

## Preliminary Note

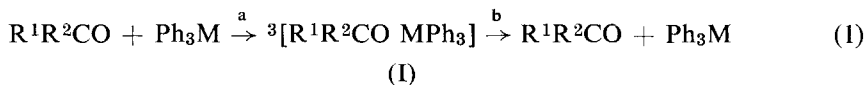
### Carbonyl triplet quenching by Group V organometallics

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(Received October 24, 1973)

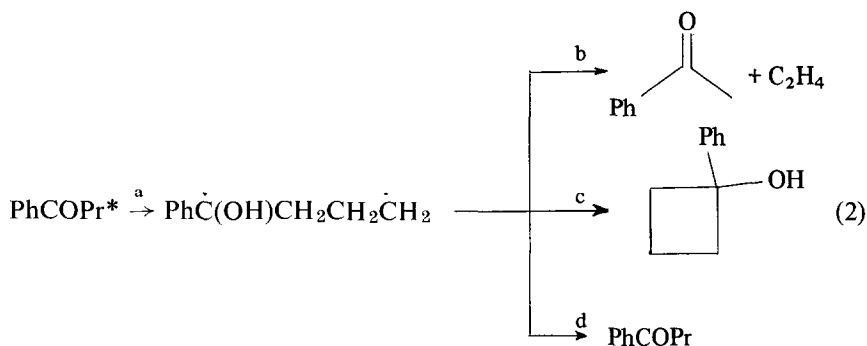
Triarylaminines and triarylphosphines are known to be efficient quenchers of the triplet state of carbonyl compounds<sup>1-3</sup>. The interaction results mainly in physical quenching, although chemical reaction has been also detected in some cases<sup>4</sup>. The process is believed to involve an exciplex, which provides an energy wasting mechanism:



Alkoxy radicals are known to react with organophosphorus compounds *via* an intermediate<sup>5-8</sup>, the structure of which can conceivably be similar to that of (I).

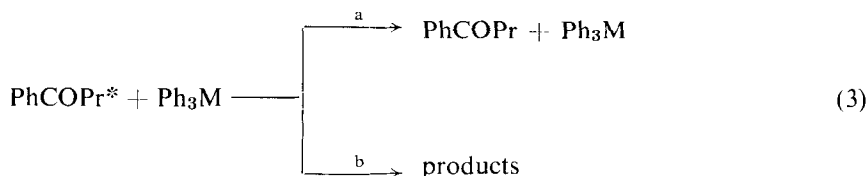
No examinations seem to have been carried out of the interaction of carbonyl triplets with compounds having arsenic, antimony or bismuth as the metallic centre. We have examined the interaction of a series of compounds of general formula  $\text{Ph}_3\text{M}$  ( $\text{M} = \text{N}, \text{P}, \text{As}, \text{Sb}, \text{Bi}$ ) with butyrophenone triplets at 28°C in non-polar solvents.

In the absence of the organometallic compound the behaviour of butyrophenone triplets can be represented by:



\* Part of this work was carried out at the Universidad Técnica del Estado (Chile).

In the presence of an organometallic substrate, reaction (3) competes with reaction (2):



The kinetic behaviour of the system can be represented by eqn. (4), provided that the relative values of  $k_{2b}$ ,  $k_{2c}$  and  $k_{2d}$  are not modified by the presence of the organometallic compound.

$$\frac{\Phi^0}{\Phi} = 1 + k_3 \tau [\text{Ph}_3\text{M}] \quad (4)$$

where  $\Phi^0$  and  $\Phi$  are the quantum yields of one of the molecular products in reaction (2) in the absence and presence of quencher respectively and  $\tau$  is the lifetime of the carbonyl triplet in the absence of quencher.

The irradiations were carried out in a 'merry-go-round' apparatus, using a Hanovia 125 W medium pressure mercury arc as light source. No filters were used for  $\text{Ph}_3\text{N}$ ,  $\text{Ph}_3\text{As}$ , while a soda glass, combined with a Corning 7380 filter were employed in the case of  $\text{Ph}_3\text{Sb}$  and  $\text{Ph}_3\text{Bi}$ , in order to avoid the direct photodecomposition of the organometallic substrate. The samples (1 ml) were contained in matched Pyrex tubes, and the product examined (by g. l. c.) was acetophenone. Conversions were around 2% for  $\text{Ph}_3\text{N}$ ,  $\text{Ph}_3\text{P}$  and  $\text{Ph}_3\text{As}$ , below 1% for  $\text{Ph}_3\text{Sb}$  and around or under 0.1% in the case of  $\text{Ph}_3\text{Bi}$ , in order to avoid the precipitation of metallic bismuth (in benzene) or a white solid (presumably  $\text{ClBiPh}_2$ ) in carbon tetrachloride. Spectra were recorded using a Cary 17 spectrometer.

The results obtained are shown in Table 1, using  $k_{2a} = 1.04 \times 10^7 \text{ s}^{-1}$  (i.e.  $\tau^{-1}$ )<sup>9,10</sup>. It is clear that all the substrates examined are very efficient, and

TABLE 1

KINETIC DATA ON THE INTERACTION OF BUTYROPHENONE TRIPLETS WITH GROUP V ORGANOMETALLICS

Organometallic	Solvent	$k_3 \tau / M^{-1}$ <sup>a</sup>	$k_3 / M^{-1} \text{ s}^{-1}$
$\text{Ph}_3\text{N}$	benzene	654	$6.8 \times 10^9$
$\text{Ph}_3\text{P}$	benzene	231	$2.4 \times 10^9$
$\text{Ph}_3\text{As}$	benzene	106	$1.1 \times 10^9$
$\text{Ph}_3\text{Sb}$	benzene	346	$3.6 \times 10^9$
$\text{Ph}_3\text{Bi}$	$\text{CCl}_4$	1250	$1.3 \times 10^{10}$ <sup>b</sup>
Penta-1,3-diene	benzene	6600	$6.2 \times 10^9$

<sup>a</sup> At 28°C.

<sup>b</sup> In benzene  $k_3 \sim 1.2 \times 10^{10} M^{-1} \text{ s}^{-1}$ .

although energy transfer cannot be fully disregarded at this stage, it seems probable that some type of specific interaction (e.g. formation of an exciplex) might be involved.\* It is interesting to note that the rate constant for  $\text{Ph}_3\text{Bi}$  is higher than that for penta-1,3-diene, usually considered a 'diffusion-controlled' quencher. The rates do not follow an increasing trend with decreasing ionization potential, a correlation which is usually characteristic of processes whose rate is determined by charge-transfer interactions<sup>1,13,14</sup>. Therefore, it seems certain that in addition to these interactions, the behaviour of the substrates is determined by other factors, and long range interactions involving the vacant *d* orbitals are likely to be of importance for the higher members in the series.

The photolyses of butyrophenone- $\text{Ph}_3\text{Bi}$  mixtures in benzene led to the precipitation of metallic bismuth. When the experiments were carried out in carbon tetrachloride a white photosensitive precipitate was formed, and the resulting solution contained chlorobenzene, which was formed with a limiting quantum yield of  $0.52 \pm 0.05$ . We believe that this chlorobenzene is formed in reaction (5) which follows the photosensitized formation of phenyl radicals:



We could not establish unambiguously the structure of the white precipitate mentioned above, which we believe is  $\text{ClBiPh}_2$ . The microanalysis showed only partial agreement (calc: C = 36.2%, H = 2.52%, Cl = 8.87%; found: C = 32.9%, H = 2.60%, Cl = 8.70%). We feel that the difference reflects problems which are intrinsic of obtaining a photosensitive product in a photochemical process. We are currently trying to build a 'centrifuge-merry-go-round' apparatus, hoping to overcome this problem.

Future examination of those systems should throw more light on the mechanism of interaction of metallic centres with excited species. Moreover, the possibility of using the photosensitized decomposition of  $\text{Ph}_3\text{Bi}$  as a source of phenyl radicals for kinetics studies is currently being examined.

Thanks are due to Drs. J. Grotewold and B. P. Roberts for gifts of chemicals, to Professor A. G. Davies for having the microanalysis carried out at University College London, and to the Chemical Society Research Fund for support.

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\* This type of interaction has been proposed for amines<sup>1,2</sup> organophosphines<sup>2</sup>, organoboranes<sup>11</sup> and organotin compounds<sup>12</sup>. In most of the systems the process is very efficient, while energy transfer could be highly endothermic.

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