

Competitive Types I and II Photocleavage of α,α -Dimethylvalerophenone

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Abstract: Irradiation of α,α -dimethylvalerophenone produces propylene, isobutyrophenone, 2,2,4-trimethyl-1-phenylcyclobutanols, benzaldehyde, 2-methylpentane, and 2-methylpentenes. In the presence of enough thiol to trap all free radicals, the quantum yield of α -cleavage products is only 6%. Quantum yields of type II products rise from only 12% in benzene to 45% in 1-propanol. Kinetic analysis suggests triplet state rate constants of $1.3 \times 10^7 \text{ sec}^{-1}$ for α -cleavage and $9.2 \times 10^7 \text{ sec}^{-1}$ for γ -hydrogen abstraction, a 13:87 ratio. α -Cleavage of triplet phenyl *tert*-alkyl ketones is only 0.4% as rapid as α -cleavage of triplet aliphatic *tert*-alkyl ketones. The large rate difference probably reflects simple energetics, the triplet excitation energies of the phenyl ketones being $\sim 6 \text{ kcal}$ lower than those of aliphatic ketones. Differences in triplet state geometries may also be partially responsible.

We decided to study the photochemistry of α,α -dimethylvalerophenone, α -DMVP, in order to develop a monitor for studying possible steric effects in energy transfer.² We hoped that this ketone would undergo type II elimination and cyclization in respectable yield. Our hope surely was not based on the behavior of aliphatic *tert*-alkyl ketones, whose triplet states undergo only α -cleavage,³ but rather on the fairly low rates reported for α -cleavage of triplet phenyl *tert*-butyl ketone.^{4,5} Our findings confirm the low rates of α -cleavage of phenyl *tert*-alkyl ketones.

Results

α -DMVP was prepared by methylation of valerophenone and purified *via* its oxime. Irradiation at 3130 Å of degassed solutions 0.1 *M* in ketone produces isobutyrophenone, propylene, 2-methylpentane, 2-methyl-1-pentene, 2-methyl-2-pentene, benzaldehyde, and two products which Lewis and Hilliard have identified⁶ as the expected 2,2,4-trimethyl-1-phenylcyclobutanols. A few other unidentified products which vary with solvent are formed in small yield and probably are various radical addition and coupling products. Table I lists the quantum yields of various products obtained under different conditions. Our values in benzene are somewhat larger than those Lewis has reported independently.⁶

The various polar solvents and additives were employed in an attempt to maximize type II quantum yields.^{7,8} It was ascertained that both 2,5-dimethyl-2,4-hexadiene and 2-chloronaphthalene quench formation of benzaldehyde, isobutyrophenone, and the two cyclobutanols equally. Both triplet quenchers can also completely quench the reaction. A Stern-Volmer plot of the data in Table I yields a $k_q\tau$ value of 48 M^{-1} . Since we have shown² that quenching of triplet α -DMVP is "diffusion controlled," we assume the usual⁹ value of $5 \times 10^9 \text{ M}^{-1} \text{ sec}^{-1}$ for k_q and so cal-

Table I. Product Quantum Yields from α,α -Dimethylvalerophenone^a

Solvent	Additive	Φ_{BA}^b	Φ_{I1}^c	Φ_{CB}^d	Φ_{2-MP}^e
Benzene		0.026	0.04	0.085	0.042 ^e
Benzene	0.010 <i>M</i> Q ^f			0.059	
Benzene	0.015 <i>M</i> Q			0.051	
Benzene	0.020 <i>M</i> Q			0.043	
Benzene	0.025 <i>M</i> Q			0.039	
Benzene	0.030 <i>M</i> Q			0.034	
Benzene	0.035 <i>M</i> Q			0.031	
Benzene	0.5 <i>M</i> RSH ^g	0.069	0.04	0.18	0.053 ^h
Benzene	0.1 <i>M</i> RSH	0.053	<i>i</i>	0.08	0.053 ^h
Benzene	3 <i>M</i> <i>t</i> -BuOH	0.014	0.05	0.12	<i>i</i>
Benzene	5 <i>M</i> <i>t</i> -BuOH	0.014	0.06	0.20	
<i>t</i> -BuOH		0.015	0.14	0.25	
1-Propanol		<i>i</i>	0.18	0.27	
CH ₃ CN	3% H ₂ O	0.015	0.17	0.33	
Cyclooctane		0.03	0.04	0.080	0.045 ^j

^a Degassed 0.10 *M* ketone solutions irradiated at 3130 Å. ^b Benzaldehyde. ^c Isobutyrophenone. ^d *Cis/trans* cyclobutanol ratio varies from 0.75 in hydrocarbon solvents to 1.2 in alcohols. ^e 5:5:1 ratio of 2-methylpentane:2-methyl-1-pentene:2-methyl-2-pentene. ^f Q = 2,5-dimethyl-2,4-hexadiene. ^g Dodecyl mercaptan. ^h Only 2-methylpentane. ⁱ Not measured. ^j 2.2:1 ratio of 2-methylpentane:2-methylpentenes.

culate a $1/\tau$ value of $10.5 \times 10^7 \text{ sec}^{-1}$ for triplet α -DMVP.

The thiol was added to trap the free radicals produced by α -cleavage. The identical yields of α -cleavage products at 0.1 and 0.5 *M* thiol and the complete quenching of olefin indicate that all radicals which escaped the initial solvent cage were trapped. We ascertained separately that the concentrations of thiol used would not quench the triplet ketone directly.¹⁰

Discussion

Behavior of α -DMVP. The 5–7% yield of free radicals produced by irradiation of α -DMVP, after correction for the inevitable cage recombination, indicates that only 10–15% of the triplet ketone molecules undergo α -cleavage.

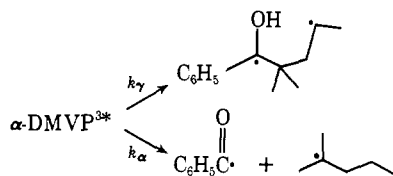
As indicated in Table I, the type II reaction of α -DMVP is unusual in that small concentrations of added

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alcohol barely affect the quantum yield. High concentrations of polar solvents (including the thiol) do produce increased quantum yields, but no leveling off to a constant maximum value (0.85–0.90 would be expected on the basis of the type I yields) is observed. The unusual behavior of the 1,4-biradical produced from α -DMVP, including its large 2/1 cyclization/elimination ratio, is discussed elsewhere.^{6,11} The type II quantum yields observed in wet acetonitrile and in propanol indicate that at least half the triplet ketone undergoes γ -hydrogen abstraction. We can calculate the actual ratio of excited state rate constants by combining Lewis' data for α,α -dimethylbutyrophenone (α -DMBP)⁶ with ours for α -DMVP as follows. The α -dimethyl substitution can be considered to introduce two unknowns into the triplet state lifetime: an inductive and/or steric effect on the rate constant for γ -hydrogen abstraction; and competitive α -cleavage.



In eq 1 k_γ^0 is the known triplet state rate constant for

$$1/\tau = k_\alpha + k_\gamma = k_\alpha + f k_\gamma^0 \quad (1)$$

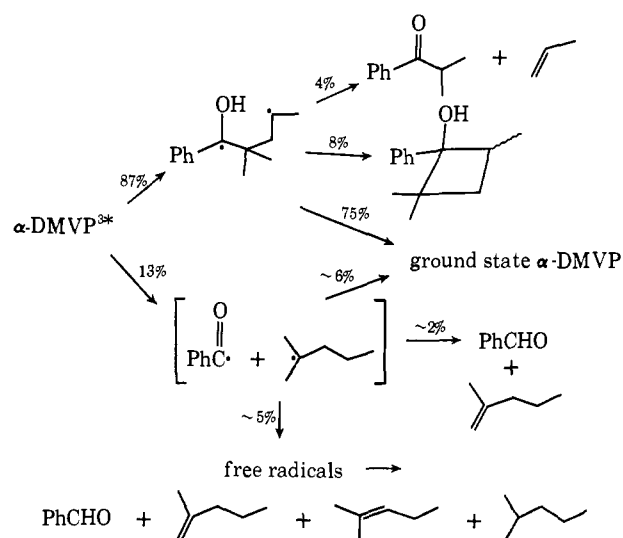
γ -hydrogen abstraction by straight chain ketones¹² and f is the unknown rate factor introduced by the α -methyls. Stern–Volmer quenching studies with naphthalenes and conjugated dienes as quenchers indicate $1/\tau$ values of 1.9×10^7 and $10.5 \times 10^7 \text{ sec}^{-1}$ for the two ketone triplets.^{2,6} Entering these values into eq 1, we can solve the resulting pair of simultaneous equations with the following results: $f = 0.74$, $k_\alpha = 1.3 \times 10^7 \text{ sec}^{-1}$, $k_\alpha/(k_\alpha + k_\gamma) = 0.13$ (DMVP) and 0.68 (DMBP).

The percentages of α -cleavage calculated for both ketone triplets are consistent with the low measured quantum yields of type I products¹³ and suggest approximately 50% cage recombination of the radicals formed by α -cleavage. We discuss the very small effect of the α methyls on the rate constant for γ -hydrogen abstraction elsewhere.¹⁴

Consideration merely of the low quantum yields of type II reactions of α -DMBP and α -DMVP in benzene⁶ might have suggested that the phenyl ketone triplets behave similarly to aliphatic ketone triplets. In fact, we can now conclude that the low type II quantum yields are only partially due to competing triplet state α -cleavage. The α -dimethyl substitution produces a large effect on the 1,4-biradical intermediates, only 13% of which go on to products, instead of the 40% found for valerophenone and butyrophenone themselves.

Scheme I represents the fate of triplet α -DMVP in hydrocarbon solvents, with polar solvents producing slight changes in the partitioning of the biradical. Note that we assume some disproportionation of radicals

Scheme I



in the initial solvent cage, even though no olefin is detected in the trapping experiments, simply because disproportionation is the only likely mode of benzaldehyde formation in unreactive solvents. (In the trapping experiments, the thiol apparently selectively removes olefin products, since propylene formation is also strongly quenched.)

Rates of α -Cleavage. The value of k_α which we deduce for α -DMVP is slightly lower than the values of $2.3 \times 10^7 \text{ sec}^{-1}$ ⁴ and $3.0 \times 10^7 \text{ sec}^{-1}$ ⁵ already reported for phenyl *tert*-butyl ketone and verifies that the former value is real and not an artifact caused by diene trapping of benzoyl radicals.¹⁵ This value of $\sim 2 \times 10^7 \text{ sec}^{-1}$ for α -cleavage of phenyl *tert*-alkyl ketones is only 0.004 as large as the comparable rate constant for aliphatic *tert*-butyl ketones^{3,16} and the large rate difference has apparently escaped previous attention. In fact, the rate of α -cleavage of triplet phenyl *tert*-alkyl ketones is very nearly equal to that for excited singlet *tert*-butyl alkyl ketones.^{3,15} We are faced with the odd situation that triplet phenyl ketones closely resemble triplet aliphatic ketones in rates of hydrogen abstraction¹⁷ and singlet aliphatic ketones in rates of α -cleavage.

It is possible to eliminate several possible causes for the reduced reactivity of phenyl ketone triplets. For one thing, the effect is not due to any increased π, π^* character in the lowest triplet state, since we have already reported that α -dimethyl substitution stabilizes the n, π^* triplet of phenyl alkyl ketones.¹⁵ Moreover, it is hard to rationalize why the rate of hydrogen abstraction would not also be affected.

Walling and Padwa's results with alkyl hypochlorites¹⁹ indicate that the relative rates of cleavage and of intramolecular hydrogen abstraction in alkoxy radicals are very similar to those observed for triplet aliphatic ketones. We make this comparison to point out that the cleavage reaction in excited ketones is triggered by the nonbonding electron on oxygen. Therefore,

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(13) Professor Lewis has kindly informed us that the yield of type I products from α -DMBP is five times that from α -DMVP, in excellent agreement with our estimated rate ratios.

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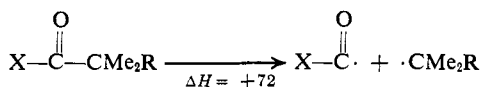
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the fact that the excited electron resides in a primarily benzene-like π^* orbital in the phenyl ketone triplet probably is not the cause for that state's lowered reactivity.

A referee has suggested that delocalization of the nonbonding orbital into the benzene ring, as suggested by Goodman,²⁰ might explain low reactivity. But, again, such an explanation might be true only if triplet phenyl ketones showed greatly reduced reactivity in hydrogen abstraction reactions as well as in α -cleavage, which they do not.

The lowered reactivity of phenyl ketones is probably due primarily to energetic differences and possibly also to geometric differences. Recent epr²¹ and kinetic²² studies indicate that the free electron of the benzoyl radical is not conjugated with the benzene ring, in contrast to the behavior of the 1-phenylvinyl radical.²³ Thermochemical data²⁴ then indicate that the α -cleavage of *tert*-alkyl ketones is 72 kcal/mol endothermic whether X is alkyl or phenyl. However, conjugation with the phenyl ring does provide extra stabilization to ketone



triplets, the excitation energy of acetophenone being ~ 74 kcal²⁵ vs. 78–80 kcal for acetone.²⁶ Although α -dimethyl substitution stabilizes the n, π^* triplet of phenyl ketones¹⁸ and the n, π^* singlet of aliphatic ketones,²⁷ it does not seem to stabilize the n, π^* triplet of aliphatic ketones.²⁷ Consequently, as Figure 1 shows, α -cleavage of triplet α -DMVP is roughly thermoneutral while α -cleavage of pinacolone could be ~ 5 kcal exothermic. Although the large positive entropy change resulting from homolytic cleavage would make both reactions proceed with a loss of free energy, the enthalpy difference could well explain much of the rate difference between the two kinds of ketones.

There is one other factor which may be partially responsible for the rate difference between phenyl and aliphatic ketone triplets. Conjugation with a phenyl ring apparently keeps the triplet carbonyl planar.²⁸ If aliphatic ketones imitate formaldehyde, their excited singlets are only slightly nonplanar while their triplets approach being tetrahedral (sp^3 -hybridized at the carbonyl carbon). It has been suggested that α -cleavage from n, π^* states of formaldehyde is a direct result of state mixing caused by the *nonplanarity* of the excited state.²⁹ Further theoretical justification for this suggestion has not been forthcoming, but the idea, if true, might explain part of the rate differences we note here.

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(b) S. W. Benson, *et al.*, *ibid.*, **69**, 279 (1969).

(25) This figure is a *gemisch* of the 72.5 kcal 0–0 phosphorescence band in solution, and the 74.5 kcal 0–0 phosphorescence and 75.6 kcal 0–0 phosphorescence excitation bands in hydrocarbon glasses at 77°K.

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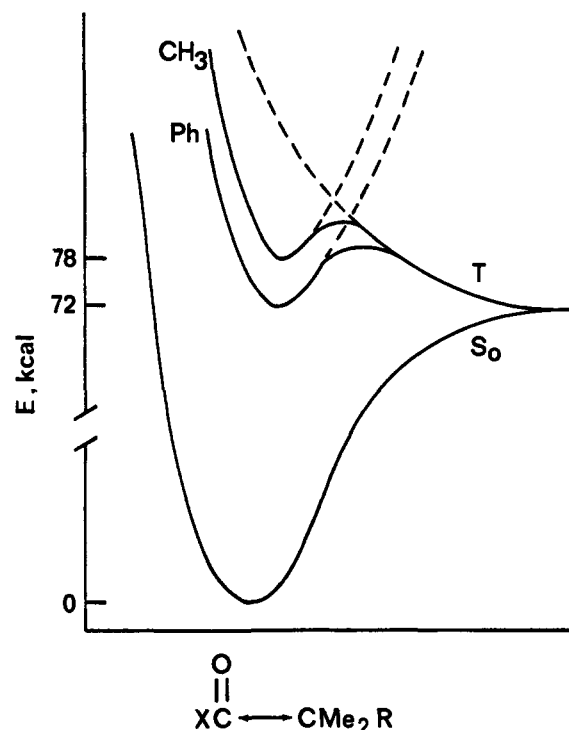


Figure 1. Potential energy diagrams for α -cleavage of the n, π^* triplets of aliphatic and phenyl *tert*-alkyl ketones.

Experimental Section

Hydrocarbon solvents were purified by washing with sulfuric acid followed by distillation from phosphorus pentoxide. Alcohols were distilled from sodium and acetonitrile was distilled from potassium permanganate. Chemical Samples Co. 2,5-dimethyl-2,4-hexadiene and Aldrich dodecyl mercaptan were used as received. α, α -Dimethylvalerophenone was prepared by methylating valerophenone.³⁰ An ether slurry of 1.8 mol of sodium hydride was added over 1 hr to 300 ml of dry ether containing 0.6 mol of valerophenone and 1.5 mol of methyl iodide, all of which was stirred under a nitrogen atmosphere. The solution was refluxed for 40 hr and then cooled to 0°. Water was added to destroy excess hydride. A 91% yield of crude ketone was obtained from the ether layer. The ketone was purified *via* its oxime (mp 132°). The recrystallized (from ethanol) oxime (50 g) was refluxed in 600 ml of 12% aqueous hydrochloric acid for 2 hr, whereupon the solution was steam distilled. Pure ketone was then collected by vacuum distillation (bp 70° at 0.3 Torr). Glpc analysis indicated a purity >99%.

Quantum yield measurements were made as usual. After solutions containing the desired concentrations of reactants were prepared, 3-ml aliquots were syringed into 13 × 100 mm Pyrex culture tubes which were then degassed and sealed. All tubes were irradiated in parallel on a rotating turntable assembly. The 3130-Å region of a mercury arc was isolated with an alkaline potassium chromate filter solution. Actinometry was provided by parallel irradiation of 0.1 M valerophenone in benzene.

Analyses for high boiling products were performed on Varian Model 1200 gas chromatographs, with 10 ft × 1/8 in. columns containing 4% QF-1 and 1% Carbowax 20M. Pentadecane or 1-decanol were used as internal standards for quantitative measurement of yields. The C₆ products were analyzed relative to cyclohexane on a 25-ft column containing 25% 1,2,3-tris(β -cyanoethoxy)propane.

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