DICARBONYL AND RELATED COMPOUNDS AS SENSITIZERS FOR PHOTO-OXIDATIVE DESULPHURIZATION AT PENTAVALENT PHOSPHORUS

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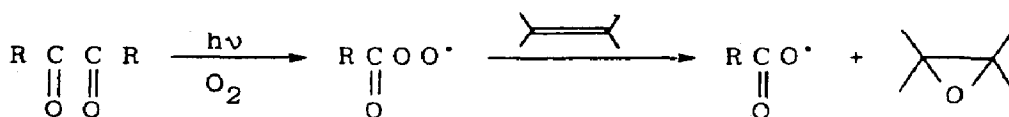
(Received March 6, 1986; in revised form May 16, 1986)

Summary

Many 1,2-dicarbonyl compounds, some quinones and benzoin sensitize the photo-oxidation of sulphur at pentacovalent phosphorus. Singlet oxygen and diacyl peroxides are ruled out as intermediates. It is suggested that either acylperoxy or peroxy radicals and/or biradicals derived by reaction of the triplet sensitizer with oxygen are responsible for reaction.

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1. Introduction

Interest in the use of 1,2-dicarbonyl compounds as sensitizers for photo-oxidation reactions stems from the fact that when olefins are used as substrates oxiranes are produced [1 - 5]. Although many 1,2-dicarbonyl compounds can sensitize singlet oxygen formation from their triplet state [1, 3], this reaction to give oxiranes often competes very successfully with reactions associated with the chemistry of singlet oxygen. A recent study [6] has shown that the efficacy with which 1,2-dicarbonyl compounds sensitize reactions involving singlet oxygen compared with that of reactions involving acylperoxy radicals is dependent upon the structure of the diketone. The sensitizers have also been shown to be consumed in the reactions [2 - 4] and oxidation products are formed. Indeed it has been known for some time that 1,2-dicarbonyl compounds suffer photo-oxidation to give products such as carboxylic acids, carboxylic anhydrides and percarboxylic acids [5, 7 - 10].

$$R\underset{\overset{\|}{O}}{C}\underset{\overset{\|}{O}}{C}R \xrightarrow[O_2]{h\nu} R\underset{\overset{\|}{O}}{C}OO^{\cdot} \xrightarrow{} R\underset{\overset{\|}{O}}{C}O^{\cdot} \; + \; \text{(oxirane)}$$

The finding that benzoin photosensitizes oxirane formation [11] has been attributed to reaction of benzoylperoxy radicals with the olefin, the

radicals being generated via a Type I cleavage followed by scavenging of the radicals by oxygen. However, there is some confusion in the literature as to whether 1,2-dicarbonyl compounds undergo simple bond homolysis in an excited state to give acyl radicals. Thus in the case of benzil there are two reports of failure to detect benzoyl radical formation [2, 12], one possible indication of inefficient benzoyl radical formation [13] and some evidence that there is a thermal activation energy barrier to cleavage in an excited state [14]. There is also strong evidence to suggest that aliphatic 1,2-dicarbonyl compounds such as esters of α-oxocarboxylic acids do not undergo simple C—C bond homolysis on irradiation in solution [15]. Undoubtedly many of these 1,2-dicarbonyl compounds are stable towards irradiation in poorly hydrogen-donating solvents and in the absence of oxygen but are highly reactive in the presence of oxygen. To rationalize these observations it has been proposed that the excited states of 1,2-dicarbonyl compounds such as benzil, biacetyl and acenaphthaquinone react with oxygen from their triplet state to give a 1,4-biradical [1 - 5, 7 - 10] as well as undergoing energy transfer to give singlet oxygen [10].
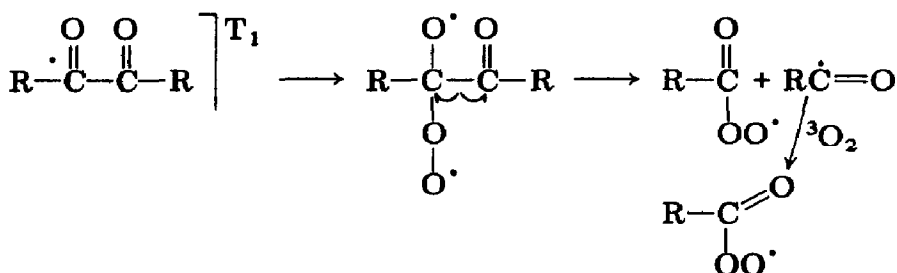
We now show that many 1,2-dicarbonyl compounds and related species photosensitize the oxidation of sulphur at pentavalent phosphorus. Earlier work has shown that *N*-oxides such as 3-methylpyridazine-2-oxide in their excited states undergo an oxygen transfer reaction with phosphine sulphides [16]. Such oxidation reactions are of considerable ecological importance owing to widespread use of thionates and thiolates as agricultural insecticides [17].

2. Results

The photo-oxidative desulphurization of the following compounds was investigated: triphenylphosphine sulphide (1), *O*-ethyl diphenylphosphinothioate (2), *O,O*-diethyl phenylphosphonothioate (3), *O,O,O*-triethyl phosphorothioate (4), *O,O*-diethyl-*S*-methyl phosphorothioate (5) and *O,O*-diethyl-*S*-pentyl phosphorothioate (6). Irradiation of oxygenated solutions of these compounds containing typical singlet oxygen sensitizers such as rose bengal and methylene blue led to no observable reaction. However, use of many 1,2-dicarbonyl compounds as sensitizers led to the desired reac-

TABLE 1

Photo-oxidative desulphurization[a] of the phosphorus compounds 1 - 4 using 1,2-dicarbonyl compounds as sensitizers

Compound	Sensitizer (amount)[b]	Recovered starting material (%)	Oxidation product (%)
1	Benzil (2)[c]	0	85
2	Benzil (2)[c]	17	72
3	Benzil (2)[c]	35	53
4	Benzil (2)[c]	42	44
1	Biacetyl (4)	0	84
2	Biacetyl (4)	0	84
3	Biacetyl (4)	13	69
4	Biacetyl (4)	17	63
1	Acenaphthaquinone (2)	2	96
2	Acenaphthaquinone (1.4)	26	68
3	Acenaphthaquinone (1.2)	29	67
4	Acenaphthaquinone (1.0)	39	39
1	9,10-Phenanthraquinone (2)	91	4
1	Pyruvic acid (4)	0	88
2	Pyruvic acid (4)	0	92
3	Pyruvic acid (4)	20	68
4	Pyruvic acid (4)	52	38
1	Methyl pyruvate (4)	0	94
2	Methyl pyruvate (4)	2	86
3	Methyl pyruvate (4)	30	62
4	Methyl pyruvate (4)	39	44
1	t-Butyl pyruvate (4)	46	48
2	t-Butyl pyruvate (4)	54	39
3	t-Butyl pyruvate (4)	72	14
4	t-Butyl pyruvate (4)	77	16

[a]Irradiated in acetonitrile solution under oxygen using black-light fluorescent lamps for 10 h.
[b]Number of equivalents of sensitizer relative to amount of compound employed.
[c]Replacement of the benzil by dibenzoyl peroxide led to a 26% yield of triphenylphosphine oxide from the sulphide.

tion (Table 1). In all cases the P=S group was cleanly oxidized to the P=O group. Since the oxidation reactions may involve acylperoxy radicals the oxidation of compounds 1 - 4 using benzoin as sensitizer (a known precursor of benzoyloxy radicals) was carried out and the results are shown in Table 2. The ability of 1,4-quinones to sensitize these reactions was also studied. There is some indication that the excited triplet state of quinones can react with oxygen to give 1,4-biradicals which can be trapped by olefins [18]. The observed products can also be interpreted as arising via an initial reaction occurring between the quinone and the olefin (path b).
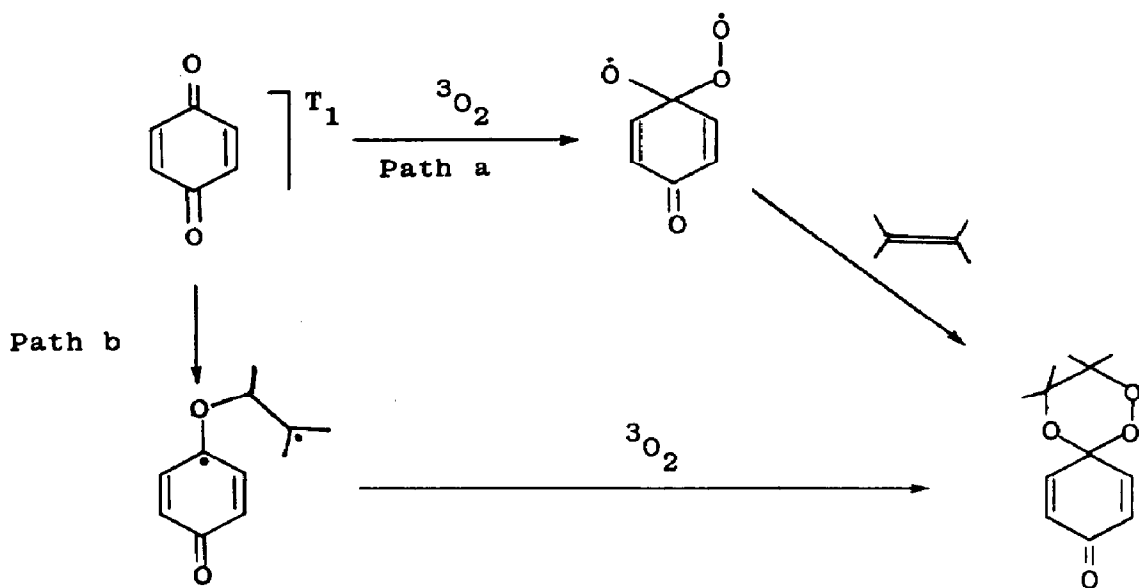
TABLE 2

Photo-oxidative desulphurization[a] of the phosphorus compounds 1 - 4 using benzoin and 1,4-quinones as sensitizers

Compound	Sensitizer (amount)[c]	Recovered starting material (%)	Oxidation product (%)
1[b]	Benzoin (2)	0	98
2	Benzoin (2)	0	88
3	Benzoin (2)	0	86
4	Benzoin (2)	0	95
1	2,3-Dichloro-5,6-dicyanobenzoquinone (2)	0	95
2	2,3-Dichloro-5,6-dicyanobenzoquinone (2)	33	53
3	2,3-Dichloro-5,6-dicyanobenzoquinone (2)	56	24
4	2,3-Dichloro-5,6-dicyanobenzoquinone (2)	43	17
1	2,3,5,6-Tetrachlorobenzoquinone (2)	65	31
2	2,3,5,6-Tetrachlorobenzoquinone (2)	88	12

[a]Irradiated in acetonitrile solution under oxygen using black-light fluorescent lamps for 10 h (except where stated otherwise).
[b]Irradiation carried out for 1 h only.
[c]Number of equivalents of sensitizer relative to amount of compound used.

The results in Table 2 show that quinones can act as sensitizers for the oxidation of P=S bonds to P=O bonds. There is also the possibility that the quinones lead to superoxide anion formation. The latter reacts inefficiently with the substrates and can be discounted as being a participating intermediate [19].

In many of the reactions it became obvious that the sensitizers were being degraded. Certain reactions were selected in order to verify this point and also to establish whether the phosphorus thionates were protecting the sensitizers in any way. The results shown in Table 3 indicate that, on the whole, the phosphorus sulphides have little protective action. In the case of acenaphthaquinone the principle photodegradation product was found, in agreement with earlier work, to be 1,8-naphthalic anhydride [5, 7 - 9]. Interestingly it was found that the presence of a thiophosphorus compound enhanced the yield of 1,8-naphthalic anhydride (Table 4).

TABLE 3

Percentage dicarbonyl compound sensitizer consumed during irradiation[a] in the presence and absence of triphenylphosphine sulphide

Sensitizer (amount) [b]	Sulphide present	Sulphide absent
Benzoin [c] (2)	67	76
Benzil (2)	89	88
Biacetyl (4)	81	91
Acenaphthaquinone (2)	100	100
p-Chloranil (2)	23	26
Pyruvic acid (4)	98	96
Methyl pyruvate (4)	85	86
t-Butyl pyruvate (4)	54	65

[a]Irradiated in acetonitrile solution under oxygen with black-light fluorescent lamps for 10 h (except where stated otherwise).
[b]Number of equivalents relative to sulphide present and used at the same concentration in the absence of sulphide.
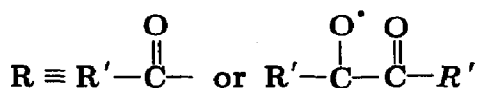[c]Irradiated for 20 min.

TABLE 4

Yield of 1,8-naphthalic anhydride obtained by photo-oxidation[a] of acenaphthaquinone in the presence and absence of 1 and 4

Concentration of acenaphthaquinone ($\times 10^{-2}$ M)	Phosphorus compound concentration (M)	Yield of 1,8-naphthalic anhydride (%)
1.36	1 6.79×10^{-3}	54
1.36	1 None	44
2.05	4 2.0×10^{-2}	60
2.05	4 None	42

[a]Solutions irradiated in acetonitrile under oxygen with black-light fluorescent lamps for 10 h.

The range of sensitizers found to effect oxidation of phosphorus compounds 1 - 4 was also found to oxidize 5 and 6 at sulphur in the following way.

$$(EtO)_2\underset{\underset{O}{\|}}{P}SR \longrightarrow (EtO)_2\underset{\underset{O}{\|}}{P}OH$$

5 R ≡ CH$_3$

6 R ≡ (CH$_2$)$_4$CH$_3$

The results are shown in Table 5. The oxidation of these compounds by the dicarbonyl compounds appears to be less efficient than for compounds 1 - 4.

TABLE 5

Photo-oxidative desulphurization[a] of the phosphorus thioate compounds 5 and 6[b]

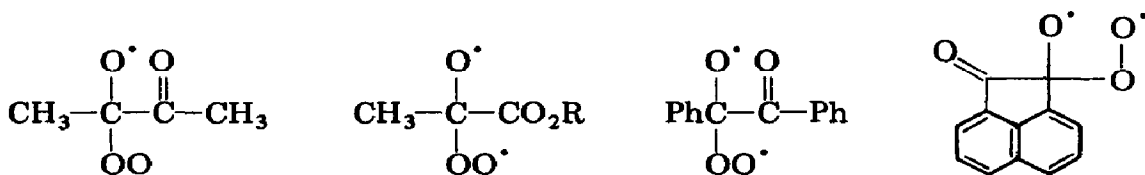| Compound	Sensitizer (amount)[c]	Recovered starting material (%)	Oxidation product (%)
5	Benzoin (2)	0	77
6	Benzoin (2)	0	90
5	Benzil (4)	57	42
6	Benzil (4)	51	41
6	Biacetyl (6)	5	93
5	Acenaphthaquinone (6)	68	11
6	Acenaphthaquinone (6)	84	14
5	Pyruvic acid (6)	53	25
6	Pyruvic acid (6)	13	67
5	Methyl pyruvate (6)	55	31
6	Methyl pyruvate (6)	54	41

[a] Irradiated in acetonitrile under oxygen with black-light fluorescent lamps for 10 h.
[b] Determined as the methyl ester after treatment with diazomethane.
[c] Number of equivalents of sensitizer relative to amount of compound used.

3. Discussion

3.1. Species responsible for oxidation

There are a number of potential candidates for the oxidizing species. Many of the 1,2-dicarbonyl compounds are known to give diacyl peroxides upon photo-oxidation. However, the finding that dibenzoyl peroxide oxidizes triphenylphosphine sulphide to its oxide slower than benzil suggests that the peroxide is not an important species in the oxidation reaction sensitized by diketone. The results with the dyes as sensitizers suggest that singlet oxygen plays little if any part. The two clearest contenders are acyl-peroxy radicals and the 1,4-biradicals generated by reaction of ground state oxygen and the triplet sensitizer. These species may react with the thiophosphorus compound as follows:

$$\geqslant\!P\!=\!S + RO\dot{O} \longrightarrow \geqslant\!\dot{P}\!-\!S \xrightarrow{\text{Path A}} \geqslant\!P\!-\!S + R^{\bullet}$$

$$\geqslant\!P\!=\!O + S \longleftarrow \geqslant\!P\!\underset{O}{\overset{S}{\triangle}} \longleftarrow \geqslant\!\dot{P}\!-\!\underset{\dot{O}}{S} + RO^{\bullet} \qquad \geqslant\!P\!=\!O + SO$$

$$R \equiv R'\!-\!\overset{\overset{\displaystyle O}{\|}}{C}\!- \quad\text{or}\quad R'\!-\!\overset{\overset{\displaystyle O^{\bullet}}{|}}{C}\!-\!\overset{\overset{\displaystyle O}{\|}}{C}\!-\!R'$$

The fate of the sulphur in these reactions was not determined. There was no trace of precipitated sulphur in the reaction mixtures. That benzoyl-peroxy radicals can bring about desulphurization is clear from the finding that benzoin acts as a very good sensitizer for the reaction.

$$PhCO\!-\!CHOHPh \xrightarrow{h\nu} Ph\dot{C}O + Ph\dot{C}HOH$$

$$Ph\dot{C}O \xrightarrow{{}^{3}O_{2}} PhC\!\!\underset{OO^{\bullet}}{\overset{O}{<}}$$

$$Ph\dot{C}HOH \xrightarrow{{}^{3}O_{2}} PhCHOH\!-\!OO^{\bullet}$$
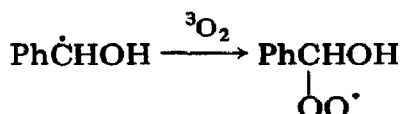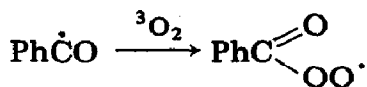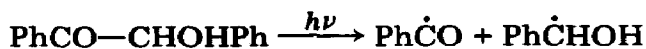
It is also likely that the alkylperoxy radical generated in this reaction oxidizes the thiophosphorus compound. The diketones may well be reacting via the 1,4-biradicals, *i.e.*

$$CH_{3}\!-\!\underset{OO}{\overset{O^{\bullet}}{C}}\!-\!\overset{O}{C}\!-\!CH_{3} \qquad CH_{3}\!-\!\underset{OO^{\bullet}}{\overset{O^{\bullet}}{C}}\!-\!CO_{2}R \qquad Ph\underset{OO^{\bullet}}{\overset{O^{\bullet}}{C}}\!-\!\overset{O}{C}\!-\!Ph$$

$$R \equiv H, Me, Bu^{t}$$

Little is known about such species. If they were to collapse to give a trioxetane the labelling studies employing ${}^{18}O_{2}$ should have led to an oxirane containing labelled and unlabelled oxygen. As this is not the case it appears that some 1,4-biradicals have a lifetime sufficiently long to enable them to undergo bimolecular reactions or else all the observable reactions are gener-

ated from their sibling acylperoxy radicals. These 1,4-biradicals may rearrange to give 1,3-biradicals and this is particularly favourable for acenaphthaquinone.
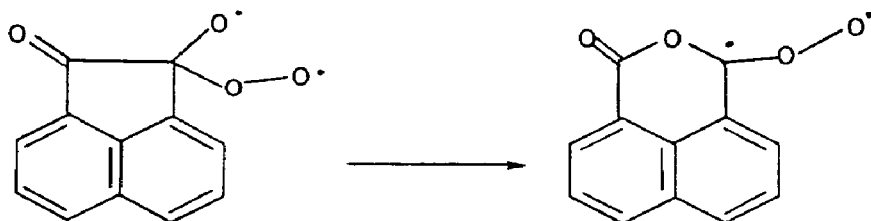
Such a radical should be a potent oxygen transfer agent and in undergoing such a reaction will produce the observed product, 1,8-naphthalic anhydride.

The fact that the presence of compounds 1 and 4 leads to a small but measurable increase in anhydride yield lends some support to the view that the 1,3-biradical and the 1,4-biradical lie along the reaction pathway. The inefficiency of phenanthraquinone as a sensitizer may be due to the fact that the biradical formed by reaction of its triplet with oxygen cannot rearrange to give a 1,3-biradical without forming a seven-membered ring. However, it is clear that none of the experiments answer the crucial question "is the oxidizing species a biradical or an acylperoxy radical?" The finding that certain 1,4-quinones can sensitize the reaction lends some support to the view that the triplet states of these compounds can interact with oxygen to give a biradical. However, since it was found that the quinones are photodecomposed during reaction one cannot neglect the possibility that some radical degradation products react with oxygen to give species which oxidize P=S bonds.

The photo-oxidative desulphurization of the phosphorus thiolate compounds 5 and 6 leads in most cases to cleavage of the thioalkyl group with formation of the corresponding phosphorus acid (Table 3). These reactions probably involve acylperoxy radicals or their precursors, oxidizing the sulphur atom to give a thiolate S-oxide. For example
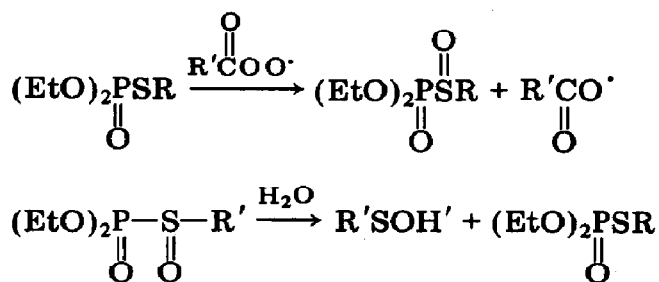

From the work of Segall and Casida [20] it is known that such compounds are powerful phosphorylating agents and the formation of the

phosphorus acids is believed to be due to the primary oxidation product reacting with adventitious traces of water.

3.2. Reactivity of the phosphorus compounds

From the data in Tables 1 and 2 it appears that the order of reactivity for the compounds 1 - 4 is

$$Ph_3P{=}S > Ph_2\underset{\underset{S}{\parallel}}{P}OEt > Ph\underset{\underset{S}{\parallel}}{P}(OEt)_2 > (EtO)_3P{=}S'$$
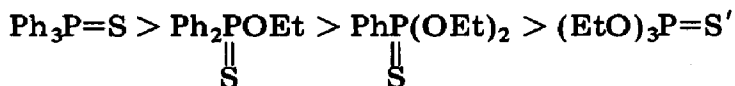
If species of the type $R_3\overset{\bullet}{P}SOR$ are intermediates in the reaction, then the order of reaction can be attributed to the ability of the substituent groups to stabilize the phosphoranyl radical.

4. Experimental details

Acetonitrile (Aldrich) was distilled under argon prior to use. All the sensitizers were recrystallized prior to use and shown to have melting points in accord with the literature values. The phosphorus compounds were prepared by standard literature methods and shown to possess spectral and physical properties in accord with literature data [21].

4.1. General procedure for photo-oxidative desulphurization of 1 - 6

A stock solution of the phosphorus compound containing the internal standard for gas–liquid chromatography (GLC) was prepared as detailed below. To 5 ml of this solution, a known amount of sensitizer was added. The solution was irradiated in a Pyrex tube by means of a circular array of black-light fluorescent tubes (16 × 8 W, Sylvania FT875/BLB). Throughout the irradiation the solution was flushed continuously with dry oxygen free of carbon dioxide. After irradiation (usually 10 h) the solutions of 1 - 6 were analysed by GLC to determine the amount of unreacted starting material and in the case of 1 - 4 the yield of product. The solutions of 5 and 6 were treated with excess diazomethane (in ether) and then analysed by GLC to determine the yield of diethyl phosphate (as the methyl ester). The solution of 6 was also analysed for the presence of pentanethiol but none could be found.

Stock solutions were prepared as follows: 1, triphenylphosphine sulphide (0.2 g) plus diphenylsulphone (0.1 g, internal standard for GLC) in acetonitrile (100 ml); 2, O-ethyl diphenylphosphinothioate (0.4 g) plus diphenylsulphone (0.2 g, internal standard for GLC) in acetonitrile (100 ml); 3, O,O-diethyl phenylphosphonothioate (0.4 g) plus di-t-butylsulphone (0.2 g, internal standard for GLC) in acetonitrile (100 ml); 4, O,O,O-triethyl phosphorothioate (0.4 g) plus dimethyl sulphone (0.2 g, internal standard for GLC) in acetonitrile (100 ml); 5, O,O-diethyl-S-methyl phosphorothioate (1.5 g) plus 1-bromodecane (1.0 g, internal standard for GLC) in acetonitrile

(100 ml); 6, *O,O*-diethyl-*S*-pentyl phosphorothioate (1.95 g) plus di-*t*-butyl-sulphone (1.0 g) in acetonitrile (100 ml).

4.2. *Gas—liquid chromatography analysis*

GLC analysis was carried out on a Perkin—Elmer Sigma 3 Gas Chromatograph (flame ionization detector) linked to a Pye—Unicam DP88 integrator. The linearity of the response was checked for the range of concentrations of substrates employed. Compounds 1 - 3 were analysed using a 20 in × 1/8 in 10% UCW 982 column and 4 - 6 were analysed on a 2 m 1.5% OV 225 on chromosorb column. Benzoin, benzil, acenaphthaquinone, *p*-chloranil, 2,3-dichloro-5,6-dicyanobenzoquinone and 1,8-naphthalic anhydride were determined using the 20 in 10% UCW 982 column and methyl pyruvate and *t*-butyl pyruvate was determined on a 2 m 15% B.B. oxydipropianitrile column. Pyruvic acid was determined as its methyl ester after esterification with diazomethane.

Acknowledgments

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