

Figure 1.

using Mo $K\alpha$ radiation with a General Electric XRD 5 diffractometer, employing stationary crystal-stationary counter techniques.³ Background was measured as an average of minimum levels on either side of the peak.

The structure was solved using the Hauptmann and Karle direct-method approach.⁴ A fully automatic computer program utilizing the symbolic addition technique⁵ determined 127 phases, all subsequently determined to be correct, from which an E map showing the positions of the iron atom was calculated. Several cycles of least-squares refinement with anisotropic temperature factors produced a final R factor of 0.043 (with zeros) and 0.068 (for all reflections).

Figures 1 and 2 show the molecule as viewed parallel and perpendicular to the COT ring, and Table I gives some of the bond lengths. The molecule is bisected by a mirror plane passing through carbon atoms C_4 and C_5 of the COT ring and the bridging carbonyl group C_1O_1 . This means that the bonding in the cyclooctatetraene ring must be symmetrical about the mirror plane, which rules out a structure with alternating single and double bonds.

Table I. Bond Lengths in $Fe_2(CO)_6COT$

Bond	Length, Å	Std dev
Fe-C ₁	1.968	(0.017)
Fe-C ₂	1.786	(0.015)
Fe-C ₃	1.802	(0.014)
Fe-C ₄	2.494	(0.015)
Fe-C ₅	2.496	(0.016)
Fe-C ₆	2.136	(0.013)
Fe-C ₇	2.113	(0.013)
Fe-C ₈	2.123	(0.013)
C ₄ -C ₅	1.392	(0.018)
C ₅ -C ₆	1.398	(0.021)
C ₆ -C ₇	1.410	(0.022)
C ₇ -C ₈	1.432	(0.022)
Fe-Fe	2.742	(0.003)

Examination of the iron-ring carbon distances shows that the carbon atoms of the COT may be divided up into two groups, one of three carbon atoms (C_5 , C_6 , and C_7) at a distance of 2.1 Å from the nearest iron atom, and one of two carbon atoms on the mirror plane (C_4 and C_8) at a distance of 2.5 Å from the iron atoms.

(3) T. C. Furnas, "Single Crystal Orienter Instruction Manual," General Electric Co., Schenectady, N. Y., 1957.

(4) See I. L. Karle, K. S. Dragonette, and S. A. Brenner, *Acta Cryst.*, **19**, 713 (1965), and references therein.

(5) R. Dewar and A. Stone, to be published.

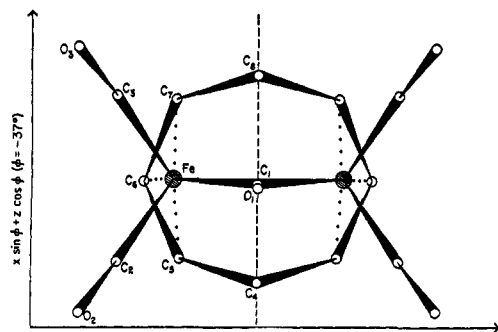
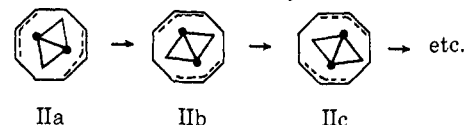


Figure 2.

The group of three carbon atoms equidistant from the iron atom suggests a π -allyl type of bonding. This leaves two carbon atoms on the mirror plane, each with a single electron available for bonding. Since the molecule is diamagnetic,² these electrons must be involved in bonding, and the structure is consistent with two three-center bonds each containing two electrons, extending over the two iron atoms and a carbon atom on the mirror plane, much as in the electron-deficient boron hydrides. Each iron atom is bonded to two terminal carbonyl groups, and an iron-iron bond is then proposed in order that each Fe attain the effective atomic number of krypton.

The structure shown in Figure 1 contains three nonequivalent hydrogen atoms; the single peak which is seen in the nmr is then explained on the basis of rapid degenerate valence tautomerism as shown. The facility of this isomerism is indicated by the fact that the spec-



trum remains as a single peak even at -80° . Structure I could well be a stable intermediate involved in this rearrangement and could offer a low-energy pathway for the extensive electronic reorganization associated with the conversion of IIa to IIb.^{6,7}

(6) The infrared absorption spectrum of the complex in the solid state shows the same major regions of absorption as those when taken in solution. This indicates that no new species having a different mode of metal-ligand bonding in which eight chemically equivalent hydrogen atoms are present is produced in solution.

(7) This work was supported by grants from the National Institutes of Health and Advanced Research Projects Agency.

(8) Alfred P. Sloan Fellow.

(9) U. S. Rubber Fellow.

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A New Method for Determining the Stereochemistry of Substitution Reactions

Sir:

There are three main methods for determining the stereochemistry of substitution reactions at carbon:¹

(1) E. Eliel, "Stereochemistry of Carbon Compounds," McGraw-Hill Book Co., Inc., New York, N. Y., 1962, pp 116-119.

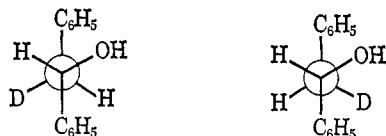


Figure 1.

(i) through the use of optically active molecules, (ii) through the use of diastereomeric acyclic molecules, and (iii) by the study of *cis-trans* pairs of substituted cyclic molecules. The relative advantages and drawbacks of these three methods are well known.

The use of asymmetrically deuterated molecules has recently found increasing favor in the study of reaction pathways.²⁻⁵ These diastereomers have the advantage that the ground states and transition states of the two isomers should not vary widely in stability.

The nmr spectra of asymmetrically deuterated diastereomers exhibit another useful property of these molecules. In the 2-deuterio-1,2-diphenyl-1-ethanol system, originally investigated by Curtin and Kellom,² the *erythro* isomer shows a rather large vicinal coupling constant whereas the *threo* isomer shows a smaller J value, indicative of predominant conformations shown in Figure 1.

In a substitution reaction in which the hydroxyl is replaced by a substituent X, one isomer should exhibit a large J value, the other a small J value. If both products occur, a mixture of the above cases should result and hopefully integration will show the amount of each isomer. Thus the steric course of a substitution reaction may be followed by nmr means if the high J value product and the low J value product can be identified with either the *erythro* or the *threo* diastereomer.

The magnitude of the coupling constant is of course dependent upon molecular conformation. Usually the largest groups (in Figure 1, the two phenyl groups) prefer a *trans* orientation. However, as the size of

Table I. Coupling Constant Assignments in the 1,2-Diphenyl-2-deuterio-1-ethyl System

Isomer	X	J_{AB} , cps	Chemical shift, H_A , ppm ^a
1 ^b <i>erythro</i>	OH	8.4	4.77
<i>threo</i>	OH	4.9	4.66
2 ^b <i>erythro</i>	Cl	7.3	4.72
<i>threo</i>	Cl	7.3	4.75
3 ^b <i>erythro</i>	Br	7.2	4.95
<i>threo</i>	Br	7.6	5.03
4 ^c <i>erythro</i>	SC ₆ H ₅	6.0	4.28
<i>threo</i>	SC ₆ H ₅	8.7	4.29
5 ^c <i>erythro</i>	SO ₂ C ₆ H ₅	4.3	
<i>threo</i>	SO ₂ C ₆ H ₅	11.1	

^a Spectra taken on a Varian A-60 instrument vs. tetramethylsilane as an internal standard taken as 0 ppm. ^b Ca. 5% CCl₄ solution. ^c Ca. 5% CDCl₃ solution.

(2) D. Y. Curtin and D. B. Kellom, *J. Am. Chem. Soc.*, **75**, 6011 (1953).

(3) (a) P. S. Skell and W. L. Hall, *ibid.*, **86**, 1557 (1964); (b) *ibid.*, **85**, 2852 (1963).

(4) F. A. L. Anet, *ibid.*, **82**, 994 (1960).

(5) D. S. Noyce, D. Hartter, and F. B. Miles, *ibid.*, **86**, 3583 (1964).

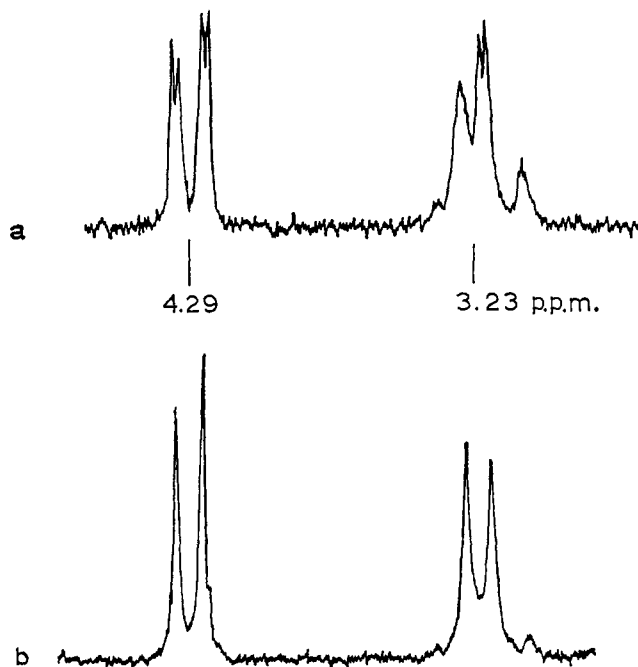


Figure 2. Nuclear magnetic resonance spectra of phenyl sulfides (3) prepared by two different reaction pathways: (a) *threo-1*, LiCl-HCl, then sodium thiophenoxide, (b) *threo-1*, SOCl₂, then sodium thiophenoxide.

the group X increases, it may prefer to be *trans* to phenyl. Thus a crossover may occur in which the *erythro* isomer may show the larger J value when the substituent is small but the smaller J value when the substituent is large. Table I shows the assignments of configuration for a variety of substituents of increasing size.

The data seem to point to a crossover in the vicinity of the chloro and bromo substituents. A similar crossover has been noted in another study⁶ except it occurred at iodo.

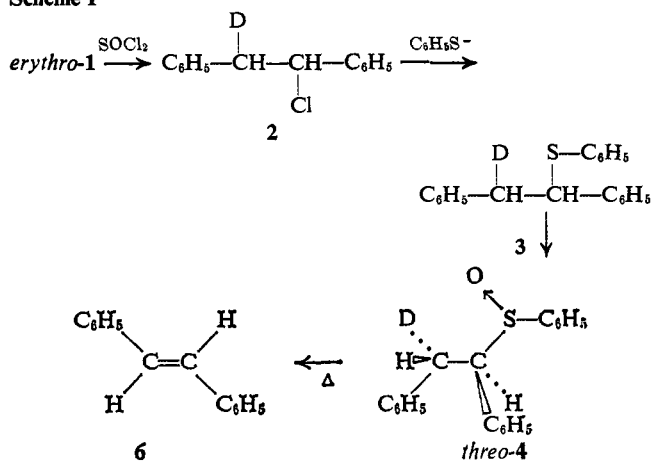
The following experiments show the attempts to determine the stereochemistry of substitution reactions. *erythro-1* was treated with SOCl₂ at low temperature, yielding the chloride 2, which was a nondistillable oil. The ratio of *erythro* and *threo* isomers could not be determined due to their close similarity of coupling constants and chemical shifts. This product was converted to the phenyl sulfide 3 in better than 80% yield. No stilbene was evident. Analysis by integration of the nmr spectra indicated that 3 was 78% *threo* isomer, 22% *erythro* (these values are considered accurate to ca. ± 10%). Oxidation of 3 with sodium metaperiodate yielded two diastereomeric sulfoxides, 4, mp 88–90°, and 5, mp 123–125°. Pyrolysis of 4 yielded stilbene (6) which retained 22.4% deuterium. As Scheme I shows *threo-4* would yield undeuterated stilbene. Thus the nmr analysis is in good agreement with deuterium analysis.

A similar sequence of reactions beginning with *threo-1* yielded 3 in good yield which exhibited 78% *erythro* and 22% *threo* isomers. Conversion to 6 as before yielded product retaining 78% deuterium. These results are consistent with a thionyl chloride reaction going by predominant retention and the thiophenoxide displacement by predominant inversion.

Optically active 1 (undeuterated), $[\alpha]^{25D} -34.88^\circ$

(6) C. A. Kingsbury and D. C. Best, unpublished results.

Scheme I



(*c* 5, EtOH), was converted into **2**, $[\alpha]^{25\text{D}} + 9.30^\circ$ (*c* 10.5, EtOH), as before.

In a second series of experiments, a reaction involving predominant racemization was investigated. *erythro-1* was treated with concentrated HCl with added LiCl to yield **2**. This product was converted into **3** in 85% yield. The phenyl sulfide **3** was 44% *erythro* and 56% *threo* isomers. Beginning with *threo-1*, product **3** again showed the product ratios 52% *erythro* and 48% *threo*, corresponding to near 100% optical racemization. Optically active **1**, $[\alpha]^{25\text{D}} + 46.88^\circ$ (*c* 5, EtOH), was treated with LiCl-HCl forming **2**, $[\alpha]^{25\text{D}} - 0.34$ (*c* 13.45, EtOH).

Figure 2 shows the partial nmr spectra of **3** prepared in stereospecific and nonstereospecific manners.

This study demonstrates the relative merits of the nmr method as opposed to the optical rotation method.

The optical rotation method is probably more accurate and will remain the method of choice where oxygen nucleophiles are to be used.

The one great advantage of the nmr method is that the amount of retention product and of inversion product can be *directly observed* in most cases, and it may find application in displacements where oxygen nucleophiles are not used.

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Structure of a Silver-Bullvalene Complex¹

Sir:

Stimulated by the prediction of the unusual properties to be expected of tricyclo[3.3.2.0^{4,6}]deca-2,7,9-triene or bullvalene (I),² and its subsequent synthesis,³ considerable interest has been exhibited in the behavior and geometry of this extreme example of a "fluxional structure."⁴⁻⁶ Allerhand and Gutowsky⁶ prepared some Ag⁺-bullvalene complexes in which the rate of self-rearrangement of bullvalene was reduced, and in

(1) This work was supported in part by the National Institutes of Health (GM 12470-02 and 5T1 GM 722-05).

(2) W. von E. Doering and W. R. Roth, *Tetrahedron*, **19**, 715 (1963).

(3) G. Schröder, *Angew. Chem.*, **75**, 722 (1963); *Angew. Chem. Intern. Ed. Engl.*, **2**, 481 (1963).

(4) W. von E. Doering and W. R. Roth, *ibid.*, **2**, 115 (1963).

(5) M. Saunders, *Tetrahedron Letters*, 1699 (1963).

(6) A. Allerhand and H. S. Gutowsky, *J. Am. Chem. Soc.*, **87**, 4092 (1965).

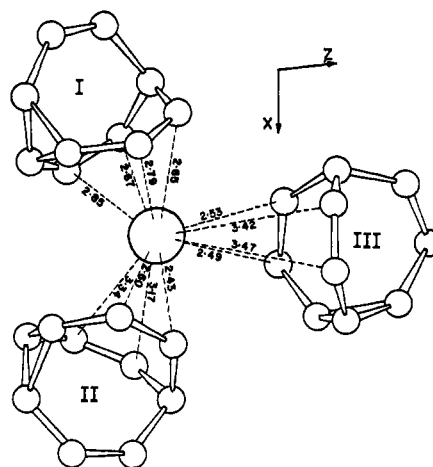
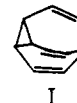


Figure 1. Perspective drawing of the Ag⁺(bullvalene)₃ portion of the molecule viewed down the *b* axis. The important Ag⁺-C (olefin) distances are shown in angstrom units.

the course of their work they isolated some solid complexes. Preliminary X-ray studies⁷ on some of these compounds indicated that they possessed a very low degree of crystallinity which might be a result of crystallographic disorder among the bullvalene tautomers. We now report the results of a single crystal structure



analysis of a new AgBF₄-bullvalene (1:3) complex, prepared by recrystallization of the previously reported 1:2 complex,⁸ which had been standing for several weeks and had apparently partially decomposed, leaving an unidentified deposit.

This (C₁₀H₁₀)₃·AgBF₄ complex⁸ crystallizes as white needles which darken on prolonged exposure to light. They belong to the monoclinic system with *a* = 12.44 ± 0.02, *b* = 10.18 ± 0.02, *c* = 19.47 ± 0.03 Å, and β = 95° 40' ± 10', as determined on a precession camera using Mo Kα radiation (λ 0.7107 Å). The space group is P2₁/c with four molecules of (C₁₀H₁₀)₃·AgBF₄ in the unit cell.⁹ A total of 1734 independent structure amplitudes was obtained from visual estimates of equiinclination Weissenberg photographs (Cu Kα, λ 1.5418 Å) taken at 4°.¹⁰

The crystal structure was solved by the heavy-atom method,¹¹ and a perspective view of the atomic arrangement looking down the *b* axis is shown in Figure 1. At the present stage of refinement the crystallographic *R* factor is 0.12.¹²

(7) I. C. Paul, unpublished work.

(8) Analytical data: Calcd: C, 61.5; H, 5.13. Found: C, 61.3; H, 5.25.

(9) We had only a few well-formed crystals, and virtually all of those were used in characterization and data collection. We have been unable to get a reliable estimate of the density from those remaining, as the complex readily dissolves in most organic solvents and all our measured values have been much higher than the calculated density of 1.59 g/cm³.

(10) The data were collected in a cold room as under these conditions no observable intensity changes were detected over a period of 4-5 days. Three crystals were required to accumulate the data used in this analysis.

(11) J. M. Robertson and I. Woodward, *J. Chem. Soc.*, 219 (1937).

(12) The fluoroborate anion appears to be partially disordered, as has been found in other structures,^{13,14} but as this ion has approximately the same *x* and *z* coordinates as the Ag⁺ ion, the details of this area of the unit cell may be subject to distortion owing to diffraction effects.

(13) M. G. B. Drew, D. M. L. Goodgame, M. A. Hitchman, and D. Rogers, *Chem. Commun.*, 477 (1965).

(14) I. C. Zimmermann, M. Barlow, and J. D. McCullough, *Acta Cryst.*, **16**, 883 (1963).