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THE PHOTOCHEMISTRY OF AROMATIC COMPOUNDS

VIII*. THE PHOTOLYSIS OF 1-NAPHTHYLTRIMETHYLTIN

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SUMMARY

1-Naphthyltrimethyltin gives naphthalene under irradiation in degassed aqueous methanol or cyclohexane/acetic acid solution. Photolysis in the corresponding CH_3OD or AcOD media gives more 1-deuterionaphthalene than 1-protionaphthalene. These findings, together with quantum yield measurements, are in agreement with a mechanism involving a competition between a bimolecular photosubstitution and a free radical dissociation. Rate constants for the photosubstitution and for radiative and radiationless processes are derived.

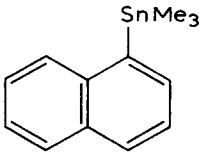
The photochemistry of most organometallic compounds involves the homolytic cleavage of the carbon–metal bond[2–6] but exceptions are found in some organosilanes[7–8] and organoboranes[9–11]. On the other hand, non-radical photosubstitutions in aromatic substrates is rather well documented[12–27]. The present work describes the behaviour of 1-naphthyltrimethyltin (I) under irradiation in weakly electrophilic solvents.

A QUANTUM YIELDS

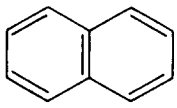
The results are summarised in the following scheme:

$$(I) \xrightarrow[\text{MeOH/H}_2\text{O (95\%/5\%)}]{h\nu} \underset{96\%}{C_{10}H_8} + \underset{60\text{–}70\%}{Me_3SnOH} + Me(Me_2Sn)_nMe$$

$$(I) \xrightarrow[\text{C}_6\text{H}_{12}\text{+AcOH (0 4 M)}]{h\nu} \underset{95\%}{C_{10}H_8} + \underset{70\%}{Me_3SnOAc} + Me(Me_2Sn)_nMe$$



(I)



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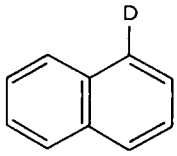

(III)

* For Part VII see ref 1

Photolysis in CH_3OD/D_2O yields $64 \pm 1\%$ of monodeuterionaphthalene (III) and $35 \pm 1\%$ of (II), whereas in cyclohexane containing AcOD (85% isotopic purity) the yields are $53 \pm 1\%$ (III) and $46 \pm 1\%$ (II).

The naphthalene may conceivably be formed by two main mechanistic pathways: (*a*) a homolytic cleavage of the carbon–tin bond or (*b*) a heterolytic or molecular photosubstitution in the excited state.

(*a*). The hypothesis of the homolytic cleavage was examined on the basis of the following experiments. 1-Iodonaphthalene is known to photodecompose into iodine atoms and 1-naphthyl radicals[28–29]; when it was irradiated in CH_3OD, we found over 97% of unlabelled naphthalene (II), and over 95% of (II) from AcOD/C_6H_{12} photolyses. It is thus clear that the relatively high yields of (III) cannot originate from homolysis of the carbon–tin bond. Another possible source of free radicals is the biphotonic "energy transfer to the solvent"[30–37]. The contribution of such a process was estimated in the following way: since (I) and (II) have very similar absorption spectra, irradiation of naphthalene in the same conditions should yield an approximate value for the importance of this potential source of free radicals. The photolysis of (II) in CH_3OD/D_2O gave 3–4% of $C_{10}H_7D$ after the same irradiation time, and irradiation in AcOD/C_6H_{12} gave 5–6% of $C_{10}H_7D$. The large amounts of labelled naphthalene formed from the aryltin thus cannot originate from such a process.

Considering the electrochemical properties of naphthalene and methanol or acetic acid, a photoinduced electron transfer from the reagent to the excited aryltin would be endothermic by some 15 kcal/mole, excluding thus[38] the possibility of a heterolytic or radical reaction of a naphthyltin radical-anion.

(*b*). Mackor[14] has shown that the localisation energies in aromatic hydrocarbons are lower in excited states than in the ground state; this has been substantiated by pK_a measurements[19] Such an enhanced reactivity may then account for the fact that the aryltin, which reacts rapidly with HCl in methanol[39] but not in pure methanol, is cleaved by the weak electrophiles CH_3OH or dilute AcOH, when excited to a higher electronic state. The labelled naphthalene (III) would then originate from a photosubstitution process, analogous to ground state electrophilic substitutions.

The fact that both labelled and unlabelled naphthalenes are formed shows that both processes, the direct photosubstitution and the homolytic cleavage, occur simultaneously.

The results are collected in Table 1

The first observation is that the quantum yields are very low; this is due to the short lifetime of the excited species and to their low intrinsic reactivity.

The reaction in methanol goes mainly through the triplet state, the contribution of the excited singlet state to the quantum yield being of the order of experimental error (0.003 ± 0.003); on the other hand, the singlet contribution is appreciable (0.016 ± 0.004) in cyclohexane/0.4 *M* acetic acid. There seems to be no contribution from the singlet state in pure cyclohexane.

Solvent isotope effects seem to be negligible; the meaning of this observation is however far from being as clear as it would be for a ground state reaction The interpretation of isotope effects depends on two major hypotheses; the first is the very existence of a transition state, the second is the assumption of a definite mechanism. Whereas a transition state in equilibrium with ground state reactants seems to be a

TABLE 1

QUANTUM YIELDS FOR THE PHOTODESTANNYLATION OF 1-NAPHTHYLTRIMETHYLTIN

Medium	$10^3\ \Phi$ (*direct*, 289 *nm*)	$10^3\ \Phi$ (*sensit*, 313 *nm*)
C_6H_{12}	0 9±0 1	1 0±0 1
C_6H_{12}/0 4 *M* AcOH	2 6±0 3	1 0±0 1
C_6H_{12}/0 8 *M* AcOH	4 6±0 6	
CH_3OH/H_2O	3 0±0 3	3 3±0 3
	3 4±0 3	
CH_3OD/D_2O	3 2±0 3	
CH_3OD	3 4±0 3	

reasonable concept, it may be a misleading picture when one of the partners is an electronically excited molecule, even when vibrationally relaxed.

Should there be anything like a transition state, one must still assume a mechanism for the reaction. Ground state aromatic electrophilic substitutions proceed in two discrete steps; isotope effects have been very useful to analyse these processes, and the solvent isotope effect in the acetolysis of aryltrimethyltins[41] has been used to ascertain that attack by the electrophile is the rate-determining step If such were the case for the methanolysis of the naphthyltin excited state, it would mean that the transition state for the proton transfer is very dissymetric Since the excited state of the aryltin is much more reactive than the ground state, it might well be that the proton is still strongly bound to the methanol, and only weakly to the substrate.

The quantum yield for the destannylation in $AcOH/C_6H_{12}$ increases as the concentration of acetic acid is raised, suggesting a first order reaction with respect to the electrophile.

B DEACTIVATION RATE CONSTANTS

In the absence of reactions, the behaviour of the excited states of 1-naphthyltrimethyltin (I) is summarized in the following scheme:

$$\begin{array}{lll}
I(S_0) \xrightarrow{h\nu} I(S_1) & & \text{rate} = I_a \\
I(S_1) \rightarrow I(S_0) + h\nu & & k_f \cdot [I(S_1)] \\
I(S_1) \rightarrow I(S_0) & & k_{1d} \cdot [I(S_1)] \\
I(S_1) \rightarrow I(T_1) & & k_T \cdot [I(S_1)] \\
I(T_1) \rightarrow I(S_0) & & k_{3d} \cdot [I(T_1)]
\end{array}$$

where S_0, S_1 and T_1 are the ground state, the lowest excited singlet and the lowest excited triplet states respectively The quantum yield for the chemical reactions is so low that the physical properties may safely be assumed to be unaffected by decompositions.

The quantum yield Φ_F^0 for fluorescence of (I) was measured relative to that of naphthalene, and quenching by molecular oxygen (Φ_F^Q) gave the lifetime of the fluorescent state according to eqn (1), where $\tau(S_1) = 1/(k_f + k_{1d} + k_T)$ is the natural lifetime of the excited state and k_Q is the (diffusion-controlled) rate constant for quenching

TABLE 2

FLUORESCENCE QUANTUM YIELDS AND LIFETIMES OF I(S_1)

Solvent	$10^2 \times \Phi_F^O$	Φ_F^O/Φ_F^Q	k_Q[42]	*Solub of* O_2[43] (25°, 1 *atm*)	$k_f + k_{1d} + k_T$	$\tau(S_1) \times 10^8$ (*sec*)	k_f
Hexane	1 4±0 4[a]	5 0	2 1 × 10^{10}	0 022 *M*	(1 0±0 8) × 10^8	1 0±0 8	1 4 × 10^6
Methanol	1 4±0 4	2 4	1 1 × 10^{10}	0 010 *M*	(0 8±0 6) × 10^8	1 2±0 7	1 7 × 10^6

[a] This fluorescence is not affected by added acetic acid

$$\Phi_F^O/\Phi_F^Q = 1 + k_Q \cdot \tau(S_1) \cdot [O_2] \quad (1)$$

by O_2. From the date collected in Table 2, the value of k_f can be calculated since $\Phi_F = k_f \cdot \tau(S_1)$.

The low values for k_f are to be related to the weak intensity of the ^1L_b transition. Application of the Förster relation[44] gives the approximate area for the absorption as 10^5 ε/cm; since the ^1L_a and ^1B_b bands have high ε's (over 5000) against $\varepsilon \approx 50$ for the ^1L_b band, the latter must be the origin of the emission. Moreover, the fluorescence spectrum is found to be the mirror image of the first transition.

The quantum yield for triplet formation Φ_T has been determined by comparison with that of naphthalene (Φ_T^N 0.80)[45] by flash photolysis and found to be 0.96 Since $k_T/k_f = \Phi_T/\Phi_F$, the rate constant for intersystem crossing k_T is deduced to be approximately 10^8 sec^{-1}. Comparison with the corresponding value for naphthalene ($\approx 10^6$ sec^{-1}) shows the importance of spin-orbit coupling due to the heavy ($Z_{Sn} = 50$) tin atom.

From the values of Φ_F, Φ_T, k_f and k_T, it is found that k_{1d} is very small; this is in agreement with the results published by Wilkinson and Horrocks[46] who show that for many aromatic systems $\Phi_F + \Phi_T$ is near unity and that radiationless decay from S_1 to S_0 is negligible.

The decay of the triplet state of (I) has been followed by monitoring the disappearance of its T–T absorption in kinetic flash photolysis; the unimolecular rate constant k_{3d} were found to be $(2.6 \pm 0.2) \times 10^4$ sec^{-1} in cyclohexane and $(2.3 \pm 0.4) \times 10^4$ sec^{-1} in methanol. These are probably upper limits because of unavoidable traces of residual oxygen, as suggested by Porter and Hoffman[47].

C KINETICS OF THE PHOTODESTANNYLATION IN METHANOL

The quantum yield for the direct and sensitized destannylation in methanol are the same within experimental error, suggesting that the singlet contribution can be neglected. The following kinetic scheme, where k_{3h} and k_{3s} are rate constants for homolytic cleavage and for photosubstitution in the triplet state respectively, leads

$I(S_0) \rightarrow I(S_1)$	rate $= I_a$
$I(S_1) \rightarrow I(S_0)$	$k_f \cdot [I(S_1)]$
$I(S_1) \rightarrow I(T_1)$	$k_T \cdot [I(S_1)]$
$I(T_1) \rightarrow I(S_0)$	$k_{3d} \cdot [I(T_1)]$
$I(T_1) \rightarrow 1\text{-}C_{10}H_7^{\cdot} + Me_3Sn^{\cdot}$	k_{3h} $[I(T_1)]$
$I(T_1) + CH_3OD \rightarrow 1\text{-}C_{10}H_7D + Me_3SnOMe$	$k_{3s} \cdot [I(T_1)] \cdot [CH_3OD]$

to eqn. (2) for the quantum yield Φ_3 of the demetallation from the triplet Since $\Phi_T = 0.97$, $k_{3d} = 2.3 \times 10^4$ and $\Phi_3 = 3.2 \times 10^{-3}$

$$\Phi_3 = \Phi_T \ (k_{3h} + k_{3s} \ [\mathrm{MeOD}])/(k_{3d} + k_{3h} + k_{3s} \ [\mathrm{MeOD}]) \tag{2}$$

this leads to

$$k_{3h} + k_{3s} \ [\mathrm{CH_3OD}] = k_{3d}/(\Phi_T/\Phi_3) - 1 = 76 \ \mathrm{sec}^{-1} \tag{3}$$

If we assume that the ratio 64/36 of 1-$C_{10}H_7D$ to $C_{10}H_8$ found in preparative runs reflects the ratio of the rates of substitution to homolysis reactions, one finds, after correcting for the 5% of $C_{10}H_7D$ formed in the subsequent irradiation of unlabeled naphthalene

$$k_{3s} \cdot [\mathrm{CH_3OD}]/k_{3h} = (64\text{-}5)/(36\text{-}5) = 1\ 44$$

and introduction of this value in eqn. (3) gives ultimately $k_{3s} = 1.8 \ \mathrm{l \cdot m^{-1} \cdot sec^{-1}}$ (if we assume that the molar volumes of CH_3OH and CH_3OD are the same; this leads to a 25 *M* concentration of neat CH_3OD).

An upper limit for the substitution rate in the excited singlet state can be estimated in the following way: the singlet contribution to the direct irradiation is within the experimental error (5%) of the total quantum yield, and is thus less than $5 \times 10^{-2} \times 3.2 \times 10^{-3} = 1\ 6 \times 10^{-4}$ Since the quantum yield for photosubstitution in the singlet excited state is given by $\Phi_{1s} = k_{1s} \cdot [\mathrm{CH_3OD}]/(k_f + k_T + k_{1s} \cdot [\mathrm{CH_3OD}])$, taking $k_f + k_T = 8 \times 10^7$, one finds that this rate constant k_{1s} is less than $5.10^2 \ \mathrm{l \cdot m^{-1} \cdot sec^{-1}}$

D KINETICS OF THE PHOTODESTANNYLATION IN CYCLOHEXANE/ACETIC ACID

The quantum yields in pure cyclohexane are the same for the direct and for the sensitized irradiations, suggesting that the reaction originates solely from the triplet state. Adding acetic acid accelerates the direct photolysis without affecting the sensitized reaction although some 8% deuterionaphthalene is formed in these conditions. These observations lead to the following kinetic scheme:

$\mathrm{I}(S_0)$	$\rightarrow \mathrm{I}(S_1)$	rate $= \mathrm{I}_a$
$\mathrm{I}(S_1)$	$\rightarrow \mathrm{I}(S_0)$	$k_f \cdot [\mathrm{I}(S_1)]$
$\mathrm{I}(S_1) + \mathrm{AcOD}$	$\rightarrow$ 1-$C_{10}H_7D$ + MeSnOAc	$k_{1s} \ [\mathrm{I}(S_1)] \ [\mathrm{AcOD}]$
$\mathrm{I}(S_1)$	$\rightarrow \mathrm{I}(T_1)$	$k_T \cdot [\mathrm{I}(S_1)]$
$\mathrm{I}(T_1)$	$\rightarrow \mathrm{I}(S_0)$	$k_{3d} \cdot [\mathrm{I}(T_1)]$
$\mathrm{I}(T_1) + \mathrm{AcOD}$	$\rightarrow$ 1-$C_{10}H_7D$ + Me_3SnOAc	$k_{3s} \cdot [\mathrm{I}(T_1)] \ [\mathrm{AcOD}]$
$\mathrm{I}(T_1)$	$\rightarrow$ 1-$C_{10}H_7^{\cdot}$ + $Me_3Sn^{\cdot}$	$k_{3h} \cdot [\mathrm{I}(T_1)]$

Since no isotope effect was found on going from AcOH to AcOD, the quantum yield for the formation of naphthalene (labeled and unlabeled) is given by eqn. (4), where (AcOD) stands for [AcOH] + [AcOD]; the triplet contribution Φ_3 being $1\ 0 \times 10^{-3}$ (1) and practically independent of acid concentration, the steady-state

$$I_a \cdot \Phi = k_{1s} \cdot (\mathrm{AcOD}) \cdot [\mathrm{I}(S_1)] + k_{3s} \cdot (\mathrm{AcOD}) \cdot [\mathrm{I}(T_1)] + k_{3h} \cdot [\mathrm{I}(T_1)] \tag{4}$$

TABLE 3

REACTIVITY OF I(S_1) TOWARDS AcOD IN CYCLOHEXANE

$(AcOH)$	$\Phi \times 10^3$	$\Phi - \Phi_3$	$k_{1s} = (\Phi - \Phi_3)k_T/(AcOH)$
0 0	1 0	0 0	
0 4	2 6	$1 6 \times 10^{-3}$	$4 0 \times 10^5$
0 8	4 6	$3 6 \times 10^{-3}$	$4 5 \times 10^5$

concentration of I(S_1) is equal to

$$I(S_1) = I_a/[k_f + k_T + k_{1s}\ (AcOD)] \approx I_a/k_T$$

Rewriting then eqn. (4) in the form $I_a \cdot (\Phi - \Phi_3) = k_{1s}$ (AcOD) [I(S_1)], one finds

$$k_{1s} = (\Phi - \Phi_3) \cdot k_T \cdot (AcOD)$$

The relevant data summarized in Table 3 show that $k_{1s} = (4.2 \pm 0.3) \times 10^5$ l $m^{-1} \cdot sec^{-1}$.

On the other hand, an indirect estimate of the rate for photosubstitution in the triplet state can be deduced from preparative runs, which showed that 46% of 1-$C_{10}H_7D$ were formed during irradiation in cyclohexane/CH_3COOD. These 46% account for all sources of deuterionaphthalene, *i.e.* 8% from the triplet state and about 6% from further reaction of the formed naphthalene, leaving 32% originating from the singlet excited state. The rate from the singlet state being $k_{1s} \cdot [I(S_1)] \cdot (AcOD)$, we find that

$$\frac{k_{1s} \cdot [I(S_1)] \cdot (AcOD)}{k_{3s} \cdot [I(T_1)] \cdot (AcOD)} = \frac{32}{8} = 4$$

if we assume that the rate equation is the same for the reaction from I(T_1), and since the steady state concentration of I(T_1) is related to that of I(S_1) by the relation $I(T_1) = I(S_1) \cdot k_T/k_{3d}$ this leads to

$$\frac{k_{1s}}{k_{3s}} \cdot \frac{k_{3d}}{k_T} = 4$$

The rate constants k_{1s}, k_{3d} and k_T being approximately 4.2×10^5 sec^{-1}, 2.6×10^4 sec^{-1} and 10^8 respectively, k_{3s} turns out to be 27 sec^{-1}.

Table 4 summarizes the rate constants k_s for the second order deuteriodestannylation rate constants, given in $l \cdot m^{-1} \cdot sec^{-1}$.

TABLE 4

SECOND-ORDER RATE CONSTANTS (in l m^{-1} sec^{-1}) FOR THE DEMETALLATION OF 1-NAPHTHYLTRIMETHYLTIN

Medium	*Ground state*	*Excited triplet*	*Excited singlet*
C_6H_{12}/CH_3COOD	$< 10^{-5}$	≈ 27	4×10^5
CH_3OD/D_2O	$< 10^{-9}$	1 8	$(< 5 \times 10^2)$

In cyclohexane/acetic acid, the reactivity increases strongly on going from the ground state to the lowest excited triplet and then to the lowest excited singlet. This sequence qualitatively follows the pK_a data for aromatic hydrocarbons, whose equilibrium properties place the triplet between the ground and excited singlet states[8]. This sequence is less clear in aqueous methanol, where both excited states show at best similar reactivities. It is clear from these results that photoexcitation leads to a tremendous increase in reactivity[19], in agreement with calculations of localisation energies[14]; however our present understanding of the reactivity in excited states does not allow any deeper discussion of the data.

EXPERIMENTAL

Reagents and solvents

1-Naphthyltrimethyltin was synthesised[48] and its purity, as checked by gas–liquid chromatography (20% SE30 on diatoport W) was 99 5%; it contained 0 5% of naphthalene.

UCB cyclohexane was freed from traces of benzene by percolation through activated silica gel[49]; CH_3OD (over 99% O-D) was from Radio Electro and D_2O (over 99.75%) from Merck (Uvasol) AcOD was made by hydrolysing acetic anhydride with D_2O and avoiding any contact with moisture during the work-up and use

Photolyses

1. *Preparative runs.* Water (5%, vol/vol) was added to the methanol (and 5% D_2O to CH_3OD) to swamp out any adventitious moisture. The 0.033 *M* solutions of 1-naphthyltrimethyltin in methanol, or in cyclohexane with 0.4 *M* of acetic acid, were degassed by freeze-pump-thaw cycles till the residual pressure was 10^{-4} mm, and were then irradiated with HPK 125 Philips medium pressure mercury arcs. After the photolysis the solutions are injected as such in the VPC analytical apparatus, or concentrated and analysed by mass spectrometry (Hitachi–Perkin–Elmer RMU 6). Naphthalene was identified by its melting point and mass spectrum, and was estimated by VPC (using an internal standard) and UV spectrophotometry. The labelling of 1-deuterionaphthalene was checked by mass spectrometry and repeated integrations of NMR spectra (Varian A60); IR spectra were found compatible with the other data Trimethyltin hydroxide was too unstable to analyse accurately; it was identified by comparison of its IR spectrum and VPC behaviour with those of an authentic sample. Trimethyltin acetate was identified by IR, melting point and mixed melting point, and estimated by weighing.

2. *Quantum yields.* The light source was a Super Pressure Osram H.B.O. 200 W mercury lamp, followed by a High Intensity Bausch & Lomb monochromator using the 180–400 nm grating. The spectral distribution of the light beam was checked with a Hilger Medium Quartz Spectrograph. A beam splitter was used to irradiate the organotin solution simultaneously with a benzophenone/hexane actinometer. The conversion in both cells was followed by spectrophotometry (Cary 14). The organotin solutions absorbed 80% to 99% of the incident light; the corresponding corrections were taken into account for the calculation of the quantum yields

In the case of the runs sensitized with triphenylene, the conversion was determined by a quantitative iododestannylation of unreacted 1-naphthyltrimethyltin

with a known amount of iodine, the remaining I_2 being then estimated spectrophotometrically (Beckman B) as I_3^-.

Fluorescence quantum yield of 1-*naphthyltrimethyltin*

The fluorescence quantum yield of 1-naphthyltrimethyltin was determined relative to that of naphthalene by comparison of the emission intensities from solutions having the same absorbance (0.28/cm) at the exciting wavelength (280 nm), with a Cary 14 Spectrophotometer equipped with the Three-port Illuminator Accessory.

Triplet yield for 1-*naphthyltrimethyltin*

(*a*). *Determination of the extinction coefficient of the* $T_1 \rightarrow T_n$ *transition in the triplet state.* Absorption spectra of excited triplet naphthyltin were photographed by flash photolysis. The absorbance of the transient at 430 nm decreases when more dilute solutions are used, but the relative absorbance $D/[\mathrm{ArSn}]_0$ *increases* steadily and levels off when the conditions are such that one may assume that all the molecules populate the lowest triplet state. From the horizontal part of this concentration dependence, it is concluded that the T_1-T_n transition observed at 430 nm has an ε of about 7700.

(*b*). *Determination of* Φ_T. The spectra of naphthalene and 1-naphthyltrimethyltin being very similar, it is possible to estimate the Φ_T for the aryltin relative to that ($\Phi_T = 0.80$) of the parent hydrocarbon. The solvent used was purified (Merck Uvasol) liquid paraffin, to increase the lifetime of the transients. Solution of the compounds were flashed through a nickel sulphate solution filter transparent in the 240–310 nm region. The decay of the triplets was monitored at their respective maximum absorption wavelength (naphthalene: 420 nm; aryltin: 430 nm). Taking into account the relative intensity of the various lines of the flash lamps together with the absorption spectrum of both molecules, it is possible to estimate the relative amount of light absorbed by the solutions. If one now assumes the following kinetic scheme, where A is either naphthalene or 1-naphthyltrimethyltin:

$$\begin{array}{lll} \mathrm{A}(S_0) \rightarrow \mathrm{A}(S_1) & \text{rate: } I_a & \\ \mathrm{A}(S_1) \rightarrow \mathrm{A}(S_1) + h\nu & & k_f \cdot [\mathrm{A}(S_1)] \\ \mathrm{A}(S_1) \rightarrow \mathrm{A}(T_1) & & k_T \cdot [\mathrm{A}(S_1)] \\ \mathrm{A}(T_1) \rightarrow \mathrm{A}(S_0) & & k_d \cdot [\mathrm{A}(T_1)] \end{array}$$

one finds that

$$\frac{\Phi'_T}{\Phi} = \frac{D'_T \cdot \varepsilon_{TT} \cdot I_a}{D_T \cdot \varepsilon'_{TT} \cdot I'_a}$$

where the primed symbols refer to the aryltin and the unprimed to naphthalene, D_T is the initial absorbance of the triplet having an extinction coefficient ε_{TT} at the monitoring wavelength, and I_a is the amount of light absorbed. We accept for ε_{TT} of naphthalene the value 10000 suggested by Porter and Windsor[50]. In our conditions, it was observed that $D_T = D'_T$ and $I_a/I'_a = 0.93$, so that $\Phi'_T = 0.80 \times 10{,}000/7{,}700 \times 0.93 = 0.96$.

When a 1.3×10^{-3} M solution of the aryltin in cyclohexane containing benzo-

phenone was flashed through filters which allowed absorption only by the ketone, the same transient was observed as in the direct photolyses, showing that it is the triplet state of the substrate Assuming by analogy with other naphthalene derivatives[51] that the lowest triplet energy of the aryltin is not higher than 60 kcal/mole, these conditions are those which allow complete quenching of the benzophenone triplet state by the substrate.

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REFERENCES

1 J Nasielski, A Kirsch-Demesmaeker and R Nasielski-Hinkens, *Tetrahedron*, 28 (1972) 3767
2 K C Bass, *Organometal Chem Rev*, 1 (1966) 391
3 J McDonald Blair, D Bryce-Smith and B W Pengilly, *J Chem Soc*, (1959) 3174
4 E E van Tamelen, J I Brauman and L E Ellis, *J Amer Chem Soc*, 87 (1965) 4964
5 G A. Razuvaev and V N Pankratova, *Zh Obsch Khim*, 36 (1966) 1702
6 D B Peterson, D A G Walmsley, R J Povinelli and M Burton, *J Phys Chem*, 71 (1967) 4506
7 A G Brook and J M Duff, *J Amer Chem Soc*, 89 (1967) 454
8 H G Kuivila and P L Maxfield, *J Organometal Chem*, 10 (1967) 41, *Inorg Nucl Chem Lett*, 1 (1965) 29
9 J L R Williams, P J Grisdale, J C Doty, M E Glogowski, B E Babb and D P Maier, *J Organometal Chem*, 14 (1958) 53
10 J L R Williams, J C Doty, P J Grisdale, R Searle, T H Regan, G P Happ and D P Maier, *J Amer Chem Soc*, 89 (1967) 5153
11 J L R Williams, J C Doty, P J Grisdale, T H Regan, G P Happ and D P Maier, *J Amer Chem Soc*, 90 (1968) 53
12 D H R Barton, T Nakano and P G Sammes, *J Chem Soc C*, (1968) 322
13 D A De Bie and E Havinga, *Tetrahedron*, 21 (1965) 2359
14 J P Colpa, C Mac Lean and E L Mackor, *Tetrahedron, Suppl* 2, 19 (1963) 65
15 J Kroh and A M Plonka, *Bull Acad. Pol Sci, Ser Sci Chim*, 14 (1966) 331, 16 (1968) 383, 387
16 J Kroh and E Hankiewicz, *Chem Phys Lett*, 1 (1968) 542, J Kroh, E Burzynska, *Bull Acad Pol Sci, Ser Sci Chim*, 16 (1968) 509
17 M G Kuzmin, B M Uzhinov, G Szent Gyorgy and I V Berezin, *Zh Fiz Khim*, 41 (1967) 769
18 M G Kuzmin, V L Ivanov and O E Yakimchenko, *Khim Vys Energ*, 1 (1967) 443
M G Kuzmin, V. L Ivanov and Y Y Kulis, *Khim Vys Energ*, 2 (1968) 228.
19 E Vander Donckt, D Liétaer and J. Nasielski, *Bull Soc Chim Belg*, 79 (1970) 283
20 G M J Beijersbergen van Henegouwen and E Havinga *Recl Trav Chim Pays-Bas*, 89 (1970) 907, and references cited therein
21 R L Letsinger and K E Steller, *Tetrahedron Lett*, (1969) 1401
22 S T Reid and G Subramanian, *Chem. Commun*, (1966) 245
23 A J. Kirby et A G Varvoglis, *Chem Commun*, (1967) 405.
24 J A. Barltrop, N J Bunce and A Thomson, *J. Chem. Soc, C*, (1967) 1142
25 R. H Shapiro and K Tomer, *Chem Commun*, (1968) 460
26 R Grinter, E Heilbronner, T Petrzilka and P Seiler, *Tetrahedron Lett*, (1968) 3845
27 J T Pinhey and R D G Rigby, *Tetrahedron Lett*, (1969) 1267, 1271
28 G M Badger and C P Whittle, *Aust J Chem*, 16 (1963) 440
29 W Wolf and N Kharasch, *J Org Chem*, 26 (1961) 283

30 M. Ochiai, E. Mizuta, Y Asahi and K Morita, *Tetrahedron*, 24 (1968) 5861
31 J. S. Connolly and H Linschitz, *Photochem Photobiol*, 7 (1968) 791
32 B Brocklehurst, W A Gibbons, F T Lang, G Porter and M I Savadatti, *Trans Faraday Soc*, 62 (1966) 1793
33 A Terenin, V Rylkov and V Kholmogorov, *Photochem Photobiol*, 5 (1966) 543
34 H S Judeikis and S. Siegel, *J Chem. Phys*, 43 (1965) 3625
35 H D Mettee, *Can J Chem*, 45 (1967) 339.
36 S H Ng, G P Semeluk and I Unger, *Can J. Chem*, 46 (1968) 2459
37 W Van Dusen and W H Hamill, *J Amer Chem Soc*, 84 (1962) 3648
38 H Knibbe, K Röllig, F P Schäfer and A Weller, *J Chem. Phys*, 47 (1967) 1184
39 O Buchman, M Grosjean and J Nasielski, *Helv Chim Acta*, 47 (1964) 1695
40 A Beckett and G Porter, *Trans Faraday Soc*, 59 (1963) 2038.
41 J. Nasielski, O Buchman, M Grosjean and M Jauquet, *J. Organometal Chem*, 19 (1969) 353
42 W R. Ware, *J Phys Chem*, 66 (1962) 455
43 *Gmelins Handbuch der Anorganischen Chemie*, Vol 3, 8e ed, 1958, pp 485, 491
44 T Förster, *Fluorescenz Organischen Verbindungen*, Vandenhoeck und Ruprecht, Göttingen, 1951
45 A R Horrocks, A Hearvell, K Tickle and F. Wilkinson, *Trans Faraday Soc*, 62 (1966) 3393.
46 A. R Horrocks and F Wilkinson, *Proc Roy Soc., Ser, A*, 306 (1968) 257
47 M. Z. Hoffman and G Porter, *Proc Roy Soc, Ser, A*, 268 (1962) 46
48 O Buchman, M Grosjean and J Nasielski, *Bull Soc Chim. Belg*, 71 (1962) 467
49 S A Ashmore, *Analyst (London)*, 72 (1947) 206
50 G Porter and M. W Windsor, *Proc Roy. Soc, Ser A*, 245 (1958) 238
51 J G Calvert and J N Pitts Jr, *Photochemistry*, Wiley, London, 1966, p 297, 298.