Triphenylphosphine Deoxygenation of Malonyl Peroxides, A Novel Route to Malonyl Anhydrides

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Summary Treatment of di-n-butylmalonyl peroxide (**1**; R = Bu^n) with triphenylphosphine produced quantitatively triphenylphosphine oxide, 40—45% di-n-butylmalonyl anhydride (**2**; R = Bu^n), 55—60% carbon dioxide, and 45—50% di-n-butylketen (**3**; R = Bu^n) (trapped with methanol as its methyl ester).

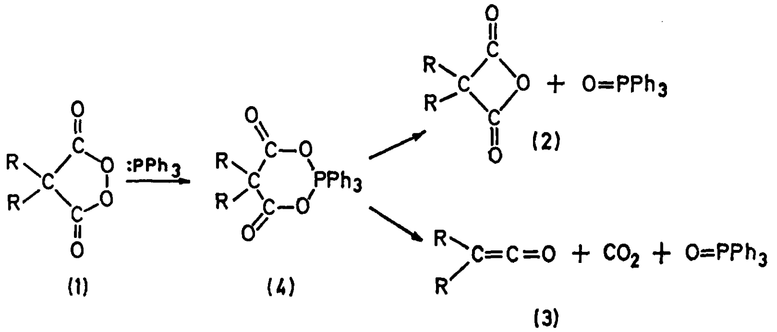
Previously we have shown that in the reaction of di-isopropyl peroxydicarbonate and triphenylphosphine the fragmentation into carbon dioxide and di-isopropyl carbonate competes with simple deoxygenation into di-isopropyl pyrocarbonate.[1] However, in the triphenylphosphine deoxygenation of β-peroxylactones only small amounts of β-lactones were formed, since fragmentation into olefin and carbon dioxide or into ketone and keten predominated.[2] Thus, it was of interest to examine the reaction of malonyl peroxides (**1**) with triphenylphosphine, since simple deoxygenation might provide a convenient method for preparing malonyl anhydrides (**2**), while fragmentative deoxygenation would afford ketens (**3**) and carbon dioxide (see Scheme).

When a cyclohexane solution of (**1**;R = Bu^n), prepared by cyclization of the malonic acid with 98% H_2O_2 (CAUTION),[3] was treated with equimolar amounts of triphenylphosphine at room temperature, precipitation of triphenylphosphine oxide occurred with evolution of carbon dioxide. It was shown that 95—100% (by weight) triphenylphosphine oxide was formed. The carbon dioxide was collected in a gas burette, identified by mass spectroscopy, and shown to be formed in 55—60% by volume.

I.r. analysis of the supernatant solution from the reaction indicated strong bands at 2100 cm^{-1} (keten) and at 1815 and 1760 cm^{-1} (anhydride). Treatment of this solution with methanol, caused the keten band at 2100 cm^{-1} to change completely to the methyl 2-n-butylhexanoate band at 1735 cm^{-1}. This was identified by comparison of i.r. spectra and t.l.c. retention times with those of an authentic sample, prepared by decarboxylation of the malonic acid and esterification with diazomethane. Quantitative g.c. analysis of the methyl 2-n-butylhexanoate showed that 45—50% di-n-butylketen (**3**; R = Bu^n) was formed in the deoxygenation of (**1**; R = Bu^n).

The di-n-butylmalonyl anhydride (**2**; R = Bu^n) was identified by comparison of i.r. spectra and t.l.c. retention times with those of an authentic sample, prepared *via* cyclization of di-n-butylmalonic acid with benzenesulphonyl chloride in pyridine.[4] Quantitative i.r. analysis established that 40—45% of di-n-butylmalonyl anhydride (**2**; R = Bu^n) was formed in the deoxygenation of (**1**: R = Bu^n).

Control experiments showed that the anhydride (**2**; R = Bu^n) is stable towards triphenylphosphine under the reaction conditions, while thermal decarboxylation into keten (**3**; R = Bu^n) can only be effected at elevated temperatures (>100 °C). Unfortunately, the rate of the reaction is too great for the kinetics of the deoxygenation to be measured; however, by analogy with previous studies in our laboratory,[1,2] we suggest that phosphorus insertion gives the cyclic phosphorane (**4**), a precursor of the observed products (see Scheme). Although fragmentation into anhydride (**2**) and keten (**3**) was expected, the formation of the strained heterocycle is remarkable.



SCHEME

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[1] W. Adam and A. Rios, *J. Org. Chem.*, 1971, **36**, 407.

[2] W. Adam, J. R. Ramirez, and S. C. Tsai, *J. Amer. Chem. Soc.*, 1969, **91**, 1254.

[3] W. Adam and R. Rucktäschel, *J. Amer. Chem. Soc.*, 1971, **93**, 557.

[4] Anhydride (**2**; R = Bu^n) has been prepared by C. Duckworth (*J. Org. Chem.*, 1962, **27**, 3146) as a partially crystalline semi-solid. Recrystallization from methanol afforded analytically pure, colourless prisms, m.p. 120—120·5° (R. Rucktäschel, unpublished results from this laboratory).