

Extent of Charge Transfer in the Photoreduction of Phenyl Ketones by Alkylbenzenes

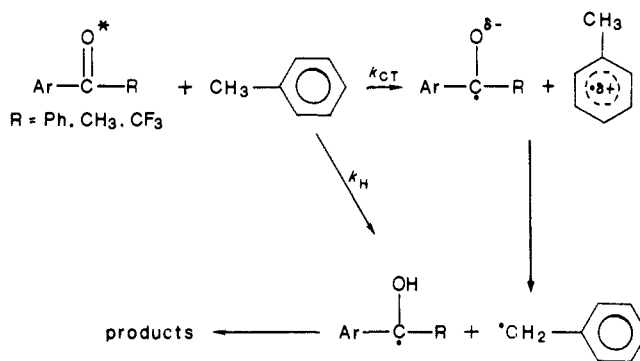
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Abstract: Rate constants for triplet-state reaction of various ring-substituted benzophenones (BPs), acetophenones (APs), and α,α,α -trifluoroacetophenones (TFAs) with toluene and *p*-xylene have been determined by a combination of flash kinetics, steady-state quenching, and quantum yield measurements. The relative amounts of primary and tertiary radicals formed by reaction of the same ketones with *p*-cymene have also been measured. For all three types of ketones, rate constants correlate well with triplet ketone reduction potentials. The magnitude of the kinetic isotope effects observed with toluene- d_8 and *p*-xylene- d_{10} diminishes as the ketones become easier to reduce. All of the ketone triplets react with alkylbenzenes primarily by a charge-transfer mechanism, with the rate-determining step changing from complexation to hydrogen transfer as the ketones become harder to reduce. The least reactive AP triplets probably react significantly via simple hydrogen atom abstraction as well. Those ketones with n,π^* lowest triplets (all BPs and some APs) react with *p*-cymene to give primary/tertiary radical ratios that vary no more than a factor of 2 from the 0.40 value displayed by *tert*-butoxy radicals; those with π,π^* lowest triplets (TFAs and some APs) give ratios that favor primary radicals and that vary by an order of magnitude with the triplet ketone reduction potential. The variation in cymene product ratios reflects different orientations for attack on cymene by n,π^* and π,π^* triplets and differing degrees of partial electron transfer within the exciplexes, which are *not* tight radical ion pairs. The variation seen for π,π^* triplets represents a stereoelectronic effect within face-to-face exciplexes, as evidenced by the exceptional behavior of *p*-diacylbenzenes, which give the highest ratio of tertiary radicals from cymene. There is no set intrinsic ratio of reactivity for π,π^* triplets vs. n,π^* triplets in these CT reactions. The two types of triplets show similar reactivity for the more easily reduced triplets, with the harder to reduce π,π^* triplets being only one-tenth as reactive as n,π^* triplets of comparable triplet reduction potential. When the extent of electron transfer in the exciplex is small, hydrogen transfer is rate determining and π,π^* reactivity drops. A study of two radical reactions which generate benzyl and α -hydroxy- α -methylbenzyl radicals indicates that radical disproportionation cannot explain the low quantum yields (<0.10) of most ketone-toluene photoreductions, which apparently involve substantial radiationless decay by the exciplex intermediates.

One particularly intriguing aspect of the well-studied ketone photoreduction reaction is the fact that hydrogen atom abstraction by triplet ketones can occur directly or in two steps: charge transfer followed by proton transfer.^{1,2} The charge-transfer (CT) path was first evident for amine donors, which are orders of magnitude more reactive than would be simple hydrogen atom sources.^{3,4} We showed some years ago that even weak electron donors like alkylbenzenes reduce highly electron-deficient triplet ketones by a CT process.⁵ Such CT processes are now generally considered to involve nonemitting exciplex intermediates (excited charge-transfer complexes). At that time we pointed out the possibility that photoreduction might occur under certain conditions by a combination of competing charge transfer and direct hydrogen atom abstraction. Since the oxidation of alkylbenzenes is of widespread interest and importance, we have completed a thorough study of how alkylbenzenes reduce triplet phenyl ketones. Knowing substituent effects on direct hydrogen atom abstraction by n,π^* ketone triplets,⁶ we can determine the extent to which such direct abstraction competes with electron transfer for benzophenones with n,π^* triplets, α,α,α -trifluoroacetophenones with π,π^* triplets, and acetophenones with equilibrating mixtures of both triplets.

This paper describes how ring substituents affect rate constants for the interaction of the three types of phenyl ketone triplets with toluene or *p*-xylene.⁷ In that sense it represents a completion of work first reported 15 years ago.⁸ It also describes how primary/tertiary radical ratios formed by triplet ketone reaction with



p-cymene reflect the type of triplet-state interaction and the extent of electron transfer in the exciplexes.⁹ Finally, it analyzes low product quantum yields in terms of radical-radical disproportionation and exciplex decay.

Results

Photoreduction by Toluene and *p*-Xylene. The products obtained by irradiating benzophenone (BP),¹⁰ acetophenone (AP),¹¹ and α,α,α -trifluoroacetophenone (TFA)⁵ with toluene are well-known to be bibenzyl, pinacols, and benzylcarbinols, all products of radical coupling reactions. Since bibenzyl is the one product common to photoreduction of any ketone by toluene, we have performed steady-state kinetics by measuring the effects of toluene (or *p*-xylene) and quencher concentrations on the quantum yields of bibenzyl (bixylyl) formation. In every case that we checked, product ratios are the same at all concentrations of reactants and quenchers, as long as the quenchers do not trap radical inter-

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Table I. Photoreduction of Substituted α,α,α -Trifluoroacetophenones by Toluene in Acetonitrile^a

substituent	Φ_{BB}^{maxb}	k_r/k_d^b	$k_q\tau, M^{-1b,c}$	$10^{-7}k_r, M^{-1} s^{-1d}$
<i>m</i> -CF ₃	0.016 (0.05)	49	135 [0.10]	78 (100)
<i>p</i> -CF ₃	0.06 (0.10)	15	107 [0.10]	44 (72)
<i>p</i> -CF ₃ ^e			3	310
<i>m</i> -Cl	0.05 (0.07)	16	190	4.7 (4.9)
<i>p</i> -MeCO	0.026	4	246	3.2
<i>p</i> -MeCO ^e	0.09	93		74 ^f
<i>p</i> -F	0.06	50	9970 [0.05]	1.7
H	0.024 (0.04)	3.2	810	0.94 (1.1)
H ^g	0.05	1.2		0.73
H ^e	0.11 (0.04) ^g	29	42	23 (9.7) ^g
H ⁱ	0.06	16.5	100	9.4
<i>p</i> -Cl	0.054 (0.07)	4.2	1780	0.42 (0.49)
<i>p</i> - <i>t</i> -Bu	0.03	1.3		
<i>p</i> -CH ₃	0.056 (0.07)	1.4	7500	0.074 (0.09)
<i>m</i> -CH ₃	0.039 (0.03)	0.60	5600	0.068 (0.23)
<i>m</i> -CH ₃ ^e	0.11	7.4	300	2.9
3,4-(CH ₃) ₂	0.047	0.90	15700 [1.6]	0.023
<i>p</i> -CH ₃ O	0.064 (0.06)	0.20	21300	0.008 (0.005)
<i>p</i> -CH ₃ O ^e	0.09	4.6	3780	0.22

^a 313- or 365-nm irradiation of 0.05 M ketone solutions at ambient temperature. Values in parentheses from ref 2. ^b Average reproducibility for two to three runs was ± 10 –15%. ^c 1 M toluene unless noted otherwise in brackets. ^d Accuracy estimated at ± 20 %. ^e With *p*-xylene. ^f Same k_d assumed as with toluene. ^g Reference 5, in benzene. ⁱ *p*-Diisopropylbenzene.

Table II. Photoreduction of Substituted Benzophenones by *p*-Xylene in Acetonitrile^a

substituent	Φ_{BB}^{maxb}	k_r/k_d^b	$k_q\tau, M^{-1b,c}$	$10^{-7}k_r, M^{-1} s^{-1d}$
<i>m</i> -CF ₃	0.04	23	610	3.0
<i>p</i> -CN	0.12	80	660	3.0
<i>m</i> -Cl	0.053	32	660	2.8
<i>p</i> -CF ₃	0.056	54	735	2.6
4,4'-Cl ₂	0.13	32	2230	0.83
4,4'-F ₂	0.091	18	2540	0.76
<i>p</i> -Cl	0.092	19	2490 [0.2]	
H	0.08	18	2950 [1.0]	0.31
4,4'- <i>t</i> -Bu ₂	0.24	2.8	4770	0.24
4,4'-Me ₂	0.21	2.3	6130	0.17
4,4'-(OMe) ₂	0.20	0.7	6370	0.084

^a 313- or 365-nm irradiation of 0.02–0.05 M ketone solutions at ambient temperature. ^b Average reproducibility for two to three runs was ± 10 –15%. ^c Xylene concentrations = 0.5 M unless noted. ^d Accuracy estimated at ± 20 %.

mediates. Likewise, bibenzyl (or bixylyl), benzylcarbinol, and pinacol are formed in ratios very close to 1:2:1 for several ketones.



Tables I–III list the results obtained by measuring bibenzyl or bixylyl quantum yields as a function of alkylbenzene concentration. Plots of reciprocal quantum yield vs. reciprocal donor concentration^{10,12} (eq 1) are linear with intercepts equal to $1/(\alpha\Phi_{isc})$ and slope/intercept values equal to k_d/k_r . The rate constants k_r and

$$\Phi^{-1} = \alpha^{-1}\Phi_{isc}^{-1}(1 + k_d/k_r[\text{ArCH}_3]) \quad (1)$$

$$\Phi^0/\Phi = 1 + k_q\tau[Q] \quad (2)$$

$$1/\tau = k_r[\text{ArCH}_3] + k_d \quad (3)$$

k_d describe reaction of triplet ketone with donor and the sum of all other triplet decay reactions, respectively. All measured intersystem crossing yields (Φ_{isc}) of phenyl ketones which do not undergo rapid intramolecular photoreactions are unity,¹³ so intercepts are listed solely as $1/\alpha$, the maximum quantum yield for formation of bibenzyl. Because of the fairly long extrapolations necessary, some of these values are accurate probably to no better

Table III. Photoreduction of Substituted Acetophenones by *p*-Xylene in Acetonitrile^a

substituent	Φ_{BB}^{maxb}	k_r/k_d^b	$k_q\tau, M^{-1b,c}$	$10^{-7}k_r, M^{-1} s^{-1d}$
<i>m</i> -CN	0.032	15	395	1.5
<i>m</i> -CF ₃	0.14	11	925	0.64
<i>p</i> -CF ₃	0.21	16	1270	0.47
<i>m</i> -Cl	0.105	5.4	1960	0.28
<i>p</i> -CN	0.13	14	3350	0.18
H	0.28 (0.10) ^e	0.30	2930	0.070 (0.07) ^e
<i>m</i> -CH ₃	0.16	0.44	9470	0.027
<i>p</i> - <i>t</i> -Bu	0.05	0.9	18300	0.020
<i>p</i> -Cl	0.15	2.8	25600	0.020 ^g
<i>p</i> -CH ₃	0.11	0.18	17200	0.008 ^g
3,4-Me ₂	0.023	0.10	26000	0.0034 ^g
<i>p</i> -MeO	0.04	0.19	43500	0.0034 ^g
<i>p</i> -COCH ₃	0.06			0.014 ^f

^a 313- or 365-nm irradiation of 0.01–0.03 M ketone solutions at ambient temperature. Values in parentheses from ref 2. ^b Average reproducibility for two to three runs was ± 10 –15%. ^c Xylene concentration = 1.6 M. ^d Accuracy estimated at ± 20 %. ^e reference 5, in benzene. ^f Measured by flash kinetics. ^g Accuracy only ± 50 % because of strong dependence on concentration.

Table IV. Isotope Effects on Triplet Ketone Reactivity^a

ketone	donor	Φ^{maxb}	k_r/k_d^b	$10^{-6}k_r, M^{-1} s^{-1}$
TFA ^c	toluene	0.053	0.83	7.3
TFA ^c	toluene- <i>d</i> ₈	0.015	0.83	7.3
<i>p</i> -MeO-TFA	<i>p</i> -xylene			0.56 ^d
<i>p</i> -MeO-TFA	<i>p</i> -xylene- <i>d</i> ₁₀			0.29 ^d
<i>p</i> -CF ₃ -BP	toluene	0.22	1.6	0.61
<i>p</i> -CF ₃ -BP	toluene- <i>d</i> ₈	0.065	1.15	0.43 ^d
4,4'-(CN) ₂ -BP	toluene			0.85 ^d
4,4'-(CN) ₂ -BP	toluene- <i>d</i> ₈			0.78 ^d
<i>p</i> -Cl-BP	<i>p</i> -xylene			8.7 ^d
<i>p</i> -Cl-BP	<i>p</i> -xylene- <i>d</i> ₁₀			5.4 ^d
BP	toluene			0.46 ^d
BP	toluene- <i>d</i> ₈			0.20 ^d
BP	toluene	0.093	0.90	0.35 (0.41) ^e
BP	toluene- <i>d</i> ₈	0.078	0.36	0.14 ^f
BP	<i>p</i> -xylene			2.5 ^d
BP	<i>p</i> -xylene- <i>d</i> ₁₀			1.6 ^d
<i>p</i> -CN-AP	<i>p</i> -xylene			1.5 ^d
<i>p</i> -CN-AP	<i>p</i> -xylene- <i>d</i> ₁₀			0.61 ^d
AP	<i>p</i> -xylene			1.1 ^d
AP	<i>p</i> -xylene- <i>d</i> ₁₀			0.33 ^d

^a Generally 0.01–0.05 M ketone in CH₃CN, irradiated at 313 nm. ^b From double reciprocal plots. ^c From ref 2. ^d Measured by flash kinetics, 0.001 M ketone, 337-nm excitation. ^e Reference 14. ^f Calculated on the assumption of constant k_q .

than ± 50 %. For bibenzyl, the largest possible value for α is 0.25, the maximum chemical yield in most circumstances. Table I contains results for TFA and its ring-substituted derivatives, Table II for substituted BPs, and Table III for substituted APs.

The photoreduction of each ketone at a given toluene or xylene concentration was quenched with naphthalene. Stern–Volmer plots (eq 2) were linear; their slopes are listed as $k_q\tau$ values in the same three tables. Lifetimes were determined on the basis that $k_q = 1 \times 10^{10} M^{-1} s^{-1}$.¹⁴ The k_r values in the tables were determined from the k_r/k_d ratios and from eq 3. They agree well with previous measurements in acetonitrile⁷ but are twice as large as values in benzene.⁵ The values of k_d include impurity, solvent, and ground-state ketone quenching^{5,7} and will not be considered further.

Isotope Effects. Table IV lists several experiments comparing the reactivity of selected ketones toward toluene and toluene-*d*₈ or *p*-xylene and *p*-xylene-*d*₁₀. The photoreductions of BP and *p*-(trifluoromethyl)benzophenone were studied as a function of toluene concentration in acetonitrile. Triplet lifetimes of several ketones as a function of alkylbenzene concentration also were measured by flash kinetics both in benzene and in acetonitrile. The steady-state and flash experiments gave k_r values which

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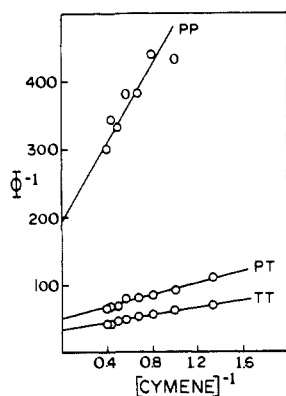
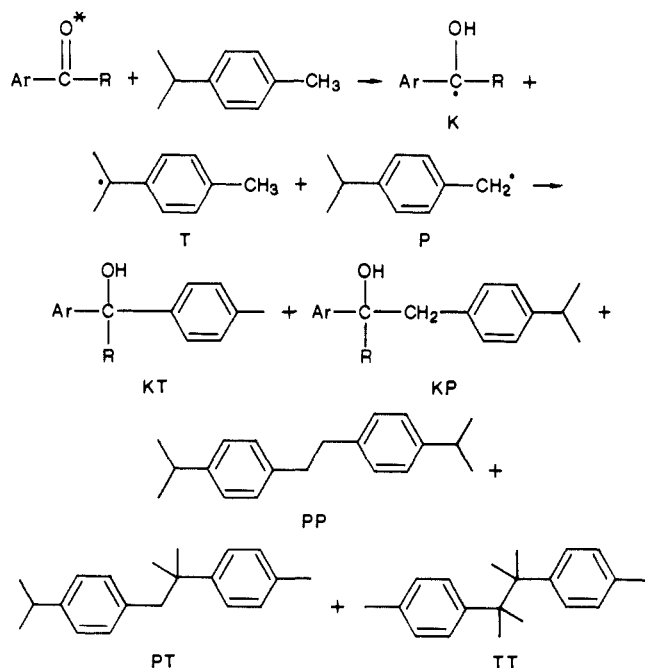


Figure 1. Dependence of hydrocarbon product quantum yields on cymene concentration for acetophenone in benzene.

usually agree closely, although a couple of values do disagree by a factor of 3. Not listed in the table is an isotope effect of 2.4 for 4,4'-dimethylbenzophenone, as measured by phosphorescence quenching with toluene or toluene- d_8 in benzene.

In a separate experiment, benzene and benzene- d_6 were found to quench the photoreduction of TFA by toluene in acetonitrile with the same efficiency. Therefore ring deuteriums do not influence the measured isotope effects.

Photoreduction by *p*-cymene gives a more complicated mixture of products, since both primary (P) and tertiary (T) radicals are formed from the cymene. These couple with each other to give hydrocarbons PP, PT, and TT and with the hemipinacol radical (K) to yield KP and KT.



The products resulting from photoreduction of TFA with *p*-cymene were isolated by a combination of column chromatography and sublimation. A mixture of the three hydrocarbon products, each of the two cross-coupled alcohols, and the pinacols were readily separated on an alumina column. One of the pinacols could not be isolated pure, but IR and NMR spectra of a 50:50 mixture of the two diastereomers indicated nothing but pinacol. The hydrocarbons were individually separated by fractional sublimation, the two symmetrically coupled products PP and TT each subliming more readily than the unsymmetrical PT. Photoreduction of TFA gave mixtures rich in PP; photoreduction of AP gave mixtures rich in TT.

The material balance for production of the three hydrocarbons, the two cross-coupled alcohols, and pinacol was 82% at three different cymene concentrations in benzene at 66% conversion of

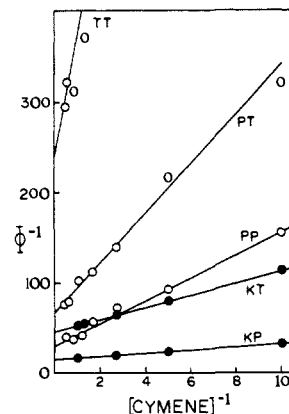


Figure 2. Dependence of product quantum yields on cymene concentration for trifluoroacetophenone in benzene: (O) hydrocarbons; (●) cross-coupled alcohols.

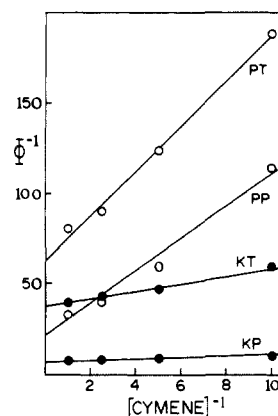


Figure 3. Dependence of product quantum yields on cymene concentration for trifluoroacetophenone in acetonitrile: (O) hydrocarbons; (●) cross-coupled alcohols.

Table V. Photokinetics for Reaction of Acetophenone and TFA with *p*-Cymene^a

quantity	AP(benzene)	TFA(benzene)	TFA-(CH ₃ CN)
$\Phi_{\text{PP}}^{\text{max}}$	0.005	0.031	0.045
$\Phi_{\text{PT}}^{\text{max}}$	0.023	0.015	0.015
$\Phi_{\text{TT}}^{\text{max}}$	0.031	0.004	0.0036
$\Phi_{\text{KP}}^{\text{max}}$		0.077	0.133
$\Phi_{\text{KT}}^{\text{max}}$		0.026	0.028
$\Phi_{\text{KK}}^{\text{max}}$		0.044	0.038
k_r/k_d	0.86 ± 0.12	5 ± 1	29 ± 5
$10^{-7}k_r, \text{M}^{-1} \text{s}^{-1b}$	0.05	4	9

^a Generally 0.05 M ketone, irradiated at 313 nm. ^b Calculated on assumption of same k_d values as measured in ref 2 and Table I.

TFA. The ratio of KP/KT was 3.3:1. Figures 1–3 show double reciprocal plots of product formation for AP and TFA in benzene. Table V lists the results in benzene and in acetonitrile solvent.

Table VI lists ratios of the three hydrocarbon products formed from each of the substituted ketones, where other products did not prevent GC analysis, and primary/tertiary (P/T) radical ratios were calculated therefrom. The somewhat low material balance is probably due to some para coupling of the radicals,¹⁵ which would not affect P/T ratios significantly. Cymene was also reacted with two different sources of *tert*-butoxy radicals. Degassed benzene solutions 1 M in cymene and containing various concentrations of *tert*-butyl hypochlorite were irradiated and analyzed by GC. The only products from cymene were the primary chloride, *p*-isopropylbenzyl chloride, and α ,*p*-dimethylstyrene. The latter product resulted from quantitative dehydrochlorination of the

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Table VI. Substituent Effects on Primary/Tertiary Radical Formation from *p*-Cymene in CH₃CN^a

substituent	%PP	%PT	%TT	P/T ^b
Trifluoroacetophenones				
<i>m</i> -CF ₃	59	41	0	3.9
<i>m</i> -CF ₃ ^c	71	29	0	4.7
<i>p</i> -CF ₃	48	52	0	2.8
<i>m</i> -Cl	56	37	8	2.8
<i>p</i> -F	60	35	5	3.4
H	71	23	6	4.7
H ^c	62	30	8	3.4
<i>p</i> -Cl	47	43	11	2.1
<i>p</i> -Cl ^c	40	44	16	1.6
<i>m</i> -CH ₃ ^c	<i>d</i>	81	19	2.1
<i>p</i> - <i>t</i> -Bu	35	44	21	1.3
<i>p</i> -CH ₃	43	42	16	1.7
<i>p</i> -CH ₃ ^c	40	45	15	1.7
3,4-Me ₂	33	46	22	1.2
<i>p</i> -CH ₃ O	32	46	23	1.2
<i>p</i> -CH ₃ O ^c	31	45	24	1.1
<i>p</i> -CH ₃ CO	15	43	42	0.57
Benzophenones				
<i>p</i> -CN	19	42	40	0.66
3,4-Cl ₂	17	41	42	0.60
4,4'-Cl ₂	16	41	43	0.57
<i>p</i> -CF ₃	15	42	43	0.56
<i>m</i> -CF ₃	10	34	56	0.37
4,4'-F ₂	13	41	46	0.50
<i>p</i> -Cl	10	42	48	0.45
<i>m</i> -Cl	11	39	51	0.43
H	8	44	49	0.42
H ^c	<i>d</i>	45	55	0.42
4,4'- <i>t</i> -Bu ₂	5	31	64	0.26
4,4'-Me ₂	8	34	59	0.33
3,3'-Me ₂	7	32	61	0.30
4,4'-MeO ₂	8	33	59	0.32
4,4'-MeO ₂ ^c	<i>d</i>	40	60	0.33
Acetophenones				
<i>p</i> -CN	24	52	25	0.96
<i>p</i> -Cl	27	44	29	0.98
3,4-C ₂	24	48	29	0.91
<i>m</i> -CN	20	45	35	0.74
<i>m</i> -CF ₃	19	45	36	0.71
<i>m</i> -CF ₃ ^c	<i>d</i>	50	50	0.53
<i>p</i> -CF ₃	19	44	38	0.68
<i>m</i> -Cl	19	44	37	0.69
<i>p</i> -F	16	43	41	0.60
<i>p</i> -F ^c	20	35	45	0.59
<i>p</i> -CH ₃ O	17	42	41	0.61
<i>m</i> -CH ₃	15	41	45	0.54
<i>p</i> -CH ₃	14	40	47	0.51
<i>p</i> - <i>t</i> -Bu	12	41	48	0.47
3,4-Me ₂	13	40	48	0.49
H	11	41	47	0.47
H ^c	8	39	53	0.36
<i>p</i> -CH ₃ CO	6	30	64	0.19

^a 1 M *p*-cymene, 0.1 M ketone, 313 nm, room temperature. ^b (2PP + PT)/(PT + 2TT). ^c In benzene. ^d Peak obscured by other products.

tertiary chloride in the GC injector port, as tests on cumyl chloride established. The styrene/primary chloride product ratio at low hypochlorite concentrations was 2.4 ± 0.1 . Another experiment was performed by irradiating degassed benzene solutions containing 0.6 M cymene and 0.1 M di-*tert*-butyl peroxide at 313 nm. The three hydrocarbon radical coupling products were formed in a TT/PT/PP ratio of 7.5:5.9:1, which corresponds to a 2.7:1 T/P ratio.

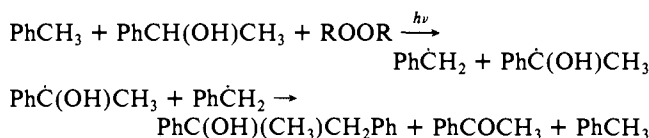
Independent Generation of Intermediate Radicals. Two separate methods were used to independently generate benzyl and hemipinacol radicals in order to measure their disproportionation vs. coupling ratios. Table VII lists the products formed by 313-nm irradiation of degassed solutions containing 1 M toluene, 0.1 M 1-phenylethanol, and various concentrations of di-*tert*-butyl peroxide. The 10:1 substrate ratio was to assure equal production of benzyl and hemipinacol radicals via hydrogen abstraction by the photogenerated *tert*-butoxy radicals.¹⁶ Irradiations were

Table VII. Product Yields for Decomposition of Di-*tert*-butyl Peroxide in Mixtures of 1 M Toluene and 0.1 M 1-Phenylethanol or 1-Phenyl-2,2,2-trifluoroethanol^a

[peroxide], M	solvent	[ketone] ^b	[BK] ^c	[BB] ^d	[pinacol]
0.02	benzene	1.0	2.5	1.2	3.3
0.03	benzene	2.2	2.8	1.5	3.2
0.05	benzene	2.1	1.6	1.0	1.5
0.10	benzene	4.5	2.6	1.8	2.2
0.15	benzene	7.2	3.4	2.5	2.7
0.05	CH ₃ CN	1.0	1.9	1.1	1.0
0.10	CH ₃ CN	1.9	3.0	1.8	1.7
0.15	CH ₃ CN	2.7	4.1	2.3	2.3
0.4 M Toluene-PhCH(OH)CF ₃					
0.05	benzene	0.6	3.8	1.9	1.1
0.1 M <i>p</i> -Xylene-PhCH(OH)CF ₃					
0.05	benzene	0.24	4.0	2.0	1.5
0.1 M Cumene-PhCH(OH)CF ₃					
0.05	benzene	1.3	2.1	0.6	1.05

^a Irradiated at 313 nm for 15–19 h; product yields in units of 10⁻³ M. ^b PhCOCH₃ or PhCOCF₃. ^c Cross-coupled alcohol. ^d Bibenzyl.

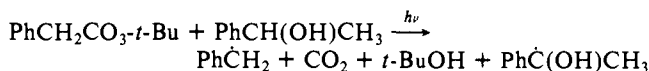
conducted to low conversions in order to minimize reaction of the acetophenone product, which absorbs far more strongly than the peroxide. The table also contains results for 0.05 M peroxide, 0.5 M 1-phenyl-2,2,2-trifluoroethanol, and various concentrations of alkylbenzenes.



Since peroxide decomposition is induced by hemipinacol radicals with the formation of ketone,¹⁷ not all of the acetophenone formed in the above experiments comes from benzyl-hemipinacol radical-radical disproportionation. This problem is evident from the large concentration dependence of the acetophenone/benzylcarbinol ratios in benzene but not in acetonitrile. The value extrapolated to zero peroxide is ~ 0.5 in acetonitrile and probably is not much different in benzene. Therefore, at most one-third of the benzyl-hemipinacol radical-radical reactions results in disproportionation to ketone and toluene.

Similar experiments with the trifluoroethanol give much lower ketone/benzylcarbinol ratios for toluenes and xylene. Radical disproportionation is a very minor reaction in these systems but appears to be more pronounced with cumyl radicals.

We also studied the decomposition of *tert*-butyl phenylperacetate in the presence of 1-phenylethanol. Thermolysis of benzene solutions at 80 °C produced toluene and acetophenone but no benzylcarbinol or pinacol. The reaction presumably proceeds almost entirely by induced decomposition. In contrast, 313-nm irradiation of a degassed solution containing 0.02 M perester and 0.1 M 1-phenylethanol at room temperature gave the products expected from *tert*-butoxy, benzyl, and hemipinacol radicals: *tert*-butyl alcohol (0.02 M), benzyl *tert*-butyl ether (0.0005 M), toluene (0.0005 M), bibenzyl (0.0033 M), 1,2-diphenyl-1-methylethanol (0.0023 M), and acetophenonepinacol (0.0048 M). That the total yield of the benzyl radical products is only 50% indicates that induced decomposition of the perester also occurred. Some toluene could be formed by attack of benzyl radicals on phenylethanol. Therefore the 0.21 ratio of toluene to diphenylmethylethanol is a maximum value for the disproportionation/coupling ratio of the benzyl and hemipinacol radicals, somewhat less than the value gleaned from Table VII.



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Table VIII. Ketone Triplet Energies and Reduction Potentials

substituent	E_T^a	$-E(A^-/A)^b$	$-E_{red}^{*c}$
Trifluoroacetophenones			
<i>p</i> -CH ₃ CO	395 (72.4)	1.15 (26.5)	45.9
<i>m</i> -CF ₃	405 (70.6)	1.21 (27.8)	42.8
<i>p</i> -CF ₃	405 (70.6)	1.20 (27.6)	43.0
<i>m</i> -Cl	413 (69.2)	1.25 (28.7)	40.5
H	409 (69.9)	1.38 (31.9)	38.0
<i>p</i> -F	408 (70.1)	1.47 (33.9)	36.2
<i>p</i> -Cl	423 (67.6)	1.32 (30.6)	37.0
<i>m</i> -CH ₃	428 (66.8)	1.42 (32.9)	33.9
<i>p</i> - <i>t</i> -Bu	423 (67.6)	1.54 (35.5)	32.1
<i>p</i> -CH ₃	425 (67.3)	1.57 (36.2)	31.1
3,4-Me ₂	430 (66.5)	1.61 (37.1)	29.4
<i>p</i> -CH ₃ O	434 (65.9)	1.63 (37.5)	28.4
Benzophenones			
<i>p</i> -CN	428 (66.8)	1.42 (32.7)	34.1
<i>p</i> -CF ₃	419 (68.3)	1.58 (36.4)	31.9
<i>m</i> -CF ₃	414 (69.1)	1.64 (37.8)	31.3
<i>m</i> -Cl	416 (68.8)	1.67 (38.4)	30.3
4,4'-Cl ₂	417 (68.6)	1.67 (38.5)	30.1
4,4'-Fe ₂	407 (70.3)	1.78 (41.0)	29.3
<i>p</i> -Cl	415 (68.9)	1.75 (40.3)	28.6
H	413 (69.2)	1.83 (42.1)	27.1
4,4'- <i>t</i> -Bu ₂	413 (69.2)	1.87 (43.1)	26.1
4,4'-Me ₂	414 (69.1)	1.90 (43.8)	25.3
4,4'-MeO ₂	412 (69.4)	2.02 (46.5)	22.9
Acetophenones			
<i>m</i> -CN	392 (73.0)	1.75 (40.3)	32.7
<i>p</i> -CN	413 (69.2)	1.58 (36.4)	32.8
<i>p</i> -CH ₃ CO	426 (67.1)	1.56 (35.9)	31.2
<i>p</i> -CF ₃	399 (71.7)	1.81 (41.7)	30.0
<i>m</i> -CF ₃	392 (73.0)	1.90 (43.8)	29.2
<i>m</i> -Cl	394 (72.6)	1.94 (44.7)	27.9
H	389 (73.5)	2.14 (49.3)	24.2
<i>p</i> -Cl	399 (71.7)	2.10 (48.3)	23.4
<i>m</i> -CH ₃	401 (71.3)	2.12 (48.8)	22.5
<i>p</i> - <i>t</i> -Bu	394 (72.6)	2.21 (50.9)	21.7
<i>p</i> -CH ₃	396 (72.2)	2.19 (50.4)	21.8
3,4-Me ₂	407 (70.3)	2.20 (50.7)	19.6
<i>p</i> -CH ₃ O	408 (70.1)	2.23 (51.4)	19.2

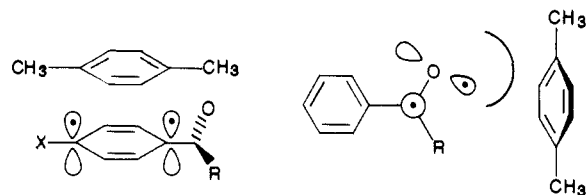
^a0,0 band in nm (kcal/mol), MTHF solvent. ^bHalf-wave reduction potential vs. SCE in eV (kcal/mol), CH₃CN solvent. ^c $E_T - E(A^-/A)$, kcal/mol.

Spectroscopy. Phosphorescence of all the ketones was measured at 77 K in methyltetrahydrofuran, an aprotic solvent like the acetonitrile used for kinetics. Reduction potentials of all the ketones were measured in acetonitrile vs. a standard calomel electrode. All the 0-0 triplet energies and reduction potentials are listed in Table VIII. The former are in good agreement with those measured in other solvents.^{7,18,19} The relative values of the latter also agree well with literature values,^{7,19,20} although absolute values vary by as much as 0.1 eV. We measured values for all the ketones so that our internal comparisons would be accurate and not rely on measurements made under differing conditions.

Discussion

Our measured variations in triplet reactivity and product selectivity as a function of ring substituents can be summarized as follows. Rate constants for triplet ketone reaction with alkylbenzenes vary tremendously for TFAs, substantially for APs, and only modestly for BPs. Likewise, product ratios from *p*-cymene vary the most for the substituted TFAs and less so for the substituted APs and BPs. Isotope effects are insignificant for the more easily reduced ketoens but significant for the harder to reduce ketones. We shall interpret these effects in terms of the nature of the reactive triplet and the competition between hydrogen

Chart I



abstraction and reversible CT exciplex formation. We emphasize and reiterate here that those ketones that show negligible isotope effects must undergo rate-determining, *irreversible* complexation.⁵ Those which show isotope effects may undergo *reversible* complexation prior to hydrogen transfer and/or independent hydrogen atom transfer.

Before proceeding, we shall consider the geometries of the possible reactions between ketone triplets and alkylbenzenes, since this factor shall be important in all of our subsequent discussion. Hydrogen abstraction is well-known to involve attack of the half-empty oxygen *n*-orbital on a C-H bond.² The generally accepted model for exciplex structure assumes maximum overlap of donor HOMO and acceptor LUMO orbitals.²¹ In our case, the HOMO is an alkylbenzene π -orbital and the LUMO is either a benzoyl π -orbital (π, π^*) or the carbonyl *n*-orbital (*n*, π^*). We presume that alkylbenzenes form relatively tight face-to-face complexes with the π, π^* triplets and looser complexes with *n*, π^* triplets involving π -overlap with the carbonyl *n*-orbital, as Singer first proposed (Chart I).²² We shall explore whether these quite different exciplex structures can cause differences either in their rates of formation (kinetics) or in their subsequent reactions (product selectivities).

It is now well established that the π, π^* triplets of aryl ketones are no more than 10^{-3} times as reactive as their *n*, π^* triplets in direct hydrogen atom abstraction reactions.²³⁻²⁵ Ketones with π, π^* lowest triplets undergo hydrogen abstraction with reduced observed rate constants and often with reduced efficiency from low populations of their *n*, π^* triplets. We have just shown that inductive substituent effects on rate constants for hydrogen abstraction by *n*, π^* triplets are quite small,⁶ as originally anticipated.²³ Substituent effects get large only when the lowest triplets are π, π^* ²⁶ and the equilibrium constant for triplet level interconversion becomes part of the observed rate constant.²³

CT quenching occurs efficiently for ketones with both *n*, π^* and π, π^* lowest triplets,²⁷⁻²⁹ and it has not been established whether there is any intrinsic difference in reactivity between the two types of triplets.^{2,7} We have shown that triplet TFA reacts very rapidly with alkylbenzenes by a CT process⁵ and that substituents on the TFA modify the rate constant by 4 orders of magnitude.⁷ We pointed out that the large substituent effects might be due to changing proportions of *n*, π^* and π, π^* triplets, with the former more reactive, as well as to changes in the thermodynamics for electron transfer.⁷ These considerations, plus the knowledge that hydrogen abstraction by π, π^* triplets is very slow, produce the three-component eq 4 for the rate constants which we have measured, where χ_n and χ_π indicate the equilibrium fractions of

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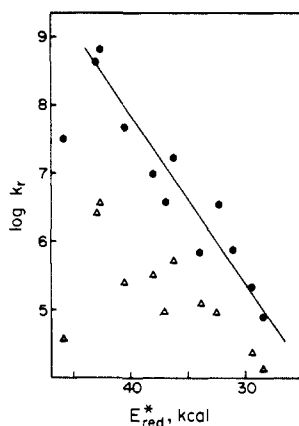


Figure 4. Bimolecular reaction rate constants for triplet trifluoroacetophenone as a function of triplet ketone reduction potential: (●) toward toluene in acetonitrile; (Δ) toward cyclopentane ($\times 1/4$).

n, π^* and π, π^* triplets and k_H and k_{CT} represent rate constants for hydrogen atom abstraction and for exciplex formation.

$$k_r^{\text{obsd}} = \chi_n k_H^n + \chi_n k_{CT}^n + \chi_\pi k_{CT}^\pi \quad (4)$$

We shall now analyze the rate behavior of each type of ketone and then the substituent effects on product selectivity before making overall conclusions. First, it is important to note that n, π^* ketone triplets are well-known to show the same reactivity and selectivity as alkoxy radicals in hydrogen abstraction reactions.³⁰⁻³² The *tert*-butoxy radical displays relative reactivities toward cyclopentane, *p*-xylene, and toluene of 4:4:1, respectively.³² We shall base our analysis on the expectation that any triplet ketone that reacts with the alkylbenzenes only by hydrogen atom abstraction would display the same ratio of rate constants. Inasmuch as CT complexation competes, k_r^{obsd} values will be larger than one-quarter of or 1 times the k_H values measured toward cyclopentane,⁶ which has too high an oxidation potential to function as an electron donor.

Trifluoroacetophenones. All of these ketones have π, π^* lowest triplets.⁷ Figure 4 displays the dependence of k_r values on triplet ketone reduction potentials (as derived in Table VIII). There is a good linear free energy dependence, as expected for a CT process, with a slope of $0.4/RT$. The diketone is markedly less reactive than expected. The triangles in Figure 4 represent rate constants for hydrogen abstraction from cyclopentane, divided by 4 so as to represent rate constants for the hypothetical "pure" hydrogen atom abstraction from toluene.³² The various substituted TFAs are all 10–100 times more reactive toward toluene than would be expected for simple hydrogen atom abstraction; therefore >90% of the reaction with toluene can be attributed to a CT interaction.

The slope of Figure 4 is double that for the quenching of triplet TFA itself by various substituted benzenes of different oxidation potentials.^{5,7} We previously suggested that the slope of a less extensive plot might be hiding an S-shaped curve because of changing proportions of n, π^* triplets.⁷ There does not appear to be any experimentally distinguishable S shape, which would be apparent only if the most reactive ketones had n, π^* lowest triplets and if the intrinsic $n, \pi^*/\pi, \pi^*$ reactivity ratio were at least 100. Neither condition appears to hold.

We can gauge the influence of varying $n, \pi^*-\pi, \pi^*$ populations as follows. Since hydrogen abstraction rate constants are dominated by the $n, \pi^*-\pi, \pi^*$ equilibrium, the dotted line through the triangles in Figure 4 represents the change in n, π^* fractional population. (A good linear correlation could not have been expected, since hydrogen abstraction rate constants do not correlate with triplet energies.⁶) Rate constants toward toluene vary by 4 orders of magnitude, whereas those toward cyclopentane vary by only 2. Thus, if n, π^* reaction competed significantly with π, π^*

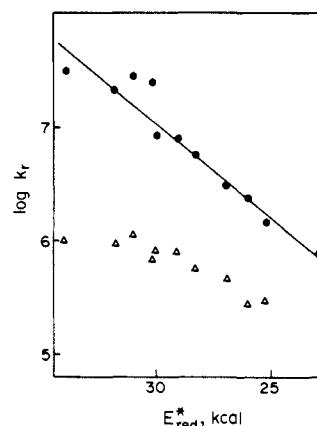


Figure 5. Bimolecular reaction rate constants for triplet benzophenone as a function of triplet ketone reduction potential: (●) toward *p*-xylene in acetonitrile; (Δ) toward cyclopentane.

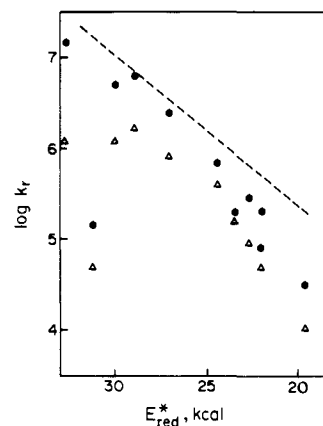


Figure 6. Bimolecular reaction rate constants for triplet acetophenone as a function of triplet ketone reduction potential: (●) toward *p*-xylene in acetonitrile; (Δ) toward cyclopentane.

reaction, roughly half of the toluene slope would represent changes in n, π^* population and half would represent changes in redox potentials. However, there is no sign of curvature over a n, π^* fractional population which we now know⁶ ranges from $\leq 0.1\%$ to $\sim 50\%$. Therefore Figure 4 provides no evidence for any intrinsic difference in n, π^* and π, π^* reactivity. We conclude that most of the reaction comes from the π, π^* triplets, as verified by the correlation of TFA and BP reactivities discussed below. A separate study of the effects of successive α -fluorination shows that k_{CT} continues rising when the lowest triplet switches from n, π^* to π, π^* , whereas k_H begins to decrease.³³

Benzophenones. All of these ketones have n, π^* lowest triplets.³⁴ Therefore direct hydrogen atom abstraction might be expected to be more competitive with CT quenching than is the case for the TFA triplets. Figure 5 plots rate constants for the reaction of triplet BPs with *p*-xylene as a function of excited ketone reduction potential. The linearity of the plot suggests that triplet reaction is dominated by charge transfer. This conclusion is reinforced by the fact that reactivity toward xylene is 5 times greater than toward cyclopentane for the least reactive BPs and up to 30 times greater for the most reactive BPs. Thus direct hydrogen atom abstraction can contribute only 3–20% to the total reactivity observed toward xylene. The slope of the plot is $0.2/RT$, one-half that observed for TFAs with toluene.

The small isotope effects observed for the CN- and CF_3 -substituted BPs, which have the highest reactivity of the BPs, demand the predominance of a CT mechanism, as concluded earlier for TFA.⁵ However, there are significant isotope effects for the more

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Table IX. Comparison of Isotope Effects with Triplet Reactivity^a

ketone	low T	substrate	E_{red}^{*b}	k_r^H/k_r^D	k_r^c	k_H^d
TFA	π, π^*	toluene ^e	38	1.0	230	1.4
4,4'-(CN) ₂ -BP	n, π^*	toluene ^e	>34	1.1	>30	2.3
<i>p</i> -CF ₃ -BP	n, π^*	toluene	32	1.4	26	1.2
<i>p</i> -Cl-BP	n, π^*	xylene	28.6	1.6	7.2	0.7
<i>p</i> -MeO-TFA	π, π^*	xylene	28.4	1.9	2.2	<0.02
BP	n, π^*	toluene	27	2.4		
BP	n, π^*	xylene	27	1.5	3.1	0.6
4,4'-Me ₂ -BP	n, π^*	toluene ^e	25	2.4	1.7	0.5
<i>p</i> -CN-AP	π, π^*	xylene	33	2.5	1.8	0.3
AP	n, π^*	xylene	24	3.3	0.7	0.5

^aAll rate constants in units of $10^6 \text{ M}^{-1} \text{ s}^{-1}$, CH₃CN solvent. ^bkcal/mol. ^cWith xylene, from Tables I-III. ^dWith cyclopentane, ref 6. ^eIn benzene.

electron-rich and less reactive BPs and APs, despite the fact that overall reactivity is too high to represent simple hydrogen atom abstraction. We shall return to this point below.

Walling and Gibian reported a Hammett ρ value of -1.16 for the selectivity that triplet BP displays toward ring-substituted toluenes.³¹ At the time they thought that the value for *tert*-butoxy radical was similar, but later work showed its ρ value to be <0.4 .³⁵ This large difference in ρ values between triplet ketone and alkoxy radical is further evidence for the importance of CT complexation with the triplet ketones. Mallory and co-workers reported a ρ value of $+0.87$ for the reaction of ring-substituted BPs with benzhydrol.³⁶ This value is almost double what we just reported for cyclopentane as hydrogen donor,⁶ perhaps indicative of partial CT even with as reactive a substrate as benzhydrol.

Acetophenones. Figure 6 compares rate constants for the reaction of triplet acetophenones with *p*-xylene and with cyclopentane. All but one of the substituted APs are 3–10 times more reactive toward xylene. The line, which comes from Figure 5, correlates the reactivities of the benzophenones toward xylene. Only those substituted APs with n, π^* lowest triplets (*m*-CN, *m*-CF₃, *p*-CF₃, and *m*-Cl) lie close to that line. Those APs with π, π^* lowest triplets (*p*-CN, *p*-Cl, and all electron-donating substituents) display reactivities about one-tenth that interpolated for n, π^* triplets with the same reduction potentials. *p*-Acetylacetophenone, like *p*-acetyltrifluoroacetophenone, has unusually low reactivity. The falloff in reactivity toward xylene is comparable to that observed toward cyclopentane and therefore presumably has the same cause, namely, low populations of reactive n, π^* triplets. The π, π^* triplets clearly can be no more than 1–10% as reactive as the n, π^* triplets. The least reactive APs appear to show the S-shaped plot originally sought for the TFAs,⁷ and it is likely that they react from both triplet levels.

The fact that the APs are the hardest ketones to reduce and also show reactivity closest to that displayed toward cyclopentane verifies our strategy of comparing reactivities to detect CT reaction competing with (and dominating) hydrogen abstraction.

Rate-Determining Step. Table IX lists the primary isotope effects measured for various ketones as a function of their triplet reduction potentials and triplet reactivity. It is apparent that all of the ketones with triplet reduction potentials below about 30 kcal/mol show significant isotope effects. Moreover, the size of the isotope effect correlates well with E_{red}^* and even better with actual k_r values, independently of the nature of the lowest triplet. Since we have just concluded from the magnitude of the k_r values that all of the ketones react predominantly by CT complexation, we now can further conclude that the rate-determining step changes smoothly from complex formation to hydrogen transfer as triplet ketone reduction potentials increase and as the overall reaction becomes slower.

Figure 7 portrays the variations in activation energies for charge transfer and hydrogen transfer as the thermodynamics for electron transfer change. This figure emphasizes how charge separation facilitates hydrogen transfer. For complexation to be both

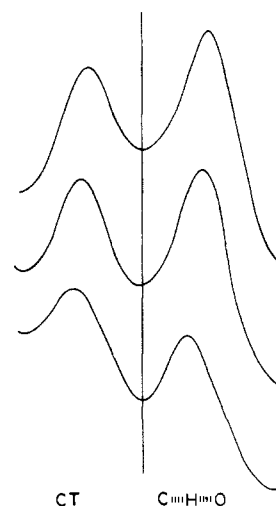


Figure 7. Representative potential energy diagrams for CT complexation followed by hydrogen transfer: top, $E_{red}^* > 30$ kcal/mol; middle, ~ 28 kcal/mol; bottom, < 26 kcal/mol. Note that the left and right half represent two different reaction coordinates.

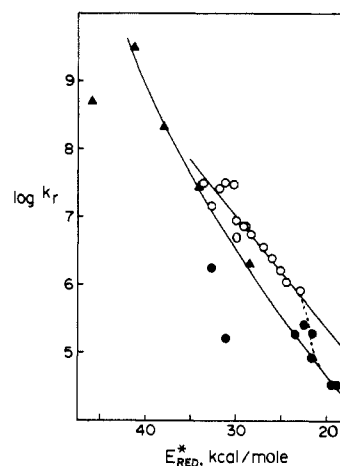


Figure 8. Overall dependence of rate constants for triplet ketone reaction with *p*-xylene on triplet ketone reduction potential: (▲) TFAs; (○) BP and AP n, π^* triplets; (●) AP π, π^* triplets.

rate-determining and much faster than hydrogen transfer, as is the case for TFA, the charge separation within the exciplex must substantially increase the rate of hydrogen transfer to oxygen. For the least reactive ketones, there is so little charge separation that reactivity is enhanced only a fewfold relative to normal hydrogen abstraction. As the ketones become easier to reduce, charge separation increases and hydrogen transfer from within the complex becomes faster until, around 28 kcal/mol, hydrogen transfer becomes faster than reverse complexation. At this point the isotope effect shrinks and becomes insignificant for ketones with triplet reduction potentials above 30 kcal/mol. *p*-Cyanacetophenone is the only exception; as discussed below, it has unusually low reactivity.

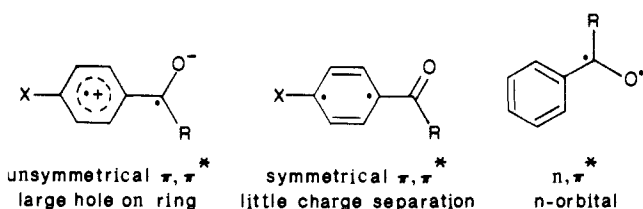
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Toluene produces a larger isotope effect with BP than does the more reactive xylene. This difference further strengthens the composite picture since the donor oxidation potential must influence the energetics of charge transfer as much as does the acceptor reduction potential.

Comparison of n,π^* and π,π^* Triplets. Figure 8 compares the triplet reactivities toward *p*-xylene of all ketones studied as a function of triplet reduction potential. The filled markers indicate ketones with π,π^* lowest triplets. Whereas the n,π^* triplets show a good linear correlation, the π,π^* triplets (except for the *p*-diketones) show a curved correlation. The curvature explains why substituted TFA reactivity seems to correlate well with n,π^* reactivity, while that of AP π,π^* triplets does not. The latter are reacting at least partially from their n,π^* triplets, as deduced above from the fact that substituents on AP cause very similar variations in rate constants for attack on both xylene and cyclopentane. However, the product ratios discussed below and the S shape in Figure 6 (emphasized by the dotted line in Figure 8) indicate significant involvement of π,π^* triplets.

Why is the free energy plot curved for π,π^* triplets, giving a variable ratio of $\pi,\pi^*/n,\pi^*$ reactivity, and why are the diketones so unreactive? We believe that the answer involves two factors: the extent of CT-induced activation of benzylic C-H bonds and the different types of π,π^* excitation possible in substituted benzenes. It is well established that 1,4-positioning of two electron-withdrawing substituents results in a lowest π,π^* triplet that basically is a 1,4-biradical with no significant charge separation.²⁵ The low reactivities of the diketones and of 4-cyanoacetophenone presumably reflect the lack of charge separation and the delocalized half-empty π -orbital in their triplets. In contrast, ketones substituted with electron-donating substituents have a strong ring-to-carbonyl CT component in their lowest triplets.³⁷ The charge separation and the presumed localization of the "hole" near the electron-donating group may well facilitate exciplex formation. This reasoning is based on the assumption that exciplex formation involves the donor-acceptor orbital overlap discussed above and on the corollary that rate constants reflect the ease of achieving this overlap.



The TFA triplets (except *p*-acetyl) all presumably have a strong internal CT component because of the great electron-attracting nature of the COCF_3 group. That they and n,π^* triplets have similar reactivities is coincidental. The n,π^* triplets have no significant charge separation but a highly localized hole orbital for interaction with the donors. TFA π,π^* triplets show high reactivity because the significant charge separation promotes proton transfer to oxygen. AP π,π^* triplets do not produce as much charge separation or as much negative charge on oxygen, so hydrogen transfer is promoted only weakly and remains rate-determining. The curved dependence of π,π^* reactivity on reduction potential, which results in the large apparent slope when only TFAs are plotted,⁷ reflects stereoelectronic as well as energetic effects, the former due to differing types of activation induced by CT interactions of different π,π^* triplets.

Comparison of Intra- and Intermolecular Quenching. Scaiano and co-workers recently concluded that intramolecular CT quenching in triplet β -phenylpropiophenones occurs only from the n,π^* triplets.³⁸ This reaction is the intramolecular equivalent of toluene quenching triplet AP.³⁹ We believe that their con-

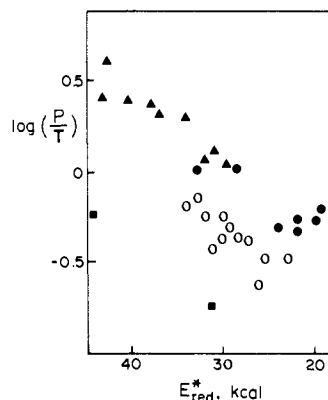


Figure 9. Variation of primary/tertiary selectivity toward cymene as a function of triplet ketone reduction potential: (▲) TFA and (●) AP π,π^* triplets; (○) BP and AP n,π^* triplets; (■) diketone triplets.

clusion is correct but not general. Conformational preferences probably retard parallel overlap of the two benzene rings in β -phenylpropiophenone, so the less reactive π,π^* triplet cannot be quenched. It is interesting that triplet γ -phenylbutyrophenone undergoes type II elimination in high quantum efficiency and is 3 times more reactive than triplet valerophenone,^{30b} exactly the ratio of γ -hydrogen abstraction rates predicted by alkoxy radicals.³² Thus there is no evidence for any intramolecular CT complexation in this compound. We have already discussed the huge difference between β - and γ -vinyl ketones in this regard.⁴⁰ The behavior of the ω -phenyl ketones is another manifestation of conformational restrictions on intramolecular reactivity.

Product Selectivity. The meaning of the slopes of plots such as in Figures 4 and 5 remains ill-defined. Weller originally showed that slopes of similar plots for endothermic electron transfer can equal $1/RT$ (0.7/kcal),⁴¹ although some treatments of electron-transfer theory predict smaller values.⁴² The slopes of CT quenching in systems such as ours where full electron transfer is too endothermic to afford rate constants as high as observed are typically 20–40% the maximum value possible.^{5,7,28,43} We⁵ and others⁴³ once suggested that these deviations from $1/RT$ reflect the degree of charge separation in the exciplexes. Subsequent reflection raised skepticism that, say, *p*-methoxytrifluoroacetophenone would accept as much electron density from toluene as would *p*-(trifluoromethyl)trifluoroacetophenone. Therefore we decided to investigate product selectivity in order to separate exciplex reactivity from the kinetics of exciplex formation.

Figure 9 plots ratios of primary and tertiary radicals formed from *p*-cymene as a function of triplet ketone reduction potential. The ratio found for the *tert*-butoxy radical itself (the model hydrogen atom abstractor) is similar to that displayed by many of the BPs and APs. One might wonder whether P/T values greater than 0.4 reflect CT complexation competing with simple hydrogen atom abstraction by n,π^* triplets. However, since it was concluded above that most of the ketones, including all of the TFAs, react almost exclusively by CT interaction, few of these P/T ratios reflect such a mixed mechanism.

Looking first at the individual types, we see a good linear free energy relationship for the substituted TFAs,^{9b} although the actual P/T values vary over a factor of only 4. With substituted BPs, the values all cluster within a factor of 2 around the *tert*-butoxy radical value, although para electron-withdrawing substituents definitely increase P/T values. Exactly the opposite trend occurs for hydrogen abstraction from 2,3-dimethylbutane, where electron-donating substituents on BP increase P/T ratios.⁶ Therefore

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the selectivity displayed in Figure 9 definitely reflects the dominance of a mechanism other than simple hydrogen abstraction. The behavior of the substituted APs, which have the most negative reduction potentials of all the ketones studied, is interesting in that those with π, π^* lowest triplets give P/T ratios 50% greater than those of the comparable BPs. Those with n, π^* lowest triplets give ratios not much different from those of the comparable BPs. This difference suggests, as indicated above, that the former react at least partially from their π, π^* levels.

If we now consider all the data, we see that ketones with π, π^* lowest triplets in general form relatively more primary radical than do ketones with n, π^* triplets. Within experimental error, all the monoketones with π, π^* lowest triplets show a good correlation covering an order of magnitude in P/T values, while actual k values cover 5 orders of magnitude in range. The two diketones, with very low P/T ratios, are dramatic exceptions in both respects. Those ketones with n, π^* lowest triplets show a weaker correlation, with P/T values only two-thirds as large as those for π, π^* triplets of the same reduction potential.

These observations prompt three important questions. (1) Why do product ratios correlate so well with the thermodynamics for electron transfer, especially for π, π^* triplets? (2) Why does P/T selectivity appear to be higher for π, π^* than for n, π^* triplets? (3) Why are the two diketones such exceptions? Since there is so much independent evidence that the products arise by hydrogen transfer within an exciplex, we view the often high primary selectivity as corroboration of the CT nature of the exciplex and consider the above questions in terms of the quite different exciplex structures described at the beginning of the Discussion.

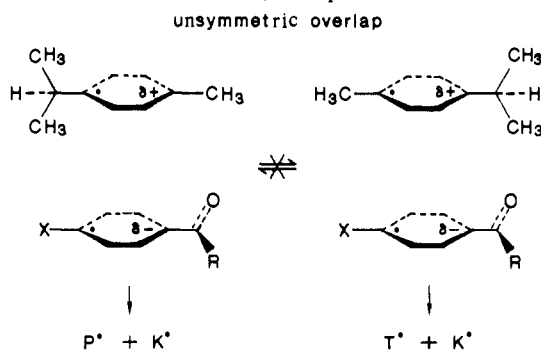
The correlation of product selectivity with reduction potential of π, π^* triplets is so significant that selectivity surely is dominated primarily by electronic factors. Simple steric factors are relatively unimportant. For example, the *p*-*tert*-butyl ketones are if anything more reactive than the *p*-methyl ketones and produce almost the same P/T ratios. We suggested preliminarily that the variation in P/T selectivity represents a kinetic acidity effect.⁹ With the TFAs, exciplex formation apparently involves a sufficient degree of electron transfer that hydrogen transfer within the exciplex resembles proton transfer. Primary protons thus are transferred more rapidly to the basic carbonyl oxygen than are tertiary protons. With the harder to reduce ketones, the degree of electron transfer in the exciplex is smaller, and hydrogen transfer takes place with very little change in charge separation. Thus the more stable radical is formed preferentially.

Although there are several reports of high primary/tertiary selectivity accompanying hydrogen transfer from radical cation-like species,⁴⁴⁻⁴⁸ there also are several reports of more normal selectivity;⁴⁹ it is not easy to explain the differences. It is difficult to determine from the electrochemical literature the exact selectivity of deprotonation that should be expected for pure cymene radical cation. Some reports indicate large P/T radical ratios,⁴⁸ while others report large T/P ratios.⁵⁰ It is evident that the base/solvent combination is important, but more research is needed to afford reliable predictive capabilities. Thus cymene is oxidized primarily at the methyl group in protic solvents containing added acetate base but primarily at the tertiary carbon in aprotic solvents.⁵¹

Lewis has demonstrated that photooxidation at the α -carbons of amines, which also shows a strong preference for primary vs. tertiary hydrogens,⁴⁵ has a strong stereoelectronic component.⁴⁶ The dramatic difference in P/T selectivity between our mono-

and diketones with π, π^* lowest triplets indicates that selectivity probably is determined by orientational factors similar to those thought to determine the regiochemistry of cycloalkenone cycloadditions to alkenes.⁵² Inasmuch as an alkyl group stabilizes the positive charge on the donor and the acyl group stabilizes the negative charge on the ketone, the carbons bearing these substituents on each benzene ring would approach each other as closely as possible so as to minimize charge separation. If we presume the face-to-face complex geometry described above, such an arrangement would assure that the benzyl protons of toluene are within bonding distance of the carbonyl. With cymene, however, such an arrangement would result in at least two distinct complexes. Since each is formed irreversibly, at least from the most reactive ketones, one would lead exclusively to a primary radical, the other only to a tertiary radical, *provided that the two benzene rings do not rotate much with respect to each other.*

That this picture is essentially correct is demonstrated by the behavior of the two diketones. They form effectively only one complex with cymene, both alkyl groups being within equal distance of a carbonyl in any face-to-face arrangement. Since these diketones have π, π^* lowest triplets,²⁵ excitation presumably is centered on the benzene ring, with each carbonyl a potential electron and proton acceptor. (NMR analysis indicated that only the CF_3CO gets reduced in *p*-acetyltrifluoroacetophenone. However, independent work³³ indicates that rapid and irreversible hydrogen transfer occurs from PhC(OH)CH_3 hemipinacol radicals to TFA.) The strong preference for formation of the thermodynamically preferable tertiary radical indicates that the "kinetic acidity effect" for monoketones is primarily stereoelectronic in origin. We therefore conclude that the large changes in product selectivities with increased charge transfer are also primarily stereoelectronic. These changes are far more evident for π, π^* triplets, which presumably form complexes with more rigidly defined orientations than do n, π^* triplets.



What now needs explanation is the source of this stereoelectronic effect for monoketones. It has been suggested that the well-known preference of isopropyl groups on benzene for a conformation with the benzylic proton in the plane of the ring explains high P/T ratios for the cymene radical cation.⁴⁸ This explanation seems incomplete, since benzylic conjugation of incipient cumyl intermediates and nonbonded interactions of the isopropyl methyls are opposed no matter how much positive charge resides on the cymene. Moreover, the actual quantum efficiencies with which toluene and cumene react are comparable.⁵ Therefore the P/T selectivity with cymene must arise from preferential formation of one of the two different exciplex geometries discussed above. We suggest that this differentiation involves inefficient hyperconjugative stabilization by an isopropyl group of the positive charge on an alkylbenzene radical cation. As decreasing ketone reduction potential causes the alkylbenzene to develop increasing positive charge, the exciplex geometry with the methyl group near the acyl group becomes increasingly favored since the methyl group better stabilizes the positive charge. This same reasoning explains the greater reactivity of toluene relative to cumene, which we originally attributed to a steric effect.⁵ Thus, the P/T ratios appear to be

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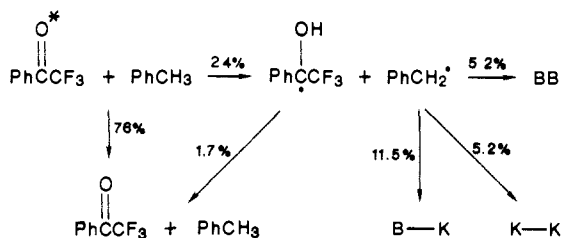
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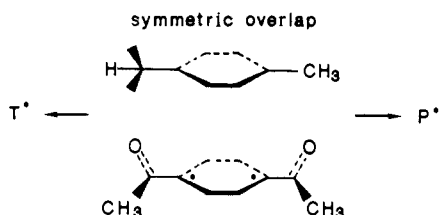
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Chart II



sensitive measures of the extent of electron transfer in π, π^* -derived exciplexes.



The validity of this model is supported by the reported EPR spectra of cumene and cymene radical cations.⁵³ At temperatures below 130 K, conformations are favored in which the tertiary C-H bonds lie almost parallel to the benzene π -system. At higher temperatures the isopropyl group undergoes free rotation. Therefore the need for hyperconjugative stabilization of the radical cation by benzylic C-H bonds appears to be so great as to partially offset the steric hindrance produced by in-plane methyl groups.

That there are changes in exciplex behavior attributable to the ease of electron transfer in forming the exciplex indicates that the various ketones form exciplexes with different structures. They cannot all be contact radical ion pairs; therefore they must be excited CT complexes with only partial but variable charge separation. We have already pointed out that complete electron transfer with formation of solvent-separated radical ions is too endothermic to occur with significant rates in these systems^{5,7,54} and probably is not involved even with the more easily oxidized aliphatic amines.^{3c}

Quantum Efficiencies. Lower than expected quantum efficiency is one of the classic indications that photoreactions proceed via exciplexes.^{1,2,5} Radiationless decay of the exciplex invariably competes with proton transfer, so that radical yields are lower than in the absence of CT interactions. Thus there are isotope effects on *quantum yields* but not on rate constants for TFA photoreduction.⁵

Since the actual chemical yield of bibenzyl averages 25% for these photoreductions, the fraction of triplet ketone-donor interactions which proceed to give stable photoproducts is some 4 times higher than α in eq 1. Given 100% efficient intersystem crossing, α values lower than 0.25 reflect disproportionation of radicals back to ground-state ketone and any other inefficiencies which occur after triplet reaction and before product formation. Our measurements indicate that disproportionation accounts for no more than one-quarter to one-third of benzyl-hemipinacol radical-radical reactions. Therefore maximum bibenzyl quantum yields of $\sim 20\%$ are expected. Most of the ketones studied show α values much smaller than that value. The α values for the TFAs are about one-half those for the APs, as expected from earlier work,⁵ and one-half to one-quarter those for the BPs. Only the BPs with electron-donating substituents, and unsubstituted acetophenone, give α values near the maximum expected. This behavior reinforces the conclusion that most of these ketones react via an exciplex, with only the hardest to reduce n, π^* triplets reacting primarily by direct hydrogen abstraction. Chart II dissects the quantum efficiency of the various decay paths followed by triplet TFA. Our conclusions contrast with the suggestion put

forth by the Brandeis group that ketone photoreduction by amines is inefficient only because of radical-radical disproportionation.⁵⁵

The large experimental errors inherent in determining α values by extrapolation make any further analysis of individual α values unprofitable.

Overall Comparison of Results. We set out to determine how much CT complexation and direct hydrogen abstraction compete, the extent of electron transfer in CT complexation, and whether n, π^* and π, π^* triplets differ in reactivity. We shall summarize our conclusions in reverse order and emphasize from the outset that our conclusions are based on the patterns displayed by all of the ketones.

It appears that n, π^* and π, π^* triplets both react with alkylbenzenes predominantly by CT complexation, since rate constants are much larger than expected for simple hydrogen atom abstraction. Because rate constants, isotope effects, and product selectivities all show good correlations with triplet ketone reduction potential, we conclude that both the formation and reaction of the intermediate CT complex are sensitive to and reflect the degree of electron transfer involved in complexation. For this reason the rate-determining step of the reaction (as revealed by the isotope effects) shifts from complexation to hydrogen transfer as the triplet ketone becomes harder to reduce.

Despite sharing the same gross mechanism and displaying similar isotope effects, π, π^* and n, π^* triplets do interact differently with alkylbenzenes. The former have variable, often lower, reactivity relative to n, π^* triplets and apparently form complexes of significantly different structure. A comparison of *p*-methoxytrifluoroacetophenone and *p*-chlorobenzophenone, which have the same triplet reduction potential, clearly illustrates the differences. The n, π^* triplet is the more reactive while the π, π^* triplet gives twice as large a primary/tertiary radical ratio with cymene. Nonetheless, they show similar *partial* isotope effects; for both ketones, complexation and hydrogen transfer are equally rate-determining.

The reactivity of n, π^* triplets shows a good linear correlation with triplet ketone reduction potential, whereas the reactivity of π, π^* triplets shows a curved correlation. Therefore there is no fixed intrinsic ratio of n, π^* and π, π^* reactivity in these CT reactions. The nonlinear correlation between rate constant and triplet reduction potential for π, π^* triplets reflects varying degrees of n, π^* reaction for the hardest to reduce ketones, a shift from rate-determining hydrogen transfer to rate-determining complex formation, and different types of π, π^* excitation.

The π, π^* triplets show evidence for large variations in the amount of electron transfer within the exciplex, as judged from P/T selectivity with cymene. This product selectivity reflects a stereoelectronic effect: the greater the degree of electron transfer in the complex, the more the cymene methyl group is positioned near the carbonyl in the presumed face-to-face exciplex. The exceptional behavior of the diketones confirms this model.

The n, π^* alkylbenzene complexes all yield primarily tertiary radicals, with only slight variations in selectivity. These complexes apparently have considerable rotational freedom, such that the more stable radical product is formed preferentially.

The overall reaction by n, π^* triplets more nearly resembles simple hydrogen atom abstraction than does the reaction by π, π^* triplets. However, maximum quantum efficiency for radical production is lowered for both n, π^* and π, π^* triplets whenever the thermodynamics favor significant electron transfer during CT complexation. Exciplex radiationless decay apparently occurs independent of initial electronic configuration.

Although CT complexation followed by hydrogen transfer is the major pathway followed by all of the ketones studied, we conclude that direct hydrogen abstraction without prior complexation can compete to varying degrees. It would not be proper to invoke a single mechanism which involves varying degrees of charge transfer in the transition state. Indeed there are varying degrees of polarization in the transition state for hydrogen ab-

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straction, as we have already reported,⁶ but these differences are too small to explain the large variation in k_r and in product ratios that we report here.

Probably the most important conclusion from this work is that the extent of electron transfer in the exciplex intermediates in these ketone photoreductions appears to increase as the barrier for forming the complex decreases. Since charge separation enhances the rate of benzylic hydrogen transfer to oxygen, the rate-determining step for the overall reaction changes over the range of triplet reduction potentials studied. The easiest to reduce ketones react by irreversible, rate-determining complexation. The harder to reduce ketones complex reversibly with the alkylbenzenes. Whether the hydrogen-transfer step is wholly or partially rate-determining depends on the extent of electron transfer in the complex. The distinct change in product selectivity observed over the same range of reduction potentials indicates that the complexes differ as a function of thermodynamics. Therefore they cannot all be contact radical ion pairs (which involve complete electron transfer) and instead must be charge-transfer complexes with a variable extent of charge separation, as was first postulated for these⁵ and similar^{3c} reactions.

Experimental Section

Chemicals. Acetonitrile solvent for steady-state studies was reagent grade material purified as described previously;⁵⁶ Aldrich Gold Label spectroscopic grade was used as received for flash studies. Benzene and the alkylbenzenes were all reagent grade materials that were washed with sulfuric acid, neutralized, dried, and distilled from P₂O₅: benzene, bp 80.0 °C; toluene, bp 110.5 °C; *p*-xylene, bp 137.5 °C; *p*-cymene, bp 177 °C; and *p*-diisopropylbenzene, bp 210 °C. Both toluene-*d*₈ and *p*-xylene-*d*₁₀ were Aldrich Gold Label and were used as received. Various alkanes used as internal standards for GC analysis were available from previous work. Alkyl benzoates either were commercial materials or were synthesized from the appropriate alcohol and benzoyl chloride. All were distilled before use. Naphthalene was recrystallized from ethanol, mp 79–80 °C. Chemical samples 2,5-dimethyl-2,4-hexadiene and 1,3-pentadiene were used as received. Aldrich di-*tert*-butyl peroxide was used as received. Commercial 1-phenylethanol was treated with NaBH₄ and then distilled, such that <0.01% acetophenone was present.

Trifluoroacetophenone was reduced with NaBH₄ in ethanol to prepare 1-phenyl-2,2,2-trifluoroethanol. The alcohol was purified by vacuum distillation: bp 117 °C (25 torr); IR (CCl₄) 3400, 3040, 1455, 800 cm⁻¹; ¹H NMR (CDCl₃) δ 3.1 (s, 1 H), 4.8 (quartet, 1 H, *J* = 7 Hz), 7.3 (m, 5 H); ¹⁹F NMR δ 78.4 (d, *J* = 7 Hz).

tert-Butyl phenylperacetate was prepared exactly as described by Neuman and Behar⁵⁷ by treating phenylacetyl chloride with *tert*-butyl hydroperoxide at –20 °C. It was chromatographed on dried Florisil with CH₂Cl₂ eluent. The resulting clear liquid was 70% active as determined by thiosulfate titration. GC and IR analysis revealed some alcohol impurity but no significant toluene.

Trifluoroacetophenones were usually prepared by a modification of the Dishart and Levine procedure,⁵⁸ namely, by adding the appropriate arylmagnesium bromide to lithium trifluoroacetate in ether or THF. The lithium salt was prepared by adding trifluoroacetic acid dropwise to 8 M aqueous LiOH until a Bromcresol Green end point was reached. The water was distilled off and the product dried under vacuum in a dessicator. The ketones were prepared by first making the appropriate Grignard reagent and then adding it dropwise to a rapidly stirred solution of the acid salt (40% excess). The solution was then refluxed for 2 h, cooled, and added to water containing excess HCl. Normal workup procedures following ether extraction gave oils which were distilled under vacuum to give 40–60% yields. All ketones were purified by spinning-band distillation or by recrystallization. Those substituted trifluoroacetophenones which had been studied previously had the same spectroscopic properties as already reported.⁷

p-Fluoro- α,α,α -trifluoroacetophenone: bp 152 °C, IR (neat) 1710 cm⁻¹; ¹H NMR (CDCl₃) δ 7.1 (m, 2 H), 8.0 (m, 2 H); MS (70 eV), *m/e* 192, 173, 123.

p-Acetyl- α,α,α -trifluoroacetophenone was prepared similarly from the ethylene glycol ketal of *p*-bromoacetophenone. Prouct was obtained by refluxing its ketal for 6 h in acetone containing 2 mL of sulfuric acid. Removal of the solvent left a yellow oil which was purified by dissolution in methanol (which left behind some yellow polymer) and recrystalliza-

tion: mp 99 °C; IR (Nujol) 1630 cm⁻¹; NMR (CD₃CN) δ 2.6 (s, 3 H), 7.73 (d, 2 H, *J* = 8 Hz), 7.93 (d, 2 H, *J* = 8 Hz); MS, *m/e* 216, 201, 173.

3,4-Dimethyl- α,α,α -trifluoroacetophenone was prepared by Friedel-Crafts acylation of 1.1 mol of *o*-xylene with 0.63 mol of trifluoroacetic anhydride and 0.65 mol of AlCl₃ in 1 L of CS₂. The anhydride was added over 6 h. After the solution was stirred overnight, it was refluxed for 3 h and then worked up routinely. The ketone was purified by spinning-band distillation: bp 203 °C; IR 1710 cm⁻¹; NMR δ 2.25 (s, 6 H), 7.0–7.8 (m, 3 H); MS, *m/e* 203, 133, 105.

p-*tert*-Butyl- α,α,α -trifluoroacetophenone was prepared by a similar Friedel-Crafts acylation of *tert*-butylbenzene: mp 41–44 °C; NMR δ 1.4 (s, 9 H), 7.5 (d, 2 H, *J* = 8 Hz), 7.95 (d, 2 H, *J* = 8 Hz); MS, *m/e* 231, 215, 200, 161.

Acetophenone and its *m*-methyl, *p*-methyl, *m*-chloro, *p*-chloro, *p*-trifluoromethyl, *m*-trifluoromethyl, *m*-methoxy, and *p*-methoxy derivatives were all commercially obtained materials which were distilled under vacuum before use. The *p*-cyano ketone was recrystallized from ethanol. Their IR, NMR, and mass spectra were all checked for consistency with the advertised structures.

p-Diacetylbenzene (Aldrich) was dissolved in acetone, treated with Norit, and then recrystallized from methanol.

m-Cyanoacetophenone was obtained from Dr. E. Siebert.²⁵

p-*tert*-Butylacetophenone was prepared by Friedel-Crafts acetylation of *tert*-butylbenzene: bp 239 °C; IR (neat) 1680 cm⁻¹; NMR (CDCl₃) δ 1.2 (s, 9 H), 2.6 (s, 3 H), 7.4 (d, 2 H, *J* = 8 Hz), 7.85 (d, 2 H, *J* = 8 Hz); MS, *m/e* 161, 146, 133, 115, 105, 91.

3,4-Dimethylacetophenone was prepared by Friedel-Crafts acetylation of *o*-xylene: bp 244 °C; IR (neat) 1700 cm⁻¹; NMR δ 2.3 (s, 3 H), 2.5 (s, 3 H), 7.2 (s, 1 H), 7.6–7.7 (m, 2 H); MS, *m/e* 148, 133, 105.

Benzophenone and its *p*-chloro, 4,4'-dichloro, 4,4'-dimethyl, and 4,4'-dimethoxy derivatives were commercial materials recrystallized from ethanol. The 3,3'-dimethyl derivative was obtained from Dr. M. Thomas.³⁷

m-Chlorobenzophenone was prepared by Friedel-Crafts acylation of benzene with 3-chlorobenzoyl chloride: mp 79–80 °C; IR (Nujol) 1640 cm⁻¹; MS (relative intensity), *m/e* 218, 216 (44), 181 (5), 141, 139 (20), 105 (100).

3,4-Dichlorobenzophenone was prepared by acylation of benzene with 3,4-dichlorobenzoyl chloride: mp 101.5–102 °C; IR (Nujol) 1650 cm⁻¹; MS (relative intensity), *m/e* 252, 250 (12), 173 (15), 145, 105 (100).

4,4'-Di-*tert*-butylbenzophenone was prepared by adding 0.3 mol of *tert*-butylbenzene to a rapidly stirred mixture of 0.15 mol of CCl₄ and 0.15 mol of AlCl₃ in 300 mL of CS₂. The mixture was stirred at room temperature for 36 h and then poured onto ice. Normal ether extraction and workup provided the crude dichlorodiarlylmethane, which was refluxed for 12 h in 300 mL of water. The resulting dark oil was treated with hot heptane, from which ketone was obtained and recrystallized from ethanol: mp 132–133 °C; NMR δ 1.33 (s, 18 H), 7.4 (d, 4 H, *J* = 8 Hz), 7.7 (d, 4 H, *J* = 8 Hz); MS (relative intensity), *m/e* 294 (22), 279 (100), 161 (8).

p-Cyanobenzophenone was prepared by Friedel-Crafts acylation of benzene with *p*-cyanobenzoyl chloride: mp 110–110.5 °C; MS (relative intensity), *m/e* 207 (15), 130 (8), 105, (100), 77 (90).

p-(Trifluoromethyl)benzophenone was prepared by adding benzaldehyde to the Grignard of *p*-bromobenzotrifluoride and oxidizing the resulting alcohol with dichromate: mp 113–113.5 °C; IR (Nujol) 1640 cm⁻¹; MS (relative intensity), *m/e* 250 (30), 173 (25), 145 (20), 105 (100).

m-(Trifluoromethyl)benzophenone was prepared likewise from *m*-bromobenzotrifluoride: mp 49–52 °C; IR (Nujol) 1630 cm⁻¹; MS, *m/e* 250, 173, 145, 105.

Identification of Photoproducts. Bibenzyl, bixyl, and the ketone pinacols were identified in earlier work.⁵ They were measured quantitatively by their GC retention times. 1-Methyl- and 1-(trifluoromethyl)-1,2-diphenylethanol were prepared by addition of benzyl Grignard to acetophenone or trifluoroacetophenone.

The photoproducts of cymene with trifluoroacetophenone were isolated by column chromatography of benzene solutions which had been irradiated to complete reaction. After solvent removal, the oil residue was eluted through alumina with hexane. The first fraction contained three hydrocarbons; the next two fractions contained the two separate alcohols. With chloroform added to the hexane, pinacol then eluted last. Sublimation of the hydrocarbon mixture provided pure PP. A mixture rich in TT was prepared by similar irradiation of an acetophenone-cymene solution; TT also sublimated more readily than PT. The unsymmetrical hydrocarbon PT was obtained from the combined residues of the two sublimations.

1,1,1-Trifluoro-2-phenyl-3-methyl-3-(4-methylphenyl)-2-butanol: IR (neat) 3560, 2990, 1145 cm⁻¹; ¹H NMR (CDCl₃) δ 1.3 (s, 3 H), 1.6 (s,

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3 H), 2.3 (s, 3 H), 2.6 (s, 1 H), 7.0 (br s, 4 H), 7.3 (m, 5 H); ^{19}F NMR δ 67.2 (s); MR (relative intensity), m/e 308, 175 (100).

1,1,1-Trifluoro-2-phenyl-3-(4-isopropylphenyl)-2-propanol: IR (neat) 3540, 2945, 1150, 820 cm^{-1} ; ^1H NMR (CDCl_3) δ 1.1 (d, 6 H), 2.6 (s, 1 H), 2.9 (septet, 1 H), 3.5 (s, 2 H), 7.0 (br s, 4 H), 7.3 (m, 5 H); ^{19}F NMR δ 68.2 (s); MS, m/e 308.

1,2-Bis(4-isopropylphenyl)ethane (PP): ^1H NMR (CDCl_3) δ 1.1 (d, 12 H), 2.8 (s, 4 H), 2.9 (septet, 2 H), 7.0 (br s, 8 H); MS, m/e 266.

2,3-Bis(4-methylphenyl)-2,3-dimethylbutane (TT): ^1H NMR (CDCl_3) δ 1.2 (s, 12 H), 2.3 (s, 6 H), 6.9 (br s, 8 H); MS, m/e 266.

1-(4-Isopropylphenyl)-2-(4-methylphenyl)-2-methylpropane (PT): ^1H NMR (CDCl_3) δ 1.1 (d, 6 H), 1.3 (s, 6 H), 2.3 (s, 3 H), 2.8 (s, 2 H), 2.9 (septet, 1 H), 6.9 (s, 4 H), 7.0 (s, 5 H); MS, m/e 266.

Irradiation procedures were as in earlier work.⁵ Samples of known concentration were prepared; 2.8-mL aliquots were placed in 13 \times 100 Pyrex tubes which were then degassed in three freeze-pump-thaw cycles before being sealed. Samples were irradiated in a "merry-go-round" apparatus⁵⁹ immersed in a water bath. A water-cooled 450-W Hanovia mercury arc provided UV radiation. One of two filter systems was used: 313 nm, 0.002 M K_2CrO_4 in 1% aqueous K_2CO_3 ; 365 nm, Corning 7-83 glass filters.

Flash kinetics were conducted as described previously⁶ at the NRCC.⁶⁰ Solutions were prepared ~ 0.01 M in ketone such that they had optical densities of 0.2 at 308 nm or 0.6 at 337 nm in 7- \times 7-mm cells. They were deaerated by bubbling purified nitrogen through them for a few minutes. An excimer laser (~ 80 mJ/4 ns pulse) was used for 308-nm excitation, a nitrogen laser (~ 10 mJ/8 ns pulse) for 337 nm. Triplet decay was followed typically at 375 nm for the APs and TFAs, 600 nm for the BPs. Plots of $1/\tau$ vs. concentrations of added alkylbenzene provided k_t values.

Analytical Procedures. Analyses of product yields were performed on Varian Model 1400 gas chromatographs fitted with flame-ionization detectors and digital integrators. Calibration factors for response to various reactants, products, and internal standards were determined independently under the same conditions of column, temperature, and nitrogen flow rate as used for each particular analysis. Almost all analyses of ketone-toluene and ketone-xylene reactions were performed on an 8-ft column containing 5% QF-1 and 1.25% Carbowax 20M on 60/80 DMSC-treated Chromosorb G. Ketone/*p*-cymene product ratios were measured either on the same column or on one containing 5% SE-30 on 60/80 Chromosorb W. Analysis of products from peroxide and perester decompositions was done on a column containing 20% SE-30, programmed from 50 to 225 $^\circ\text{C}$.

Spectroscopic Measurements. Reduction potentials were measured with Bioanalytical cyclic voltammetric equipment, relative to a standard

calomel electrode. Aldrich Gold Label acetonitrile solutions 10^{-4} M in ketone and 0.1–1.0 M in tetraethylammonium perchlorate were bubbled with argon for several minutes. With a scan rate of 400–500 mV/s, most ketones showed fully or partially reversible reduction. Standard potentials were measured as the average of the forward and reverse wave maxima, which typically differed by 8–14 mV.

Phosphorescence spectra were recorded on a Perkin-Elmer MPF-44A spectrophotometer equipped with a differential-corrected spectrum unit and a Hitachi phosphorescence accessory. MTHF solutions 10^{-4} M in ketone were placed in 5-mm-i.d. quartz tubes and submerged in liquid nitrogen. Slit widths were 12 mm, and spectra were run at a scan rate of 60 nm/min, with 290-nm excitation.

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Registry No. *m*- $\text{CF}_3\text{C}_6\text{H}_4\text{COCF}_3$, 721-37-9; *p*- $\text{CF}_3\text{C}_6\text{H}_4\text{COCF}_3$, 74853-66-0; *m*- $\text{ClC}_6\text{H}_4\text{COCF}_3$, 321-31-3; *p*- $\text{MeCOC}_6\text{H}_4\text{COCF}_3$, 86988-49-0; *p*- $\text{FC}_6\text{H}_4\text{COCF}_3$, 655-32-3; PhCOCF_3 , 434-45-7; *p*- $\text{ClC}_6\text{H}_4\text{COCF}_3$, 321-37-9; *p*-*t*- $\text{BuC}_6\text{H}_4\text{COCF}_3$, 73471-97-3; *p*- $\text{MeC}_6\text{H}_4\text{COCF}_3$, 394-59-2; *m*- $\text{MeC}_6\text{H}_4\text{COCF}_3$, 1736-06-7; 3,4- $\text{Me}_2\text{C}_6\text{H}_3\text{COCF}_3$, 75833-26-0; *p*- $\text{MeOC}_6\text{H}_4\text{COCF}_3$, 711-38-6; *m*- $\text{CF}_3\text{C}_6\text{H}_4\text{COPh}$, 728-81-4; *p*- $\text{NCC}_6\text{H}_4\text{COPh}$, 1503-49-7; *m*- $\text{ClC}_6\text{H}_4\text{COPh}$, 1016-78-0; *p*- $\text{F}_3\text{CC}_6\text{H}_4\text{COPh}$, 728-86-9; 4,4'- $\text{ClC}_6\text{H}_4\text{COC}_6\text{H}_4\text{Cl}$, 90-98-2; 4,4'- $\text{FC}_6\text{H}_4\text{COC}_6\text{H}_4\text{F}$, 345-92-6; *p*- $\text{ClC}_6\text{H}_4\text{COPh}$, 134-85-0; PhCOPh , 119-61-9; 4,4'-*t*- $\text{BuC}_6\text{H}_4\text{COC}_6\text{H}_4\text{Bu-t}$, 15796-82-4; 4,4'- $\text{MeC}_6\text{H}_4\text{COC}_6\text{H}_4\text{Me}$, 611-97-2; 4,4'- $\text{MeOC}_6\text{H}_4\text{COC}_6\text{H}_4\text{OMe}$, 90-96-0; *m*- $\text{NCC}_6\text{H}_4\text{COMe}$, 6136-68-1; *m*- $\text{F}_3\text{CC}_6\text{H}_4\text{COMe}$, 349-76-8; *p*- $\text{F}_3\text{CC}_6\text{H}_4\text{COMe}$, 709-63-7; *m*- $\text{ClC}_6\text{H}_4\text{COMe}$, 99-02-5; *p*- $\text{NCC}_6\text{H}_4\text{COMe}$, 1443-80-7; PhCOMe , 98-86-2; *m*- $\text{MeC}_6\text{H}_4\text{COMe}$, 585-74-0; *p*-*t*- $\text{BuC}_6\text{H}_4\text{COMe}$, 943-27-1; *p*- $\text{ClC}_6\text{H}_4\text{COMe}$, 99-91-2; *p*- $\text{MeC}_6\text{H}_4\text{COMe}$, 122-00-9; 3,4- $\text{Me}_2\text{C}_6\text{H}_4\text{COMe}$, 3637-01-2; *p*- $\text{MeOC}_6\text{H}_4\text{COMe}$, 100-06-1; *p*- $\text{MeCOC}_6\text{H}_4\text{COMe}$, 1009-61-6; H_2 , 1333-74-0; D_2 , 7782-39-0; $\text{PhCH}_2\text{C}(\text{O})\text{O}(\text{O})\text{Bu-t}$, 3377-89-7; PhCH_2COCl , 103-80-0; Me_3COOH , 75-91-2; $\text{F}_3\text{CCO}_2\text{Li}$, 2923-17-3; *p*- $\text{FC}_6\text{H}_4\text{Br}$, 460-00-4; *o*- $\text{MeC}_6\text{H}_4\text{Me}$, 95-47-6; $\text{F}_3\text{CC}(\text{O})\text{OC}(\text{O})\text{CF}_3$, 407-25-0; PhBu-t , 98-06-6; C_6H_6 , 71-43-2; *m*- $\text{ClC}_6\text{H}_4\text{COCl}$, 618-46-2; 3,4- $\text{Cl}_2\text{C}_6\text{H}_3\text{COPh}$, 6284-79-3; 3,4- $\text{Cl}_2\text{C}_6\text{H}_3\text{COCl}$, 3024-72-4; CCl_4 , 56-23-5; *p*- $\text{NCC}_6\text{H}_4\text{COCl}$, 6068-72-0; PhCHO , 100-52-7; PhMe , 108-88-3; *p*- $\text{MeC}_6\text{H}_4\text{Me}$, 106-42-3; *p*-*i*- $\text{PrC}_6\text{H}_4\text{Me}$, 99-87-6; *p*-*i*- $\text{PrC}_6\text{H}_4\text{Pr-i}$, 100-18-5; $\text{F}_3\text{CCH}_2\text{OH}$, 75-89-8; $\text{F}_3\text{CCO}_2\text{H}$, 76-05-1; *p*-*t*- $\text{BuC}_6\text{H}_4\text{CCl}_6\text{H}_4\text{Bu-t}$, 78828-12-3; *p*- $\text{BrC}_6\text{H}_4\text{CF}_3$, 402-43-7; *p*- $\text{F}_3\text{CC}_6\text{H}_4\text{CH}(\text{OH})\text{Ph}$, 395-23-3; *m*- $\text{BrC}_6\text{H}_4\text{CF}_3$, 401-78-5; *m*- $\text{F}_3\text{CC}_6\text{H}_4\text{CH}(\text{OH})\text{Ph}$, 728-80-3; *p*- $\text{MeC}_6\text{H}_4\text{C}(\text{Me}_2)\text{C}(\text{Ph})(\text{CF}_3)\text{OH}$, 104762-34-7; *p*-*i*- $\text{PrC}_6\text{H}_4\text{CH}_2\text{C}(\text{Ph})(\text{CF}_3)\text{OH}$, 104762-35-8; *p*,*p'*-*i*- $\text{PrC}_6\text{H}_4(\text{CH}_2)_2\text{C}_6\text{H}_4\text{Pr-i}$, 36716-22-0; *p*,*p'*- $\text{MeC}_6\text{H}_4\text{C}(\text{Me}_2)_2\text{C}_6\text{H}_4\text{Me}$, 734-17-8; *p*,*p'*- $\text{MeC}_6\text{H}_4\text{C}(\text{Me}_2)\text{CH}_2\text{C}_6\text{H}_4\text{Pr-i}$, 71523-10-9; *p*-bromoacetophenone ketal, 4360-68-3.

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