development of optical activity shows that in the transfer step there exists some kind of diastereoisomeric relationship between the systems constituted by one enantiomer of *trans*-DPC or the other and the sensitizer. This probably implies preferential orientation of sensitizer and substrate to allow maximum π overlap.[13] Although the absolute configurations of both are known, the extent of the induced asymmetry is too small to allow one to predict which enantiomer of *trans*-DPC is approached most easily by (*R*)-(−)-3-methyl-1-indanone.

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Photochemistry of 1-Benzoyl-4-*p*-anisoylbutane. Reaction from Equilibrating Upper Triplets[1]

Sir:

The problem of energetically proximate excited states has aroused much interest, both spectroscopic[2] and chemical,[3] but remains puzzling. In the particular case of ketones with π,π^* lowest triplets, it is difficult to differentiate whether n,π^*-like chemical reactivity is induced by vibronic mixing with a nearby n,π^* state[4] or actually emanates from low equilibrium concentrations of the upper n,π^* triplet. We have already reported evidence for the latter possibility.[5] We now report unequivocal evidence for reaction from at least one and probably two upper triplets of a molecule with a π,π^* lowest triplet. Not only does this evidence provide further support for the hypothesis of efficient equilibration of triplet excitation within one chromophore, it clearly demonstrates chemical reaction *via* equilibration of excitation between two chromophores.

Upon uv irradiation in degassed benzene containing 0.5 *M* pyridine[6] 1-benzoyl-4-anisoylbutane (**1**) undergoes normal type II photoelimination[8] reactions from each end, producing acetophenone, *p*-methoxyphenyl allyl ketone, *p*-methoxyacetophenone, and phenyl allyl ketone. The former two are formed in equal yield, as are the latter two, with the overall yield of the former pair (type II from the benzoyl group) far surpassing that of the latter pair (type II from the anisoyl group). The benzoyl–anisoyl product ratio is independent of excitation wavelength (313 or 365 nm) and decreases with increasing temperature, as indicated in Table I.

Table I. Temperature Effect on Ratio of Products Obtained from **1**[a]

T, °C[b]	Acetophenone/ *p*-Methoxyacetophenone[c]
25	19.4[d]
30	18.4
90	11.5
116	9.5

[a] 0.01 *M* diketone, 0.5 *M* pyridine in degassed benzene, irradiated at 313 nm. [b] All the temperatures were controlled within ±0.5°. [c] Product ratios measured by vpc and corrected for different FID responses. [d] Same value obtained with 365-nm irradiation.

Four further products are formed in 5–6% total yield at all temperatures and are assumed to be the expected cyclobutanols.[9] The total quantum yield of products at 25° equals 0.21. Addition of various concentrations of 2,5-dimethyl-2,4-hexadiene results in quenching of both benzoyl and anisoyl reactions with almost the same efficiency, $k_q\tau$ values of 240 and 370 M^{-1} being measured.[10]

Like several other molecules in which two chromophores are separated by more than one methylene group,[11] **1** manifests no evidence for significant ground-state electronic interaction between the two aroyl groups, *i.e.*, the uv spectrum of **1** is nearly identical with the spectrum of an equimolar mixture of valerophenone and *p*-methoxyvalerophenone. The phosphorescence of **1** in an ethanol glass at 77°K is identical in both spectral shape and lifetime with that of *p*-methoxyvalerophenone (71 kcal 0–0 band, 0.4 sec lifetime), indicating that the lowest triplet of **1** is the π,π^* state of the anisoyl group. The second lowest triplet of **1** should be the n,π^* state of the benzoyl group, since we have shown that such states of simple phenyl alkyl ketones have an excitation energy of 72 kcal in solution.[12] Scheme I depicts our best estimate of the various triplet energy levels in **1** (in kilocalories).

We chose compound **1** for this study because it has been shown that exothermic triplet energy transfer[11d] and charge transfer[13] between groups separated by four methylenes both proceed with a rate ~3 × 10^9 sec^{-1}. This rate is appreciably faster than the 5 × 10^7 sec^{-1}

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(1) We are grateful to the National Science Foundation, Grant No. GP-19850, for support of this work.

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(4) (a) N. C. Yang and R. Dusenbery, *ibid.*, **90**, 5899 (1968); (b) C. D. DeBoer, W. G. Herkstroeter, A. P. Marchetti, A. G. Schultz, and R. G. Schlessinger, *ibid.*, **95**, 3963 (1973).

(5) P. J. Wagner, A. E. Kemppainen, and G. N. Schott, *ibid.*, **92**, 5280 (1970); **95**, 5604 (1973).

(6) The pyridine maximizes type II yields by suppressing reverse hydrogen transfer in the biradical intermediate,[7] thus ensuring that product ratios actually equal triplet rate ratios.

(7) P. J. Wagner, I. Kochevar, and A. E. Kemppainen, *J. Amer. Chem. Soc.*, **94**, 7489 (1972).

(8) P. J. Wagner, *Accounts Chem. Res.*, **4**, 168 (1971).

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(10) $k_q\tau$ values for 1,4-dibenzoylbutane and 1,4-dianisoylbutane are 55 and 1000 M^{-1}, respectively. The observed quenching is triplet quenching; supposition of singlet quenching would demand an incredibly long singlet lifetime for **1** of at least 10^{-7} sec.

(11) (a) O. Schnepp and M. Levy, *J. Amer. Chem. Soc.*, **84**, 172 (1962); (b) A. A. Lamola, P. A. Leermakers, G. W. Byers, and G. S. Hammond, *ibid.*, **87**, 2322 (1965); (c) A. A. Lamola, *ibid.*, **92**, 5045 (1970); (d) D. O. Cowan and A. A. Baum, *ibid.*, **93**, 1153 (1971).

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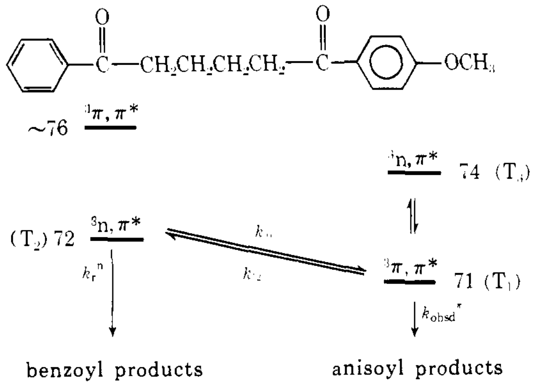
Scheme I



measured for γ-hydrogen abstraction by triplet 1,4-dibenzoylbutane.[8] The slightly endothermic energy transfer from anisoyl to benzoyl should then proceed at a rate >10⁸ sec⁻¹, much faster than the rate of decay of *p*-methoxyphenyl ketones.[5] Therefore, we expected that the lowest triplets of the two chromophores in **1** might approach thermal equilibrium before undergoing significant reaction or decay. The results verify this supposition. Most of the photoproducts of **1** clearly arise from the molecule's second triplet. Since the anisoyl group has double the extinction coefficient of the benzoyl group at 313 nm, T_2 must be populated by thermal activation of the lowest triplet. Furthermore, the comparable quenching efficiencies toward the two chromophores indicate that the two lowest triplets are nearly equilibrated, since they display almost the same lifetime.[14]

If, for the moment, we ignore the problem of whether T_1 and T_3 are equilibrated, we can first determine whether the results are quantitatively consistent with excitation being equilibrated between the two chromophores. Under conditions such that T_1 and T_2 are totally equilibrated, the relative yields of products derived from γ-hydrogen abstraction by the two aroyl groups are described by eq 1. The various rate constants are defined in Scheme I. The value of the rate ratio k_r^n/k_{obsd}^π has been shown to average 200/1 for several pairs

$$\frac{\Phi \text{ benzoyl}}{\Phi \text{ anisoyl}} = \frac{\chi_2 k_r^n}{\chi_2 k_{obsd}^\pi} \qquad (1)$$

$$\chi_2 = 1 - \chi_1 = k_{12}/(k_{12} + k_{21}) \qquad (2)$$

of ketones at 25°.[5] Since the quenching data indicate that T_1 and T_2 are very nearly equilibrated, the observed product ratios indicate a χ_2 value of 0.09 at room temperature and thus a 1.4 kcal energetic difference between T_1 and T_2, well within the range of uncertainties in our Scheme I estimate.

If we now return to the problem of equilibration of excited states within the *p*-methoxybenzoyl chromophore, the validity of our previous conclusion[5] that such ketones react from equilibrium concentrations of their n,π* triplets depends on reversible internal conversion of the two triplets being much faster than any irreversible decay modes of either individual triplet. Our present observation that *inter*chromophore energy transfer is sufficiently rapid to allow almost complete equilibration before any chemical reaction certainly lends support to the supposition of rapid *intra*chromophore energy transfer. The temperature effects observed for **1** also are consistent with the interpretation that the anisoyl derived products arise from T_3. An Arrhenius plot of the data in Table I yields a $\Delta\Delta H^\ddagger$ of 1.70 ± 0.05 kcal/mol and a $\Delta\Delta S^\ddagger$ of 0. If all the chemistry of triplet **1** arises from two n,π* triplets 1.7 kcal apart, each of which abstracts a similar secondary hydrogen with the same activation energy (~4 kcal/mol),[15] then T_3 and T_1 are indeed 3 kcal apart, as previously deduced.[5]

Although these temperature effects are nicely consistent with the equilibrium description of reactivity, they alone cannot rule out the possibility that T_1 actually reacts with a coincidental 3 kcal higher activation energy than T_2. The only evidence *against* reaction from the π,π* triplet, perhaps induced by vibronic coupling, is that presented in our previous papers.[5]

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Neighboring Group Effect in Heme–Carbon Monoxide Bonding[1,2]

Sir:

One of the factors contributing to the stability of oxymyoglobin relative to oxyheme is thought to be that the protein holds the imidazole "snugly in place"[3] on the iron. This implies some special stability to the geometrically positioned proximal imidazole group relative to the binding of free imidazole to iron in a simple heme–base interaction.[4] In order to quantitatively probe this "chelating" or "neighboring group" effect, we have prepared a series of simple heme compounds having the base covalently attached to a side chain on the porphyrin in such a way as to lead to approximately the same base-to-heme geometry as that in myoglobin.[6] Typical structures are shown in Figure 1.

Compounds **1** and **2** were synthesized by coupling mesoporphyrin IX to one equivalent mole of 3-(3-pyridyl)-1-propanol *via* acid chloride, followed by tlc purification and iron insertion. Compound **3** was then prepared from peptide coupling of **2** to the requisite amine by DCC method.[7,8] All compounds had nmr,

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(1) This work was supported by the National Institutes of Health, Grant USPHS HE 13581.

(2) Previous papers in this series are (a) H. Diekmann, C. Chang, and T. G. Traylor, *J. Amer. Chem. Soc.*, **93**, 4068 (1971); (b) C. K. Chang and T. G. Traylor, *ibid.*, **95**, 5810 (1973).

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(4) Other factors such as the nature of the proximal base and the solvent[5] or hydrophobic pocket effect will be discussed in subsequent papers. See also ref 2b.

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(7) 3-(3-Pyridyl)-1-propanol was obtained from Aldrich and redistilled over calcium hydride before use. 4-(Aminomethyl)imidazole·2HCl was synthesized according to Turner's procedure, mp 243°.[8]

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