The following procedure for the conversion of cyclohexanone to 2-(cyclopentylmethyl)cyclohexanone is representative. A dry 1-l. flask equipped with a water condenser, septum inlet, pressure-equalizing dropping funnel, and magnetic stirrer was flushed with nitrogen and then maintained under a static pressure of the gas. The preparation of tricyclopentylborane was achieved by the dropwise addition of 100 ml of a 2 *M* solution of borane (0.2 mol) in tetrahydrofuran to the flask containing a solution of 53.2 ml (0.06 mol) of cyclopentene in 100 ml of tetrahydrofuran. The solution was stirred for 1 hr at room temperature, and then 100 ml of a water solution containing 19.2 g (0.1 mol) of 2-(dimethylaminomethyl)cyclohexanone hydrochloride was added. Quaternization was achieved by adding 14 ml (0.22 mol) of methyl iodide, followed by the addition of 33.3 ml of 3 *M* solution of potassium carbonate (0.1 mol). The reaction mixture was stirred at room temperature for 24 hr to complete the reaction. *n*-Octane was added as an internal standard. Glpc analysis indicated a 90% yield. The tetrahydrofuran layer was separated and washed once with water saturated with sodium chloride. The residual organoboranes were oxidized[6] by the addition of 66 ml of 3 *M* sodium hydroxide followed by dropwise addition of 55 ml of 30% hydrogen peroxide, while the temperature was maintained under 40°. Distillation at reduced pressure gave 16 g (85%) of 2-(cyclopentylmethyl)cyclohexanone, bp 78° (0.5 mm).

Many types of organic molecules with reactive α positions are readily converted into Mannich bases.[4,5] This suggests the possibility that the present reaction may make it possible to achieve the alkylation of many other such derivatives *via* organoboranes. We continue to explore these developments.

[6] This conversion of the dialkylborinic acid to boric acid and the alcohols greatly simplified the distillation to isolate the product.

[7] National Science Foundation Postdoctorate Fellow at Purdue University, 1967–1968.

[8] Graduate research assistant on Grant GM 10937 from the National Institutes of Health.

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Received April 3, 1968

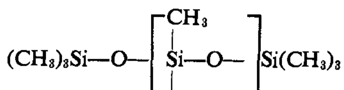
Far-Ultraviolet Optical Activity of Crystals in Mulls. I. Cystine[1]

Sir:

In studying the correlation of the screw sense of aliphatic disulfides with the signs of their circular dichroic bands, we have measured the untraviolet circular dichroism (CD) spectra of several forms of crystalline cystine to 190 mμ.

Several papers have reported ORD and CD spectra of cystine and derivatives of cystine in solution,[2–4] but the interpretation of results in terms of inherent or induced asymmetry has been hindered by uncertainty concerning rotational equilibration about the disulfide bond. A recent report by Carmack and Neubert on disulfides stereospecifically constrained within rings has shown that the longest wavelength CD band was oppositely signed in rings having opposite disulfide handedness.[5] The crystalline materials were examined because X-ray diffraction studies show that, while hexagonal L-cystine crystallizes with the disulfide as a left-handed screw,[6,7] the dihydrochloride has opposite chirality.[8,9] Corresponding bands due to inherent asymmetry of the two materials should, therefore, have opposite signs.

The method requires that samples be suspended in a chemically inert medium having little or no ultraviolet absorption and no optical activity of its own. These requirements are met by a silicon polyether called SE-30,[10] which has the formula



$$(CH_3)_3Si{-}O{-}\left[\begin{array}{c} CH_3 \\ | \\ Si{-}O{-} \\ | \\ CH_3 \end{array}\right]_n Si(CH_3)_3$$

The technique involves placing a small amount (50–75 mg) of mulling matrix on a glass surface; an overturned beaker is suitable. If necessary, the material is pressed flat with a spatula, and the sample of crystals (2–10 mg) is spread onto it. The mixture is then alternately rolled and kneaded with the spatula until a uniform distribution of crystals is obtained. It is next rolled into a ball if possible and placed at the center of the outer window of an involuted cylindrical cell. A second cell is now pressed onto the first, squeezing the mixture out into a thin, flat layer between them. The whole assembly is finally placed in the appropriate instrument.

Microscopic examination showed that the crystals were often oriented in a nonrandom manner. Linear dichroism artifacts arising from this were tested for by pulverizing the samples with an agate mortar and pestle; the very small crystals that resulted were oriented more randomly when made into mulls. These mulls, however, scattered so much of the input light that measurements at short wavelengths became impossible. The scattering was reduced by mixing 60% spectroanalyzed dodecane (n-$C_{12}H_{26}$) with 40% SE-30. The mixture is prepared by dissolving 0.4 g of silicone in spectroanalyzed methylene chloride or spectroanalyzed chloroform, pipetting in 0.6 g of dodecane, and, after mixing, removing solvent in a stream of dry nitrogen. When as much of it has been removed as seems possible by this method, the mixture is evacuated at room temperature for about 5 min. Care must be taken to avoid loss of dodecane through excessive exposure to low pressure. Solvent removal is considered complete when no odor of it is detected after brief, gentle warming followed by a few minutes of standing.

The materials whose spectra are reported in Figures 1 and 2 are hexagonal plates of D- and L-cystine, L-cystine dihydrochloride, which crystallizes as long white

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[1] This work was supported in part by grants from the U. S. Public Health Service (Research Grant No. GM 10576) and from the National Science Foundation (Research Grant No. GB 7128).

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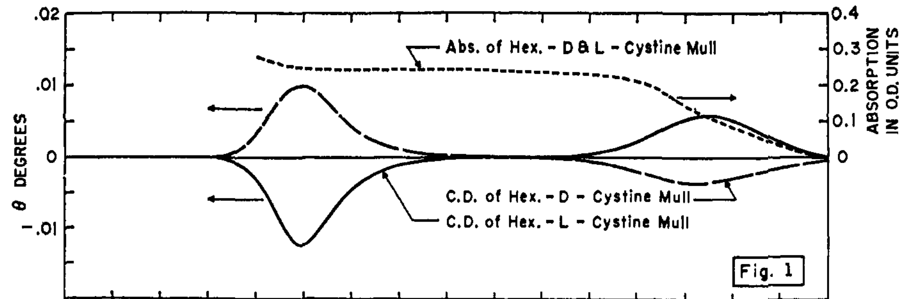
[10] The substance is marketed as a stationary phase in gas chromatography by the Pierce Chemical Co., Rockford, Ill.



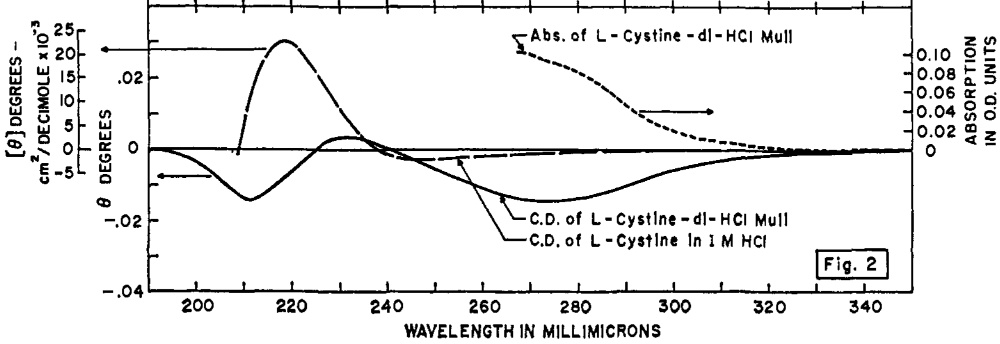


Figure 1. CD of hexagonal L-cystine mull: whole crystals (———). CD of hexagonal D-cystine mull: whole crystals (— — —). Absorption of hexagonal D- and L-cystine mulls: whole crystals (- - - - - - - - -). Sample is that used for CD of hexagonal L material. Although the matrix is everywhere optically inactive, it has significant absorption below 230 mμ. Absorption spectra at shorter wavelengths are, accordingly, not shown.

Figure 2. CD of L-cystine dihydrochloride mull: pulverized crystals (———). CD of L-cystine in 1 *M* HCl (— — —). Absorption of L-cystine dihydrochloride mull: pulverized crystals (- - - - - - - - -). Same sample as that used for CD spectrum. Data corrected for light scattering according to Leach and Scheraga.[13] Because the scattering correction is excessively large below 265 mμ, the absorption data below that wavelength are unreliable and are therefore not shown.

needles, and DL-cystine dihydrochloride, which forms shorter, more blunt needles. The hexagonal materials were obtained from Mann Research Laboratories, Inc., as was amorphous DL-cystine. The former were each recrystallized twice,[7] and the dihydrochloride of the L form was prepared from hexagonal material.[11] DL-Cystine is difficult to crystallize, so it was converted to its dihydrochloride,[12] and it, too, was recrystallized twice.

As a check for artifacts, each sample was scanned, the cell assembly turned around so that the light passed through it in the opposite direction, and the sample scanned again. If the two scans did not agree, the sample was remulled and the scanning repeated. The presence of bubbles led to spectra that were not reproducible in this way, but pulverization had no effect. Reproducible spectra, however, were harder to obtain from ground samples, in which the detection of bubbles and their removal by squeezing was more difficult. Nevertheless, a comparison between large crystals and ground samples should always be made over the mutually accessible spectral range before trusting measurements on the former. In the samples whose spectra are reported here, the L- and DL-dihydrochloride crystals were pulverized, while those of the hexagonal forms were not.

In addition to the above tests, the sample in some measurements was rotated about the axis of the incoming light by approximately 120°. Spectra that were unchanged by the tests described above were also unchanged in this way.

The dichroic spectra of hexagonal D- and L-cystine are opposite to one another. Moreover, samples of the racemic DL-dihydrochloride having up to twice the absorbance of the optically active samples had no optical activity. Because the latter samples were more concentrated than the optically active ones, their CD spectra were noisier. The maximum deviation from the base line was 3–4 mdeg and was less at most wavelengths. Repeated scanning of the same sample and scans of several different samples made it clear that the material was optically inactive.

The dichroic spectra of hexagonal L-cystine and the L-dihydrochloride, however, bear little resemblance to one another. In the region from 260 to 300 mμ, where the latter shows substantial negative dichroism, the former exhibits no bands. Moreover, the hexagonal material shows significant absorption in this region, indicating that transitions occur which generate feeble optical activity or none. Neither solid-state spectrum resembles that of L-cystine in solution in 1 *M* HCl, and the spectra of such solutions do not depend on the form of the crystals used in preparation of the solutions. It is worth noting that bands at wavelengths greater than 300 mμ have been observed previously only for cyclic disulfides and not, as is the case here, for open-chain compounds.

All CD measurements shown here were made on a Cary 60 recording spectropolarimeter equipped with a Cary CD attachment. Before the Cary instrument became available, however, spectra were taken on a modified Jouan Dichrograph, which has a somewhat longer sample-to-detector distance but which could not pene-

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(12) J. Greenstein and M. Winitz, ref 11, p 1900.

(13) S. J. Leach and H. A. Scheraga, *J. Amer. Chem. Soc.*, **82**, 4790 (1960).

trate below 220 mμ with the samples used. The data so obtained were identical with those produced by the newer machine at the same wavelengths. Depolarization due to scattering would not, therefore, seem to be a serious problem in this case. Absorption measurements were made on a Cary 15 recording spectrophotometer.

The interpretation of these data requires an analysis of the crystal structures and of relevant solution measurements. This work is in progress and will be reported in the near future.

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Received April 6, 1968

Ligand Exchange and Isomerization in Tris(triphenylphosphine)chlororhodium(I)

Sir:

Osborn, Jardine, Young, and Wilkinson[1,2] have reported that $Rh\{P(C_6H_5)\}_3Cl$ and its Br and I analogs effectively catalyze the homogeneous hydrogenation of olefins. On the basis of molecular weight data they suggested that these complexes are highly dissociated in solution to $Rh\{P(C_6H_5)_3\}_2X + P(C_6H_5)_3$ and considered the bisphosphine complex to be the catalytically active species. We therefore included these compounds as part of a more extensive study of the mechanisms of ligand exchange of phosphine complexes with the expectation of finding a dissociative (first-order) mechanism for exchange rather than the associative (second-order) mechanism previously demonstrated for both square-planar[3] and tetrahedral[4] d^8 complexes. We do indeed find a dissociative mechanism for ligand exchange but have also obtained some evidence suggesting that the dissociation is a two-step process and wish to suggest that the existence of such a mechanism has relevance to the problem of understanding why these complexes are catalytically active.

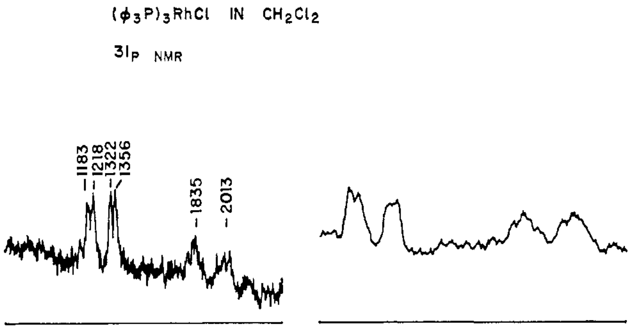

Figure 1. ^{31}P nmr spectra at 40.5 Mc/sec of tris(triphenylphosphine)rhodium chloride in methylene chloride at +30° (reference, 85% H_3PO_4).

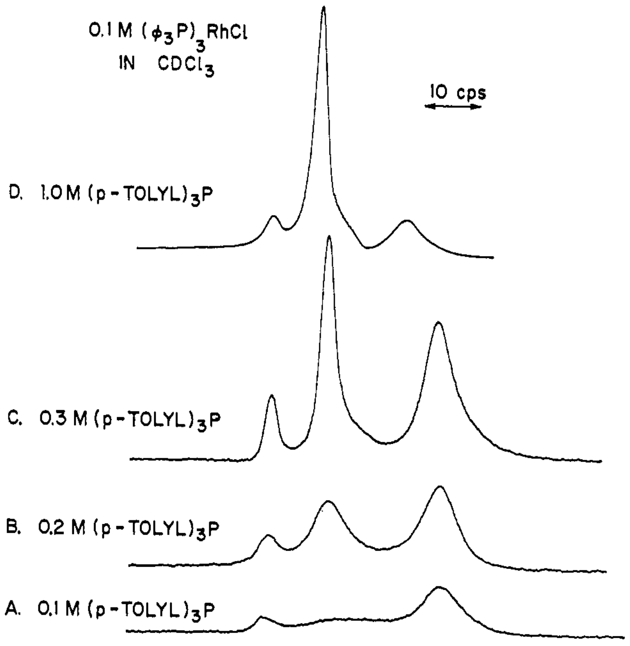

Figure 2. 220-Mc/sec ^1H nmr spectra of CH_3 resonance of 0.1 *M* tris(triphenylphosphine)rhodium chloride and tri-*p*-tolylphosphine in $CDCl_3$ at +23°.

The ^{31}P nmr spectrum of $Rh\{P(C_6H_5)_3\}Cl$ (Figure 1) has the expected pattern with different chemical shifts for *cis* and *trans* phosphines, each split by ^{103}Rh and by ^{31}P. Free triphenylphosphine cannot be detected. Addition of triphenylphosphine gives a resonance at the expected frequency but causes no other change. Therefore, the complex does not dissociate extensively at these concentrations (>0.1 *M*) and ligand exchange is slow by the nmr criterion. Additional peaks which appear after about 30 min of standing are ascribed to the dimer reported by Wilkinson.[1] These conclusions have been verified by examination of the H spectra at 220 Mc/sec. The lines are broad at room temperature, but the spectrum is analyzable at −35°. Again no resonance can be ascribed to the free ligand (the most intense line of which does not coincide with the complex lines) and addition of free ligand gives an additional line in the expected place. These observations set a lower limit for the lifetimes of free and complexed ligand of $\sim 10^{-2}$ sec and an upper limit for the degree of dissociation. These nmr experiments have been extended to concentrations as low as 10^{-3} *M* by using a computer of average transients (CAT). Below 10^{-2} *M* there is some evidence for free ligand, and additional resonance lines appear. However, the principal new lines have been identified as triphenylphosphine oxide which must arise from the presence of adventitious oxygen. It is very difficult to eliminate these lines at low concentrations even though the solvents were carefully degassed and all manipulations carried out in a drybox. At the lowest concentration (10^{-3} *M*) there are additional lines not due to triphenylphosphine oxide. We therefore deduce that there is some dissociation of the complex but that contrary to the molecular weight evidence the degree of dissociation is small (<5%) at concentrations above 10^{-2} *M*. Spectra obtained with the addition of halide ions provide no evidence for ionic dissociation.

A lower limit to the rate can be obtained by studying the exchange with tri-*p*-tolylphosphine and examining

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