-2-methyl-1,3-pentadiene as the major isomeric product at 25°, the major 2,4-hexadiene derived from each methylvinylcyclopropane is the *trans,trans* isomer. The only 2,4-hexadienes that are consistently formed in significant quantities from *cis*-1,4-hexadiene are the *trans,cis* and *cis,cis* isomers which may be derived solely or in part from the "direct" migration of the 1,4-hexadiene terminal double bond.[10] Also, the half-life at 25° for the conversion of *cis*-1,4-hexadiene into products, under the conditions listed in Table I, was *ca.* 5 min, whereas the corresponding half-lives for the methylvinylcyclopropanes were *ca.* 60 min. Therefore, the entries in Table I do not accurately reflect the relative rates of conversion into products at 25°. Interestingly, *cis*-1,4-hexadiene, when mixed with the catalyst components at −22°, remains unchanged during a 3-hr period but is rapidly converted to a product mixture containing 64% *trans,cis*- and 26% *cis-cis*-2,4-hexadienes after ethylene is introduced. *trans*-2-Methyl-1,3-pentadiene and *trans,trans*-2,4-hexadiene were minor components of the mixture.



Ethylene may facilitate the transfer of the elements of nickel hydride to and from hydrocarbon substrates. This would explain the rapid double bond migration in *cis*-1,4-hexadiene at −22° which can occur by a metal hydride addition–elimination sequence and the enhanced rates of rearrangement of **3** and **4** if the rate-determining steps involve metal hydride transfer. Apparently the ratios of products derived from the methylvinylcyclopropanes at −22° in the presence of ethylene are regulated mainly by kinetic control. A rapid and irreversible elimination of metal hydride from the organometallic products generated in the ring-opening reactions of **2a** and **2b** would lead to a product mixture with a "kinetically controlled" composition.

Acknowledgment. Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, and to the University of North Dakota grant-in-aid program for support of this research.

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[8] The product mixtures were analyzed by glpc. Products described herein were collected *via* preparative glpc and identified by comparison of infrared and nmr spectra with those of authentic samples. Reaction mixtures and aliquots therefrom were quenched with isopropyl alcohol.

[9] Two diastereomers of **2a** and of **2b** would be expected to result. It is clear that in any concerted ring-opening reaction, the geometry of the internal double bond of the *primary* products will be determined by the configuration at the carbinyl carbon in **2a** and **2b**.

[10] *trans*-1,4-Hexadiene affords *trans,trans* and *trans,cis* isomers as the only 2,4-hexadiene products under similar conditions.

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The Structure of Thiepin 1,1-Dioxide

Sir:

The question of π-electron delocalization involving sulfones is an intriguing one.[1] Thiepin 1,1-dioxide (**1**) offers a promising situation for the observation of this

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[1] For a critical summary, see D. J. Cram, "Fundamentals of Carbanion Chemistry," Academic Press Inc., New York, N. Y., 1965, pp 71–84; also D. J. Cram and T. A. Whitney, *J. Am. Chem. Soc.*, **89**, 4651 (1967).

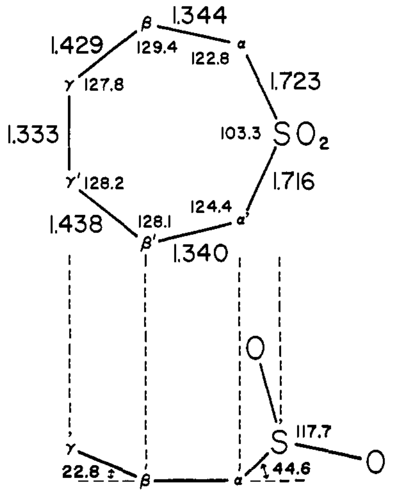
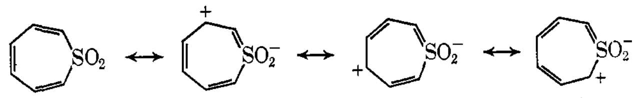


Figure 1. Bond length (Å, larger numbers) and angles (deg, smaller numbers) for thiepin 1,1-dioxide. The S–O lengths not shown are 1.439 Å (upper) and 1.448 Å (lower). The C–S–O angles not shown are C(α)–S–O (upper) = 109.2°, C(α)–S–O (lower) = 108.3°, C(α')–S–O (upper) = 109.1°, and C(α')–S–O (lower) = 108.2°. Estimated standard deviations are C–C = 0.005, C–S = 0.003, and S–O = 0.002 Å for bond lengths and *ca.* 0.3° for angles.

effect, in that one may draw canonical forms (**1a–c**) analogous to those responsible for the basicity and



1 1a 1b 1c

planarity of tropone. The valence shell expansion of sulfur required by structures **1a–c** may be effected utilizing the atom's unfilled 3d orbitals. The dπ–pπ orbital overlap is favored[2] if the second-row atom, without multiple bonds, is positively charged.

Thiepin 1,1-dioxide has been recently synthesized by one of us.[3] The chemical and spectral properties of this molecule are largely consistent with a localized triene structure.[4] This is a report of the results of an X-ray crystallographic investigation of thiepin 1,1-dioxide, undertaken with the hope that a knowledge of the precise molecular geometry could be used to assess the possibility of π-electron delocalization in the molecule.

Thiepin 1,1-dioxide crystallizes in the monoclinic space group $P2_1/n$ as colorless needles elongated along *c*. Cell parameters and intensity data were measured on a General Electric automatic diffractometer with Mo Kα radiation. The cell constants are $a = 6.788$, $b = 13.173$, $c = 7.596$ Å, and $\beta = 109.10°$. Intensity data were collected with the 2θ scan technique to $\sin \theta/\lambda = 0.64$; 1092 (66.5%) of the 1402 reflections examined had net peak intensities $\geq 1.5\sigma$ of the measurement and were designated as "observed" data.

The structure was solved utilizing the "heavy-atom" technique and has been refined with full-matrix least-squares to an *R* index[5] of 0.055. Anisotropic temperature factors were used for the carbon, oxygen, and sulfur atoms, and the hydrogen atoms were included with individual isotropic temperature factors.

Bond lengths and angles for the carbon, oxygen, and sulfur atoms are shown in Figure 1. Thiepin 1,1-dioxide exists in the boat conformation predicted by Mock.[3] Two aspects of the X-ray structure deserve special comment. First, all bond lengths appear to have typical values except for (a) the C(β)–C(γ) bonds (1.429, 1.438 Å), which are significantly less than values normally found for C(sp^2)–C(sp^2) single bonds (1.48 Å),[6] and (b) the carbon–sulfur bonds (1.723, 1.716 Å), which are not representative of the values usually measured for this bond type (1.75–1.80 Å).[7] The carbon–sulfur values are, however, in excellent agreement with the carbon–sulfur distance reported for thiophene (1.714 Å).[8] This correspondence becomes even more striking by contrast with the carbon–sulfur bond length found in 2,5-di-*t*-butylthiophene 1,1-dioxide (1.79 Å[9]).[10]

Second, we note the lack of coplanarity in the formally double C(α)–C(β) bonds of **1**. These possess torsional angles[11] of 8.4°. The formally single C(β)–C(γ) bonds exhibit torsional angles of 29.5°.[12] Because of the constraints of the ring system, π-type overlap in the former bond can only be improved at the expense of the latter bond and *vice versa.* Hence, a possible interpretation of this structural feature is that a compromise has been achieved between a minimally strained boat conformation and a more planar delocalized ring. The feature could also arise from σ bonding between C(α) and C(α'), *i.e.*, participation of a norcaradiene-type structure. However, this explanation is disfavored on the basis of chemical and other physical information.[4] Whatever the origin, the X-ray evidence suggests that some unusual bonding effects are being observed, resulting in a flattening of the hydrocarbon portion of the ring of thiepin 1,1-dioxide. (In agreement with this conclusion, the internal bond angles of the ring are somewhat enlarged at carbon; see Figure 1.)

More detailed analysis of the structure in terms of chemical bonding leads to ambiguity. Mesomeric π-electron delocalization into the sulfone (inferred from the short carbon–sulfur bond lengths) accords with the partial double-bond order apparent in the

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(2) A detailed discussion of the structural characteristics essential for 3d orbital participation in valence-shell expansion may be found in H. H. Jaffé and M. Orchin, "Theory and Applications of Ultraviolet Spectroscopy," John Wiley and Sons, Inc., New York, N. Y., 1962, Chapter 17.

(3) W. L. Mock, *J. Am. Chem. Soc.*, **89**, 1821 (1967).

(4) The chemistry of this ring system will be reported separately: W. L. Mock and W. E. Hatch, work in progress.

(5) $R = \Sigma|F_o - F_c|/\Sigma|F_o|$.

(6) (a) For 1,3-butadiene: A. Almenningen, O. Bastiansen, and M. Traetteberg, *Acta Chem. Scand.*, **12**, 1221 (1958); (b) 1.477 Å: M. J. S. Dewar and H. N. Schmeising, *Tetrahedron*, **5**, 166 (1959).

(7) R. K. Bullough and P. J. Wheatley, *Acta Cryst.*, **10**, 233 (1957); A. I. M. Rae and E. N. Maslen, *ibid.*, **15**, 1285 (1962); S. R. Hall and E. N. Maslen, *ibid.*, **18**, 301 (1965); C. J. Brown and D. E. Corbridge, *ibid.*, **21**, 485 (1966); A. M. O'Connel and E. N. Maslen, *ibid.*, **22**, 134 (1967); S. R. Hall and E. N. Maslen, *ibid.*, **22**, 216 (1967).

(8) B. Bak, D. Cristensen, L. Hansen-Nygaard, and J. Rastrup-Anderson, *J. Mol. Spectry.*, **7**, 58 (1961).

(9) L. G. Vorontsova, *J. Struct. Chem.*, **7**, 234 (1966).

(10) Caution must be exercised in forming conclusions upon this comparison since an equally reasonable analog, 2H-thiapyran 1,1-dioxide, has recently been shown to possess a short S–C(sp^2) bond (1.730 Å): E. Boelema, G. J. Visser, and A. Vos, *Rec. Trav. Chim.*, **86**, 1275 (1967).

(11) Defined as the amount by which these and adjacent ring atoms fail to lie in a common plane; *e.g.*, the dihedral angle between the planes defined by S–C(α)–C(β) and C(α)–C(β)–C(γ) is 8.4°.

(12) The torsional angle about C(γ)–C(γ') is 0.9°.

$C(\beta)$–$C(\gamma)$ bonds and the tendency toward coplanarity of the carbon portion of the ring. Reduction of the torsional angles about the $C(\beta)$–$C(\gamma)$ bonds and concomitant relaxation of the planarity requirements for the $C(\alpha)$–$C(\beta)$ bonds are implied by structures **1a–c**. Unfortunately, a "donor–acceptor" type of conjugation involving the sulfur 3d orbitals does not lead to clear stereochemical predictions.[2,13] Orbital symmetry considerations indicate the availability of a suitable 3d orbital in a hypothetical planar molecule (Case I).[13] However, when the sulfone group is not coplanar with the rest of the molecule, another geometry is approached (Case II),[13] and delocalization into a different 3d orbital may be anticipated.[14] Independent evidence regarding the relative merits of the two types of conjugation is inconclusive,[1] and it may *not* be assumed that optimal delocalization requires a planar thiepin 1,1-dioxide ring. We finally note that nonbonded interactions and orbital rehybridization phenomena[6a] which cannot be quantitatively assessed also may influence the observed structure.

We feel that the preceding data are evidence for electron delocalization in thiepin 1,1-dioxide. Conclusions regarding the nature and extent of the effect must, however, be formed with consideration of the chemical properties of the molecule.[4]

Acknowledgment. We gratefully acknowledge the Committee on Research, University of California, the Computer Science Center, University of Maryland, and the Biochemistry Section, Walter Reed Army Medical Center, for financial support.

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(13) H. P. Koch and W. E. Moffitt, *Trans. Faraday Soc.*, 47, 7 (1951).

(14) The highest filled (donor) 1,3,5-hexatriene molecular orbital (ψ_3) has b_2 symmetry. It is, therefore, necessary that the available sulfur 3d orbital (acceptor) also have b_2 symmetry (Case I)[13] or that a compatible symmetry (a_1, as in Case II) be available. Carbon–sulfur orbital overlap in the latter case would be favored by as large an angle as possible between the $C(\alpha)$–S–$C(\alpha')$ and $C(\alpha)$–$C(\beta)$–$C(\beta')$–$C(\alpha')$ planes.

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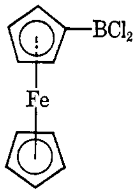
The Interaction of Diboron Tetrachloride with Ferrocene

Sir:

We wish to report the preparation of a new boron derivative of ferrocene, ferrocenyldichloroborane, from the reaction of diboron tetrachloride and ferrocene. The study of this reaction was undertaken as a part of our general investigation of the interactions of boron trihalides and diboron tetrahalides with organometallic compounds of the transition metals. Ferrocene readily forms a charge-transfer complex with tetracyanoethylene, a π acid.[1] Although the original work indicated that the tetracyanoethylene might be complexed with the iron, recent crystallographic studies have shown that the acid is bonded to the cyclopentadienyl rings.[2] Since it has been suggested that B_2Cl_4 acts as a π acid in its reactions with olefins,[3,4] it was of interest to investigate the possibility that B_2Cl_4 would interact with the ferrocene cyclopentadienyl rings as a π acid.

With hexane as the reaction medium, ferrocene and B_2Cl_4 were found to react readily at temperatures between −23 and 0°.[5,6] After approximately 2 days at 0°, the main reaction product, a red, crystalline solid, was separated from gray-green insoluble reaction products by extraction with hexane at 0°. The reaction products which were readily volatile at room temperature were distilled into a vacuum line (*vide infra*); unreacted ferrocene was removed by prolonged pumping at 10^{-6} mm and room temperature.

The infrared and ^1H nmr spectra of the red solid indicated that the substance was a monosubstituted ferrocene derivative. Ferrocene and its monosubstituted derivatives display characteristic absorption bands near 1000 and 1110 cm^{-1}.[7] While the presence of these bands is not conclusive proof of monosubstitution, they are very often indicative of derivatives of this type. We observed these bands at 1000 and 1107 cm^{-1}. In addition, bands assigned to B–Cl vibrations were observed at 887 (s) and 922 cm^{-1} (m). The ^1H nmr spectrum of the solid dissolved in benzene consisted of a pair of triplets at τ 5.57 and 5.65 (total relative intensity 4, J = 2 Hz) and a singlet at τ 6.08 (relative intensity 5). Characterization of the red material by complete elemental analysis was difficult due to problems in handling the air-sensitive, low-melting (33°) solid. However, a chloride analysis and a molecular weight determination indicated that the substance was $C_{10}H_{10}BCl_2Fe$.[8] It may be concluded from the spectral and analytical data that the red solid is ferrocenyldichloroborane (I). This new boron derivative of ferrocene was best characterized as the orange-yellow trimethylamine adduct II.[9] The solid amine complex was only slightly air-sensitive and was sublimable at 110–120° *in vacuo*. The complex exhibited an infrared



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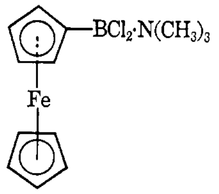

II

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(1) M. Rosenblum, R. W. Fish, and C. Bennett, *J. Amer. Chem. Soc.*, **86**, 5166 (1964).

(2) E. Adman, M. Rosenblum, S. Sullivan, and T. N. Margulis, *ibid.*, **89**, 4540 (1967).

(3) R. W. Rudolph, *ibid.*, **89**, 4216 (1967).

(4) M. Zeldin, A. R. Gatti, and T. Wartik, *ibid.*, **89**, 4217 (1967).

(5) The reactions described in this communication were carried out in an all-glass *zweikugel*. Diboron tetrachloride and the appropriate solvents were distilled into the apparatus from a vacuum line. The reaction and extraction of soluble materials were carried out in this apparatus; solids were handled in a drybox.

(6) Diboron tetrafluoride does not react with ferrocene under similar conditions: W. J. Painter, unpublished results.

(7) M. Rosenblum, "Chemistry of the Iron Group Metallocenes," Part I, John Wiley and Sons, Inc., New York, N. Y., 1965, p 38.

(8) *Anal.* Calcd for $C_{10}H_9BCl_2Fe$: Cl, 2.66; mol wt, 267. Found: Cl, 2.57; mol wt, 254 (by freezing point depression in benzene).

(9) *Anal.* Calcd for $C_{13}H_{18}BCl_2NFe$: C, 47.9; H, 5.57; B, 3.32; N, 4.30; Fe, 17.1; mol wt, 326. Found: C, 47.7; H, 5.66; B, 2.94; N, 4.33; Fe, 16.3; mol wt, 332 (by ebulliometry in benzene).