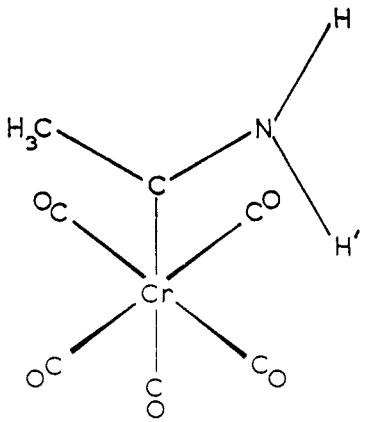
pentacarbonyl,[1] an immediate color change occurs. Upon removal of the benzene by distillation under reduced pressure, pale yellow crystals form which can be recrystallized from a 9:1 hexane–ether mixture at −95°. The diamagnetic crystals melt at 76–77°. They are soluble in polar and nonpolar organic solvents and insoluble in water. In the absence of oxygen, the water-saturated ether solutions are remarkably stable. Total elemental analysis and molecular weight determination in benzene are in good agreement with the formation of $Cr(CO)_5CCH_3(NH_2)$. Gas chromatographic analysis of the solvent shows that methanol was the only other product.

Anal. Calcd for $C_7H_5CrNO_5$: C, 35.76; H, 2.12; Cr, 22.11; N, 5.96; O, 34.0. Found: C, 36.12; H, 2.08; Cr, 22.11; N, 5.91; O, 33.8.

The nmr spectrum of this complex in deuterated acetone exhibits a broad triplet centered at τ −0.25, J_{N-H} = 50 cps, as well as a singlet at τ 7.16 in the area ratio of 2:3, respectively. Upon addition of deuterium oxide, the broad triplet disappears and a band due to hydroxyl protons appears. This observation as well as the broadness of the band, which is due to the nuclear electric quadrupole of the nitrogen atom, suggests that the two hydrogen atoms are attached to the nitrogen atom. The triplet may then arise from the coupling of the nitrogen-14 with the protons attached to it. The singlet is attributed to the three CH_3 protons. This methyl group is not attached to the nitrogen atom; otherwise a multiplet due to spin–spin coupling with the NH_2 group should be observed.[2]

We believe, therefore, that the structure might be as shown below. In this structure the $Cr-CCH_3(NH_2)$



atoms define a plane, except for the CH_3 protons. In order to minimize steric interactions between the NH′ hydrogen atom and a *cis*-CO group, the plane might bisect the angle formed by two *cis*-CO groups and the Cr atom. This structure is then similar to that of the phenylmethoxycarbenechromium pentacarbonyl,[3] except that the C_6H_5 and OCH_3 groups have been replaced by the CH_3 and NH_2 groups.

A C_{4v} symmetry of the $Cr(CO)_5$ moiety is consistent with the four infrared CO stretching frequencies (hexane solution) at 2057, 1964, 1949, and 1941 cm^{-1}. Although it is predicted that only three bands should be observed,[4] other $M(CO)_5L$ molecules, where L represents a variety of ligands and M = Cr, Mo, and W, exhibit also four bands.[5,6]

The much slower reaction of $Cr(CO)_5CCH_3(OCH_3)$ with thiophenol yields methylthiophenoxycarbenechromium pentacarbonyl. The dark brown crystals have physical properties that are similar to the methylaminocarbene complex. The compound is monomeric in benzene and melts at 67–68°.

Anal. Calcd for $C_{13}H_8CrO_5S$: C, 47.56; H, 2.46; Cr, 15.84; O, 24.4; S, 9.8. Found: C, 47.62; H, 2.50; Cr, 15.99; O, 24.6; S, 9.2.

The nmr spectrum of this compound in deuteriobenzene exhibits lines at τ 3.10, 3.45, and 7.08 with relative intensities of 3:2:3, respectively. The two bands at τ 3.10 and 3.45 are assigned to the C_6H_5 protons; the line at τ 7.08 is due to the CH_3 protons. Only three CO stretching frequencies (hexane solution) are observed at 2064, 1986, and 1960 cm^{-1}. Both of these observations are consistent with a structure similar to that of $(CO)_5CrCCH_3(NH_2)$ except that an SC_6H_5 group is in the place of the NH_2 group.

The mass spectra of these new carbene complexes show a pattern similar to that of methylmethoxycarbenechromium pentacarbonyl.[7] This is additional proof for their structure. The complexes are therefore formed by replacement of the methoxy group by NH_2 or SC_6H_5 without any other rearrangements.

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(2) We thank Dr. E. Moser for the interpretation of the nmr spectrum.
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(7) We wish to thank Dr. J. Müller for this information in advance of publication and for his helpful discussions.

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The Circular Dichroism of L-Tryptophan by an Improved Dichrograph[1]

Sir:

The circular dichroism (CD) measurements of proteins and polypeptides have revealed the presence of well-defined ellipticity bands in the aromatic absorption region.[2-4] The origins of these bands have been associated with various aromatic amino acid side chains, although the specific information necessary for such correlation is rather limited, especially in those cases which exhibit poor signal-to-noise ratios due to either relatively high absorptivity, or to low rotatory strengths, or to both. Even in cases in which the signal-to-noise

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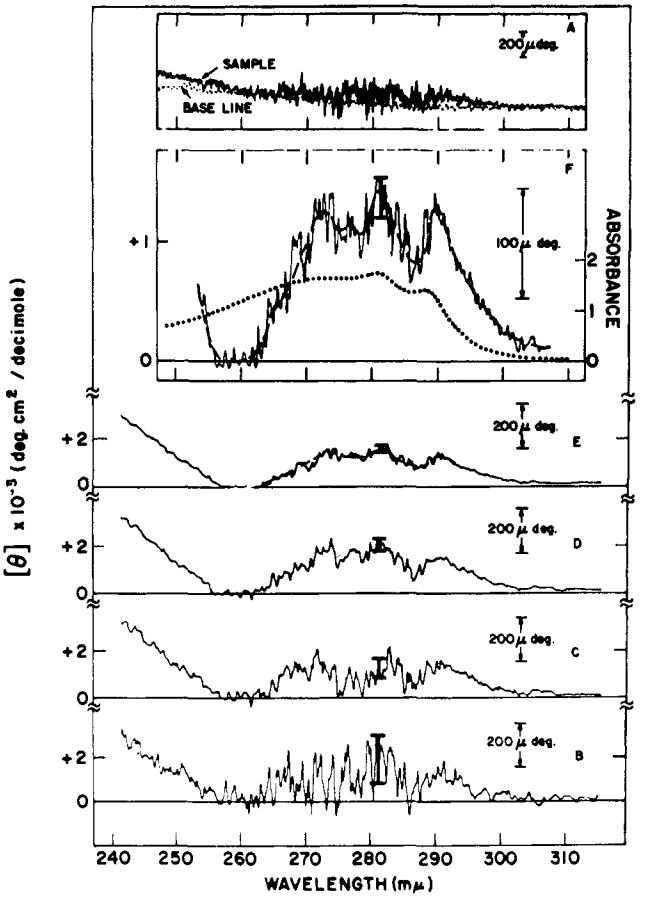

Figure 1. Circular dichroism and absorption spectra of L-tryptophan in H_2O at pH 7.0. Concentration, 7.42 mg/100 ml; 1-cm path length; temperature, 25°. (A) Original recording from the instrument at sensitivity of 0.002°/full scale, gain setting of 4 and scanning speed of 2 mμ/min; (B) readout from the computer after a single scan; (C) readout after four scans; (D) readout after eight scans; (E) readout after 16 scans; (F) 5-fold Y axis expansion of E. ———, Actual CD tracings; ------, electrical mean of the computer output; ·····, absorption spectrum.

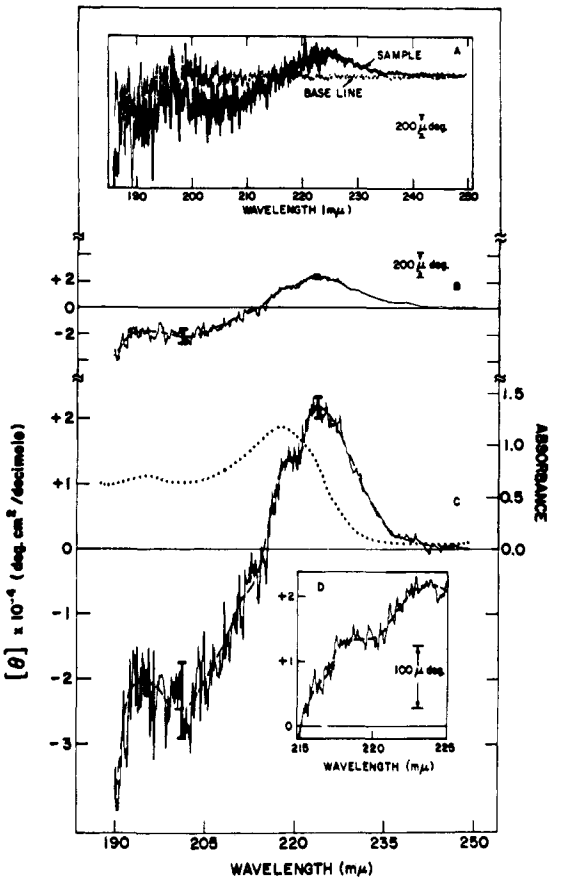

Figure 2. Circular dichroism and absorption spectra of L-tryptophan in H_2O at pH 7.0. Concentration, 7.02 mg/100 ml; 1-mm path length; temperature, 25°. (A) Original recording from the instrument at sensitivity of 0.002°/full scale, gain setting of 4 and scanning speed of 2 mμ/min; (B) readout from the computer after 16 scans; (C) 5-fold Y axis expansion of B; (D) 5-fold Y axis and 2-fold X axis expansion of B. ———, Actual CD tracing; ------, electrical mean of the computer output; ·····, absorption spectrum.

ratios are favorable, such measurements are limited to wavelengths higher than 210 mμ[5,6] because of unfavorable conditions at low wavelengths. Similar difficulties are also encountered during measurements of proteins.

The use of the average transient computer for the analysis of nuclear magnetic resonance spectra[7] and of low-temperature spectra[8] has resulted in marked improvement in signal-to-noise ratio; we have applied the same technique to CD measurements of amino acids and proteins. Details of the modification of the dichrograph and preliminary results of CD spectra of L-tryptophan (Sigma Chemical Co., Lot 75B-1660) in water at pH 7.0, wavelength region 310–190 mμ, are reported.

The Jasco ORD/CD/UV-5 spectropolarimeter was modified by addition of a ten-turn precision potentiometer with the central tap driven by the mechanical servo mechanism of the instrument with a gear ratio of 1:1. A constant potential of 6 v dc was applied to the potentiometer. The input of the average transient computer (Technical Measurement Corp., catalog no. 1024) was connected to the central whipping contact of the potentiometer and the floating ground of the power supply. The position of the potentiometer was adjusted so as to yield 0 v at the central position, which also corresponded to zero deflection on the recorder of the dichrograph. The signal necessary for the triggering of the computer was provided by a mechanical microswitch operative from the drum. The repeated scan of the instrument was carried out manually. The scanning of the sample and of the solvent in the same cell was carried out one after the other with the mode switch of the computer in the position of summation at the time of the sample run and in the position of subtraction for the solvent run, which automatically corrected for background contributions. The readout of the information stored in the memory unit was made on a Sargent multirange recorder. The calibration of the modified instrument was made with *d*-camphorsulfonic acid.

As shown in Figures 1 and 2, both the precision and the sensitivity of the measurements have been improved severalfold. Since the magnitude of the signal increases linearly with the number of scans and the signal-to-noise ratio with the square root of the number of scans,[7] an improvement of at least 3-fold in the signal-to-noise ratio, peak to peak, is thus obtained by 16-fold rerecording. The multirange of the recorder and of the out-

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put from the computer permits the magnification of the tracing to the desired level (Figure 1, F; Figure 2, C and D), which increases the sensitivity of the technique and is necessary for careful evaluation of the position and the magnitude of the ellipticity bands.

The CD spectrum of L-tryptophan in the wavelength region 250–300 mμ consists of at least three positive dichroic bands, centered at 291, 281, and 272 mμ. The positions of these bands are approximately the same as those of the absorption peaks of the indole chromophore, thus suggesting their origin. Below 250 mμ, of the four ellipticity bands, only two seem to reflect their counterparts in the absorption spectrum. The shoulder at about 218 mμ corresponds to the exceedingly strong indole absorption peak at 218 mμ (Figure 2, C), and the negative dichroic band centered at about 200 mμ possibly reflects the carboxyl transition (absorption maximum at 194 mμ). Since there seems to be no directly perceivable absorption band corresponding to the relatively large positive ellipticity peak at about 224 mμ, any comments without further investigations would be presumptive. We are currently investigating the ORD and CD spectra of various amino acids and their derivatives and of peptides containing aromatic amino acids. These and other results will be reported in due course.

The use of the modified technique, as described, results in an improvement of about 3–4-fold in the signal-to-noise ratio and a 4–6-fold decrease in the uncertainty of the absolute value. This, with the scale expansion (Figures 1 and 2), shows that a more than 10–12-fold increase in the sensitivity is readily obtainable by this technique. There is no reason, however, to believe that this represents the limit of the improvement of the data. Further refinement of the measurements can be attained by employing a larger number of scans. Because of the time factor required for repeated scanning, this may, in certain cases, be a practical limitation. The fundamental limitation of this modified instrument still lies in the capability of the basic instrument, the minimum dichroic absorption detectable by the dichrograph. The other limitation may be the limited number of memory locations available in the computer. This could be overcome by covering small sections of wavelength region at a time and utilizing all the 1024 locations. This technique should, therefore, be useful in obtaining CD spectra of greater precision, especially in unfavorable situations. Since the basic instrument used for modification is a combination of dichrograph, polarimeter, and absorption spectrophotometer, this technique may also be applied to ORD and absorption spectrophotometric measurements.

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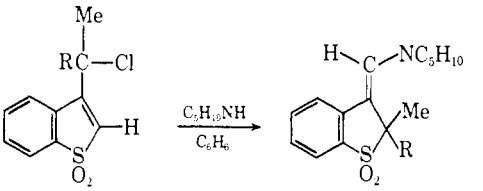
Concerning an Unusual SNi′ Rearrangement and the Application of the SN2′ Mechanistic Label

Sir:

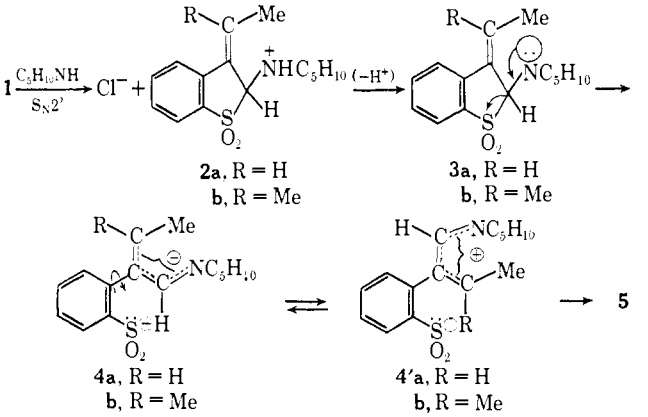
When 3-(α-chloroalkyl)benzo[*b*]thiophene 1,1-dioxides **1a** and **1b** are treated with piperidine in benzene they react rapidly to form enamines **5a** and **5b** in good yields.



1a, R = H
b, R = Me

5a, R = H
b, R = Me

The rate of release of chloride ion is in each instance first order in piperidine. For **1b** the rate (titrimetric) is equal to the rate of product formation (spectrophotometric rate). For **1a** the spectrophotometric rate was considerably slower than the titrimetric rate and was independent of piperidine concentration. When the latter reaction was interrupted after four titrimetric half-lives an intermediate was present which was identified as **3a** from its nmr spectrum; further reaction of **3a** with piperidine gave **5a**. These data indicate that **1** undergoes an SN2′ reaction with piperidine to give **2**, which rapidly loses a proton to form **3**; the latter rearranges to **5** in a final step (a special type of SNi′ reaction). Dipolar ion **4** is visualized as being formed from **3**. Rotation of the cationic part of **4** around the Ar–C bond interchanges the positions of the C-1 and C-3 carbon atoms in the allyl grouping leading to **4′**. Restoration of the C–S bond gives **5**. For **1a** the rate-controlling step in formation of the product is the SNi′ reaction whereas for **1b** it is the SN2′ reaction. The rate data are summarized in Table I.



2a, R = H
b, R = Me

3a, R = H
b, R = Me

4a, R = H
b, R = Me

4′a, R = H
b, R = Me

Table I. Kinetic Data for the Reactions of **1a** and **1b** with Piperidine in Benzene at 50°

Halide	k, M^{-1} sec^{-1}	E_a, kcal mole^{-1}	$\Delta S^{\ddagger}$, eu
1a	2.1×10^{-3}	10	−42
1a	$(4 \times 10^{-5})^{a,b}$	20	−18
1a	$(3.4 \times 10^{-2})^{c}$	8	−43
1b	1.6×10^{-4}	11	−43
1b	$(1.4 \times 10^{-4})^{a}$		
1b	$(1.8 \times 10^{-5})^{d}$	17	−32

[a] Spectrophotometric rate. [b] First-order constant, sec^{-1}. [c] Rate for the corresponding bromide. [d] Rate in methanol at 50°.

The titrimetric rates for **1a** and **1b** are about 500-fold greater and 50-fold greater, respectively, than the rate of the (SN2′) reaction of diethylamine with α-methylallyl chloride in benzene.[1] The unusual facility of the SN2′

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