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## Nonselective Proton Transfer from *p*-Cymene as the Radical-Cation Half of an Exciplex

Sir:

Several years ago we demonstrated that the photoreduction of  $\alpha, \alpha, \alpha$ -trifluoroacetophenone (AF<sub>3</sub>) with reductants such as toluene and cumene proceeds via charge transfer followed by proton transfer from aromatic to ketone.<sup>1</sup> This mechanism is analogous to that for the photoreduction of ketones by amines.<sup>2</sup> Since the reductants assume radical-cation character in the charge transfer (exciplex) intermediate, there is the possibility that reductants possessing more than one kind of activated hydrogen might show unusual relative proton labilities. Such selectivities have not been measured heretofore in aprotic media; we report the first example in this paper.

Irradiation of either acetophenone, AH<sub>3</sub>, or AF<sub>3</sub> in *p*-cymene produces the expected six radical coupling products: three hydrocarbons, two alcohols, and the pinacol. These products account for over 80% of the reacted ketones and only traces of other products were detectable by VPC analysis. The hydrocarbons were separated from the other products by vacuum distillation and from each other by sublimation. With AH<sub>3</sub>, the bicumyl TT<sup>3</sup> was the major radical coupling product, whereas with AF<sub>3</sub> the bibenzyl PP was the major product. Product ratios were independent of conversion and of cymene concentration (0.1–0.6 M for AF<sub>3</sub>, 0.75–2.5 M for AH<sub>3</sub>) and were comparable in either benzene or acetonitrile as solvent. Table I lists representative quantum yields.

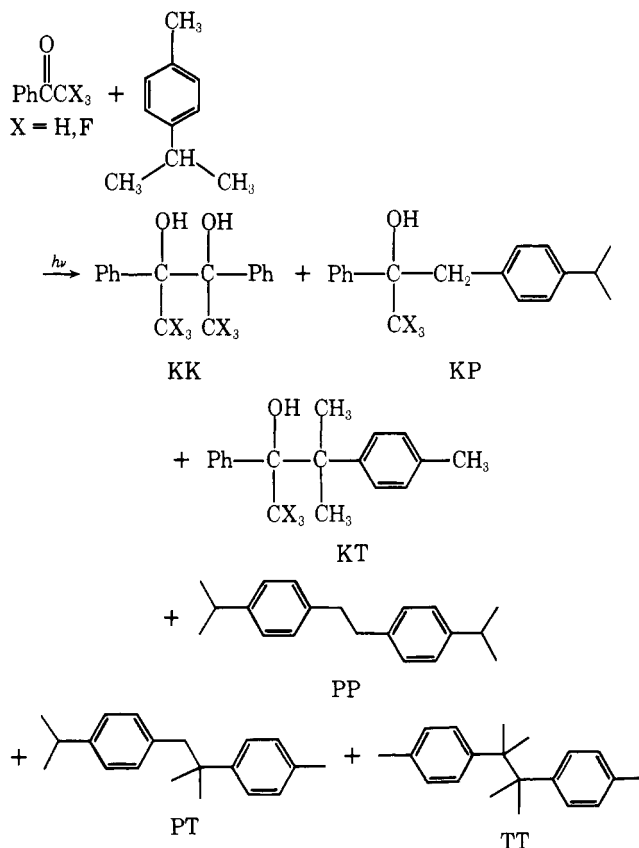
With AF<sub>3</sub>, the KP/KT ratio averages 3.4; the (PP/TT)<sup>1/2</sup> ratio averages 3.2; and the total P/T ratio in the three hydro-

**Table I.** Product Quantum Yields in the Photoreduction of Acetophenone and Trifluoroacetophenone by Cymene<sup>a</sup>

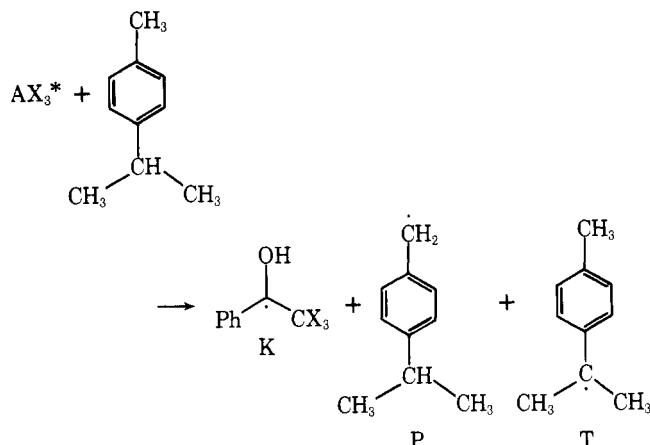
product	PhCOCF <sub>3</sub> <sup>b</sup>	PhCOCH <sub>3</sub> <sup>c</sup>
TT	0.0014	0.012
TP	0.0065	0.008
PP	0.0130	0.002
KT	0.013	<i>d</i>
KP	0.043	<i>d</i>

<sup>a</sup> 313-nm excitation, 25 °C, benzene solvent. <sup>b</sup> 0.6 M *p*-cymene.

<sup>c</sup> 2.5 M *p*-cymene. <sup>d</sup> Not yet determined.



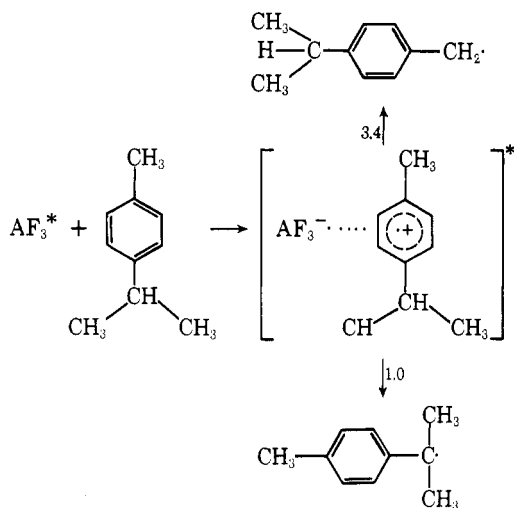
carbons averages 3.4. We can therefore conclude that the benzylic radicals P and T are formed in 3.4:1 ratio. Moreover,



the ketyl radicals do not preferentially react with one or the other benzyl radical. If we assume that the ketyl radicals from AH<sub>3</sub> behave likewise, the hydrocarbon product ratios from AH<sub>3</sub> indicate that P and T are formed in a 1:2.6 ratio.

The preference for tertiary radical formation with AH<sub>3</sub> is expected for direct hydrogen atom abstraction<sup>5</sup> and agrees closely with the 2.4-fold greater reactivity toward triplet AH<sub>3</sub> of cumene relative to toluene.<sup>1</sup>

The 3.4-fold preference for primary over tertiary radical formation with AF<sub>3</sub> is unprecedented and does not parallel the 1.7-fold greater reactivity toward triplet AF<sub>3</sub> of toluene relative to cumene. In fact, a standard double reciprocal plot<sup>6</sup> of product quantum yield as a function of cymene concentration indicates that *p*-cymene reacts with triplet AF<sub>3</sub> with the same rate constant as does *p*-xylene,  $1 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$ , 14 times faster than does toluene.<sup>1</sup> Product ratios are not coupled with rates of reaction with triplet ketone because of the intervention of a CT complex (triplet exciplex).<sup>1</sup> Benzyl radical formation involves transfer of an electron-deficient hydrogen from



cymene to the partially anionic (and basic) ketyl.

After statistical correction, primary protons are seen to be 1.1 times as reactive as tertiary protons in the chemical decay of this exciplex, in total disregard for C-H bond strengths. It might be concluded that all selectivity has vanished, but further work is required before that generalization can be justified. In fact, any competitive direct hydrogen atom abstraction by triplet ketone would raise the observed P/T ratio. We estimated a maximum rate constant of  $1 \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$  for direct H abstraction from cumene by triplet  $AF_3$ .<sup>1</sup> Since *p*-alkyl groups increase reactivities by a factor of three,<sup>1,5</sup> we estimate a maximum of 3% direct H abstraction from *p*-cymene. Correction for this small percentage raises the exciplex-derived P/T to 3.7, 1.2 per proton.

What seems most remarkable is that the 10-fold change in selectivity, in the direction opposed to bond strengths, results from only a small fraction ( $\sim 20\%$ ) of electron transfer<sup>1,7</sup> in the triplet exciplex. It is difficult to find results with which to compare these. Cohen observed that methyl groups of dimethylbutylamine are preferentially photooxidized by ketones in alkaline aqueous media.<sup>2,8</sup> Co(III) catalyzed oxidation of *p*-cymene in acetic acid, a process which has been interpreted to involve the aromatic radical cation,<sup>9</sup> gives products resulting from a 19:1 ratio of P/T radical formation.<sup>10</sup> Therefore, our much lower 3.4–3.7 ratio might be due to the partial rather than full positive charge on the H being abstracted. However, the presence of chloride ions reverses the Co(III) selectivity to 1:3 P/T, more in line with the 1:2 P/T ratio observed in the electrochemical oxidation of cymene in methanol.<sup>11</sup> The relative acidities of protons in aromatic radical cations apparently are strongly solvent and base sensitive.

The photoreduction of dimethyl terephthalate by *p*-cymene, a reaction which probably involves substantial charge transfer,<sup>12</sup> has been reported to yield TT as the only hydrocarbon and cross-coupling products analogous primarily to KP!<sup>13</sup> No clear-cut P/T ratio can be gleaned from this earlier study.

We are currently investigating the relative proton labilities of various other aromatic systems as well as the effects of external protons.<sup>14</sup>

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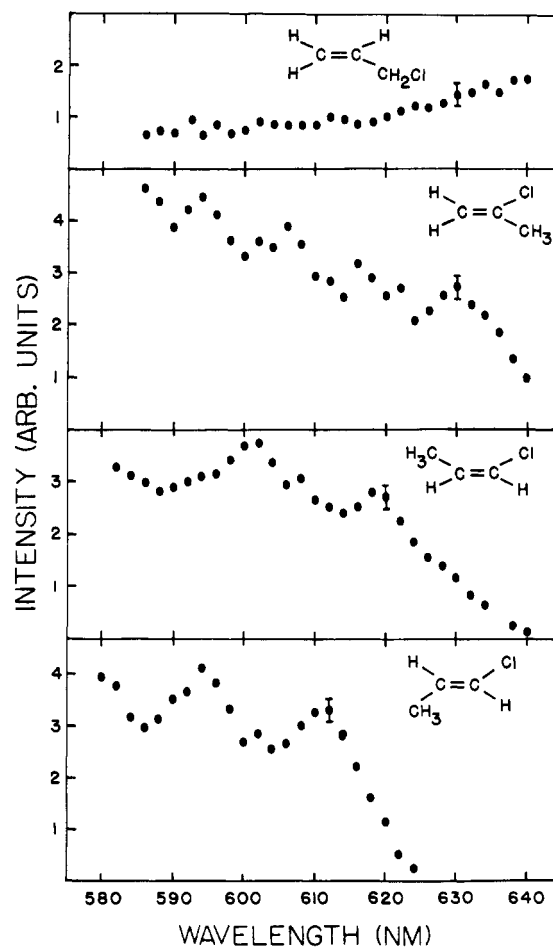
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## Structure of Reactively Produced Choropropene Cations by Laser Photodissociation

Sir:

The unambiguous identification of reaction products by spectroscopic means is an indispensable tool of mechanistic investigation which has until very recently been denied to the gas-phase ion-molecule reaction investigator. This situation has been changed by the recent advent of the technique of photodissociation spectroscopy. By observing the extent of dissociation as a function of wavelength, a photodissociation spectrum of a cation can be obtained which reflects many of the same characteristics as its optical absorption spectrum. Over the past several years this technique has been utilized



**Figure 1.** Laser photodissociation spectrum of the isomers of chloropropene cation from top to bottom: allyl chloride cation, 2-chloropropene cation, *cis*-1-chloropropene cation, and *trans*-1-chloropropene cation.