













intermolecular nyarogen abstractions			
Some hydro	gen abstraction rate co	onstants	
(in units of 10 <sup>6</sup> M	<sup>-1</sup> s <sup>-1</sup> )		
	Benzophenone triplet	(CH <sub>3</sub> ) <sub>3</sub> CO•	
Cyclohexane	0.45	1.6	
Methanol	0.21	0.29	
Benzhydrol	7.5	7.2	
Triethylsilane	9.6	5.7	
Ph2CO* +	R-H→ Ph₂COH	+ R•	



## What determines <u>rate constants</u> for hydrogen abstraction?

- Nature of the excited state: n, \* states are radical-like and react faster
- Triplet energy ...... high is better
- Strength of the R-H (frequently C-H) bond broken
- · Number of hydrogen atoms available
- Steric effects
- · Polar effects ..... most excited carbonyl states are electrophillic
- In intramolecular examples, the ability to form an unstrained transition state ..... 6-center is good
- · Entropic factors can be quite important in intramolecular cases
- ..... and the usual temperature, solvent, etc.





![](_page_12_Figure_0.jpeg)

![](_page_13_Figure_0.jpeg)

![](_page_14_Figure_0.jpeg)

![](_page_15_Figure_0.jpeg)

![](_page_16_Figure_0.jpeg)

![](_page_17_Figure_0.jpeg)

![](_page_18_Figure_0.jpeg)

![](_page_19_Figure_0.jpeg)

all rate constants in units of  $10^8 \ M^{-1} s^{-1}$ 

![](_page_20_Figure_0.jpeg)

![](_page_21_Figure_0.jpeg)

![](_page_22_Figure_0.jpeg)

![](_page_23_Figure_0.jpeg)

![](_page_24_Figure_0.jpeg)

![](_page_25_Figure_0.jpeg)

Compound	k <sub>CT</sub> , (Mxsec)	-1
Benzene	<b>7.6</b> x 10 <sup>5</sup>	
Toluene	<b>4.2</b> x 10 <sup>6</sup>	since the more electron rich
Pyridine	6.3 x 10 <sup>6</sup>	molecules are the best queneners
o-Xylene	<b>2.4</b> x 10 <sup>7</sup>	
m-Xylene	3.6 x 10 <sup>7</sup>	
p-Xylene	4.3 x 10 <sup>7</sup>	
Durene	5.5 x 10 <sup>7</sup>	
Anisole	8.4 x 10 <sup>7</sup>	
Mesitylene	2.4 x 10 <sup>8</sup>	

![](_page_27_Figure_0.jpeg)

![](_page_28_Picture_0.jpeg)

![](_page_29_Figure_0.jpeg)

## Carbonyl triplet addition to electron poor olefins Some general characteristics

- Only S<sub>1</sub> (n, \*) forms oxetanes with cyanoethylenes
- The cis-trans isomerization is a side reaction which is not affected by quenching of the S<sub>1</sub> (n, \*) state.
- Quenching of the  $T_1$  (n, \*) state sensitizes reactions of cyanoethylene, but it does not lead to oxetane (although the reaction does take place with electron rich\*olefins).
- Oxetane formation from  $S_1(n, *)$  is stereospecific.
- Oxetane formation from  $S_1(n, *)$  is regiospecific.

![](_page_30_Figure_6.jpeg)

![](_page_31_Figure_0.jpeg)

![](_page_32_Figure_0.jpeg)