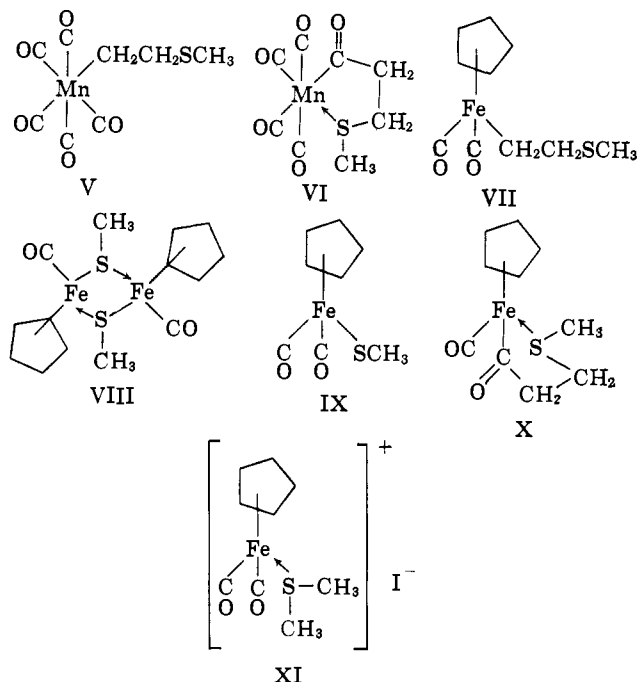


and dimethyl disulfide¹⁵; (3) $[\text{C}_5\text{H}_5\text{Fe}(\text{CO})_2]_2$; (4) brown crystalline $\text{CH}_3\text{SFe}(\text{CO})_2\text{C}_5\text{H}_5$ (IX), m.p. 67–69°⁶; and (5) red crystalline $\text{CH}_3\text{SCH}_2\text{CH}_2\text{COFeCO}-\text{C}_5\text{H}_5$, m.p. 70°⁶, exhibiting a single strong terminal metal carbonyl band at 1934 cm^{-1} and a single strong acyl carbonyl band at 1618 cm^{-1} in its infrared spectrum clearly indicating structure X analogous to the structure VI proposed for $\text{CH}_3\text{SCH}_2\text{CH}_2\text{COMn}(\text{CO})_4$.

The monomeric product $\text{CH}_3\text{SFe}(\text{CO})_2\text{C}_5\text{H}_5$ (IX) is the first example of a methylthio derivative of a transition metal where the sulfur atom does not bridge between two metal atoms. This organosulfur derivative may also be obtained in 13% yield from $\text{C}_5\text{H}_5\text{Fe}(\text{CO})_2\text{H}$ ¹⁶ and dimethyl disulfide.⁶ Similar reactions of dimethyl disulfide with $\text{HMn}(\text{CO})_5$ and $\text{C}_5\text{H}_5\text{Mo}(\text{CO})_3\text{H}$ have previously been shown to give the dimeric derivatives $[\text{CH}_3\text{SMn}(\text{CO})_4]_2$ and $[\text{CH}_3\text{SMo}(\text{CO})_2-\text{C}_5\text{H}_5]_2$.¹⁸

The chemical properties of $\text{CH}_3\text{SFe}(\text{CO})_2\text{C}_5\text{H}_5$ are consistent with its formulation as IX. Thus, on heating to 70° at atmospheric pressure, gas is evolved and the dimeric derivative $[\text{CH}_3\text{SFeCO}(\text{C}_5\text{H}_5)]_2$ (VIII) may be isolated in 26% yield. Treatment of $\text{CH}_3\text{SFe}(\text{CO})_2\text{C}_5\text{H}_5$ with excess methyl iodide forms an exothermic reaction yellow solid $[\text{C}_5\text{H}_5\text{Fe}(\text{CO})_2-\text{S}(\text{CH}_3)_2]\text{I}$ (XI), m.p. 104° dec.⁶

Detailed aspects of the chemistry outlined in this communication will be presented in future papers.



(15) R. B. King, P. M. Treichel, and F. G. A. Stone, *J. Am. Chem. Soc.*, **83**, 3600 (1961).

(16) Prepared *in situ* from $\text{NaFe}(\text{CO})_2\text{C}_5\text{H}_5$ and $(\text{CH}_3)_2\text{CCl}$ in tetrahydrofuran solution.¹⁷

(17) M. L. H. Green and P. L. I. Nagy, *J. Organometal. Chem.*, **1**, 58 (1963).

(18) P. M. Treichel, J. H. Morris, and F. G. A. Stone, *J. Chem. Soc.*, 720 (1963).

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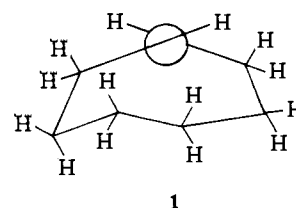
The Absolute Configuration of *trans*-Cyclooctene

Sir:

The complete resolution of *trans*-cyclooctene was reported recently.¹ The absolute configuration of

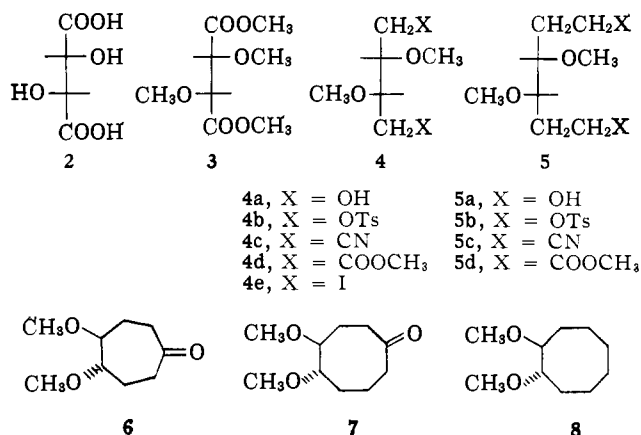
(1) A. C. Cope, C. R. Ganellin, H. W. Johnson, Jr., T. V. Van Auken, and H. J. S. Winkler, *J. Am. Chem. Soc.*, **85**, 3276 (1963).

trans-cyclooctene has now been determined and the levorotatory enantiomer is assigned the (*R*)-configuration² as shown in the Newman projection formula (1).



(1*S*:2*S*)-1,2-Dimethoxycyclooctane (8) was synthesized from the dextrorotatory (2*R*:3*R*)-tartaric acid (2) and its sign of rotation was shown to be identical with that of the same diether obtained from (–)-*trans*-cyclooctene.

(+)-Tartaric acid (2) was esterified³ with methanolic hydrogen chloride and the resulting dimethyl (2*R*:3*R*)-tartrate was methylated⁴ with methyl iodide and silver oxide to give 3. Lithium aluminum hydride reduction of the dicarboxylic ester (3) afforded the



4a, X = OH
4b, X = OTs
4c, X = CN
4d, X = COOCH₃
4e, X = I

5a, X = OH
5b, X = OTs
5c, X = CN
5d, X = COOCH₃

glycol (4a) in 62% yield. The distilled glycol crystallized on cooling and was recrystallized from chloroform-ether (1:1) at 0°, m.p. 37–38°.⁵ The reaction of 4a with *p*-toluenesulfonyl chloride and pyridine yielded the ditosylate⁶ (4b, 94%). The corresponding diiodide (4e) was prepared⁶ from the ditosylate (4b) with sodium iodide and anhydrous acetone. Alkylation of either the ditosylate (4b) or the diiodide (4e) with acetonitrile did not give a satisfactory yield of the dinitrile (5c). An alternative sequence of reactions was therefore utilized.

The ditosylate (4b) was converted to (3*S*:4*S*)-3,4-dimethoxy-1,6-hexanedinitrile (4c)⁷ with sodium cyanide in dimethyl sulfoxide. Optimum yields (65–78%) were obtained with a reaction time of 6 days and careful control of the temperature at $20 \pm 3^\circ$. The dinitrile (4c) was converted to dimethyl (3*S*:4*S*)-3,4-dimethoxyadipate (4d) by treatment with methanolic hydrogen chloride followed by hydrolysis of the bis-

(2) The nomenclature for absolute configuration used throughout is that of R. S. Cahn, C. K. Ingold, and V. Prelog, *Experientia*, **12**, 81 (1956).

(3) A. Skrabal and L. Herman, *Montash.*, **43**, 633 (1922).

(4) T. Purdie and J. C. Irvine, *J. Chem. Soc.*, **79**, 957 (1901).

(5) Posternak and Susz⁸ had prepared the same glycol as an oil by its isolation from reduction as the diacetate followed by saponification of the purified diacetate with methanolic barium hydroxide. We isolated the glycol by treating the aluminate salt with a minimum of aqueous base and repeated washing of the filter cake with acetone as the glycol is sparingly soluble in ether.

(6) Th. Posternak and J. Ph. Susz, *Helv. Chim. Acta*, **39**, 2032 (1956).

(7) Satisfactory analytical data were obtained for all major intermediates in this synthesis. The assigned structures are supported by spectral data.

imino ether hydrochloride intermediate.⁸ In most preparations the presence of some free carboxylic acid was shown by infrared spectroscopy; hence the product mixture was esterified with methanol and thionyl chloride. The yield of the dicarboxylic ester (**4d**) was about 90%.

The dicarboxylic ester (**4d**) was converted (63%) to the next higher homolog, dimethyl (4*S*:5*S*)-4,5-dimethoxysuberate (**5d**), by the same sequence of reactions used for the transformation of **3** to **4d**. Under the conditions of the acyloin condensation⁹ the dicarboxylic ester (**5d**) did not yield any of the desired (5*S*:6*S*)-2-hydroxy-*trans*-5,6-dimethoxycyclooctanone. The major product isolated (31% yield), (4*S*:5*S*)-2-carbomethoxy-*trans*-4,5-dimethoxycycloheptanone, resulted from a Dieckmann condensation.

Hydrolysis of (4*S*:5*S*)-2-carbomethoxy-*trans*-4,5-dimethoxycycloheptanone gave (4*S*:5*S*)-4,5-dimethoxycycloheptanone (**6**). However, a better yield (57%) of the cycloheptanone (**6**) was obtained by Thorpe-Ziegler cyclization¹⁰ of the dinitrile (**5c**) followed by hydrolysis with 30% aqueous sulfuric acid.

The cycloheptanone (**6**) was converted to the cyanohydrin which was hydrogenated catalytically. The resulting amino alcohol on treatment with sodium nitrite and acetic acid yielded (4*S*:5*S*)-4,5-dimethoxycyclooctanone (**7**, 23% from ketone **6**).¹¹

Wolff-Kishner reduction¹² of the cyclooctanone (**7**) gave (1*S*:2*S*)-1,2-dimethoxycyclooctane (**8**) [$[\alpha]^{31,5D} + 50.3^\circ$ (*c* 4.63, CHCl₃)].¹³

The identical diether (**8**) having $[\alpha]^{31D} + 49.5^\circ$ (*c* 4.337, CHCl₃) was obtained from (–)-*trans*-cyclooctene, by treatment of the olefin with osmium tetroxide yielding (+)-*trans*-1,2-cyclooctanediol¹⁴ followed by methylation.¹⁵

Thus, (2*R*:3*R*)-tartaric acid (**2**) has been related to (–)-*trans*-cyclooctene and the only assumption in assignment of the (*R*)-configuration to the olefin is that osmium tetroxide attacks from the side of the double bond not hindered by the ring methylene groups. In the osmium tetroxide oxidation of 5 α ,22 α -spirost-2-ene it has been reported¹⁶ that the product is the 2 α ,3 α -diol which results from the approach of the reagent to the $\Delta^{2,3}$ -bond from the less hindered α -side of the steroidal nucleus.

During the course of this work, Moscowitz and Mislou¹⁷ reported on the basis of theoretical considerations that (–)-*trans*-cyclooctene has the (*S*)-configuration, contrary to these results.

(8) The method was similar to that of W. Davey and D. J. Tivey [*J. Chem. Soc.*, 1230 (1958)].

(9) The procedure was similar to that of N. L. Allinger [*Org. Syn.*, **36**, 79 (1956)].

(10) Carried out essentially according to the method of N. L. Allinger, M. Nakazaki, and V. Zalkov [*J. Am. Chem. Soc.*, **81**, 4074 (1959)] for the preparation of *cis*-bicyclo[5.2.0]nonan-4-one.

(11) The cyanohydrin was prepared according to the procedure of G. C. Ayerst and K. Schofield [*J. Chem. Soc.*, 3445 (1960)] but was not isolated pure. The subsequent steps followed essentially the method of C. D. Gutsche [*J. Am. Chem. Soc.*, **71**, 3513 (1949)].

(12) Huang-Minlon, *ibid.*, **68**, 2487 (1946).

(13) Optical rotations were determined with a Zeiss photoelectric polarimeter which gave values at 546.1 and 577.8 m μ and the value at the sodium D-line (589.2 m μ) was calculated by extrapolation using the first approximation of Drude's formula for normal rotation dispersion.

(14) A. C. Cope, R. A. Pike, and C. F. Spencer, *J. Am. Chem. Soc.*, **75**, 3212 (1953).

(15) M. Neeman, M. C. Caserio, J. D. Roberts, and W. S. Johnson, *Tetrahedron*, **6**, 36 (1959).

(16) C. Djerassi, L. B. High, T. T. Grossnickle, R. Ehrlich, J. A. Moore, and R. B. Scott, *Chem. Ind. (London)*, 474 (1955).

(17) A. Moscowitz and K. Mislou, *J. Am. Chem. Soc.*, **84**, 4605 (1962).

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F¹⁹ Magnetic Resonance Determination of σ -Constants for the –ICl₂ Functional Group

Sir:

Iodobenzene dichloride and its derivatives have been the subject of several recent publications by Keefer and Andrews.^{1–11} They have reported the effect of substituents and solvents on the rates and equilibria of dissociation of substituted iodobenzene dichlorides into chlorine and substituted iodobenzenes^{1–6} and the behavior of the complex as a chlorinating agent.^{7–11} Little information has been obtained concerning the effect of the –ICl₂ functional group on the chemical or physical properties of aromatic compounds. We have obtained the F¹⁹ n.m.r. spectra of *m*-fluoriodobenzene dichloride and *p*-fluoriodobenzene dichloride and have utilized Taft's correlations of F¹⁹ chemical shifts in *m*- and *p*-substituted fluorobenzenes with σ -constants^{12–16} to determine these parameters for the –ICl₂ group.

Fluorine-19 magnetic resonance spectra were obtained at 56.4 Mc./sec. using a Varian HR-60 spectrometer and associated equipment on dilute solutions of the substituted fluorobenzenes in carbon tetrachloride in 15-mm. tubes. *p*-Difluorobenzene was employed as an internal reference and chemical shifts were obtained by the standard side-band technique. The chemical shifts are presented in Table I in p.p.m. with respect to fluorobenzene. Similar but less precise shifts were obtained using fluorobenzene as an external reference.

TABLE I

F¹⁹ CHEMICAL SHIFTS

| Compound | Conditions | Chemical shifts, p.p.m. with respect to fluorobenzene |
|---------------------------------------|------------|---|
| <i>p</i> -Fluoriodobenzene dichloride | <i>a</i> | –7.1 |
| <i>p</i> -Fluoriodobenzene dichloride | <i>b</i> | –7.0 |
| <i>m</i> -Fluoriodobenzene dichloride | <i>a</i> | –7.2 |
| <i>m</i> -Fluoriodobenzene dichloride | <i>b</i> | –7.2 |
| <i>p</i> -Fluoriodobenzene | <i>c</i> | +1.6 |
| <i>m</i> -Fluoriodobenzene | <i>c</i> | –2.4 |

^a Spectra obtained on supernatant liquids above the solid formed by treatment of 2% solution of ArI in CCl₄ with chlorine gas. ^b Spectra obtained on saturated CCl₄ solutions prepared from the washed solid referred to in *a*. ^c Spectra obtained on 2% solutions in CCl₄.

The shifts listed for *m*- and *p*-fluoriodobenzene in Table I are in good agreement with the values reported elsewhere.^{13,16} When carbon tetrachloride solutions of these compounds were treated with chlorine, the F¹⁹

- (1) R. M. Keefer and L. J. Andrews, *J. Am. Chem. Soc.*, **80**, 277 (1958).
- (2) R. M. Keefer and L. J. Andrews, *ibid.*, **80**, 5350 (1958).
- (3) R. M. Keefer and L. J. Andrews, *ibid.*, **81**, 2374 (1959).
- (4) L. J. Andrews and R. M. Keefer, *ibid.*, **81**, 4218 (1959).
- (5) R. M. Keefer and L. J. Andrews, *ibid.*, **81**, 5329 (1959).
- (6) L. J. Andrews and R. M. Keefer, *ibid.*, **82**, 3059 (1960).
- (7) R. M. Keefer and L. J. Andrews, *ibid.*, **79**, 4348 (1957).
- (8) R. M. Keefer and L. J. Andrews, *ibid.*, **82**, 4547 (1960).
- (9) L. J. Andrews and R. M. Keefer, *ibid.*, **82**, 5823 (1960).
- (10) R. M. Keefer and L. J. Andrews, *ibid.*, **83**, 376 (1961).
- (11) J. L. Cotter, L. J. Andrews, and R. M. Keefer, *ibid.*, **84**, 793 (1962).
- (12) R. W. Taft, Jr., *ibid.*, **79**, 1045 (1957).
- (13) R. W. Taft, Jr., S. Ehrenson, I. C. Lewis, and R. E. Glick, *ibid.*, **81**, 5352 (1959).
- (14) R. W. Taft, Jr., E. Price, I. R. Fox, I. C. Lewis, K. K. Andersen, and G. T. Davis, *ibid.*, **85**, 709 (1963).
- (15) R. W. Taft, Jr., E. Price, I. R. Fox, I. C. Lewis, K. K. Andersen, and G. T. Davis, *ibid.*, **85**, 3146 (1963).
- (16) R. W. Taft, Jr., *J. Phys. Chem.*, **65**, 1805 (1960).