sequitor).) The carbon magnetic resonance spectrum of unlabeled streptovaricin D (**1**) showed peaks for the expected 40 carbon atoms. Relevant carbon atom signals were assigned (Table II) with the help of the

Table II. Important Carbon Magnetic Resonance Peaks for Streptovaricin D (**1**)

Carbon atom[a]	δc[b]	Rel enrichment[c]
C-1	169.4	0.7
C-3	134.7	0.0
C-5	144.1	1.3
C-7	83.6	0.8
C-9	77.6	1.1
C-11	73.4[d]	1.0
C-13	70.4[d]	0.8
C-15	153.6	1.1
C-17	169.0	0.0
C-19	159.6	1.3
C-21	188.7	0.0

[a] Numbering for **1** is shown in Figure 1. [b] Ppm from TMS; CD_2Cl_2 = 53.80. [c] Calculated by measuring peak heights in the spectrum of enriched streptovaricin D relative to the height (arbitrarily assigned the value 1.00) of the peak at 153.6 ppm (the tallest of these peaks in the unenriched spectrum), then dividing those relative heights by the relative heights of the same peaks (calculated the same way, from an assigned value 1.00 for the peak at 153.6 ppm) in the natural abundance spectrum. The relative enrichments, which of necessity are rough approximations, have been normalized so their sum is 8.0. [d] May be interchanged.

carbon magnetic resonance spectra of other streptovaricins; of standard chemical shift data;[7] and of complete, off resonance, and specific proton[8] decoupling.[9]

The carbon magnetic resonance spectrum of ^{13}C-labeled streptovaricin D showed eight clearly enriched peaks of similar intensity for C-1, C-5, C-7, C-9, C-11, C-13, C-15, and C-19. Most important, the present data establish that the amide-head pathway (path a) is that followed, since the amide carbon (C-1) and C-5 are labeled by propionate carboxyl but C-3 is not. That one of the ring carbons (C-19) is labeled by propionate carboxyl implies a continuous sequence of propionate and acetate units leading from C-20 through C-1. We assume acetate (or malonate) as the origin of C-3 and C-4 and of C-17 and C-18.

The quinone carbonyl (C-21) is unlabeled by propionate, as are C-26 and C-24, the carbons adjacent to the remaining methyl group at C-25.[10] The lack of a methyl at the carbon in rifamycin[3] corresponding to C-25 suggests that our C-25 methyl group comes from methionine. The origin of the benzenoid aromatic ring and the quinone carbonyl carbon (C-21 through C-27) remains to be established. Experiments along these lines are in progress.

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Supplementary Material Available. A more detailed description of assigned chemical shifts will appear following these pages in the microfilm edition of this volume of the journal. Photocopies of the supplementary material from this paper only or microfiche (105 × 148 mm, 20× reduction, negatives) containing all of the supplementary material for the papers in this issue may be obtained from the Journals Department, American Chemical Society, 1155 16th St,, N.W., Washington, D. C. 20036. Remit check or money order for $3.00 for photocopy or $2.00 for microfiche, referring to code number JACS-73-5793.

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(10) After our presentation of these streptovaricin biosynthesis results,[2a] we were informed by Dr. P. Sensi, Gruppo Lepetit, Milan, Italy, that workers in his laboratory had reached similar conclusions on the biosynthesis of rifamycin, employing carbon-13 label, again contradicting the earlier (unpublished) results.[4]

Collision-Induced Negative Ion Mass Spectrometry[1]

Sir:

We have previously shown that certain classes of organic compounds will accept an electron to produce molecular anions which may then undergo characteristic decompositions.[2,3] It has been demonstrated[4–6] that molecular anions may be formed by secondary electron capture under these conditions,[7] and it follows that our spectra may be produced by the decomposition of molecular anions with thermal or near thermal energies. This has been substantiated for the case of the 2-aryl-1,3-oxathianes.[8]

There are many molecular anions which do not decompose, and there are some functional groups which show no fragmentation in the negative mode. It is

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(7) Conditions used: Hitachi Perkin-Elmer R.M.U. 7D instrument, source pressures 2–5 × 10^{-7} Torr, electron beam energy 70 eV.

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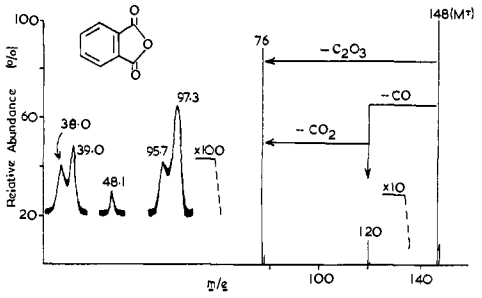

Figure 1. Collision induced negative ion mass spectrum of phthalic anhydride.

therefore of interest to devise a method by which initially unreactive molecular anions gain enough internal energy to enable fragmentation to occur. Collision excitation has recently been used to investigate the properties of collision-induced dissociations in positive ion spectra,[9-11] and adaptation of this technique to negative ions enables collision-induced fragmentation to be achieved. Sample pressures of *ca.* 5×10^{-7} Torr in the ion source are used, and collision gas is introduced through a separate inlet system into the first field-free region of the mass spectrometer to give a pressure of 10^{-5} Torr. The collision gas should (a) not produce negative ions under the reaction conditions and (b) not react with negative ions to produce ion–molecule product ions. We have successfully used krypton, nitrogen, benzene, and toluene for this purpose, but the use of aliphatic hydrocarbons (*e.g.*, methane[12]) as collision gases is to be avoided because of the risk of ion–molecule reactions producing anomalous peaks.

The spectra produced by this technique contain new peaks due to both fragmentation in the ion source[13] and to collision-induced dissociations in the field-free regions. Differential pumping of the ion source should be used if a spectrum is required which contains only fragment ions produced by collision-induced dissociations. The spectra reported in this communication were obtained with the differential pumping unit inoperative.

The first three examples to be discussed are those of molecular anions which give no fragmentation in the absence of collision gas. The spectrum[14] (Figure 1) of phthalic anhydride[15] shows the decompositions M − CO − CO_2 and M − C_2O_3. Collision-induced peaks[16] are observed for these processes and also for processes which do not occur in the ion source. Examples of the latter type are the decompositions M − CHO· (collision induced peak (cip) at *m/e* 95.7) and M − C_2HO_3· (cip at *m/e* 38.0). The spectrum of maleic anhydride shows the following fragment ions: *viz.*, $(M - CO)\cdot^-$ (cip at *m/e* 50.0), $CO_2\cdot^-$, and C_2H^-. The naphthoquinone molecular anion does not fragment in the ion source, but pronounced collision-induced peaks are produced in both field-free regions. These peaks are observed at *m/e* 105.3 and 64.6, produced by the unusual decompositions M − CHO· and M − (CHO· + CO).

The final example is that of a functional group which does not fragment under normal conditions. The conventional negative ion spectrum of *p*-nitroacetophenone[17] shows the decompositions M − NO· and M → NO_2^-. The collision-induced spectrum shows the following decompositions of the COMe group in the field-free regions: *viz.*, (M − NO·) − Me·, (M − NO· − Me·) − CO, (M − NO·) − MeCO·, and (M − NO·) − CH_2CO.

In summary, collision excitation allows the observation of fragmentations of moieties which do not decompose under the normal conditions used for the formation of molecular anions and shows considerable potential for the study of the reactivities of negative ions in the gas phase and for the structure determination of some types of organic compounds.

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(14) Hitachi Perkin-Elmer R.M.U. 7D instrument, sample pressure 5×10^{-7} Torr, toluene as collision gas, total pressure 3×10^{-5} Torr, electron beam energy 70 eV, and accelerating potential 3600 V. Identical conditions were used for other spectra.
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Influence of Trans Ligands on the Bonding Mode of Thiocyanate in Cobalt(III) Complexes. Evidence for Adjacent and Remote Attack during Electron-Transfer Reactions

Sir:

We report here the stereoselective formation and subsequent linkage isomerization of complexes of the type *trans*-$LCo(DH)_2SCN$, where L = amine, phosphine, or phosphite ligand and DH = monoanion of dimethylglyoxime. These complexes were prepared *in situ* from isomeric mixtures of $CNpyCo(DH)_2SCN$–$CNpyCo(DH)_2NCS$, where CNpy = 4-cyanopyridine, by addition of ligand, L. The reactions are examples of a new class of ligand-exchange reactions[1] which proceed only in the presence of catalytic amounts of $LCo^{II}(DH)_2$ according to eq 1–3. The slow step is

$$\text{slow} \quad LCo(DH)_2X + L'Co(DH)_2 \longrightarrow L'Co(DH)_2X + LCo(DH)_2 \quad (1)$$

$$\text{fast} \quad LCo(DH)_2 + L' \rightleftharpoons L'Co(DH)_2 + L \quad (2)$$

$$LCo(DH)_2X + L' \longrightarrow L'Co(DH)_2X + L \quad (3)$$

believed to involve an inner-sphere electron transfer.

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