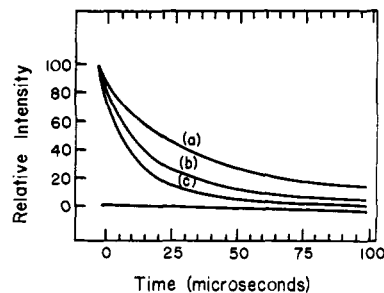


**Figure 1.** Absorption and luminescence spectra of heterobis-chelated complexes of Ir(III): (a)  $[\text{IrCl}_2(\text{phen})(5,6\text{-Me}(\text{phen}))]\text{Cl}$ ; (b)  $[\text{IrCl}_2(\text{phen})(\text{bipy})]\text{Cl}$ ; (—) absorption spectra in water at room temperature; (---) luminescence spectra in ethanol-methanol glass (4:1, v/v) at 77°K.

times were measured at the peak of the first three bands in the vibrational progression of the luminescence spectra of each complex (472, 507, and 540 nm for  $[\text{IrCl}_2(\text{phen})(\text{bipy})]\text{Cl}$  and 486, 523, and 564 nm for  $[\text{IrCl}_2(\text{phen})(5,6\text{-Me}(\text{phen}))]\text{Cl}$ ). The luminescence decay of  $[\text{IrCl}_2(\text{phen})(\text{bipy})]\text{Cl}$  was found to be only slightly nonexponential. Lifetimes measured in the first three vibrational bands of the emission spectrum were found to be  $6.33 \pm 0.05$  (473 nm),  $6.70 \pm 0.06$  (507 nm), and  $7.13 \pm 0.05$   $\mu\text{sec}$  (540 nm). Measurements of the lifetimes of  $[\text{IrCl}_2(\text{phen})_2]\text{Cl}$  and  $[\text{IrCl}_2(\text{bipy})_2]\text{Cl}$  in the vibrational bands of their emission spectra showed that these complexes also have a slight variation in their lifetimes with emission wavelength. However, the variation is only about 50% of that displayed by the  $[\text{IrCl}_2(\text{phen})(\text{bipy})]\text{Cl}$  complex. Previous measurements of the lifetimes of  $[\text{IrCl}_2(\text{phen})_2]\text{Cl}$ <sup>7</sup> and  $[\text{IrCl}_2(\text{bipy})_2]\text{Cl}$ ,<sup>8</sup> which were done under conditions where the entire emission spectrum was monitored, were found to be  $6.92 \pm 0.05$  and  $5.94 \pm 0.05$   $\mu\text{sec}$ , respectively. The luminescence decay curve for  $[\text{IrCl}_2(\text{phen})(5,6\text{-Me}(\text{phen}))]\text{Cl}$  was found to be nonexponential and to have a shape which was dependent upon the wavelength at which the emission was monitored. Luminescence decay curves measured at three different wavelengths for this complex are shown in Figure 2. From these curves it is apparent that the decay contains at least two components. From the latter part of the decay curve at 485 nm, the lifetime of the longer-lived component is estimated to be about 70  $\mu\text{sec}$ . Analysis of the initial part of the decay curve at 560 nm yields a lifetime of about 10  $\mu\text{sec}$ . These lifetimes are comparable to the values of 66.3  $\mu\text{sec}$  for  $[\text{IrCl}_2(5,6\text{-Me}(\text{phen}))_2]\text{Cl}$ <sup>6</sup> and 6.95  $\mu\text{sec}$  for  $[\text{IrCl}_2(\text{phen})_2]\text{Cl}$ .<sup>7</sup>

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**Figure 2.** Luminescence decay curves of  $[\text{IrCl}_2(\text{phen})(5,6\text{-Me}(\text{phen}))]\text{Cl}$  in ethanol-methanol glass (4:1, v/v) at 77°K excited at 337 nm: (a) luminescence monitored at 486 nm; (b) luminescence monitored at 523 nm; (c) luminescence monitored at 564 nm.

These results indicate that at least two nonthermally equilibrated states are responsible for the luminescence decay of  $[\text{IrCl}_2(\text{phen})(5,6\text{-Me}(\text{phen}))]\text{Cl}$ . Due to the dependence of the shape of the decay curves on the emission wavelength, these levels must both emit light. By comparison with previous results reported for  $[\text{IrCl}_2(\text{phen})_2]\text{Cl}$  and  $[\text{IrCl}_2(5,6\text{-Me}(\text{phen}))_2]\text{Cl}$ , it appears likely that the longer lived of these nonthermally equilibrated states has a  $\pi\pi^*$  orbital parentage and is localized in the 5,6-Me(phen) part of the complex. The shorter-lived component probably has a  $d\pi^*$  orbital parentage and is localized in the region of the complex encompassing the phen ligand and the central metal. We are currently determining the time resolved spectrum of  $[\text{IrCl}_2(\text{phen})(5,6\text{-Me}(\text{phen}))]\text{Cl}$  as well as several closely related complexes in order to further elucidate the orbital parentage of the nonequilibrated states responsible for the emission at 77°K. Studies of the photochemical reactions of this novel complex are also in progress and will be reported at a later date.

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Richard J. Watts

Department of Chemistry, University of California  
Santa Barbara, California 93106

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### Stereochemistry of Olefin Formation in Cyclopentyl Brosylate Solvolysis<sup>1</sup>

Sir:

We wish to report a determination of the stereochemistry of the solvolytic elimination of cyclopentyl brosylate based on the observed labeling patterns in the cyclopentene obtained from specifically deuterated starting material.

In earlier papers<sup>2,3</sup> deuterium isotope effects on the rate of solvolysis and the partial stereochemical results

(1) This work was supported in part by the Research Council of Croatia, in part by a PL 480 Grant administered by the National Institutes of Health, Bethesda, Md., Agreement No. 02-001-1, and in part by NSF Grant GP 32845.

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**Table I.** Olefin Yields<sup>a</sup> in Solvolysis of Cyclopentyl Brosylate in Various Solvents at 30°

| Solvent            | No. of expt. |                   | <i>cis</i> -Cyclopentyl-2- <i>d</i> <sup>b</sup> brosylate |                |                | <i>trans</i> -Cyclopentyl-2- <i>d</i> <sup>c</sup> brosylate |                |                | <i>Y</i> <sup>d</sup> |
|--------------------|--------------|-------------------|--|----------------|----------------|--|----------------|----------------|-----------------------|
|                    |              |                   | A <sup>e</sup>   | B <sup>f</sup> | C <sup>g</sup> | A <sup>e</sup>   | B <sup>f</sup> | C <sup>g</sup> |                       |
| E-W <sup>h</sup>   | 6            | Exptl             | 32.1   | 53.9           | 14.0           | 29.5   | 51.5           | 19.0           | 1.37                  |
|                    |              | Corr <sup>i</sup> | 33.4   | 55.4           | 11.2           | 26.9   | 56.2           | 16.9           |                       |
| D-W <sup>i</sup>   | 2            | Exptl             | 28.0   | 55.5           | 16.5           | 35.6   | 51.0           | 13.5           | 0.80                  |
|                    |              | Corr <sup>i</sup> | 28.2   | 56.6           | 15.2           | 33.4   | 55.3           | 11.4           |                       |
| TFE-W <sup>k</sup> | 3            | Exptl             | 17.7   | 60.3           | 22.1           | 45.4   | 47.0           | 7.6            | 0.27                  |
|                    |              | Corr <sup>i</sup> | 16.0   | 62.1           | 21.9           | 44.2   | 51.3           | 4.5            |                       |
| E + 1.5 N NaOEt    | 1            | Exptl             | 45.6   | 44.2           | 10.2           | 9.7  | 63.3           | 27.0           | 5.77                  |
|                    |              | Corr <sup>i</sup> | 49.6   | 43.2           | 7.2            | 5.3  | 69.0           | 25.6           |                       |

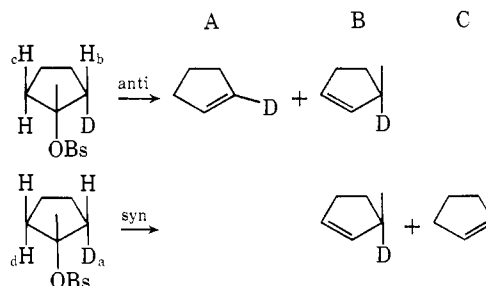
<sup>a</sup> Expressed as percentage of total olefin. <sup>b</sup> Contains 2% *d*<sub>0</sub> and 98% *d*<sub>1</sub> (7% *d*<sub>1</sub> is *trans*). <sup>c</sup> Contains 3.5% *d*<sub>0</sub>, 91.8% *d*<sub>1</sub> and 4.8% *d*<sub>2</sub>. <sup>d</sup>  $Y = k_{E(\text{anti})}/k_{E(\text{syn})}$ , calculated as described in text. <sup>e</sup> Cyclopentene-1-*d*. <sup>f</sup> Cyclopentene-3-*d*. <sup>g</sup> Cyclopentene. <sup>h</sup> Determinations were made on olefins isolated from ethanol-water mixtures of 80, 90 and 100 vol % ethanol. In each case one experiment was carried out in the pure solvent and one in the presence of excess 2,6-lutidine. The results were independent of the solvent composition and unaffected by the presence of lutidine and are given as the average of all experiments. The total olefin yields were 27, 23, and 12%, respectively. <sup>i</sup> Corrected according to deuterium content and position in starting ester. <sup>j</sup> Determinations were made on olefins isolated from 80% vol dioxane-water, one in the presence and one in the absence of 2,6-lutidine. For the same reason described in footnote *h* above, the results in the table are the averages of two experiments. The total olefin yield was 31%. <sup>k</sup> Determinations were made on olefins isolated from trifluoroethanol-water mixtures having 80 and 97.5 wt % trifluoroethanol. Products were unstable in the absence of 2,6-lutidine and the results refer only to reactions in the presence of excess base. The results are the average of one experiment in 80% and two in 97% trifluoroethanol. The total olefin yields were about 50 and 76%, respectively.

of substitution have been reported. In these studies it was concluded that the solvolysis in ethanol-water (E-W) involved rate-determining substitution and elimination of the reversibly formed intimate ion pair while in trifluoroethanol-water (TFE-W) elimination and substitution proceeded from the solvent separated ion pair after its rate-determining formation from the tight ion pair. Key observations in establishing the mechanisms in E-W solvents were moderate  $\alpha$ - and  $\beta$ -deuterium isotope rate effects and complete inversion of configuration of the reaction center in both cyclopentanol<sup>2</sup> and cyclopentyl ethyl ether<sup>4</sup> products. It was also concluded that the elimination was predominantly anti because the isotope effect on both rate and olefin formation was larger for the *trans* than for the *cis*  $\beta$ -deuterium labeled substrate.

In order to establish more precisely the ratio of anti to syn elimination, we have carried out combined <sup>2</sup>H nmr and mass spectral analysis of olefins isolated after ten half-lives of solvolysis in several solvents. The cyclopentene obtained from elimination of cyclopentyl-2-*d* brosylate was isolated by means of gas chromatography on an 8 ft  $\times$  0.25 in. column using 20% Carbowax 20 M on Chromosorb 60-80 and the ratio of undeuterated (C) to monodeuterated (B + A) olefins was determined by comparison of mass spectral peak heights at *m/e* 69 to 68 taken at 10 eV with slow scan on an AEI MS-9 double focusing mass spectrometer. Under these conditions the undeuterated cyclopentene mass spectrum showed peaks only at *m/e* 68 and *m/e* 69 (natural abundance of <sup>13</sup>C). Thus the ratio of peak heights at *m/e* 69 and 68 corrected for <sup>13</sup>C abundance corresponds directly to the ratio of monodeuterated to undeuterated olefin product. The <sup>2</sup>H nmr spectrum of the same olefin sample in carbon tetrachloride solvent was recorded on a Varian HR-220 spectrometer at 33.8 MHz. The ratio of peak areas at  $\tau$  4.75 ppm to that at 8.19 ppm relative to TMS-*d*<sub>12</sub> internal standard gave directly the concentration ratio of cyclopentene-1-*d* (A) to cyclopentene-3-*d* (B). As a check on the method

(4) Unpublished results by K. Humski, V. Sendjarević, and V. J. Shiner, Jr.

of analysis the solvolysis of cyclopentyl-1-*d* brosylate was shown to give only olefin A with the same deuterium content as the starting material. This shows that the olefin is produced by 1,2-elimination without scrambling. Scheme I shows that anti 1,2-elimination without scrambling

**Scheme I**

can give, from *cis*-cyclopentyl-2-*d* brosylate, only olefins A and B. Similarly, the same reactant proceeding via syn elimination would yield only olefins B and C. The ratio of olefins A, B, and C will thus depend on the ratio of anti to syn elimination and also on the different isotope effects caused by the differences in the position of deuterium in the several transition states. Thus, referring to Scheme I, elimination of H<sub>b</sub> will proceed with an isotope effect ( $k_{H}/k_{D}$ ) "b," H<sub>c</sub> with an effect "c," etc. It should be noted that olefin C is produced from *cis*-cyclopentyl-2-*d* brosylate only by syn elimination whereas A is produced from this reactant only by anti elimination. A similar scheme can be used to illustrate the elimination pathways and products from *trans*-cyclopentyl-2-*d* brosylate and shows that only syn elimination produces A and only anti elimination produces C. If it is assumed that the same isotope effects apply for the *cis* and *trans* deuterated reactants, then the ratio of anti to syn elimination corresponds directly to the ratio of yields of C from *trans*-cyclopentyl-2-*d* brosylate to C from *cis*-cyclopentyl-2-*d* brosylate, and also to the ratio of yields of A from *cis*-cyclopentyl-2-*d*

brosylate to A from *trans*-cyclopentyl brosylate. Using this value (*Y*) of the ratio of anti to syn elimination, the ratio of isotope effects *a/d*, *a/c*, etc., can also be calculated from the olefin yields. Table I gives the percentage of the elimination leading to the products A, B, and C from *cis* and *trans* deuterated reactants in various solvents. In ethanol–water solvents, anti elimination is found to be favored over syn by a factor of only 1.37, a relatively nonstereospecific process. This is consistent with our earlier conclusion that this is an E1 elimination process which proceeds from the intimate ion pair.<sup>2</sup> The results with sodium ethoxide in ethanol given in the last entry in the table show that the classical E2 reaction conditions favor anti over syn elimination by a factor of approximately six or more.<sup>5</sup>

It is reasonable that nucleophilic attack on the intimate ion pair proceeds with highly stereospecific inversion of configuration while proton elimination is not stereospecific; the leaving group can effectively shield the front side of the reacting carbon<sup>6</sup> but cannot effectively shield the two front-side  $\beta$ -hydrogens as well. If the cyclopentyl moiety of the intimate ion pair is assigned the planar carbonium ion structure, no strong stereoelectronic preference for *trans* elimination should obtain. On the other hand it is unreasonable to assume that substitution occurs *via* direct nucleophilic attack on the reactant (SN2) while elimination occurs in the ion pair. The observed  $\alpha$ -*d* effect of 1.15 in ethanol,<sup>2</sup> accompanied by only 12% elimination, must be predominantly on the substitution reactions; no SN2 reactions are known which show isotope effects larger than about 1.04.<sup>7</sup>

From the ratios of isotope effects in elimination, calculated from the present work, and the isotope effects in Table X, ref 2, it is possible to estimate the individual  $\beta$ -*d* effects *a*, *b*, *c*, and *d*. The primary effect "*a*" in ethanolysis is 1.72 and the secondary effects *b*, *c*, and *d* while subject to some error all appear inverse and range from 0.75 to around unity. The secondary effects are inverse presumably because elimination not only reduces the hyperconjugative demand but also forces the noneliminated  $\beta$ -hydrogen into an orientation unfavorable to hyperconjugation.

The results for solvolysis in TFE–W mixtures surprisingly indicate that syn elimination is favored over anti by a factor of about 4! This implies that elimination by the nonbasic solvent is sufficiently slow so that it is dominated at the ion pair stage by internal elimination of the  $\beta$ -hydrogen by the leaving group.<sup>8</sup> These results may require revision of our earlier analysis of this mechanism.<sup>2</sup> We must consider the possibility that internal elimination in the intimate ion pair competes with rate determining formation of the solvent separated ion pair. Additional experiments to elucidate this question are in progress.

Results on stereochemistry of elimination as well as isotope effects<sup>3</sup> and stereochemistry of substitution product formation<sup>3</sup> in D–W solvents indicate that solvol-

ysis proceeds by mixed mechanisms involving both ion pairs as intermediates from which the products are derived.

(9) Address correspondence to this author at Indiana University.

K. Humski,\* V. Sendjarević, V. J. Shiner, Jr.\*<sup>9</sup>

Faculty of Technology, University of Zagreb  
44000 Sisak, Croatia, Yugoslavia  
Institute "Rudjer Bosković"

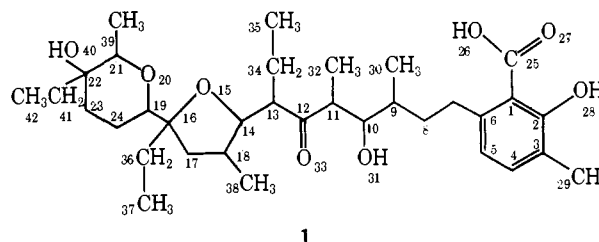
41000 Zagreb, Croatia, Yugoslavia  
Department of Chemistry, Indiana University  
Bloomington, Indiana 47401

Received May 22, 1974

### A Structural Study on the Sodium Salt of the Ionophore, X-537A (Lasalocid), by X-Ray and Nuclear Magnetic Resonance Analysis

Sir:

The "ionophore" antibiotic X-537A, lasalocid (1),<sup>1</sup>



1

has been the subject of several solution<sup>2,3</sup> and crystallographic studies.<sup>4-7</sup> We now report the results of a combined X-ray and nmr study that suggests the importance of dimeric structures when considering the behavior and mode of action of this smallest member of the acidic ionophores.

In the course of trying to get crystals of a sodium salt of X-537A suitable for X-ray structure determination, we isolated two different crystalline forms of the sodium salt of 5-Br-X-537A (2). Crystal data are shown in Table I. Crystals of modification I could be grown from ethyl acetate solution but were obtained in greatest abundance from the nonpolar carbon tetrachloride. Some crystals of modification II were obtained from ethyl acetate, but they were also obtained in high yield from acetone. Full X-ray structure analyses have been carried out on both forms. Stereoscopic pictures of the two structures are shown in Figures 1 and 2. In both cases the structures of the Na<sup>+</sup> salts are dimeric; however, the mode of assembly of the dimer is different in the two cases. If one calls the phenyl ring the "head" of the circular X-537A entity and the oxacyclohexane ring the "tail,"<sup>4</sup> then form I is "head" to

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