which have low- and high-resonance frequencies, respectively; in both cases, the dominant factor in determining carbonyl fluxionality appears to be steric strain, which results from carbonyls on adjacent layers being eclipsed. This strain is relieved by carbonyl migration on an *outer* Rh_4 or Rh_3 face, respectively.

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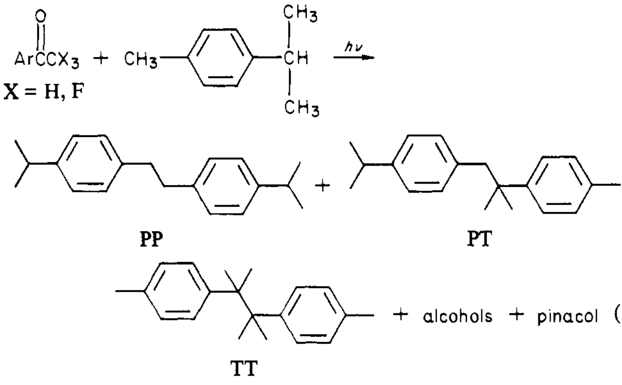
Varying Selectivities of Triplet Ketones toward *p*-Cymene: A Measure of the Extent of Charge Transfer in Triplet Exciplexes

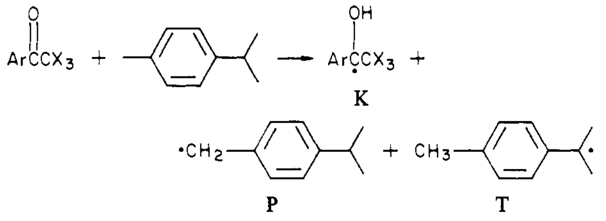
Sir:

We recently reported that triplet α-trifluoroacetophenone (AF_3) attacks *p*-cymene to yield primary and tertiary benzylic radicals in a 3.4:1 ratio, in contrast to the 1:2.8 P/T ratio observed with acetophenone (AH_3) itself (eq 1).[1] We ascribed the difference to the fact that hydrogen abstraction by triplet AF_3 proceeds via an exciplex intermediate[2] with substantial positive charge on the cymene. The 3.4:1 ratio could indicate an almost total lack of selectivity in exciplex H transfer, since it nearly equals the ratio of available benzylic hydrogens. We now find that the P/T radical ratio varies as a function of ring substitution on both AF_3 and AH_3. The apparently random ratio with AF_3 itself is just coincidental. More importantly, the P/T ratio serves as a unique probe of the extent of charge transfer in an exciplex.



(1)

Degassed benzene solutions containing various substituted ketones (0.05 M) and 0.5 M *p*-cymene were irradiated at 313 nm until 2-15% of the ketone had reacted (eq 2). The relative amounts of the three substituted bibenzyl radical coupling products were determined by gas chromatographic analysis.[1] The measured ratios are listed in Table I, as are the P/T radical ratios which would account for the product distributions.[3]



(2)

For both AF_3 and AH_3, electron-withdrawing substituents increase the P/T ratio, and electron-donating substituents decrease it, with a given substituent having roughly twice as large an effect on AF_3 as on AH_3. The effects can be related qualitatively to the degree of positive charge on the cymene in the exciplex formed with it as donor to triplet ketone, if it is accepted that high P/T selectivity results from positive charge density on the cymene.[1] There are now many examples of kinetic acidity effects dominating exciplex decay.[4] Unfortunately, as discussed earlier,[1] it is not known what P/T ratio would result from free *p*-cymene radical cation, so we cannot yet put our results on a quantitative basis.

Table I also includes some rate constants for interactions of the triplet ketones with *toluene*, which we have reported elsewhere.[5] For AF_3, there is a fourfold variation in P/T over a 10^4-fold variation in bimolecular rate constants for exciplex formation.[6] Figure 1 compares how k and P/T vary with triplet reduction potential. There have been suggestions that the slopes of plots of log k vs. ΔG for electron transfer reveal the extent of electron transfer during exciplex formation.[2,7] For example, in Figure 1, the slope of log k vs. $E_{red}{}^*$ is only 0.40/room temperature.[5] Slopes lower than 1/room temperature definitely establish that the reaction does not involve complete one-electron transfer with the formation of metastable radical ions.[8] However, it might be expected that the amount of charge separation in exciplexes formed from a common donor should vary with the reduction potential of the acceptor. Our present results, as plotted in Figure 1, provide the first experimental corroboration of this chemical intuition and indicate that linear plots of log k vs. ΔG do not demonstrate a constant degree of charge separation for all pairs plotted (e.g., 40% in the AF_3-toluene series).

Irradiation of 0.1 M di-*tert*-butyl peroxide in 0.6 M *p*-cymene produces the three bibenzyls in proportions which indicate a P/T ratio of 1:2.7, the same observed in the photoreduction of AH_3. This fact, together with a k_H/k_D value of 3.3 observed in the quenching of acetophenone phosphorescence by toluene and toluene-d_8,[9,10] might suggest that triplet AH_3 reacts with toluene by direct hydrogen atom abstraction. However, the substituent effects now observed on P/T ratios from AH_3 indicate that the photoreduction of AH_3 by alkylbenzenes generates partial positive charge on the alkylbenzene during hydrogen transfer. Given that the actual rate constant for quenching of triplet ketones by toluene correlates with toluene's oxidation potential,[7a] our present results suggest that the photoreduction of AH_3 by alkylbenzenes proceeds from a reversibly formed exciplex with a small amount of CT, possibly in competition with direct hydrogen atom abstraction.

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(1) Wagner, P. J.; Puchalski, A. E. *J. Am. Chem. Soc.* **1978**, *100*, 5948.

(2) Wagner, P. J.; Leavitt, R. A. *J. Am. Chem. Soc.* **1973**, *95*, 3669.

(3) When all three hydrocarbons were measurable, $P/T = (PP/TT)^{1/2} = (2PP + PT)/(PT + 2TT)$. When either PP or TT was present in too small an amount to be measured accurately, or when other product peaks interfered with GC analysis, $P/T = 2PP/PT = PT/2TT$. These equations reflect the statistical coupling behavior of P and T radicals and the fact that the two alcohol products containing P and T obtained from AF_3 display the same P/T ratio as measured from the hydrocarbon yields.[1]

(4) (a) Cohen, S. G.; Stein, N. M. *J. Am. Chem. Soc.* **1971**, *93*, 6542. (b) Lewis, F. D.; Tong-Ing, H. *Ibid.* **1980**, *102*, 1751.

(5) Wagner, P. J.; Lam, H. M. *J. Am. Chem. Soc.* **1980**, *102*, 4167.

(6) We are currently checking the assumption that the k values measure exciplex formation for the less reactive AF_3's just as for AF_3 itself.[2]

(7) (a) Guttenplan, J. B.; Cohen, S. G. *J. Am. Chem. Soc.* **1972**, *94*, 4040. (b) Loutfy, R. O.; Dogra, S. K.; Yip, R. W. *Can. J. Chem.* **1979**, *57*, 342.

(8) Scandola, F.; Balzani, V. *J. Am. Chem. Soc.* **1979**, *101*, 6140.

(9) Mueller, W. H., unpublished results.

(10) The primary isotope effect measured for *tert*-butoxy radicals is 5.25: Walling, C.; McGuinness, J. *J. Am. Chem. Soc.* **1969**, *91*, 2053.

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Table I. Benzyl Radical Coupling Products from Irradiation of Ring-Substituted AH_3 and AF_3 with 0.5 M *p*-Cymene in Benzene[a]

ketone	substituent	log k[b]	% P-P	% P-T	% T-T	P/T
AH_3	*p*-CH_3		*c*	0.38	0.62	0.30
AH_3	none	5.3[d]	0.09	0.37	0.54	0.38
AH_3	*m*-F		*c*	0.47	0.53	0.44
AH_3	*m*-CF_3		*c*	0.51	0.49	0.53
AF_3	*p*-OCH_3	4.7	0.31	0.45	0.24	1.2
AF_3	*p*-CH_3	6.0	0.40	0.45	0.15	1.8
AF_3	*m*-CH_3	6.4	*c*	0.81	0.19	2.1
AF_3	none	7.0	0.62	0.31	0.07	3.5
AF_3	*m*-CF_3	9.0	0.70	0.30	*c*	4.7

[a] 0.05 M ketone, irradiated at 313 nm, room temperature. [b] Bimolecular rate constant for quenching by toluene in acetonitrile, ref 5. [c] Not measurable. [d] Giering, L.; Berger, M.; Steel, C. *J. Am. Chem. Soc.* 1974, *96*, 953.

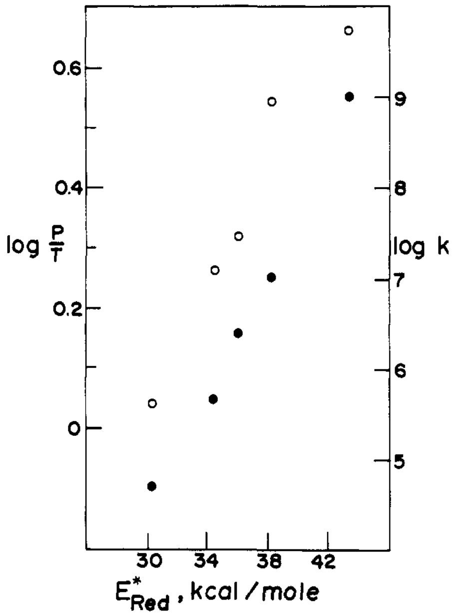

Figure 1. Correlation of rate constants and product ratios with excited ketone reduction potential for ring-substituted α-trifluoroacetophenones: (○) log (P/T) from *p*-cymene; (●) log *k* for quenching by toluene.

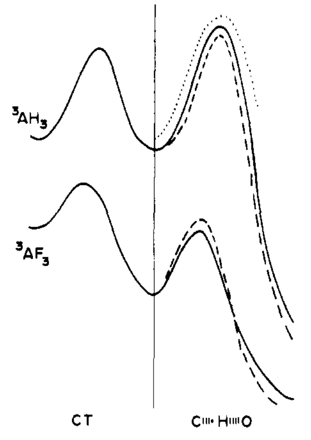

Figure 2. Partial potential-energy diagrams for triplet-state hydrogen abstraction by AH_3 (top) and AF_3 (bottom) from cymene. Reaction coordinate on left corresponds to CT complexation, that on right to H transfer from benzylic C to carbonyl O: (—) primary H; (- - -) tertiary H; (···) direct H abstraction by uncomplexed ketone triplet.

With AF_3, there is so much CT stabilization of the exciplex that proton transfer is no longer rate determining. Figure 2 compares the two situations.

We suspect that the low maximum quantum yields observed in ketone–toluene photoreductions reflect considerable exciplex decay[11] and are currently studying ketyl–benzyl radical–radical reactions to isolate chemical decay processes in photoreduction.[12]

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[11] The opposite conclusion has just been reached for ketone–amine photoreductions: Inbar, S.; Linschitz, H.; Cohen, S. G. *J. Am. Chem. Soc.* **1980**, *102*, 1419.

[12] Generous continuing NSF support (Grant No. CHE79-10831) is acknowledged.

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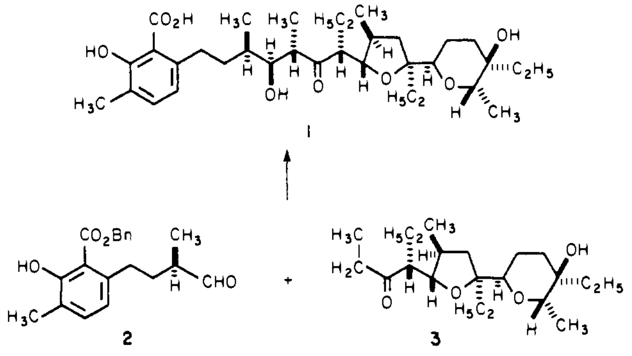
A Chiral Synthesis of the Left-Side Aldehyde for Lasalocid A Synthesis[1]

Sir:

In a recent report[2] from these laboratories, a total synthesis of the ionophore antibiotic lasalocid A (X537A) (**1**) was described. As in the first reported[3] synthesis, this approach is based on the aldol condensation between the aldehyde fragment **2** and the ketone polyether **3**. At the time, only the ketone polyether **3** had been prepared in optically pure form, and while a new and efficient synthesis of the aldehyde **2** had been developed, only racemic material was available. The total synthesis, then, relied on the previously reported synthesis[3] of the chiral aldehyde **2** and the demonstration[3] that the aldol condensation successfully generated lasalocid A. The present report describes a chiral synthesis of the aldehyde **2** and demonstrates that the previously reported[3] optical rotation of this material from synthetic and natural sources is incorrect.



A common intermediate in the two synthetic schemes is the bromopentene **10**. Previously,[3] the racemic acid **8** was resolved and subsequently transformed into the bromide **10**, $[\alpha]^{22}_D$ −4.77° (*c* 3.02, CH_3OH). In the present work, *both* enantiomers **9** and **10** of this bromopentene were prepared *independently* from *enantiomerically pure*, naturally occurring (−)-citronellene (**4**), $[\alpha]^{25}_D$ −5.63° (*c* 2.14, $HCCl_3$) (Scheme I).

The bromide **9**,[4] $[\alpha]^{25}_D$ +32.7° (*c* 2.74, CH_3OH), ultimately related to the unnatural enantiomer of the aldehyde **2**, was derived from (−)-citronellene by conversion of the vinyl terminus to the acetate **6** and then degradation of the propylidene side chain through the acid **5** to the vinyl group. The resulting olefinic alcohol was converted to the bromide **9** by displacement of the derived mesylate.

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[1] Support for this work from grants (HL-21367) from the National Heart and Lung Institute of the U.S. Public Health Service and the Hoffmann-La Roche Foundation is gratefully acknowledged.

[2] Ireland, R. E.; Thaisrivongs, S.; Wilcox, C. S. *J. Am. Chem. Soc.* **1980**, *102*, 1155–1157.

[3] Nakata, T.; Schmid, G.; Vranesic, B.; Okigawa, M.; Smith-Palmer, T.; Kishi, Y. *J. Am. Chem. Soc.* **1978**, *100*, 2933–2935.

[4] An alternate synthesis of enantiomer **9** from D-ribonic acid γ-lactone confirmed the stereochemical assignments when the *same* rotation for bromide **9** was observed: Fitzsimmons, B., unpublished experiments.

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