

allylic palladium acetate–ligand(s) systems are being pursued with a view to elucidating the nature and reactivity of such systems in catalytic processes.

John Powell

Lash Miller Chemical Laboratories, University of Toronto  
Toronto 5, Ontario, Canada

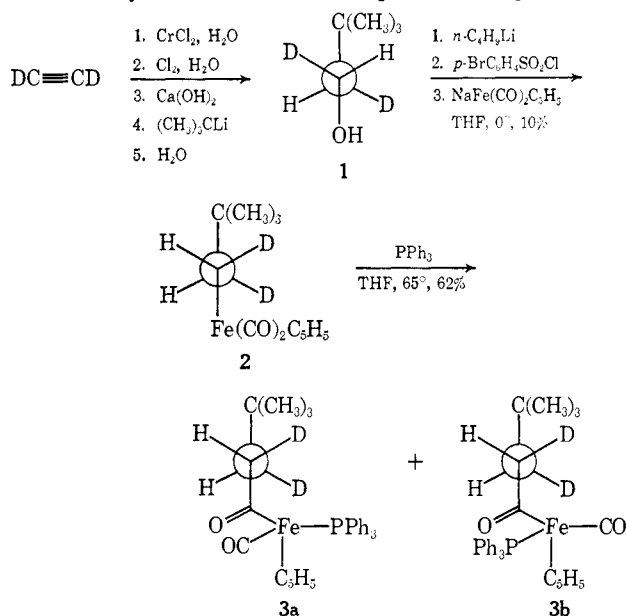
Received April 17, 1969

### Reaction of *threo*-(CH<sub>3</sub>)<sub>3</sub>CCHDCHDFe(CO)<sub>2</sub>-π-C<sub>5</sub>H<sub>5</sub> with Triphenylphosphine<sup>1</sup>

Sir:

The present understanding of the mechanism of the hydroformylation and related carbonylation reactions is based in part on studies of stereochemistry around the metal atom during the steps in which the initially formed alkylmetallic intermediates are converted to acylmetallic compounds.<sup>2</sup> Information concerning the stereochemistry at *carbon* during typical carbonylation reactions is clearly required for a complete description of the mechanisms of these reactions, but has not been reported.<sup>3</sup> We wish to describe the synthesis of π-cyclopentadienyl-dicarbonyliron *threo*-3,3-dimethylbutyl-1,2-*d*<sub>2</sub> (**2**) and evidence establishing that its reaction with triphenylphosphine to yield π-cyclopentadienylcarbonyltriphenylphosphineiron *threo*-4,4-dimethylpentanoyl-2,3-*d*<sub>2</sub> (**3**) proceeds with *retention* of configuration at carbon.

#### Scheme I. Synthesis of Deuterated Organoiron Compounds<sup>a</sup>



(1) Supported in part by the National Science Foundation, Grant GP-7266.

(2) (a) K. Noack and F. Calderazzo, *J. Organometal. Chem.*, **10**, 101 (1967); (b) R. F. Heck, *Advan. Organometal. Chem.*, **4**, 243 (1966); (c) R. F. Heck, *Accounts Chem. Res.*, **2**, 10 (1969); (d) K. Noack, M. Ruch, and F. Calderazzo, *Inorg. Chem.*, **7**, 345 (1968); (e) P. K. Maples and C. S. Kraihanzel, *J. Amer. Chem. Soc.*, **90**, 6645 (1968), and references in each. The recent demonstration that conversion of pentacarbonylmanganese methyl to pentacarbonylmanganese acetyl takes place by migration of the methyl group from manganese to an adjacent carbon monoxide ligand rather than by insertion of carbon monoxide into the carbon–manganese bond is of particular pertinence to discussions of the mechanism of carbonylation.<sup>2a</sup>

(3) The decarbonylation of optically active PhCH<sub>2</sub>CH(CH<sub>3</sub>)COMn(CO)<sub>5</sub> occurs with retention of the *sign* of rotation: F. Calderazzo and K. Noack, *Coord. Chem. Rev.*, **1**, 118 (1966).

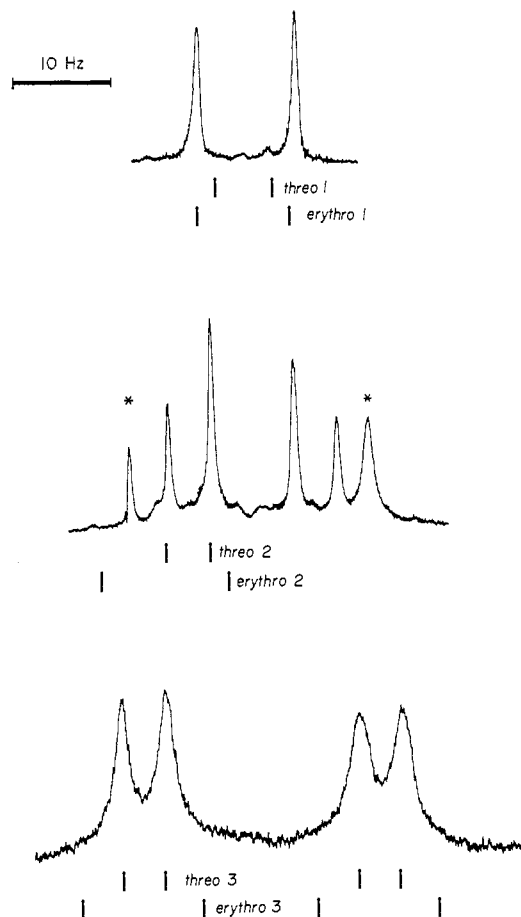


Figure 1. Deuterium-decoupled 100-MHz nmr spectra of the  $-CHDOH$  proton of **1**, the  $-CHDCHD-$  protons of **2**, and the  $-CHDCHD-$  protons of **3**. The peaks marked with an asterisk in the spectrum of **2** are due to impurities. For comparison the positions of the lines characterizing the *threo* and *erythro* diastereomers of **1**, **2**, and **3** are given below the traces; these frequencies were calculated on the basis of coupling constants obtained by analysis of the spectra of the nondeuterated analogs of these compounds.

The synthesis outlined in Scheme I was used to convert acetylene-*d*<sub>2</sub> to 3,3-dimethylbutan-1-ol-1,2-*d*<sub>2</sub> (**1**).<sup>4</sup> The deuterium-decoupled 100-MHz nmr spectrum of the *CHDCHD* protons of **1** is an AX pattern with  $\delta_A$  3.38,  $\delta_X$  1.23, and  $J = 10.0$  Hz (Figure 1). The nmr spectra of *erythro* and *threo* diastereomers of **1** are easily distinguishable on the basis of their characteristic vicinal coupling constants:  $J_{erythro} = 9.5$  and  $J_{threo} = 5.8$  Hz.<sup>5</sup> The magnitude of the coupling constant observed in the nmr spectrum of **1** confirms the *erythro* configuration expected from the method of synthesis; the absence of observable peaks in this spectrum attributable to the *threo* diastereomer indicates that the *erythro* diastereomer must constitute >95% of the 3,3-dimethylbutan-1-ol-*d*<sub>2</sub> produced.

(4) This synthesis is based on the preparation of *trans*-1,2-dideuterioethylene oxide reported by C. C. Price and R. Spector, *J. Amer. Chem. Soc.*, **88**, 4171 (1966).

(5) G. M. Whitesides, J. P. Sevenair, and R. W. Goetz, *ibid.*, **89**, 1135 (1967). The coupling constants  $J_{erythro}$  and  $J_{threo}$  are identical with the vicinal coupling constants  $J$  and  $J'$  obtained on analysis of the AA'XX' spectrum of 3,3-dimethylbutan-1-ol-*d*<sub>2</sub>. The small difference between the magnitude of the observed coupling constant for **1** and  $J_{erythro}$  obtained from the AA'XX' analysis probably reflects a solvent effect on the free-energy difference between the *gauche* and *trans* conformers of this alcohol.

Compound **1** was converted to *erythro*-3,3-dimethylbutyl-1,2- $d_2$ -*p*-bromobenzenesulfonate ( $J = 8.6$  Hz), and thence to **2** by reaction with  $\text{Na}[\text{Fe}(\text{CO})_2\text{C}_5\text{H}_5]$ . The nmr spectrum of the *CHDCHD* region of **2** consisted of a *single* AB quartet centered at  $\delta$  1.38, with  $\Delta\nu = 0.122$  ppm and  $J = 4.4$  Hz (Figure 1); the infrared spectrum of **2** in the carbonyl stretching region consisted of bands at 2005 and 1955  $\text{cm}^{-1}$ . An independent analysis of the nmr spectrum of **2-d**<sub>6</sub> established that the *threo* and *erythro* diastereomers of **2** are characterized by vicinal coupling constants  $J_{\text{erythro}} = 13.1$  and  $J_{\text{threo}} = 4.5$  Hz. Thus, transformation of **1** to **2** takes place with *inversion* of configuration.<sup>6</sup> Within the limits of detection of our experiment, no (<5%) *erythro* diastereomer is produced in this reaction.

It is worthwhile pointing out that this stereochemical result is of considerable interest in its own right. It provides the first direct evidence that nucleophilic displacement on an alkyl carbon atom by a metalate anion proceeds with inversion of configuration at carbon.<sup>7</sup> Further, the observation that no detectable loss in stereochemistry was observed in **2** on standing for >12 hr at 30° provides an indication of the configurational stability to be expected for this class of carbon-transition metal  $\sigma$  bonds.

Reaction of **2** with triphenylphosphine in THF followed by unexceptional work-up gave **3** as a yellow solid, mp 143° dec. The deuterium-decoupled nmr spectrum of the compound consists of two, equally intense, AX patterns arising from the two pairs of diastereomers represented by **3a** and **3b**.<sup>8</sup> The *-CHD-CO-* resonances of **3** occurred at  $\delta$  2.72 and 2.46; both patterns were characterized by the same vicinal coupling constant,  $J = 4.4$  Hz (Figure 1). The infrared spectrum of **3** in the carbonyl stretching region consisted of bands at 1925 and 1615  $\text{cm}^{-1}$ . *Anal.* Calcd for  $\text{C}_{31}\text{H}_{33}\text{O}_2\text{FeP}$ : C, 71.00; H, 6.34. Found: C, 70.55; H, 6.43. Comparison of the observed coupling constant with those estimated for the *threo* ( $J = 4.2$  Hz) and *erythro* ( $J = 12.5$  Hz) diastereomers of **3** from analysis of the ABXY spectrum of **3-d**<sub>0</sub> establishes that conversion of the alkyl-iron bond of **2** to the corresponding carbon-carbon bond of **3** has taken place with complete (>95%) *retention* of configuration.

Related studies of the stereochemistry of other reactions occurring at carbon-transition metal  $\sigma$  bonds will be reported later.

**Acknowledgment.** We gratefully acknowledge the experimental assistance of Dr. J. Fleming and Mr. J. Simms.

(6) A similar technique has been used to determine the stereochemistry of solvolysis of 2-phenylethyl tosylate: R. J. Jablonski and E. I. Snyder, *Tetrahedron Letters*, 1103 (1968); see also R. G. Weiss and E. I. Snyder, *Chem. Commun.*, 1358 (1968).

(7) For recent discussions of the nucleophilic reactivity of metal atoms toward saturated carbon, see R. E. Dessy, R. L. Pohl, and R. B. King, *J. Amer. Chem. Soc.*, 88, 5121 (1966); J. P. Birk, J. Halpern, and A. L. Pickard, *ibid.*, 90, 4491 (1968); J. P. Collman, *Accounts Chem. Res.*, 1, 136 (1968).

(8) A related proton diastereotropism due to chirality at iron has been observed for  $\text{C}_6\text{H}_5\text{CH}_2\text{Fe}(\text{CO})(\text{PPh}_3)(\text{C}_5\text{H}_5)$ : J. W. Faller and A. S. Anderson, *J. Amer. Chem. Soc.*, 91, 1550 (1969).

(9) National Institutes of Health Predoctoral Fellow, 1967-1969.

George M. Whitesides, David J. Boschetto<sup>9</sup>

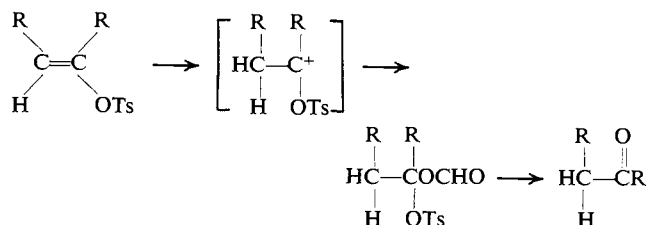
Department of Chemistry  
Massachusetts Institute of Technology  
Cambridge, Massachusetts 02139

Received April 16, 1969

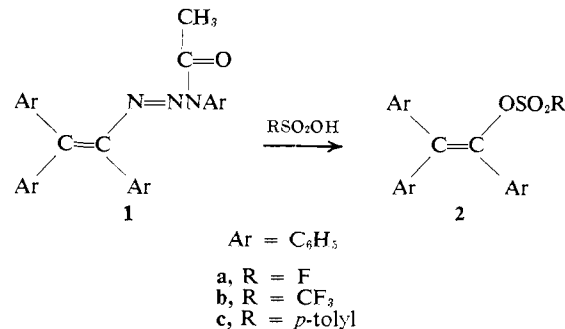
## Solvolysis of Sulfonic Acid Esters of Triphenylvinyl Alcohol by a Heterolytic Mechanism

Sir:

Although vinyl cations have finally become acceptable members of the "reactive intermediate" community,<sup>1</sup> their generation by heterolytic cleavage of a group attached directly to a double bond has been limited to vinyl diazonium ions<sup>2,3</sup> and vinyl halides.<sup>4-6</sup> To date, one mechanistic study of the solvolysis of vinyl sulfonic acid esters<sup>7,8</sup> has been reported. Although the reaction led to products that could be explained by a simple  $\text{S}_{\text{N}}1$  mechanism, the authors very elegantly showed that their products arose by an addition-elimination path.



At this time, we would like to present preliminary evidence for a simple heterolytic cleavage mechanism for the solvolysis of the following vinyl sulfonates: triphenylvinyl fluorosulfonate, triphenylvinyl trifluoromethanesulfonate, and triphenylvinyl tosylate.



All sulfonates were synthesized by allowing the acyltriazeno **1**<sup>9,10</sup> to react with the appropriate sulfonic acid<sup>11</sup> in methylene chloride at  $-50^\circ$ .

(1) H. G. Richey and J. M. Richey in "Carbonium Ions," Vol. II, G. A. Olah and P. von R. Schleyer, Ed., Interscience Publishers, New York, N. Y., in press. The authors express appreciation to Professor Richey for furnishing us with a preprint of his manuscript.

(2) M. S. Newman and A. E. Weinberg, *J. Am. Chem. Soc.*, 78, 4654 (1956); M. S. Newman and A. Kutner, *ibid.*, 73, 4199 (1951); D. Y. Curtin, J. A. Kampmeier, and B. R. O'Connor, *ibid.*, 87, 863 (1965); D. Y. Curtin, J. A. Kampmeier, and M. L. Farmer, *ibid.*, 87, 874 (1965); A. C. Day and M. C. Whiting, *J. Chem. Soc., B*, 991 (1967).

(3) W. M. Jones and F. W. Miller, *J. Am. Chem. Soc.*, 89, 1960 (1967).

(4) C. A. Grob and G. Cseh, *Helv. Chim. Acta*, 47, 194 (1964).

(5) L. L. Miller and D. A. Kaufman, *J. Am. Chem. Soc.*, 90, 7282 (1968).

(6) S. J. Huang and M. V. Lessard, *ibid.*, 90, 2432 (1968).

(7) P. E. Peterson and J. M. Indelicato, *ibid.*, 90, 6515 (1968).

(8) Very recently, G. Capozzi, G. Melloni, G. Medona, and M. Piscitelli (*Tetrahedron Letters*, 4039 (1968)) have reported that 1,2-diaryl-2-arylmethylmercaptovinyl 2,4,6-trinitrobenzenesulfonates undergo reactions suggestive of a vinyl cation mechanism. If these reactions do involve heterolysis of the sulfonate from a vinyl carbon, their rates when compared with those reported in this note would point to substantial participation of the neighboring sulfur.

(9) Synthesized by acylating the triazene<sup>9</sup> with acetyl chloride.

(10) All new compounds reported in this note showed satisfactory analyses and spectral properties agreed with structure assignments.

(11) Conversion of the acyltriazeno to the sulfonic acid ester most certainly also involves formation of a vinyl cation as evidenced by the observation that the 2,2-di-*p*-tolyl-substituted triarylvinyltriazene gives rearranged products when treated with fluorosulfuric acid.