

Free Radical Catalysed Additions to the Double Bond of Diketene: A Synthesis of Novel Oxetan-2-ones

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Free radical-catalysed additions to the exocyclic double bond of diketene are described. Thiols give unstable 4-thiomethyloxetan-2-one adducts which could be oxidised to their more stable sulfoxides or sulphones. Addition of a range of P-H compounds led, with a few exceptions, to stable phosphorus-substituted 4-methyloxetan-2-ones. The radical-catalysed chlorination of diketene by sulphuryl chloride has been shown to give 4-chloro-4-chloromethyloxetan-2-one. Further 4-halogeno-oxetan-2-ones were prepared by addition of halocarbons such as carbon tetrachloride, bromotrichloromethane, and carbon tetrabromide and of trichloromethanesulphenyl chloride to diketene.

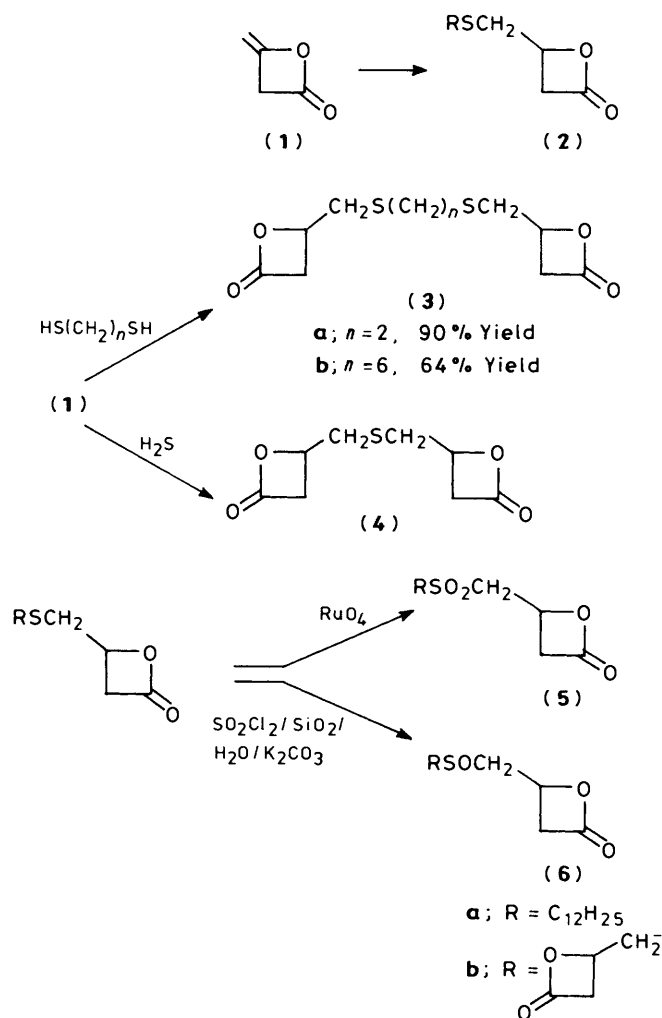
Diketene (4-methyleneoxetan-2-one) (1) is an important industrial chemical intermediate from which a large number of commercial products are manufactured. For example, acetoacetic ester and amides prepared from diketene are intermediates for important insecticides and various pigment classes. The literature of diketene is extensive and a number of reviews have been published on its chemistry.¹⁻³ Diketene has a highly reactive β -lactone ring and until recently nucleophilic ring-opening reactions have dominated its chemistry. More recently, however, attention has focused on addition reactions to the *exo*-methylene double bond of diketene⁴ and electrophilic additions,⁵ carbene additions,^{6,7} and 2 + 2 photocyclo-additions⁸ have been reported. By contrast, free radical-catalysed additions to the exocyclic double bond of diketene have remained virtually unexplored. Although resistant to radical-catalysed homopolymerisation,⁹ diketene can be readily copolymerised with, for example, maleic anhydride¹⁰ with azoisobutyronitrile as the catalyst. The addition of sulphides to diketene catalysed by azoisobutyronitrile (AIBN) was described in an early Du Pont patent⁹ and specifically exemplified with ethanedithiol. Hull *et al.*¹¹ investigated the addition of hexadecane- and octadecane-thiols to diketene and discussed the reactivity and stability of the β -lactone products (2; R = C₁₆H₃₃, C₁₈H₃₇). A report of the isolation of β -lactones (2; R = alkyl) from the reaction of diketene with thiols under acid conditions¹² was later shown to be incorrect.¹³ In this paper we report the results of our studies on the additions of sulphur, phosphorus, halocarbon, and chlorine radicals to diketene.

Results and Discussion

Addition of Mercapto Compounds.—A range of mercapto compounds add under free radical catalysis to diketene (1) to give 4-thiomethyloxetan-2-ones (2). The reactions are conveniently monitored by observing the appearance of the β -lactone carbonyl absorption at 1820 cm⁻¹.

With primary alkanethiols the reaction proceeded readily at room temperature with AIBN initiation in non-polar solvents such as cyclohexane or light petroleum, and in some cases proceeded spontaneously without addition of catalyst.¹³ With secondary or tertiary alkanethiols and thiophenols the reaction proceeded less readily but could be initiated by AIBN under u.v. irradiation at low temperature. The results are summarised in Table 1. The addition of dithiols also proceeded readily to give the bis-adducts (3) in good yield. The hydrogen sulphide adduct (4) was prepared in 69% yield by bubbling H₂S through a solution of diketene in light petroleum containing a catalytic amount of AIBN and with u.v. irradiation at 10 °C.

The 4-thiomethyloxetan-2-ones as a class are thermally unstable. Crystalline products decompose slowly on storage at



Scheme 1.

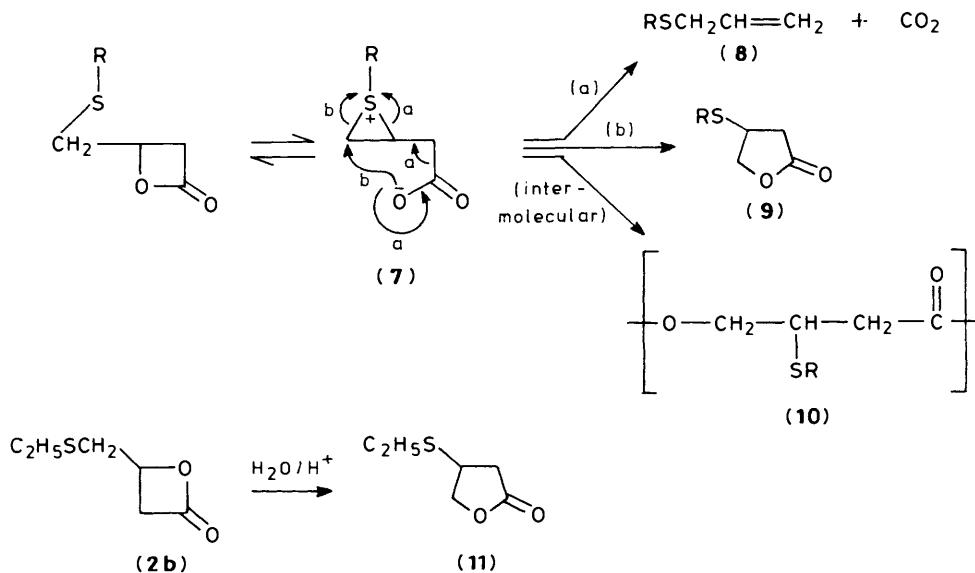
room temperature but can be stored for longer periods at 0 °C and below. The majority of the lactones (2) are, however, oils and can only be stored for shorter periods in a refrigerator, so that it is preferable to prepare the adducts as required and use immediately for further reaction. The instability of the oily adducts made characterisation other than by i.r. and n.m.r. spectroscopy difficult, but this could be overcome by oxidising them to the sulphones (5) (NaIO₄-RuO₂) which were stable, recrystallisable, well characterised solids (Table 2). The

Table 1. 4-Thiomethoxyoxetan-2-ones †

Compd.	R	Reaction * conditions	Yield (%)	M.p. (°C) decomp.	Found (%)			Mol. formula	Required (%)		
					C	H	S		C	H	S
(2a)	Me	A, ^a R.t., 2 h	100	Not isolated							
(2b) ‡	Et	B, -15 °C, 2 h	94	Oil							
(2c)	Bu	B, ^{a,b} 0 °C, 0.5 h	100	Oil							
(2d) ‡	Me(CH ₂) ₅	A, ^b <25 °C, 1 h	95	Oil	59.15	9.0	15.8	C ₁₀ H ₁₈ O ₂ S	59.37	8.97	15.85
(2e) ‡	Me(CH ₂) ₇	A, ^b <25 °C, 1 h	100	Oil							
(2f) ‡	Me(CH ₂) ₁₁	A, ^{b,c} <25 °C, 2 h	60	43—44	67.95	10.8	11.25	C ₁₆ H ₃₀ O ₂ S	67.10	10.56	11.17
(2g)	MeO ₂ CCH ₂	A, ^{b,c} <25 °C, 2 h	87	Oil	44.3	5.3	16.5	C ₇ H ₁₀ O ₄ S	44.26	5.40	16.73
(2h)	HOCH ₂ CH ₂	B, ^a -15 °C, 0.5 h	79	Oil							
(2i) ‡	Pr ⁱ	A, ^d 0 °C, 4 h	91	Oil							
(2j) ‡	c-C ₆ H ₁₁	A, B, R.t., 7.5 h	95	Oil	60.1	8.2	15.7	C ₁₀ H ₁₆ O ₂ S	59.96	8.05	16.00
(2k)	Bu ⁱ	A, -15 °C, 3 h	68	Oil	54.4	8.15	18.4	C ₈ H ₁₄ O ₂ S	55.14	8.10	18.40
(2l) ‡	Ph	C, 5 °C, 5 h	61	Oil	61.7	5.3	15.6	C ₁₀ H ₁₀ O ₂ S	61.83	5.19	16.50
(2m)	4-ClC ₆ H ₄	C, ^{e,f} R.t., 20 h	50	Oil							
(2n) ‡	2,5-Cl ₂ C ₆ H ₃	C, ^{e,g} 10 °C, 11 h	68	71—72 ^k	45.45	2.95	11.9	C ₁₀ H ₈ Cl ₂ O ₂ S	45.64	3.06	12.18
(2p)	Ac	C, -15 °C, 4 h	75	Oil	44.75	5.2	20.2	C ₆ H ₈ O ₃ S	44.99	5.03	20.01
(2q)	(EtO) ₂ PS	C, ^e -15 °C, 5 h	76	Oil	35.9	5.8	24.9	C ₈ H ₁₅ O ₄ PS ₂	35.55	5.59	23.72
(3a)	CH ₂ CH ₂	A, ^b <30 °C, 1 h	90	115—117 ^h	45.7	5.2	24.7	C ₁₀ H ₁₄ O ₄ S ₂	45.78	5.38	24.44
(3b)	CH ₂ (CH ₂) ₄ CH ₂	A, ^b <30 °C, 2 h	64	Dec. indef. ^j	52.75	7.1	20.3	C ₁₄ H ₂₂ O ₄ S ₂	52.80	6.96	20.14

* See Experimental section. † All thiomethoxyoxetan-2-ones showed characteristic absorption in the i.r. region at 1 820 cm⁻¹. ‡ Characterised as sulphone.

^a Diethyl ether used as solvent. ^b Spontaneous exothermic reaction. ^c Cyclohexane used as solvent. ^d Additional AIBN added after 2 h. ^e Excess of thiol washed out by aqueous sodium carbonate. ^f Dibenzoyl peroxide used instead of AIBN. ^g Unchanged diketene recovered. ^h Recryst. ex. acetone (lit.,⁹ m.p. 119—120 °C). ^j Recryst. ex. acetone-light petroleum. ^k Recryst. ex. CCl₄-light petroleum.



sulphoxides (6) were prepared by oxidation with SO₂Cl₂-SiO₂-H₂O.¹⁴

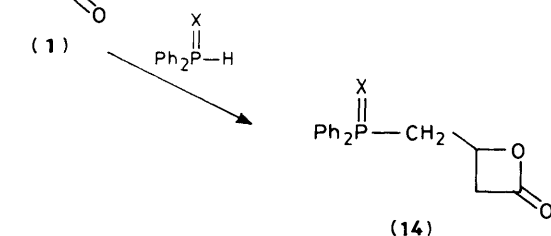
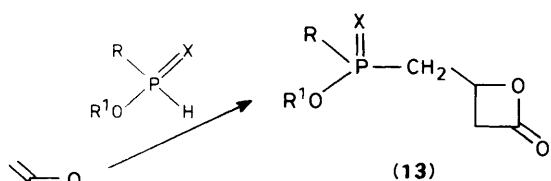
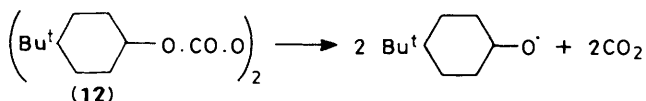
The thermal degradation products of the lactones (2; R = C₁₆H₃₃, C₁₈H₃₇) were examined by Hull, Daniher, and Conway¹¹ and found to be the allyl sulphides (8), the isomeric γ-lactones (9) along with the poly(γ-hydroxy acid) (10), all of which could be rationalised *via* the episulphonium zwitterion (7). The thermal stability of the oxidised products (5) and (6) helps to confirm the intermediacy of an episulphonium ion. We have re-examined the thermolysis of (2b) with a view to maximising the yield of the γ-lactone (11) and found that for

preparative purposes slow addition of (2b) to dilute aqueous hydrochloric acid at 20 °C gives the lactone (11) in a distilled yield of 45%.

Addition of P-H Compounds.—In the addition of sulphur radicals to diketene just described, the limiting factor for the reaction conditions was the poor thermal stability of the products. Free radical-catalysed additions of phosphorus compounds usually require more forcing conditions¹⁵ and for the additions to diketene it was important to find conditions where the decomposition and polymerisation of diketene were

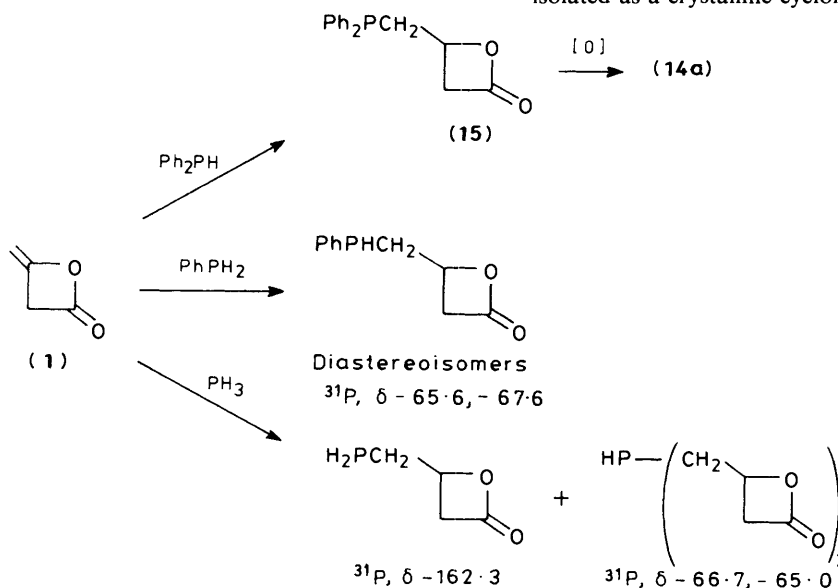
Table 2. Sulphones (5) by oxidation of sulphides (2) with $\text{NaIO}_4\text{-RuO}_2$

Compound	R	Yield (%)	M.p. (°C)	Found (%)			Mol. formula	Required (%)		
				C	H	S		C	H	S
(5a)	Et	42	83—84	40.6	5.8	17.35	$\text{C}_6\text{H}_{10}\text{O}_4\text{S}$	40.44	5.66	17.99
(5b)	$\text{Me}(\text{CH}_2)_5$	13	117—118	51.7	7.9	13.7	$\text{C}_{10}\text{H}_{18}\text{O}_4\text{S}$	51.26	7.74	13.68
(5c)	$\text{Me}(\text{CH}_2)_7$	50	133—134	55.3	8.75	12.5	$\text{C}_{12}\text{H}_{22}\text{O}_4\text{S}$	54.93	8.45	12.22
(5d)	$\text{Me}(\text{CH}_2)_{11}$	60	137—139	60.35	9.5	10.05	$\text{C}_{16}\text{H}_{30}\text{O}_4\text{S}$	60.43	9.41	9.93
(5e)	Pr^i	13	61—62	43.95	6.35	16.5	$\text{C}_7\text{H}_{12}\text{O}_4\text{S}$	43.74	6.29	16.68
(5f)	$n\text{-C}_6\text{H}_{11}$	9	89—90	51.85	7.0	13.7	$\text{C}_{10}\text{H}_{16}\text{O}_4\text{S}$	51.70	6.94	13.80
(5g)	Ph	60	100—102	53.45	4.65	13.15	$\text{C}_{10}\text{H}_{10}\text{O}_4\text{S}$	53.09	4.46	14.17
(5h)	$2,4\text{-Cl}_2\text{C}_6\text{H}_4$		139—140	40.4	2.75	10.5	$\text{C}_{10}\text{H}_8\text{Cl}_2\text{O}_4\text{S}$	40.70	2.73	10.86
(5i)	$\text{OC}(\text{O})\text{CH}_2\text{CHCH}_2$	27	242—248	41.3	4.4	13.35	$\text{C}_8\text{H}_{10}\text{O}_6\text{S}$	41.02	4.30	13.70



a; X = O, Yield 9%
b; X = S, Yield 72%

Scheme 3.



Scheme 4.

minimised. This was achieved by using freshly distilled diketene, acid-free phosphorus reagents, and particularly by the use of bis(t-butylcyclohexyl) peroxydicarbonate (BCHPC) (12) as radical initiator. This commercially available, crystalline peroxydicarbonate has a half-life of 1 h at 57 °C and 1 min at 90 °C and so allows radical additions to be carried out conveniently at temperatures below 100 °C.

In a typical experiment a mixture of diketene (1 mol) and BCHPC (1—2 mol %) was added dropwise over a period of 1 h to dimethyl phosphonate (4 mol) at 80—90 °C and heated at that temperature for a further 1 h. Distillation of the excess phosphonate followed by molecular distillation gave the β -lactones (13) usually in very good yield. The progress of the reaction and the purity of the product could readily be seen from the i.r. spectrum (1830 cm^{-1} carbonyl). Results of the reactions with phosphonates, phosphinates, thiophosphonates, and thiophosphinates are summarised in Table 3.

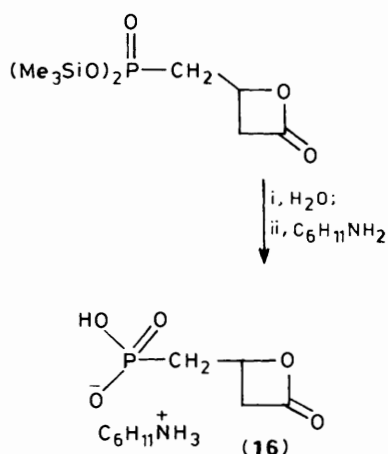
For the reactions with diphenylphosphine oxide and the corresponding sulphide, thermal initiation was not suitable. However initiation by u.v. irradiation using peroxide or AIBN at room temperature gave the lactones (14). Reactions with diphenylphosphine, phenylphosphine, and phosphine gave β -lactones which could not be isolated but were identified by a combination of i.r. and ^{31}P n.m.r., and in the case of (15) by oxidation to the stable phosphine oxide (14a).

Hydrolysis of the bistrimethylsilyl phosphonate (13f) with water (2 equiv.) in diethyl ether gave the free acid which was isolated as a crystalline cyclohexylamine salt (16).

Table 3. Phosphorus substituted 4-methyloxetan-2-ones (13)

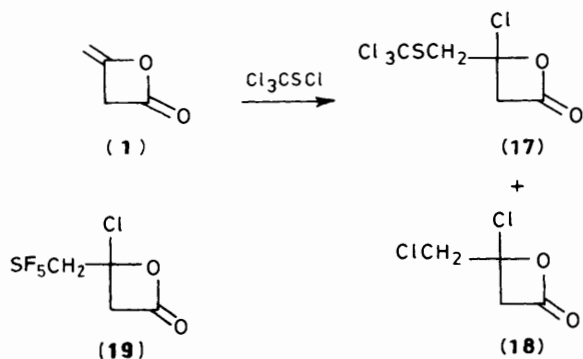
Compd.	X	R	R ¹	Catalyst	Reaction temp. (°C)	Yield (%)	Distill'n ^d temp. (°C)/ pressure (Torr)	Found (%)			Mol. formula	Required (%)			ν _{max} (film)/ cm ⁻¹ (C=O)	δ _p (CHCl ₃) ⁱ
								C	H	P		C	H	P		
(13a)	0	MeO	Me	a	80	95	140/0.2 (m.p. 47—45 °C ex. EtOAc)	37.35	6.0	15.9	C ₆ H ₁₁ O ₅ P	37.12	5.71	15.95	1830 ^b	26.4
(13b)	0	EtO	Et	a	80	96	140/0.5	42.75	7.1	14.4	C ₈ H ₁₅ O ₅ P	42.25	6.80	13.94	1830	23.76
(13c)	0	Bu	Bu	a	80	78	170/0.2	51.9	8.15	11.15	C ₁₂ H ₂₃ O ₅ P	51.80	8.33	11.13	1835	23.78
(13d)	0	Me(CH ₂) ₇ O	Me(CH ₂) ₇	a	80	55	170/0.2	62.0	10.15	7.55	C ₂₀ H ₃₉ O ₅ P	61.52	10.07	7.93	1830	23.64
(13e)	0	Pr ^o	Pr ⁱ	a	80	25	154/1.0	48.0	8.15	12.7	C ₁₀ H ₁₉ O ₅ P	48.00	7.65	12.38	1830	
(13f)	0	c-C ₆ H ₁₁ O	c-C ₆ H ₁₁	c	120	54	160/0.01	58.3	8.35	9.45	C ₁₆ H ₂₇ O ₅ P	58.17	8.24	9.37	1830	21.33
(13g)	0	Me(CH ₂) ₁₁ O	Me(CH ₂) ₁₁	c	120	65	Recryst hexane m.p. 51—52.5 °C	66.8	11.2	6.0	C ₂₈ H ₅₅ O ₅ P	67.03	10.85	6.17	1835 ^b	23.6
(13h)	0	Me(CH ₂) ₁₁ O	Me	a	80	49 ^e	150/0.01	59.2	7.8	8.85	C ₁₇ H ₃₃ O ₅ P	58.60	9.55	8.89	1830	23.0 ^g
(13i)	0	Me ₃ SiO	Me ₃ Si	b	90	84	f	49.35	8.0	14.35	C ₉ H ₁₇ O ₄ P	49.09	7.78	14.06	1835	48.6,
(13j)	0	Me	Bu ⁱ	a	80	81 ^e	115/0.01	51.75	8.45	13.45	C ₁₀ H ₁₉ O ₄ P	51.28	8.18	13.22	1820	48.9
(13k)	0	Et	Bu	a	85	87 ^e	75/0.01	56.15	6.25	12.05	C ₁₂ H ₁₅ O ₄ P	56.69	5.95	12.18	1830	52.4,
(13l)	0	Ph	Et	c	120	59 ^e	110/0.01	34.15	5.25	14.4	C ₆ H ₁₁ O ₄ PS	34.29	5.28	14.73	1830	52.7
(13m)	S	MeO	Me	a	95	29	80/0.05	41.6	6.2	12.85	C ₈ H ₁₅ O ₄ PS	40.33	6.35	13.00	1830	37.5,
(13n)	S	EtO	Et	c	120	45	60/0.01	56.2	6.4	11.35	C ₁₄ H ₁₉ O ₃ PS	56.36	6.42	10.38	1820	37.7
(13p)	S	Ph	Bu	a	85	60 ^e	115/0.01									83.2,

^a Bis(4-*t*-butylcyclohexyl) perdicarbonate. ^b *t*-Butyl perbenzoate. ^c Benzoyl peroxide. ^d Leybold-Heraeus KDS-1 wiped wall molecular still. ^e Mixture of diastereoisomers. ^f Characterised as cyclohexylamine salts of the hydrolysis product. ^g Diastereoisomers not resolved. ^h Nujol mull. ⁱ H₃PO₄ As standard.



Scheme 5.

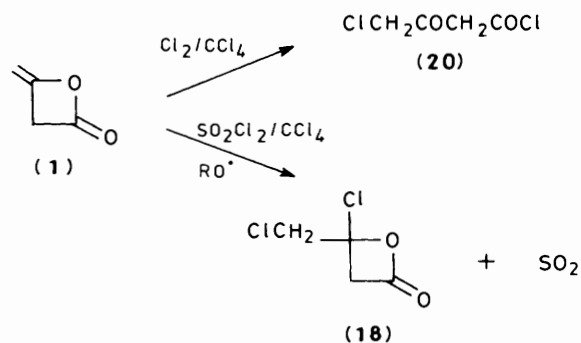
Addition of Trichloromethanesulphenyl Chloride.—U.v. irradiation of a light petroleum solution of diketene and trichloromethanesulphenyl chloride in the presence of AIBN gave a 50% yield of the 4-chloro-oxetan-2-one (17) along with small amounts of a by-product, identified as the radical chlorination product (18). Both products had a distinctive i.r. carbonyl stretch in the range 1 860—1 870 cm^{-1} . Kleeman and Seppelt¹⁶ recently reported the addition of sulphur chloride pentafluoride to diketene to give the lactone (19) with a carbonyl stretch at 1 875 cm^{-1} in almost quantitative yield.



Scheme 6.

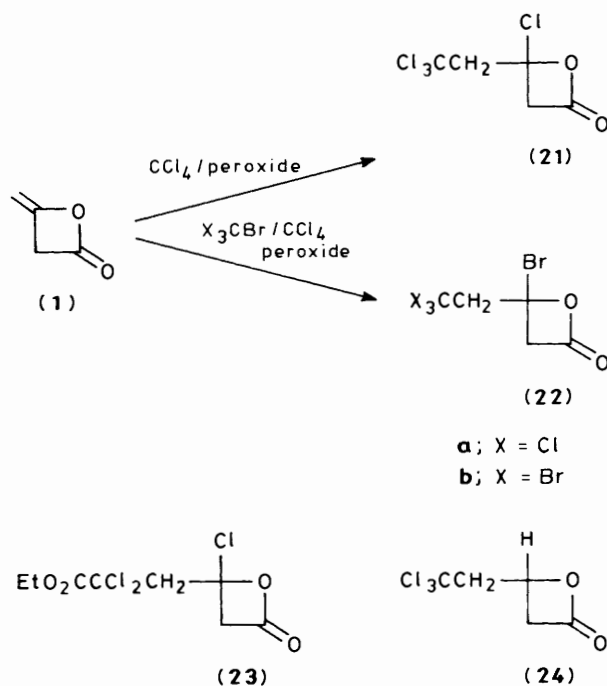
Radical Chlorination.—The ionic chlorination of diketene to give chloroacetylacetyl chloride (20) is a well known reaction which is used on an industrial scale¹⁷ for the preparation of chloroacetylacetates. We have now found that the free radical-catalysed addition of chlorine across the double bond of diketene can readily be achieved using sulphuryl chloride as chlorinating agent and peroxide catalysis to give 4-chloro-4-chloromethyloxetan-2-one (18) in 70—80% yield; the latter was stable and could be purified by vacuum distillation.

Structure (18) was considered by Hurd and Abernethy¹⁸ for the reaction product of diketene with chlorine, but then rejected. We have shown that the lactone (18) is *not* an intermediate in the formation of chloroacetylacetyl chloride from diketene and chlorine since (a) close examination of the chlorination reaction product with i.r. spectroscopy shows no sign of the characteristic β -lactone carbonyl and (b) (18) is stable in CCl_4 at -20°C when treated with chlorine (conditions for the chlorination of diketene). The lactone (18) is a stable, distillable, storable synthetic equivalent of chloroacetylacetyl chloride with interesting biocidal properties.¹⁹



Scheme 7.

Addition of Halocarbons.—BCHCP proved to be an excellent catalyst for the addition of carbon tetrachloride to diketene, allowing the reaction to be carried out at the reflux temperature of the former. The product (21) has limited thermal stability and attempted purification by vacuum distillation of larger quantities led to vigorous decomposition. However (21)



Scheme 8.

could be readily separated from telomeric side products by extraction into light petroleum, or better, by molecular distillation on a wiped wall molecular still. The product has a characteristic i.r. $\text{C}=\text{O}$ absorption at 1 860 cm^{-1} .

In the course of our work we required large amounts of (21), and although we were able to carry out a batch process on a scale large enough to give 2 kg of (21), the potential hazards in heating large quantities of (21) and diketene, led us to look for an alternative. We have developed a cascade reactor for the continuous preparation of (21) (see Figure). A dilute carbon tetrachloride solution of diketene (4.7 mol %) and BCHCP (0.17 mol %) was pumped through a two-stage cascade reactor, each reactor vessel being maintained at reflux. The product solution was collected in a reservoir, evaporated at room temperature in a cyclone evaporator, and further purified by molecular distillation. In a reactor with two 500 ml reactor flasks up to 1 kg of (21) could be prepared in a day.

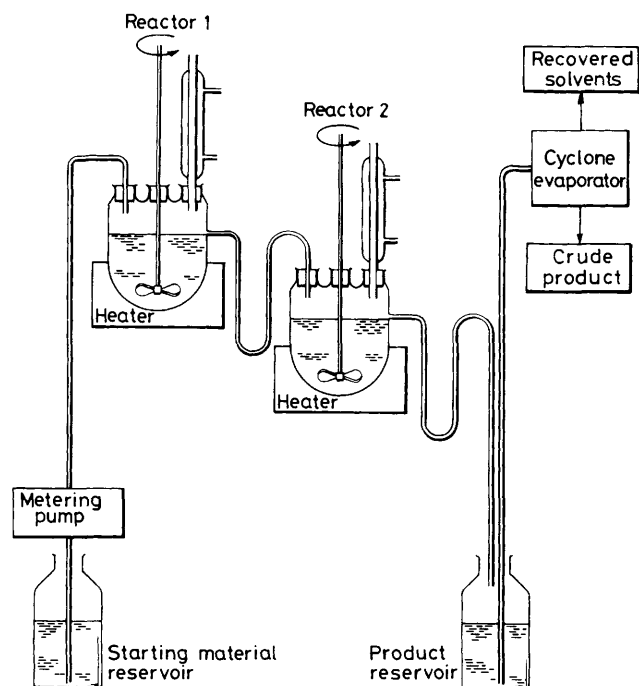


Figure. Two-stage reactor for the continuous preparation of compound (21)

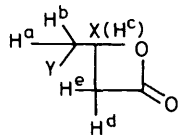
The additions of BrCCl_3 and CBr_4 proceeded readily to the corresponding 4-bromo-oxetan-2-ones (22), the lower yields reflecting the decreased thermal stability compared with (21). With trichloroacetic ester the lactone (23) was formed in <5% yield and with chloroform the i.r. spectrum [ν_{max} , 1820 cm^{-1} ($\text{C}=\text{O}$)] and n.m.r. spectrum (ring methine at C-4, m, 4.9 p.p.m.) indicate formation of the product of C-H addition also in <5% yield. The 4-chloro and 4-bromo lactones (21) and (22) also have interesting biocidal properties.²⁰

N.m.r. Spectra.—Examples of the ^1H n.m.r. spectra of the diketene adducts are shown in Table 4. Signals for the ring C-3 methylene protons appear as an AB or ABX system according to the structure of the compound. Assignment of signals to this methylene group could be made on the basis of chemical shift which in the case of the phosphorus-containing lactones (13) was confirmed by the absence of P-CH coupling. The expected non-equivalence of the exocyclic methylene protons is observed in a number of cases, the signals again appearing as an AB or ABX system. For the phosphorus substituted compounds (13) the expected P-C-H coupling of 16–20 Hz is seen. The ring methine at C-4 characteristically appears as a multiplet in the range δ 4.60–5.00 and has been used in conjunction with the i.r. carbonyl absorption to distinguish between β and γ lactones.¹³

Conclusions

The free radical, catalysed additions to diketene reported here represent a simple, versatile synthesis of a range of novel oxetan-2-ones whose chemistry will be reported later.

Table 4. ^1H N.m.r. spectra of oxetan-2-ones in CDCl_3



Compound	Y	X(H ^c)	H ^a	H ^b	H ^d	H ^e
(18a)	(MeO) ₂ P(:O)- d, 3.84, $J_{\text{P,Me}}$ 12	H, m, 4.90,	Octet, 2.33, $J_{\text{H}^a\text{H}^b}$ 16 $J_{\text{H}^a\text{H}^c}$ 8 $J_{\text{P,H}^a}$ 20	Octet, 2.61, $J_{\text{H}^b\text{H}^c}$ 16 $J_{\text{H}^b\text{H}^d}$ 6 $J_{\text{P,H}^b}$ 20	q, 3.46 $J_{\text{H}^c\text{H}^d}$ 17 $J_{\text{H}^c\text{H}^e}$ 5	q, 3.77, $J_{\text{H}^d\text{H}^e}$ 17 $J_{\text{H}^e\text{H}^f}$ 6
(18f)	(<i>c</i> -C ₆ H ₁₁) ₂ P(:O)- m, 4.35; m, 1.0–2.0	H, m, 4.70	m, 2.22, $J_{\text{H}^a\text{H}^b}$ 15 $J_{\text{H}^a\text{H}^c}$ 8 $J_{\text{P,H}^a}$ 18	m, 2.43, $J_{\text{H}^b\text{H}^c}$ 15 $J_{\text{H}^b\text{H}^d}$ 5 $J_{\text{P,H}^b}$ 18	q, 3.31, $H_{\text{H}^c\text{H}^d}$ 16 $J_{\text{H}^c\text{H}^e}$ 4	q, 3.59, $J_{\text{H}^d\text{H}^e}$ 16 $J_{\text{H}^e\text{H}^f}$ 6
(18n)	(EtO) ₂ P(:S)- t, 1.38; m, 4.20	H, m, 4.90	Octet, 2.58, $H_{\text{H}^a\text{H}^b}$ 15 $J_{\text{H}^a\text{H}^c}$ 6 $J_{\text{P,H}^a}$ 18	Octet, 2.88, $J_{\text{H}^b\text{H}^c}$ 15 $J_{\text{H}^b\text{H}^d}$ 9 $J_{\text{P,H}^b}$ 16	q, 3.53, $J_{\text{H}^c\text{H}^d}$ 17 $J_{\text{H}^c\text{H}^e}$ 5	q, 3.82, $J_{\text{H}^d\text{H}^e}$ 17 $J_{\text{H}^e\text{H}^f}$ 6
(7a)	MeS s, 2.20	H, m, 4.74	d, 2, 94 $J_{\text{H}^a\text{H}^b} = J_{\text{H}^b\text{H}^c}$		q, 3.25, $J_{\text{H}^c\text{H}^d}$ 16 $J_{\text{H}^c\text{H}^e}$ 4	q, 3.66, $J_{\text{H}^d\text{H}^e}$ 16 $J_{\text{H}^e\text{H}^f}$ 5
(7b)	EtS t, 1.26; q, 2.60, J 7	H, m, 4.60	q, 2.77, $J_{\text{H}^a\text{H}^b}$ 15 $J_{\text{H}^a\text{H}^c}$ 6	q, 2.99, $J_{\text{H}^b\text{H}^c}$ 15 $J_{\text{H}^b\text{H}^d}$ 6	q, 3.20, $J_{\text{H}^c\text{H}^d}$ 16 $J_{\text{H}^c\text{H}^e}$ 4	q, 3.54, $J_{\text{H}^d\text{H}^e}$ 16 $J_{\text{H}^e\text{H}^f}$ 6
(7j)	(<i>c</i> -C ₆ H ₁₁)S-	H, m, 4.60	q, 2.80, $J_{\text{H}^a\text{H}^b}$ 14 $J_{\text{H}^a\text{H}^c}$ 6	q, 3.05, $J_{\text{H}^b\text{H}^c}$ 14 $J_{\text{H}^b\text{H}^d}$ 6	q, 3.17, $J_{\text{H}^c\text{H}^d}$ 16 $J_{\text{H}^c\text{H}^e}$ 5	q, 3.60, $J_{\text{H}^d\text{H}^e}$ 16 $J_{\text{H}^e\text{H}^f}$ 4
(9f)	(<i>c</i> -C ₆ H ₁₁)SO ₂ - m, 2.90; m, 1.1–2.3	H, m, 4.96	q, 3.40, $J_{\text{H}^a\text{H}^b}$ 17 $H_{\text{H}^a\text{H}^c}$ 4	q, 3.76, $J_{\text{H}^b\text{H}^c}$ 17 $J_{\text{H}^b\text{H}^d}$ 5	q, 3.14, $J_{\text{H}^c\text{H}^d}$ 15 $J_{\text{H}^c\text{H}^e}$ 6	q, 3.60, $J_{\text{H}^d\text{H}^e}$ 15 $J_{\text{H}^e\text{H}^f}$ 7
(23)	Cl	Cl	2 × d, 4.08, 4.16, $J_{\text{H}^a\text{H}^b}$ 13.5		2 × d, 3.87, 4.15, $J_{\text{H}^c\text{H}^d}$ 17	
(22)	Cl ₃ CS	Cl	2 × d, 3.89, 4.07, $J_{\text{H}^a\text{H}^b}$ 14		2 × d, 3.99, 4.21, $J_{\text{H}^c\text{H}^d}$ 16	
(23)	Cl ₃ C	Cl	s, 3.78		2 × d, 3.90, 4.45, $J_{\text{H}^c\text{H}^d}$ 17	
(28a)	Cl ₃ C	Br	s, 3.86		2 × d, 4.10, 4.64, $J_{\text{H}^c\text{H}^d}$ 18	
(28b)	Br ₃ C	Br	s, 4.36		2 × d, 4.20, 4.89, $J_{\text{H}^c\text{H}^d}$ 18	

Experimental

M.p.s were determined on a Buchi melting point apparatus and are uncorrected. ^1H N.m.r. spectra were obtained on a Varian EM 360A spectrometer operating at 60 MHz using trimethylsilane as internal reference. ^{31}P N.m.r. spectra were obtained on a Jeol FX60 spectrometer operating at 24.15 MHz with 90% phosphoric acid as external reference. I.r. spectra were measured on a Perkin-Elmer 457 grating spectrometer. Molecular distillations were done on a Leybold Hereaus KDL-1 wiped wall molecular still. Irradiations by u.v. were by a Hanovia medium pressure mercury lamp contained in a water cooled quartz jacket.

Unless otherwise described, materials were purchased from B.D.H., Fluka, or Aldrich. Diketene was from the British Celanese Corporation and was distilled at reduced pressure before use. Bis(4-*t*-butylcyclohexyl) perdicarbonate was provided by Interlox Chemicals Ltd. Isobutyl methylphosphinate was a sample from Hoechst. Diphenylphosphine oxide and diphenylphosphine sulphide were obtained from Maybridge Chemicals. Lower alkyl phosphonates were purchased and generally stirred with sodium carbonate and/or distilled before use to remove acid impurities. Other phosphonates were prepared from PCl_3 and the corresponding alcohol.²¹ Bistrimethylsilyl phosphonate was made from phosphorous acid and trimethylsilyl chloride.²² Thiophosphonates were prepared from PCl_3 by successive reaction with an alcohol²³ and then hydrogen sulphide.²⁴ Ethyl phenylphosphinate was obtained by treatment of dichlorophenylphosphine with ethanol²⁵ and butyl ethylphosphinate from dichloroethylphosphine²⁶ and butanol.²⁵ Butyl phenylthiophosphinate was prepared from butoxychlorophenylphosphine²⁷ by reaction with hydrogen sulphide as described for an analogue.²⁸

Addition of Thiols to Diketene.—Method A. A mixture of diketene (0.1 mol) and the thiol (0.1–0.4 mol) in light petroleum (b.p. 40–60 °C, 300 ml) with a little azoisobutyronitrile (1.5 mmol) was stirred and if necessary* irradiated by u.v. light. The course of the reaction was followed by examination of the i.r. spectrum of the reaction mixture, β -lactone formation being indicated by appearance of a peak at 1 820 cm^{-1} . At the end of the reaction the solvent was removed under reduced pressure the temperature of the bath being kept at room temperature. Remaining traces of solvent were evaporated under high vacuum. In the majority of cases the products were oils which owing to decomposition at room temperature could not be purified satisfactorily.

Method B. A similar method to that employed in Method A was used but without the addition of a radical initiator.

Method C. A cooled mixture of diketene (0.1 mol), thiol (0.1 mol) and azoisobutyronitrile (1–5 mmol) was irradiated by u.v. light for several hours. Unchanged starting materials were removed from the product by washing with light petroleum and/or by evaporation at low pressure. In examples (2k) and (2l), excess of thiol was removed by dissolution of the reaction mixture in ether and rapid washing with 1M-aqueous sodium carbonate before drying and re-evaporating.

Addition of Hydrogen Sulphide to Diketene.—An efficiently stirred mixture of diketene (16.8 g) and azoisobutyronitrile (0.5 g) dissolved in light petroleum (b.p. 40–60 °C) (500 ml) was cooled to –10 °C and irradiated with u.v. light while a stream of hydrogen sulphide was introduced. After 2 h this reaction was essentially complete (i.r.). The precipitated solid was filtered off, washed, and dried to give (13.9 g, 69%) of bis(2-oxo-oxetan-4-ylmethyl) sulphide (4) containing a little polymeric material.

Rapid recrystallisation from acetone gave an analytical sample, m.p. 116–118 °C (decomp.) (Found: C, 47.45; H, 5.15; S, 15.65. $\text{C}_8\text{H}_{10}\text{O}_4\text{S}$ requires C, 47.52; H, 4.98; S, 15.85%).

Oxidation of the Sulphides (2) to the Sulphones (5).—**Synthesis of (5a–h).** Ruthenium trichloride (0.05 g) was added to a two-phase mixture of a solution of sodium periodate (2.54 g) in water (25 ml) and dichloromethane (100 ml). The sulphide (1.0 g) was added and the heterogeneous mixture shaken vigorously overnight at ambient temperature. The mixture was filtered through Hyflo and the organic layer separated, dried (MgSO_4), and evaporated. Crystallisation from toluene gave the pure sulphone.

Oxidation of the lactone (4) to the sulphone (5i). A solution of the lactone (4) (4.0 g) in methylene chloride (200 ml) was added to a solution of sodium periodate (10.0 g) in water (100 ml). Ruthenium trichloride (0.2 g) was added and the mixture shaken vigorously at ambient temperature overnight. The precipitated material was collected and extracted with boiling water (3 × 600 ml). The white plates crystallising from the water extracts on cooling were filtered off giving a total of 1.25 g (27%) of bis(2-oxo-oxetan-4-ylmethyl) sulphone. Crystallisation from water gave an analytically pure sample.

Oxidation of Sulphides to Sulphoxides.—(With Dr. E. Phillips) (a) **Oxidation of the lactone (2f) to the sulphoxide (6a).** A solution of sulphuryl chloride (7.6 g, 56 mmol) in methylene chloride (20 ml) was added over 1 h to a stirred, cooled (0–10 °C), heterogeneous mixture of the β -lactone (2f) (14.3 g, 50 mmol) dissolved in methylene chloride (50 ml), silica gel (2.13 g), water (2.1 g) and potassium carbonate (7.7 g, 56 mmol). The mixture was stirred at 0–10 °C for a further 2 h, water (100 ml) was added, and solid material removed by filtration. The organic layer was separated, washed with water, dried (MgSO_4), and evaporated. Recrystallisation of the residue from light petroleum (b.p. 80–100 °C) gave 4-dodecylthiomethyl-oxetan-2-one *S*-oxide (11.3 g, 75%), m.p. 95.5–96.5 °C (Found: C, 63.4; H, 10.1; S, 10.6. $\text{C}_{16}\text{H}_{30}\text{O}_3\text{S}$ requires C, 63.6; H, 10.0; S, 10.6%).

(b) **Oxidation of the lactone (4) to the sulphoxide (6b).** Sulphuryl chloride (38 g, 0.25 mol) was added over 1 h to a cooled (0–10 °C), stirred mixture of the lactone (4) (50.5 g, 0.25 mol) in methylene chloride (100 ml), silica gel (10.5 g), water (10.5 g) and potassium carbonate (38 g, 0.28 mol). Stirring was continued at 0–10 °C for 5 h after which the mixture was evaporated to dryness. The residue was extracted in a Soxhlet extractor with acetone which when evaporated gave crude product (49.5 g). Careful washing with ice-cold acetone gave pure bis(2-oxo-oxetan-4-ylmethyl) sulphoxide (6b) (17.3 g, 32%) m.p. 145–146 °C. (The cold acetone extract contained a 1:1 mixture of sulphoxide and polyester impurity). Crystallisation from acetone gave an analytical sample, m.p. 155–156 °C (Found: C, 43.7; H, 4.8; S, 14.6. $\text{C}_8\text{H}_{10}\text{O}_5\text{S}$ requires C, 44.0; H, 4.8; S, 14.6%).

Isomerisation of (2b) to γ -Lactone.—4-Ethylthiomethyl-oxetan-2-one (2b) (50 g, crude product from the radical addition of ethanethiol to diketene) was added dropwise with stirring over 2 h to 0.01M-HCl (2 l) at ambient temperature. After addition, stirring was continued for 4 h, after which the mixture was evaporated at reduced pressure. The oily residue was distilled to give the lactone of 3-ethylthio-4-hydroxybutanoic acid (11) (22.4 g, 45%), b.p. 94 °C/0.1 Torr (Found: C, 49.6; H, 6.95; S, 21.3. $\text{C}_6\text{H}_{10}\text{O}_2\text{S}$ requires C, 49.31; H, 6.90; S, 31.90%); δ_{H} (60 MHz; CDCl_3) 1.26 (3 H, t, *J* 8 Hz, Me), 2.60 (2 H, q, *J* 8 Hz, CH_2S), 2.30 (1 H, q, *J* 17 and 7 Hz, 3-H), 2.88 (1 H, q, *J* 17 and 6 Hz, 3-H), 3.72 (1 H, m, SCH), 4.04 (1 H, q, *J* 9 and 5 Hz, 5-H), and 4.53 (1 H, q, *J* 9 and 7 Hz, 5-H).

* In several cases a spontaneous reaction occurred without the need to irradiate.

Phosphorus-substituted β -Lactones (13).—Syntheses of the compounds in Table 3 are illustrated by the Examples (a)—(d) below.

(a) *Synthesis of (13a).* A mixture of diketene (84 g, 1 mol) and bis(*t*-butylcyclohexyl) perdicarbonate (6.5 g, 17 mmol) was added dropwise over a period of 1 h to dimethyl phosphonate (440 g, 4 mol) which was vigorously stirred at 80 °C under a nitrogen atmosphere. The temperature of the reaction mixture rose to 90 °C during the addition. On completion of the addition, the reaction mixture was heated for a further 40 min at 80–90 °C, after which it was cooled to room temperature. Excess of phosphonate and other volatile materials were removed by means of a rotary evaporator at a pressure of 1 Torr and a temperature rising to 100 °C. The residue was cooled and dissolved in ethyl acetate (200 ml) at room temperature. To this solution cyclohexane (750 ml) was added and the mixture stored at 0 °C for 18 h. The precipitated crystalline dimethyl 2-oxo-oxetan-4-ylmethylphosphonate (186 g, 96%), m.p. 46–47 °C was collected, washed with cyclohexane, and dried. A sample recrystallised from ethyl acetate had m.p. 47–48 °C.

(b) *Synthesis of (13j).* A solution of bis(*t*-butylcyclohexyl) perdicarbonate (3.3 g, 8 mmol) in diketene (42.0 g, 0.5 mol) was added dropwise to isobutyl methylphosphinate (2.72 g, 2.0 mol) which was stirred and heated at 80 °C. During the addition the temperature rose to 90 °C. After the addition, heating and stirring were continued for 15 min; the excess of phosphinate was then removed by twice passing the product down a wiped wall still at 55 °C/0.01 Torr. The crude product was distilled on the wiped wall still at 110 °C/0.01 Torr giving isobutyl methyl-(2-oxo-oxetan-4-ylmethyl)phosphinate (13j) (108 g, 98%). Spectroscopic examination of the product revealed several minor impurities. Further purification was effected by dissolving the product in methylene chloride (500 ml), rapid washing the solution with saturated aqueous sodium hydrogen-carbonate (100 l) and then drying (MgSO₄), evaporating, and redistilling the product on a wiped wall still; the yield of purified product was 90 g (82%).

(c) *Synthesis of (13l).* A mixture of diketene (8.4 g, 0.1 mol) benzoyl peroxide (2.4 g, 10 mmol) and ethyl phenylphosphinate (20.0 g, 0.12 mol) was added dropwise over 1 h to vigorously stirred ethyl phenylphosphinate (48.8 g, 0.28 mol) which was heated at 120 °C in an atmosphere of nitrogen. After a further hour at 120 °C the excess of phosphinate was removed by passing the reaction mixture down a wiped wall still at 80 °C at 0.01 Torr. The residue was distilled on a wiped wall still at 110 °C and 0.01 Torr and the product ethyl (2-oxo-oxetan-4-ylmethyl)phenylphosphinate, was obtained as a colourless oil (15.0 g, 59%) which was shown by ³¹P n.m.r. to be a mixture of diastereoisomers (*ca.* 1:1) having chemical shifts at δ 37.5 and 37.7 p.p.m.

(d) *Synthesis of (13n).* A mixture of diketene (16.8 g, 0.2 mol), benzoyl peroxide (4.8 g, 0.02 mol), and diethyl thiophosphonate (83.3 g, 0.54 mol) was added dropwise over 1 h to diethyl thiophosphonate (83.3 g, 0.54 mol) which was stirred at 120 °C under a nitrogen atmosphere. At the end of the reaction time, excess of starting materials and volatile impurities were removed from the product by twice passing the reaction mixture down a wiped wall still, initially at 70 °C and 15 Torr, and then at 45 °C and 0.01 Torr. The product diethyl 2-oxo-oxetan-4-ylmethylthiophosphonate was distilled on a wiped wall still at 60 °C and 0.01 Torr and was obtained as a mobile orange oil (22.0 g, 45%).

Hydrolysis of (13i).—Water (1.44 g, 0.08 mol) was added at room temperature to a stirred solution of (13i) (12.4 g, 0.04 mol) in ether (100 ml). After 40 min the ether was decanted off and the residual oil washed twice with ether. The oil was dissolved in ethanol (100 ml) at room temperature and cyclohexylamine (4.0

g, 0.04 mol) was added. After 30 min, the monocyclohexylamine salt of 2-oxo-oxetan-4-ylmethylphosphonic acid (16) (7.8 g, 74%) was collected and washed with a little ethanol; it had m.p. 132–133 °C (decomp.) (Found: C, 45.3; H, 7.95; N, 5.55; P, 11.75. C₁₀H₂₀NO₅P requires C, 45.28; H, 7.60; N, 5.28; P, 11.68%).

Addition of Diphenylphosphine Oxide to Diketene.—A mixture of diketene (4.2 g, 50 mmol), diphenylphosphine oxide (10.1 g, 50 mmol), bis-(4-*t*-butylcyclohexyl) perdicarbonate (2.3 g, 10 mmol) in toluene (70 ml) was stirred by a stream of nitrogen in a quartz apparatus at room temperature and irradiated by u.v. light. After 3 h the reaction mixture was filtered and the filtrate evaporated. The semicrystalline residue was triturated with a little toluene and the resulting crystals (1.3 g, 9%), m.p. 145–150 °C, were collected and washed with toluene. Crystallisation from toluene gave diphenyl(2-oxo-oxetan-2-ylmethyl)phosphine oxide (14a), m.p. 154–155 °C (decomp.) (Found: C, 67.25; H, 5.45; P, 10.6. C₁₆H₅O₃P requires: C, 67.3; H, 5.28; P, 10.82%).

Addition of Diphenylphosphine Sulphide to Diketene.—A mixture of diphenylphosphine sulphide (10.9 g, 50 mmol), diketene (4.2 g, 50 mmol), and azoisobutyronitrile (1.25 g, 5 mmol) in toluene (70 ml) was irradiated by u.v. light for 3.5 h at room temperature while being stirred by a stream of nitrogen. The toluene was evaporated and the residue triturated with diethyl ether (30 ml) to give white crystals, m.p. 103–106 °C (10.8 g, 72%). Crystallisation twice from a mixture of light petroleum (b.p. 100–120 °C) and toluene gave diphenyl(2-oxo-oxetan-4-ylmethyl)phosphine sulphide (14b), m.p. 106–107 °C (Found: C, 63.5; H, 5.15; P, 9.95; S, 10.7. C₁₆H₁₅O₂PS requires: C, 63.57; H, 5.00; P, 10.24; S, 10.60%).

Reaction of Phosphine with Diketene.—A mixture of diketene (8.4 g, 0.1 mol) and azoisobutyronitrile (0.25 g, 1.5 mmol) in toluene (50 ml) was irradiated by u.v. light while a slow stream of phosphine was passed into the reaction. After 2 h when *ca.* 3.4 g (0.1 mol) of phosphine had been passed in, the irradiation was stopped and the flow of phosphine discontinued. β -Lactone formation in the reaction mixture was indicated by an i.r. absorption at 1 830 cm⁻¹. A ³¹P n.m.r. spectrum on the reaction mixture showed a triplet at δ -162.3 (*J*_{PH} 194 Hz) confirming the formation of 2-oxo-oxetan-4-ylmethylphosphine and a pair of doublets at δ -66.7 (*J*_{PH} 220 Hz) and γ -65.0 (*J*_{PH} 215 Hz) corresponded to the diastereoisomers of bis(2-oxo-oxetan-4-ylmethyl)phosphine. Attempts to isolate or purify the products were unsuccessful owing to the limited stability of the adducts.

Addition of Phenylphosphine to Diketene.—A mixture of phenylphosphine (11.0 g, 0.1 mol), diketene (8.4 g, 0.1 mol), and azoisobutyronitrile (0.25 g, 1.5 mmol) in toluene (70 ml) was irradiated by u.v. light for 5 h at room temperature under a nitrogen atmosphere. The crude reaction mixture was evaporated under reduced pressure at room temperature and then kept at 0.01 Torr for 2 h to remove volatile impurities. The diastereoisomeric mixture of (2-oxo-oxetan-4-ylmethyl)phenylphosphine was obtained as an unstable oil having an i.r. spectrum characteristic of a β -lactone (C=O, ν_{\max} , 1 820 cm⁻¹) and showing a pair of doublets in the ³¹P n.m.r. at δ -65.6 (*J*_{PH} 210 Hz) and δ -67.6 (*J*_{PH} 210 Hz).

Addition of Diphenylphosphine to Diketene.—A mixture of diphenylphosphine (9.3 g, 50 mmol), diketene (4.2 g, 50 mmol), and azoisobutyronitrile (0.25 g, 1.2 mmol) in toluene (70 ml) was irradiated by u.v. light at ambient temperature under nitrogen for 22 h. Evaporation of the solvent under reduced pressure gave a yellow oil with a typical β -lactone absorption in

the i.r. at 1860 cm^{-1} . Attempts to distil this product led to decomposition. A sample of the crude β -lactone was dissolved in toluene and a stream of oxygen passed through for a total of 16 h. The solution was run onto a column of silica gel and the column eluted with toluene containing increasing proportions of ethyl acetate. Final elution with methanol gave a fraction shown to be a mixture of diphenylphosphine oxide and diphenyl(2-oxo-oxetan-4-ylmethyl)phosphine oxide (**14a**). Recrystallisation twice from toluene gave pure (**14a**) identical (i.r.) with the sample prepared in Section 2.13.

4-Chloro-4-trichloromethylthiomethyloxetan-2-one (17).—A solution of azoisobutyronitrile (0.5 g, 2.5 mmol) in diketene (16.8 g, 0.2 mol) was added to cooled (-15°C) trichloromethanesulphenyl chloride (37.2 g, 0.2 mol). The mixture was irradiated with u.v. light from a medium-pressure lamp for 4 h the temperature of the reaction being maintained between -10 and -15°C . At the end of the reaction unchanged starting materials were removed at room temperature under high vacuum giving a crude product which crystallised with time. Crystallisation from light petroleum (b.p. 60 – 80°C) gave 4-chloro-4-trichloromethylthiomethyloxetan-2-one as colourless crystals (26.8 g, 49.6%), m.p. 44 – 50°C (Found: C, 22.85; H, 1.62; Cl, 52.8; S, 11.53. $\text{C}_5\text{H}_4\text{Cl}_4\text{O}_2$ requires C, 22.85; H, 1.49; Cl, 52.53; S, 11.88%). Evaporation of the crystallisation liquors gave a clear yellow oil (10 g) which upon distillation under reduced pressure afforded a fore-run, b.p. 43 – $50^\circ\text{C}/10^{-2}$ Torr, shown to consist mainly of 4-chloro-4-chloromethyloxetan-2-one (**18**) followed by a non- β -lactone component of the mixture, b.p. 60 – $64^\circ\text{C}/10^{-2}$ Torr, $(\text{Cl}_3\text{CS})_2$. Finally further 4-chloro-4-trichloromethylthiomethyloxetan-2-one (2.5 g, 5%), b.p. 80 – 95°C was collected.

4-Chloro-4-chloromethyloxetan-2-one (18).—A mixture of diketene (84 g, 1 mol) and bis(4-t-butylcyclohexyl) perdicarbonate (13.0 g, 0.03 mol) dissolved in carbon tetrachloride (500 ml) was added dropwise over 30 min to a stirred solution of sulphuryl chloride (135 g, 1 mol) in carbon tetrachloride (1 l) which was heated under reflux in a nitrogen atmosphere. At the end of the addition, the mixture was heated under reflux for a further 30 min after which the solvent was evaporated at water-pump pressure. Distillation of the residue under reduced pressure gave the title compound (**18**) (155 g, 77%), b.p. 42 – $46^\circ\text{C}/0.03$ Torr which crystallised when cooled $<20^\circ\text{C}$ (Found: C, 30.5; H, 2.5; Cl, 45.45. $\text{C}_4\text{H}_4\text{Cl}_2\text{O}_2$ requires C, 31.00; H, 2.60; Cl, 45.75%); ν_{max} (C=O) 1850 cm^{-1} ; δ_{H} (CCl_4) 4.41 (s, 2 H), 3.82 (d, 1 H, J 17 Hz), and 4.20 (d, 1 H, J 17 Hz).

Chlorine was bubbled into a solution of 4-chloro-4-chloromethyloxetan-2-one in carbon tetrachloride at 0°C and the solution so obtained was set aside for several hours. Removal of the carbon tetrachloride and chlorine gave unchanged starting material.

Addition of Carbon Tetrachloride to Diketene.—(a) A mixture of diketene (210 g), and bis(4-t-butylcyclohexyl) perdicarbonate (30 g) dissolved in carbon tetrachloride (500 ml) was added dropwise over 1 h to carbon tetrachloride (2 l) which was then heated under reflux under a nitrogen atmosphere. Stirring at reflux temperature was continued for 1 h after which the solution was allowed to cool. The excess of carbon tetrachloride was distilled off on a rotary evaporator under a water-pump vacuum at a bath temperature of 30 – 40°C . The crude product was purified by distillation* on a wiped-wall still at 0.1 Torr

and a wall temperature of 70°C giving 4-chloro-4-(2,2,2-trichloroethyl)oxetan-2-one (**21**); typical yields were 60–70%. Distillation of a small portion gave an analytically pure sample, b.p. 70 – $75^\circ\text{C}/0.013$ Torr (Found: C, 25.45; H, 1.85; Cl, 59.6. $\text{C}_5\text{H}_4\text{Cl}_4\text{O}_2$ requires C, 25.22; H, 1.69; Cl, 59.61%).

(b) **Continuous process.** A carbon tetrachloride solution containing diketene (41.0 g l^{-1}) and bis(4-t-butylcyclohexyl) perdicarbonate (7.5 g l^{-1}) was pumped through a two-vessel cascade reactor (Figure 1) at such a rate as to give a residence time of 60 min (residence time = vessel volume/volume pumped min^{-1}) while the vessels were stirred vigorously and heated at the refluxing temperature of carbon tetrachloride. The product stream contained a little unchanged diketene, 4-chloro-4-(2,2,2-trichloroethyl)oxetan-2-one, and carbon tetrachloride. The excess of carbon tetrachloride was removed at room temperature in a cyclone evaporator and the product purified by distillation in a wiped wall still.

Addition of Bromotrichloromethane to Diketene.—A mixture of diketene (25.2 g, 0.3 mol), bis(4-t-butylcyclohexyl) perdicarbonate (1.5 g, 4 mmol) and bromotrichloromethane (62.7 g, 0.32 mol) in carbon tetrachloride (100 ml) was heated at 60°C for 2 h. The carbon tetrachloride was evaporated under reduced pressure and the residual oil crystallised twice from light petroleum (b.p. 40 – 60°C) to give 4-bromo-4-(2,2,2-trichloromethyl)oxetan-2-one (48.0 g, 55%), m.p. 54 – 55°C (Found: C, 21.3; H, 1.45. $\text{C}_4\text{H}_2\text{BrCl}_2\text{O}_2$ requires C, 21.27; H, 1.43%).

Addition of Carbon Tetrabromide to Diketene.—A mixture of carbon tetrabromide (33.1 g, 0.1 mol), diketene (8.4 g, 0.1 mol), and bis(4-t-butylcyclohexyl) perdicarbonate (0.5 g, 1.3 mmol) in carbon tetrachloride (200 ml) was heated at 60°C for 2 h. The solvent was removed under reduced pressure and the resulting crystalline residue crystallised twice from light petroleum (b.p. 40 – 60°C) to give 4-bromo-4-(2,2,2-tribromoethyl)oxetan-2-one (**22b**) (15.2 g, 37%), m.p. 71 – 73°C (Found: C, 14.3; H, 1.0. $\text{C}_5\text{H}_4\text{Br}_4\text{O}_2$ requires C, 14.45; H, 0.97%).

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