of isopentenyl-OPP and dimethylallyl-OPP. However, the drawback of the latter hypothesis is the fact that tritium was lost only in the biosynthesis of fusidic from the 2S-tritiated MVA and not from the 2R-tritiated MVA. Clarification of these points requires additional experimentation.

Communications to the Editor

Emission Characteristics of Camphorquinone[1]

Sir:

The literature on the luminescence of camphorquinone is confusing. The purpose of this note is to resolve some of that confusion.

Total luminescence spectra of camphorquinone are displayed in Figure 1. Fluorescence occurs in the 490–550-mμ region and phosphorescence in the 550–660-mμ range. The fluorescence spectrum and all phosphorescence spectra are characterized by a set of three band heads (*i.e.*, the sets $\{1, 2, 3\}$, $\{4, 5, 6\}$, and $\{7, 8, 9\}$ of Figure 1) which correspond to the set $\{$origin band, one quantum of a $>$C—C$<$ stretch mode of the carbonyl carbons, and one quantum of a $>$C$=$O stretch mode$\}$.

The phosphorescence spectrum of a glassy solution is shown in Figure 1B and is consistent with previous reports[2] which place the origin band at $\sim$556 mμ. Kuboyama and Yabe,[2a] unable to detect any $>$C$=$O stretching activity in the phosphorescence spectrum, concluded that the phosphorescence was an exception among those of the α-diketones; the observation here of a common $\sim$1700-cm^{-1} vibronic interval removes this exceptional status.

The luminescence spectrum of Figure 1A typifies that found for all solid forms of camphorquinone (*i.e.*, microcrystalline suspensions in glasses, thin films obtained from a melt, powdered solid, and single crystal) at 77°K. The phosphorescence of Figure 1A is characterized by an intense origin band at 575 mμ; this spectrum is identical, in most regards, to that observed for the solid state at 77°K by Kuboyama and Yabe[2a] (KY) and Ford and Parry[3] (FP) but quite different from that observed for the solid state at $\sim$300°K by Tsai and Charney (TC). However, as the crystal is warmed to 300°K, the intensity distribution among the 575-mμ peak and 556-mμ shoulder inverts until, at room temperature, the dominant band lies at 556 mμ and the 575-mμ band is either absent or present only as a very slight inflection. Indeed, the room temperature, solid-state phosphorescence is indistinguishable from the phosphorescence of the glassy solution at 77°K shown in Figure 1B which, in turn, is identical with the spectrum reported by TC.[4] Thus, the interrelatedness of

the results of all previous authors[2a,3,4] is now obvious.

It is clear from the vibronic analyses given in Figure 1A that the phosphorescence peaks 7, 8, and 9 refer to a defect emission which is $\sim$600 cm^{-1} lower in energy than the T_1 state of camphorquinone, as this state is found in camphorquinone solution at 77°K or in the solid state at 300°K. It is also clear from the vibronic analysis that this defect is itself camphorquinone or some molecule very closely related to camphorquinone. This view obtains further corroboration from the fact that the phosphorescence lifetimes at 77°K are 2.64 $\times$ 10^{-3} sec for the 556-mμ shoulder and 1.07 $\times$ 10^{-3} sec for the 575-mμ peak. We tend toward the view that the defect emitter is camphorquinone and that the 600-cm^{-1} energy decrement is associable with a greater coplanarity of the carbonyl units in the T_1 state of the defect molecule and/or relief of steric strain. This view, in part anyway, is suggested by the observation that in the relatively strain-free 3,3,5,5-tetramethylcyclopentanedione[5] the 0,0 absorption peak occurs at $\sim$530 mμ whereas, in camphorquinone, it is observed at $\sim$478 mμ. The dominance of the intrinsic 556-mμ phosphorescence at 300°K is, then, the result of either thermal trap depopulation or reduced exciton motion at higher temperatures.

Tsai and Charney[4] have recorded the phosphorescence excitation spectrum of the powdered solid at $\sim$300°K. Their results were quite novel and were interpreted as follows: (i) the T_1–T_2 separation is about 6700 cm^{-1}, (ii) the efficiency for phosphorescence excitation is greater upon excitation into S_2 than into S_1, (iii) item (ii) was used to infer that intersystem crossing $S_2 \rightsquigarrow T_2$ more efficient than $S_1 \rightsquigarrow T_1$. The phosphorescence excitation spectrum of a thin film of camphorquinone at 77°K is shown in Figure 2. This spectrum is of higher resolution[6] than that of TC, being a rather faithful replica of the $S_1 \leftarrow S_0$ and, in part, of the $S_2 \leftarrow S_0$ absorption bands[7] of camphorquinone. In fact, the vibronic structure of the absorption spectrum duplicates that present in the excitation spectrum. Contrary to the observations of TC, we did not detect any significant $T_1 \leftarrow S_0$ excitation process in the thin film system; however, the excitation spectrum of the powdered solid at 77°K, as shown in Figure 3, does exhibit some minimal structure in the 550–500-mμ region and one might cautiously suppose that this structure could be representative of an $T_1 \leftarrow S_0$ excitation event. The excitation efficiency in the $S_2 \leftarrow S_0$ region is higher than that in the $S_1 \leftarrow S_0$ absorption

(1) Research supported by contract between the United States Atomic Energy Commission—Division of Biomedical and Environmental Research—Physics and Technological Program and the Louisiana State University.

(2) (a) A. Kuboyama and S. Yabe, *Bull. Chim. Soc. Jap.*, **40**, 2475 (1967); (b) T. R. Evans and P. A. Leermakers, *J. Amer. Chem. Soc.*, **89**, 4380 (1967).

(3) R. A. Ford and F. Parry, *Spectrochim. Acta*, **12**, 78 (1958).

(4) L. Tsai and E. Charney, *J. Phys. Chem.*, **73**, 2462 (1969). The 525-mμ shoulder in the spectrum reported by these authors is presumably fluorescence.

(5) C. Sandris and G. Ourisson, *Bull. Chim. Soc. Fr.*, **23**, 958 (1956).

(6) The excitation monochromator was a Cary 15 spectrometer, the emission monochromator a Jarrell-Ash 0.5 m spectrometer, the light source a 500-W Sun Gun, and the detection system was phase sensitive.

(7) As obtained on a Cary 14 spectrophotometer.
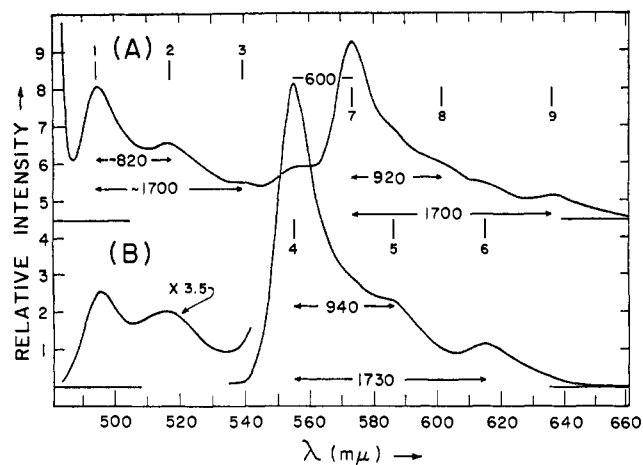
Figure 1. (A) The total luminescence spectrum of a microcrystalline suspension of camphorquinone in 3-methylpentane glass at 77°K. This spectrum is essentially identical with that of a solid film, a powdered solid, or a single crystal at 77°K. (B) The total luminescence spectrum of a glassy solution of camphorquinone in a mixed alcohol glass at 77°K. This spectrum is essentially identical with that of any of the solid samples listed above at 300°K. Vibrational analyses are indicated on the diagram.
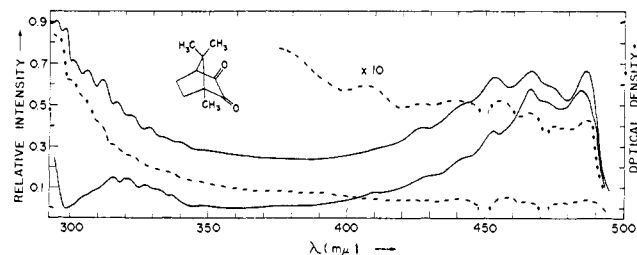
Figure 2. An uncorrected phosphorescence excitation spectrum (lower solid curve) and an absorption spectrum (upper solid curve) of a thin film of camphorquinone at 77°K. The emission wavelength monitored was 575 mμ. The thin film, which was of excellent optical quality, was grown by slow cooling of a melt between two quartz plates. This excitation spectrum, apart from some loss of resolution and some changes of relative excitation efficiency in the 380–410 and 320-mμ region, was identical with the same system at $\sim$300°K where the emission wavelength monitored was 556 mμ; the relative excitation efficiency changes were not dissimilar to those found for a powdered sample under the same variations of temperature and of emission wavelength as shown in Figure 3. A phosphorescence spectrum corrected for all vagaries of lamp, optics, monochromator, and detection systems is also shown (dashed line). The two breaks in the corrected spectrum at $\sim$450 and $\sim$470 mμ are attributable to intense lamp emission lines; data at these two breaks are uncertain.

region by a factor of $\sim$10. This observation accords with that of C T and may be similarly interpreted.[4] The excitation efficiency in the 380–410-mμ region, where TC inferred the presence of an $T_2 \leftarrow S_0$ excitation event may be supposed to corroborate the findings of TC. Thus, apart from the nonobservation of any significant $T_1 \leftarrow S_0$ excitation efficiency, our results substantiate, or may be supposed to substantiate, those of TC.

Some lower resolution excitation spectra are shown in Figure 3. Particular note should be paid to those for the powdered camphorquinone at 77 and 300°K. It is clear that these two phosphorescence excitation spectra are quite dissimilar, particularly with respect to the relative excitation efficiency in the 380–410-mμ region. The importance of this difference, vis-a-vis the $T_2 \leftarrow S_0$ excitation process, inferred by TC to lie in this energy
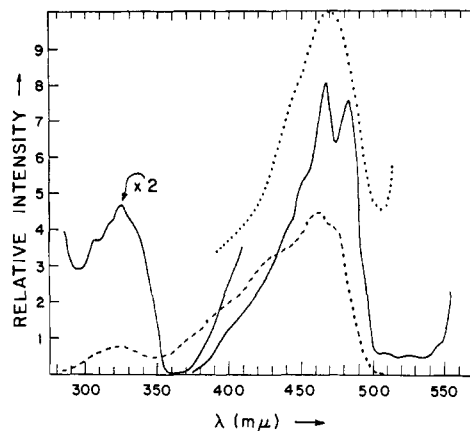
Figure 3. Excitation spectra (uncorrected) for camphorquinone luminescence: ($\cdots$) mixed-alcohol, glassy solution at 77°K; $\lambda_{\text{emission}}$ 556 mμ, (——) powdered solid at 77°K, $\lambda_{\text{emission}}$ 575 mμ; (-----) powdered solid at $\sim$300°K, $\lambda_{\text{emission}}$ 556 mμ.

range, is unknown to us but the complexity of solid state processes do indicate that this inference should be viewed as provisional.

The TC results[4,8] were interpreted on the basis of a model which implied near-degeneracy of n$_+$ and n$_-$ "nonbonding" oxygen orbitals. Since the photoelectron spectrum[9] indicates a separation of 1.7 eV between these orbitals, it is clear that the TC model of near n$_+$/n$_-$ degeneracy is called into question. A revised model has been developed and has been applied to the interpretation of the absorption and emission spectroscopy of α-dicarbonyls[10] (including camphorquinone).

(8) E. Charney and L. Tsai, J. Amer. Chem. Soc., 93, 7123 (1971).
(9) As obtained in these laboratories. See also J. R. Swenson and R. Hoffmann, Helv. Chim. Acta, 53, 2331 (1970).
(10) J. F. Arnett, G. Newkome, W. L. Mattice, and S. P. McGlynn, J. Amer. Chem. Soc., 96, 4385 (1974).

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Oxazolines. XIV. An Asymmetric Synthesis of R and S Dialkylacetic Acids from a Single Chiral Oxazoline

Sir:

We recently reported[1] an asymmetric synthesis of 2-methylalkanoic acids starting from (4S,5S)-2-ethyl-4-methoxymethyl-5-phenyl-2-oxazoline (2, R = H, R' = Me). The process involved metalation of the latter with lithium diisopropylamide (LDA) (−78°, THF) followed by introduction of an alkyl halide (−78°) producing the disubstituted oxazoline 2 (R = Me, R' = alkyl). Acidic hydrolysis (3 N HCl, 95°) gave the (S)-(+)-carboxylic acids, 3, in 60–67% optical yield. Two serious limitations, however, were noted for this scheme. (1) Although sequential alkylation of 1 with

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