Tetrahedron Vol. 39, No. 7, pp 1069 to 1074, 1983
Printed in Great Britain.

0040 4020/83/071069 06$03.00/0
Pergamon Press Ltd.

THE MECHANISM OF THE DIRECT PHOTO-OXIDATIVE DECARBOXYLATION OF α-OXO-CARBOXYLIC ESTERS

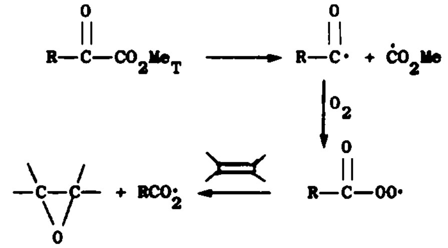
R. Stephen Davidson*, Dean Goodwin and Julie E. Pratt

Department of Chemistry, The City University, Northampton Square,
London, EC1V OHB.

(*Received in UK* 22 *November* 1982)

Abstract - A variety of α-oxo-carboxylic esters are shown to undergo direct photo-oxidation, in both polar and non-polar solvents, to produce a higher yield of carbon dioxide than under degassed conditions. In the case of n-hexyl pyruvate, hexaldehyde is also a product of the reaction. Evidence is presented which indicates that singlet oxygen plays little, if any, part in these decarboxylations. A mechanism involving electron transfer from the excited α-oxo-carboxylic ester to ground state oxygen, leading to per-acid intermediates, is proposed as being in competition with the Type II process for fragmentation of these esters.

The only report pertaining to the effect of oxygen upon the photo-reactions of α-oxo-carboxylic esters in solution concerns the epoxidation of α-methylstyrene by methyl phenylglyoxylate.[1] It was proposed that the ester underwent a Type I fragmentation to yield an acyl radical which was subsequently scavenged by oxygen to form an acyl-peroxy radical. The latter was the species thought to be responsible for the epoxidation reaction, via per-acid intermediates (Scheme 1). However, it has since been appreciated that alkyl pyruvates,[2] and other α-oxo-carboxylic esters,[3] fragment via a Type II and not a Type I process. Consequently, the mechanism of the interaction of oxygen and α-oxo-carboxylic esters leading to carbon dioxide production is of particular interest. We now report upon investigations to elucidate the role played by oxygen in the direct photo-oxidative decarboxylation of α-oxo-carboxylic esters.



SCHEME 1

RESULTS

A wide variety of α-oxo-carboxylic esters were found to undergo direct photo-oxidative decarboxylation in oxygenated acetonitrile and benzene solutions (Table 1). The yields of carbon dioxide production from the irradiation of methyl pyruvate in oxygenated acetonitrile and benzene solutions are shown in Figure 1. Surprisingly, t-butyl pyruvate, which has been shown to be photostable under degassed conditions,[2] was found to undergo efficient photo-oxidative decarboxylation (Table 1). The rates of carbon dioxide production for this ester in oxygenated acetonitrile and benzene solutions are shown in Figure 2. Table 2 shows the yields of carbon dioxide and hexaldehyde from the direct photo-oxidation of n-hexyl pyruvate in oxygenated acetonitrile solution. No appreciable solvent isotope effect was observed upon the yields of carbon dioxide from irradiation of oxygenated solutions of methyl and ethyl pyruvates (Table 3).

TABLE 1 Yields of carbon dioxide from the direct irradiation of α-oxo-carboxylic esters (10^{-2}M) under oxygen, (A) in acetonitrile and (B) in benzene solution for 3 hours.

α-Oxo-carboxylic ester	Yield (%) of carbon dioxide (A)	(B)
Methyl Pyruvate	37	34
Ethyl "	63	54
Isopropyl "	46	23
n-Butyl "	20	19
t-Butyl "	58	47
n-Hexyl "	35	33
Benzyl "	33	23
Ethyl benzoyl formate	16	18
2-(1-naphthyl)ethyl pyruvate	15	18.5
2-(2-naphthyl)ethyl pyruvate	21	11
2-(2-naphthyl)ethyl-α-oxo-octanoate	17	17

TABLE 2 Yields of carbon dioxide and hexaldehyde from the direct irradiation of n-hexyl pyruvate (5 x 10^{-2}M) in (A) oxygenated and (B) degassed acetonitrile solution for 3 hours.

Product	Yield (%) (A)	(B)
Carbon Dioxide	35	7
Hexaldehyde[a]	45	30

a - determined by g.l.c.

TABLE 3 Solvent isotope effects upon the yield of carbon dioxide from the direct irradiation, for 5 hrs, of α-oxo-carboxylic esters (10^{-2}M) in oxygenated solutions.

α-Oxo-carboxylic ester	Solvent	Yield (%) of carbon dioxide	Solvent Isotope Effect
Methyl pyruvate	Deuteriochloroform	52	1.48
" "	Chloroform	35	
Ethyl "	Deuterium oxide	15.4	0.94
" "	Water	16.3	

TABLE 4 Yield of carbon dioxide from the irradiation, for 6 hrs, of methyl pyruvate (10^{-2}M) in oxygenated acetonitrile solution containing 9,10-dicyanoanthracene (OD = 1.0 at 370 nm in order that all of the incident light is absorbed by the 9,10-dicyanoanthracene*)

Condition	Yield (%) of carbon dioxide
9,10-Dicyanoanthracene absent	50
9,10-Dicyanoanthracene present*	38

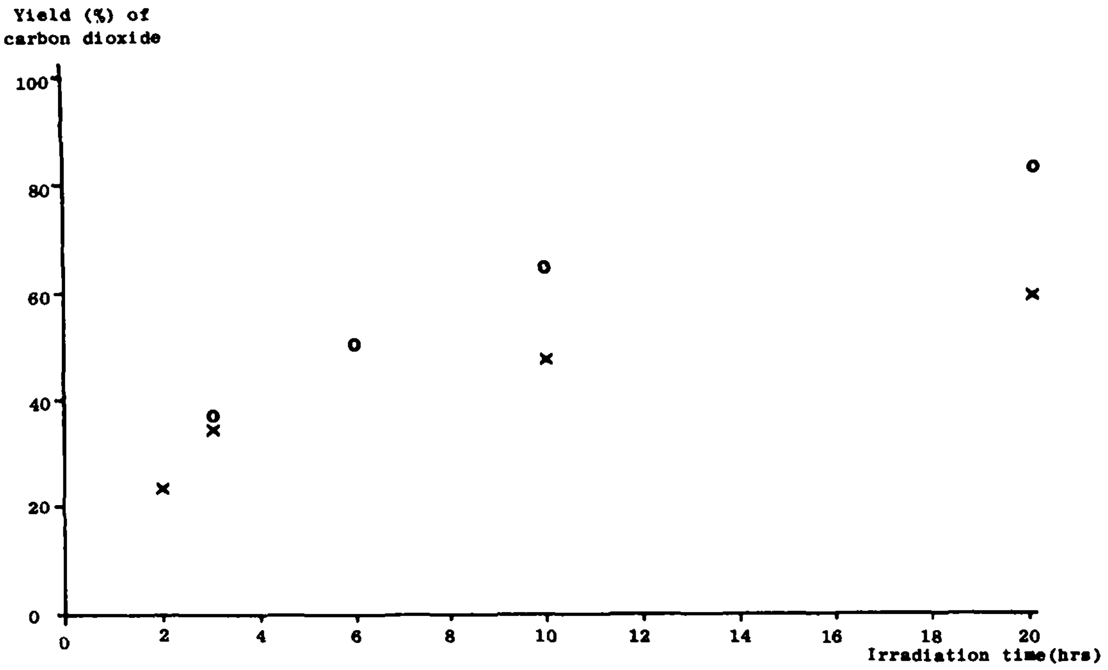


Figure 1. The yields of carbon dioxide from photolysis of methyl pyruvate (10^{-2} M) in oxygenated acetonitrile (O) and oxygenated benzene (×) solutions.

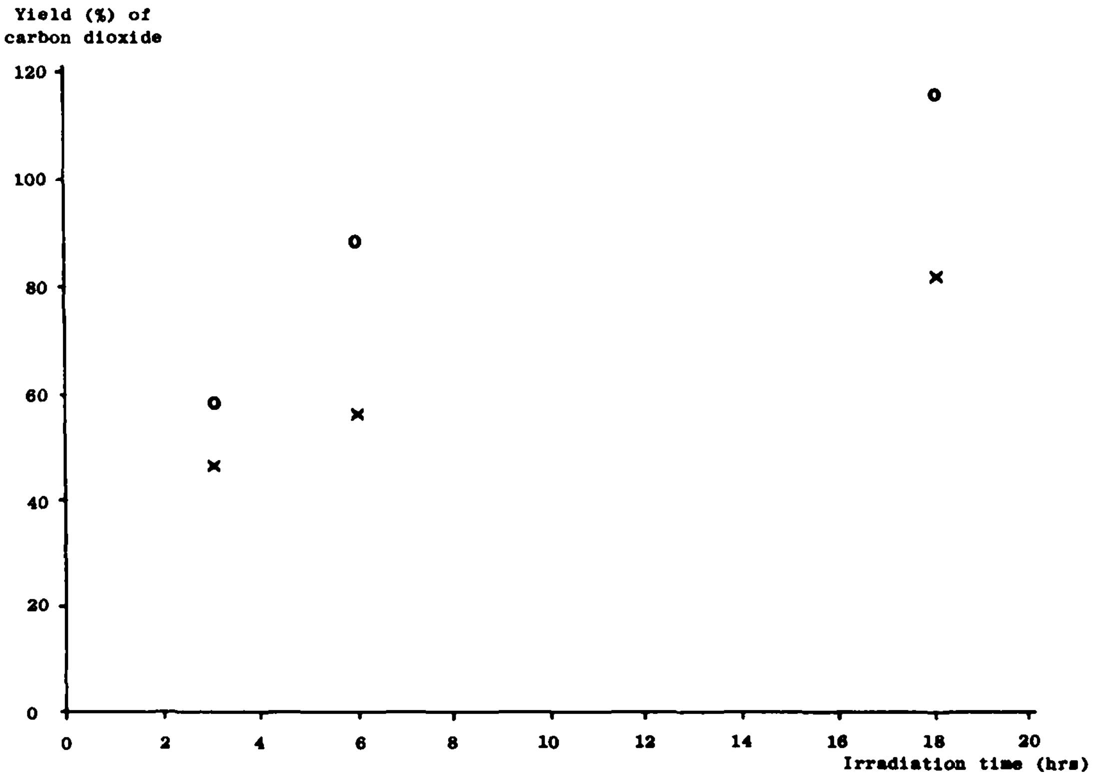


Figure 2. The yields of carbon dioxide from photolysis of t-butyl pyruvate (10^{-2} M) in oxygenated acetonitrile (O) and oxygenated benzene (×) solutions.

DISCUSSION

There are a variety of ways in which oxygen could interact with α-oxo-carboxylic esters. For those esters capable of undergoing a Type II fragmentation reaction, oxygen could intercept the intermediate 1,4-diradical[4], to yield a product which collapses to give carbon dioxide. However, the high yield of hexaldehyde, via a Type II fragmentation of n-hexyl pyruvate on irradiation in oxygenated acetonitrile solution (Table 2) would suggest that the 1,4-diradical is not intercepted by oxygen. This is consistent with the observation that oxygen does not intercept the 1,4-diradical formed by the Type II fragmentation of α-oxo-octanoic esters.[3] The yield of hexaldehyde from irradiation of n-hexyl pyruvate is higher in oxygenated than in degassed solution (Table 2). This indicates that the reduction reaction of triplet n-hexyl pyruvate by hexaldehyde[3] is being suppressed under oxygen. Presumably oxygen interacts with the triplet n-hexyl pyruvate thereby lowering the amount of triplet ester available to undergo reduction. Hence, a higher yield of hexaldehyde is observed under oxygenated than under degassed conditions. Since good yields of carbon dioxide were obtained from t-butyl pyruvate (which does not fragment via either a Type I or a Type II reaction and is photostable under degassed conditions[2,5]) decarboxylation may arise from a direct reaction between oxygen and the t-butyl pyruvate. A similar direct reaction between oxygen and the esters capable of fragmenting by a Type II process, would obviously compete with the Type II reaction for degradation of these esters.

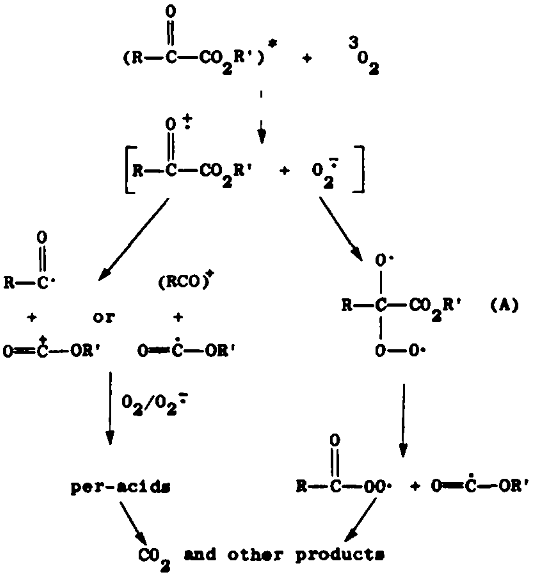
The possibility of a singlet oxygen mediated mechanism, the latter being produced from reaction of oxygen with the triplet excited ester, must obviously be considered. Any singlet oxygen produced may react with the α-oxo-carboxylic ester to yield carbon dioxide. If the singlet oxygen reaction involves a diffusional process a solvent isotope effect upon the yield of carbon dioxide would be observed.[6] The lack of a solvent isotope effect upon the decarboxylation of methyl and ethyl pyruvates (Table 3) indicates that singlet oxygen plays little, if any, part in these reactions.

Since alkyl pyruvates have been shown to reduce methyl viologen via an electron transfer reaction[5], it is conceivable that where the oxygen concentration is similar to that of the α-oxo-carboxylic ester, electron transfer from the excited ester molecule to oxygen may take place (Scheme 2).

$$(\text{ESTER})^{*} \; + \; {}^{3}O_2 \longrightarrow (\text{ESTER})^{+\cdot} \; + \; O_2^{-\cdot}$$

SCHEME 2

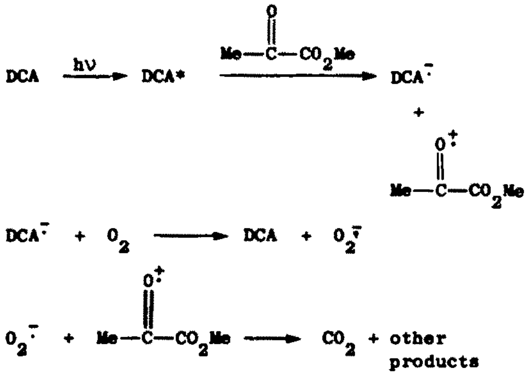
The resultant superoxide anion may then react with the ester radical cation to produce carbon dioxide. Alternatively, the radical cation of the ester may fragment to yield radicals which are subsequently scavenged by oxygen to form peroxy species, which can then undergo reactions leading to carbon dioxide formation (Scheme 3).



SCHEME 3

The formation of per-oxy species in the above mechanism would account for the previously reported epoxidation of alkenes during photo-oxidation of methyl phenylglyoxylate.[1] Species similar to (A) in the above scheme have been proposed as intermediates in the direct photo-oxidations of α-oxo-carboxylic acids,[7] non-conjugated aliphatic ketones[8] and as possible intermediates in the analogous reaction of p-benzoquinone.[9] The observation that prolonged irradiation of t-butyl pyruvate, in oxygenated acetonitrile solution, yielded more than 100% carbon dioxide indicates the involvement of per-oxy species. The production of more than 100% carbon dioxide from the photo-oxidation of pyruvic acid has been used as evidence for the participation of per-acids in the reaction.[10] The detection of per-benzoic acid from irradiation of methyl phenylglyoxylate,[1] in oxygenated benzene solution, further supports the involvement of per-acids in the photo-oxidation of α-oxo-carboxylic esters.

The ability of 9,10-dicyanoanthracene (DCA), a well known electron acceptor, to sensitise the photo-oxidative decarboxylation of methyl pyruvate, in acetonitrile, (Table 4) lends support to the proposed electron transfer reaction in Scheme 3. A possible mechanism for the above sensitised reaction is outlined in Scheme 4.



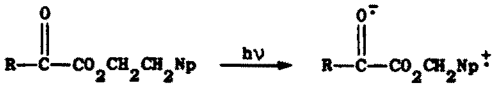
$$DCA \xrightarrow{h\nu} DCA^{*} \xrightarrow{Me-C(=O)-CO_2Me} DCA^{\overline{\cdot}} + Me-C(=O^{\cdot+})-CO_2Me$$

$$DCA^{\overline{\cdot}} + O_2 \longrightarrow DCA + O_2^{\overline{\cdot}}$$

$$O_2^{\overline{\cdot}} + Me-C(=O^{\cdot+})-CO_2Me \longrightarrow CO_2 + \text{other products}$$

SCHEME 4

It is of interest to note that 2-(2-naphthyl) ethyl pyruvate has been shown by laser flash photolysis to be capable of reducing methyl viologen.[11] However, in aqueous acetonitrile solution the addition of methyl viologen had no effect upon the fluorescence or the triplet lifetimes of this ester, so the reduction does not arise from the interaction of methyl viologen with an excited state of the ester.[11] There is however the possibility of the naphthyl-α-oxo-carboxylic esters undergoing an internal electron transfer reaction upon irradiation, to form a species containing both a carbonyl radical anion and a naphthalene radical cation group. (Scheme 5).



$$R-C(=O)-CO_2CH_2CH_2Np \xrightarrow{h\nu} R-C(-O^{\overline{\cdot}})-CO_2CH_2Np^{\dot{+}}$$

(R = Me or $Me(CH_2)_5$-, Np = 1- or 2-naphthyl)

SCHEME 5

The interaction of this species with methyl viologen will give reduced methyl viologen. Also its interaction with oxygen could lead to decarboxylation via the formation of the superoxide anion, in addition to the mechanism proposed in Scheme 3.

The carbon dioxide obtained upon irradiation of α-oxo-octanoic acid, in both oxygenated and degassed solution, is thought to arise from the pyruvic acid which is generated in the Type II fragmentation of α-oxo-octanoic acid.[10] Thus, for α-oxo-carboxylic esters capable of undergoing a Type II reaction, some decarboxylation may result from interaction between a product of the fragmentation process and oxygen.

t-Butyl pyruvate was the only ester to produce carbon dioxide in over 100% yield, the second mole of carbon dioxide may have arisen from the $O{=}\dot{C}{-}OR'$ species (Scheme 3). The latter could undergo direct decarboxylation or interact with oxygen to form an intermediate which subsequently collapses to yield the second mole of carbon dioxide. In contrast to the t-butyl pyruvate, which cannot undergo a Type II reaction, prolonged irradiation of methyl pyruvate, which is capable of fragmentation via the Type II process, did not produce high yields (i.e. > 1 mole) of carbon dioxide (Figure 1). Hence, the lower yields of carbon dioxide, obtained from irradiation of oxygenated acetonitrile solutions of methyl pyruvate, can be explained on the basis of competition between the Type II process and the mechanism outlined in Scheme 3, for the decomposition of this ester.

In conclusion, the direct photo-oxidative decarboxylation of α-oxo-carboxylic esters has been shown to produce higher yields of carbon dioxide than under degassed conditions.[5] An electron transfer reaction between the α-oxo-carboxylic ester and oxygen leading to per-acid intermediates has been proposed. This mechanism will be competition with the Type II process (which can itself lead to carbon dioxide formation as a result of subsequent reaction of the fragmentation products) for fragmentation of the ester.

EXPERIMENTAL

All melting points are uncorrected. ^1H NMR spectra were recorded at 100 MHz on a Joel JNM-MH-100 spectrometer, tetramethylsilane was used as internal standard. IR spectra were recorded on a Perkin Elmer 402 spectrophotometer. Mass spectra were recorded on a Kratos MS 30 spectrometer (connected to a DS-50-S data system) operating at 70 eV. GLC analyses were recorded on a Perkin Elmer Sigma 3 gas chromatograph, using a Perkin Elmer 10% SE 30, chromosorb W 60-80 mesh, column. Elemental analyses were carried out in the Chemistry Department at The City University, London.

9,10-Dicyanoanthracene (Eastman-Kodak), methyl pyruvate (Aldrich), ethyl pyruvate (Aldrich), deuteriochloroform (Goss) and deuterium oxide (Goss) together with the other solvents (Fisons AnalaR grade) were used as supplied. Isopropyl, n-butyl, t-butyl, n-hexyl, benzyl, 2-(1-naphthyl)ethyl and 2-(2-naphthyl)ethyl pyruvate esters were prepared by the reaction of the appropriate alcohol with pyruvoyl chloride[12] under the experimental conditions previously described.[13] Spectral and physical data confirmed the structure of the prepared esters, the details for the naphthyl ethyl esters are outlined below:

2-(1-naphthyl)ethyl pyruvate.

White crystals (petroleum ether (40-60°)/ethyl acetate) mp 50-52°C; IR (nujol) ν max 1745, 1730, 1295, 1258, 1135, 950, 800, 760cm^{-1}; NMR ($CDCl_3$) δ 8.84-8.6 (m, 2H), 8.6-8.28 (m, 2H), 8.28-7.8 (m, 4H), 5.1-4.87 (t, 2H), 3.92-3.7 (t, 2H), 2.64 (s, 3H); mass spectrum m/e 242 (M^+). Analysis calculated for $C_{15}H_{15}O_3$; C, 74.36; H, 5.82. Found: C, 73.79; H, 5.75.

2-(2-Naphthyl)ethyl pyruvate.

White crystals (petroleum ether (40-60°)/ethyl acetate) mp 82-83°C; IR (nujol) ν max 1735, 1270, 1150, 960, 827, 752 cm^{-1}; NMR ($CDCl_3$) δ 8.48-8.1 (m, 4H), 8.1-7.78 (m, 3H), 4.98-4.82 (t, 2H), 3.32-2.58 (t, 2H), 2.61 (s, 3H); mass spectrum m/e 242 (M^+). Analysis calculated for $C_{15}H_{15}O_3$: C, 74.36; H, 5.82. Found: C, 74.54; H, 5.78.

Ethyl benzoyl formate was prepared by an analogous reaction using benzoyl formyl chloride and ethanol, the structure was confirmed from spectral and physical data.

2-(2-Naphthyl)ethyl α-oxo-octanoate was prepared from α-oxo-octanoyl chloride and 2-(2-naphthyl)ethanol as a waxy solid.

IR (nujol) ν max 1724, 1270, 1124, 1078, 948, 862, 790 cm^{-1}; NMR ($CDCL_3$) δ 8.0-7.68 (m, 4H), 7.68-7.3 (m, 3H), 4.75-4.5 (t, 2H), 3.44-3.14 (t, 2H), 1.56-1.12 (m, 8H), 1.04-0.78 (m, 4H); mass spectrum m/e 312 (M^+). Analysis calculated for $C_{20}H_{24}O_3$: C, 76.92; H, 7.69. Found: C, 76.16; H, 7.80.

Photolysis tubes containing the ester solutions (25 mls) were flushed with a stream of dry, carbon dioxide free, argon or oxygen (as appropriate) for 45 mins, stoppered and rotated within a circular array of fluorescent lamps, having a maximum emission at 350 nm (16 x 8 W Sylvania F8T5/BLB). Following irradiation the solutions were flushed for 2 hrs with argon or oxygen, the exit gas being passed through a saturated solution of aqueous barium hydroxide. The precipitated barium carbonate was weighed and the percentage yield of carbon dioxide calculated on the basis of one mole of carbon dioxide being generated per mole of α-oxo-carboxylic ester.

We gratefully acknowledge financial support (maintenance and equipment grants) from the SERC and The City University. We also wish to thank Mr P Hemming for the elemental analyses and Mr C Whitehead for the mass spectral data.

REFERENCES

1. Y. Sawaki and Y. Ogata, J. Amer. Chem. Soc., <u>103</u>, 6455, (1981).
2. R.S. Davidson and D. Goodwin, J.C.S. Perkin Trans. II, 993, (1982).
3. R.S. Davidson, D. Goodwin and Ph. Fornier de Violet, Tetrahedron Letters, <u>26</u>, 2485, (1981).
4. J.C. Scaiano, E.A. Lissi and M.V. Encinas, Reviews of Chemical Intermediates, <u>2</u>, 139, (1978).
5. R.S. Davidson, D. Goodwin and J.E. Pratt, manuscript in preparation.
6. An isotope effect in the range of 8.9-10.6 would be expected for the deuteriochloroform/chloroform system and one in the range of 10-13 for the deuterium oxide/water system. [C.S. Foote and P.R. Ogilby, J. Amer. Chem. Soc., <u>103</u>, 1219, (1981); C.S. Foote and P.R. Ogilby, J. Amer. Chem. Soc., in the press, (1983)].
7. R.S. Davidson, D. Goodwin and J.E. Pratt, Unpublished results.
8. G. Quinkert, Pure and Applied Chemistry, <u>9</u>, 607, (1964).
9. R.M. Wilson, S.W. Wunderly, T.F. Walsh, A. K. Musser, R. Outcalt, F. Geiser, S.K. Gee, W. Brabender, L. Yerino, Jnr., T.T. Conrad and G.A. Tharp, J. Amer. Chem. Soc., <u>104</u>, 4429, (1982).
10. R.S. Davidson, D. Goodwin and G. Turnock, Tetrahedron Letters, <u>21</u>, 4943, (1980).
11. R.S. Davidson, D. Goodwin and Ph. Fornier de Violet, Unpublished results.
12. H.C.J. Ottenheijm and J.H.M. de Man, Synthesis, 163, (1975).
13. R.W. Binkley, J. Org. Chem. <u>41</u>, 3030, (1976).