

**Table II.** Association Constants and Thermodynamic Properties of Tetracyanoethylene Complexes in Cyclohexane

Donor	Temp, °C	$K_x$	$\epsilon_{\max}^c$	
Ferrocene <sup>a</sup>	30	30.0	474	$\Delta H_f = -3800$ cal/mole
	40	25.5	474	$\Delta S_f = -5.5$ eu
	50	21.0	469	
	60	17.5	474	
	70	15.0	479	
1,1'-Dimethyl-ferrocene <sup>b</sup>	30	52.0	462	$\Delta H_f = -4300$ cal/mole
	40	39.5	475	$\Delta S_f = -6.4$ eu
	50	31.9	472	
	60	26.5	464	
	70	21.5	472	

<sup>a</sup> Average of two separate determinations. <sup>b</sup> Average of three separate determinations. <sup>c</sup>  $\lambda_{\max}$  for ferrocene-TCNE 1000 m $\mu$ , and for 1,1'-dimethylferrocene-TCNE 1025 m $\mu$ .

in which steric interactions between the substituted donor and the acceptor component are minimized, than by structure 2.

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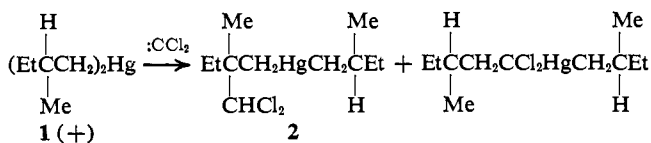
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### Insertion of Dichlorocarbene into a Carbon-Hydrogen Bond with Net Inversion of Configuration

Sir:

Recent reports have indicated an unusual and very specific preference for dichlorocarbene insertion into carbon-hydrogen bonds located  $\beta$  to either silicon,<sup>1</sup> tin,<sup>1</sup> or mercury.<sup>2</sup> The stereochemistry of this reaction is of particular interest with regard to the evaluation of possible mechanistic pathways.

(+)-Bis((*S*)-2-methylbutyl)mercury (1),  $[\alpha]^{27.5D} + 8.01^\circ$  (neat)<sup>3</sup> was prepared from 98% optically pure (*S*)-(-)-2-methyl-1-butanol (Aldrich) via the intermediate chloride. The configuration of 1 has been well



established by simple chemical transformations which allow a direct correlation with (-)-isoleucine,<sup>6,7</sup> the absolute configuration of which has been determined by X-ray diffraction studies.<sup>8</sup> Treatment of 1 with ethyl trichloroacetate and excess sodium methoxide in pentane resulted in the formation of the carbon-hydro-

(1) D. Seyferth and S. S. Washburne, *J. Organometal. Chem.* (Amsterdam), **5**, 389 (1966).

(2) J. A. Landgrebe and R. D. Mathis, *J. Am. Chem. Soc.*, **88**, 3545 (1966).

(3) Values of  $+7.65$  ( $\leq 95\%$  optical purity)<sup>4</sup> and  $+7.82^\circ$  have been previously reported.

(4) S. Murahashi, S. Nuzakura, and S. Takeuchi, *Bull. Chem. Soc. Japan*, **33**, 658 (1966).

(5) G. Frankel and D. T. Dix, *J. Am. Chem. Soc.*, **88**, 979 (1966).

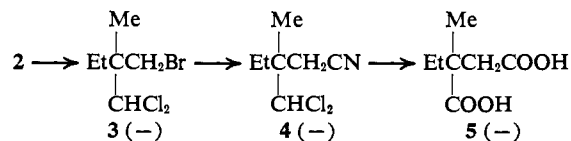
(6) W. S. Foues, *ibid.*, **76**, 1377 (1954).

(7) E. J. Badin and E. Pacsu, *ibid.*, **67**, 1352 (1945).

(8) J. Trommel and J. M. Bijvoet, *Acta Cryst.*, **7**, 703 (1954).

gen insertion product 2 and the corresponding carbon-mercury bond insertion product<sup>2</sup> in a ratio of  $\sim 93:7$ .

Purified 2 was then cleaved with bromine in carbon tetrachloride to give a mixture of (-)-1,1-dichloro-2-(bromomethyl)-2-methylbutane (3),  $[\alpha]^{25D} -1.13^\circ$



(CHCl<sub>3</sub>), and (+)-1-bromo-2-methylbutane. Trihalide 3 was converted to nitrile 4,  $[\alpha]^{25D} -1.61^\circ$  (CHCl<sub>3</sub>), in low yield by treatment with sodium cyanide in dimethyl sulfoxide (50–90°), and the nitrile was hydrolyzed and oxidized with a basic aqueous silver oxide suspension to give (*S*)-(-)- $\alpha$ -methyl- $\alpha$ -ethylsuccinic acid (5),  $[\alpha]^{25D} -6.41^\circ$  (CHCl<sub>3</sub>).<sup>9,10</sup> The method of quasi-racemates has been used to establish the relative configuration of 5 with that of each of a series of  $\alpha$ -monosubstituted and  $\alpha$ -disubstituted succinic acids,<sup>12,13</sup> including  $\alpha$ -methylsuccinic acid, the absolute configuration of which was recently established by X-ray diffraction techniques.<sup>14</sup>

The results clearly indicate that the insertion of dichlorocarbene into the  $\beta$ -carbon-hydrogen bond of 1 has occurred with *net inversion of configuration*, an unprecedented stereochemical result for a divalent carbon insertion process.<sup>2</sup> One can therefore rule out any mechanistic path which requires a direct attack of the divalent carbon atom on the carbon-hydrogen bonding electrons or a direct transfer of dichlorocarbene into the carbon-hydrogen bond *via* an ylide intermediate, as has been postulated for the analogous reaction in the tetraalkylsilane series.<sup>1</sup>

(9) Average of values for two independent conversions of 3 to 5 with an average deviation of  $\pm 0.4^\circ$ .

(10) The rotation of the resolved acid has been reported as  $[\alpha]^{25D} -5.92^\circ$  (CHCl<sub>3</sub>).<sup>11</sup>

(11) S. Stallberg-Stenhagen, *Arkiv Kemi*, **3**, 273 (1951).

(12) J. Porath, *ibid.*, **3**, 163 (1951).

(13)  $\alpha$ -Substituted succinic acids of the same configuration were shown to have the same sign of rotation.<sup>12</sup>

(14) A. T. McPhail, G. A. Sim, J. D. M. Asher, J. M. Robertson, and J. V. Silverton, *J. Chem. Soc., Phys. Org. Sect.*, 18 (1966).

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### Nuclear Magnetic Resonance of Phosphorus Compounds. III. Phosphorus-31 Overhauser Effects and Utilization of Simultaneous Observation of the Spectra of Two Types of Nuclei in Double-Resonance Experiments<sup>1,2</sup>

Sir:

In homonuclear magnetic double-resonance experiments it is possible by irradiation of one or more transitions to achieve departures from thermal spin distributions with concomitant redistribution of spectral line intensities.<sup>3</sup> Although observed signal-intensity

(1) This paper presents the results of one phase of research carried out at the Jet Propulsion Laboratory, California Institute of Technology, under Contract No. NAS7-100, sponsored by the National Aeronautics and Space Administration.

(2) Previous paper in this series: S. L. Manatt, G. L. Juvinal, R. I. Wagner, and D. D. Elleman, *J. Am. Chem. Soc.*, **88**, 2689 (1966).