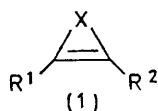


Decomposition of α -Diazo-ketones: the Oxiren–Oxocarbene Equilibrium

By S. A. Matlin and P. G. Sammes,* Chemistry Department, Imperial College, London SW7 2AY

A sensitive chemical test for the participation of oxirens in the decomposition of diazo-ketones has been developed, based on the subsequent rearrangement of oxocarbenes to $\alpha\beta$ -unsaturated ketones. In this way oxiren participation has been demonstrated in the thermal and photochemical decomposition of a variety of diazo-ketones, including 3-diazoheptan-4-one, 1-diazo-3-phenylpropan-2-one, and 2,2-dimethyl-4-diazohexan-3-one. In contrast, no oxiren participation occurred in the catalysed decomposition of the diazo-ketones with either silver or copper oxide. The importance of competing processes, such as the Wolff rearrangement, is also discussed.

THE preparation of small, unsaturated heterocyclic ring systems such as oxiren (1; X = O) is the subject of much current interest. Recently thiiren 1,1-dioxides (1; X = SO) ^{1a} and thiiren 1-oxides (1; X = SO) ^{1b} and evidence for the transient formation of both 1H-azirenes,² and thiirens³ has been presented. Oxirens have also been postulated by Strausz as transient



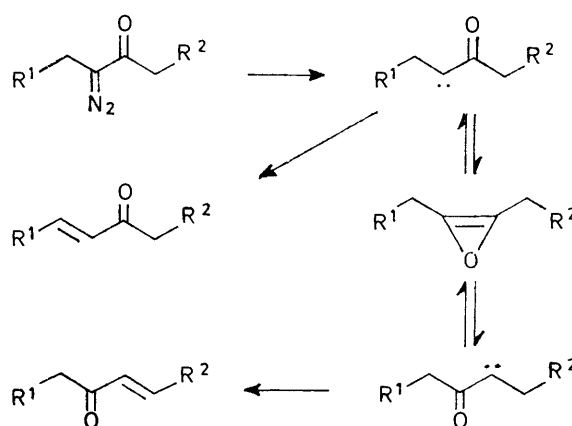
intermediates in the photochemical decomposition of diazo-ketones and diazo-esters, but their existence was demonstrated by means of ¹³C-labelling studies in the Wolff rearrangement, *viz.* the decomposition of diazo-ketones into ketenes.⁴ These results were in contrast with earlier studies, in which Huggett reported that [1-¹³C]diazoacetophenone gave only [2-¹³C]phenylacetic acid⁵ and in which Franzen reported that during conversion of [¹⁴C]- α -diazo- α -phenylacetophenone into diphenylacetic acid, no scrambling of the label occurred.⁶

¹ (a) L. A. Carpino, L. V. McAdams, R. H. Rynbrandt, and J. W. Spiewak, *J. Amer. Chem. Soc.*, 1971, **93**, 476; (b) L. A. Carpino and H.-Wu Chen, *ibid.*, p. 785.

² T. L. Gilchrist, G. E. Gymer, and C. W. Rees, *Chem. Comm.*, 1971, 1519.

³ O. P. Strausz, J. Font, E. L. Dedio, P. Kebarle, and H. E. Gunning, *J. Amer. Chem. Soc.*, 1967, **89**, 4805.

In order to clarify the evidence for the transient formation of oxirens in the decomposition of diazo-ketones a simple chemical test for their existence was developed.⁷



SCHEME 1

This was based on the observation that, when a methylene group is adjacent to the diazo-function, decomposition to the oxocarbene is followed by a 1,2-hydrogen shift to the carbenoid carbon atom, resulting in formation

⁴ G. Frater and O. P. Strausz, *J. Amer. Chem. Soc.*, 1970, **92**, 6654.

⁵ R. T. Arnold, C. Huggett, and T. I. Taylor, *J. Amer. Chem. Soc.*, 1942, **64**, 3043.

⁶ V. Franzen, *Annalen*, 1958, **614**, 31.

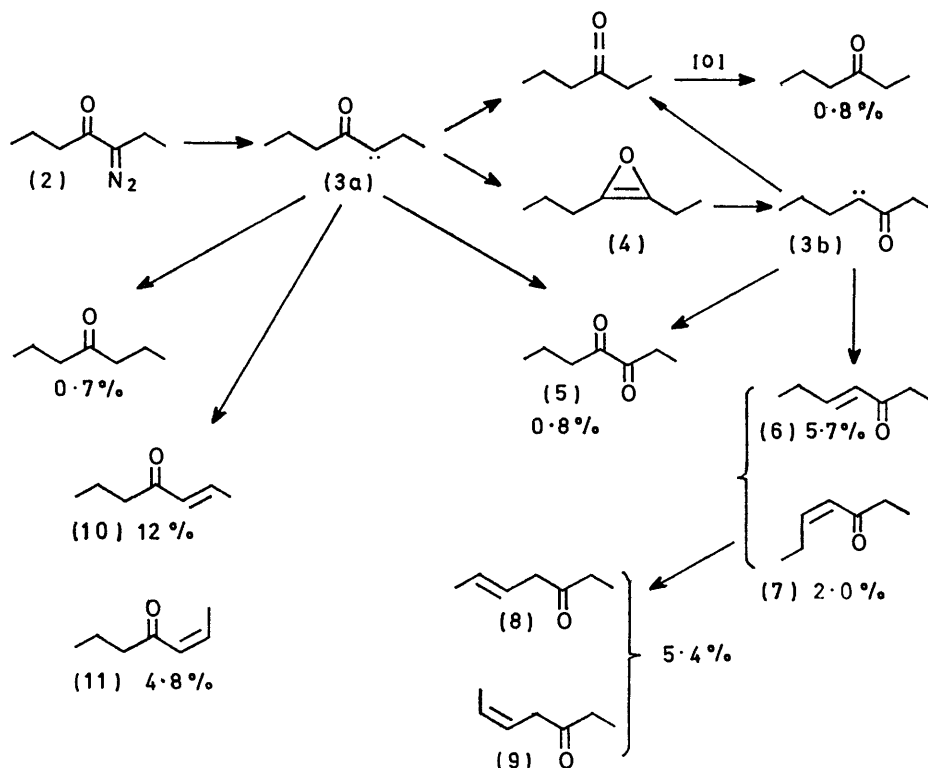
⁷ S. A. Matlin and P. G. Sammes, *Chem. Comm.*, 1972, 11.

of an $\alpha\beta$ -unsaturated ketone.⁸ Thus, for unsymmetrically substituted diazo-ketones, different $\alpha\beta$ -unsaturated ketones would form if the oxocarbene initially produced equilibrated with an oxiren intermediate (Scheme 1).

Such a scheme was successfully applied to the decomposition of 3-diazoheptan-4-one (2)⁹ under a variety of conditions. This substrate was initially chosen since it was expected that differences in the chemical behaviour of the derived oxocarbenes (3a and b, Scheme 2) would

isolated by extraction with sodium carbonate. Franzen has reported a similar result in the photolysis of dialkyl diazo-ketones.⁸

The deconjugated enones arise by a secondary photochemical process from the conjugated enones. Thus photolysis, in ether, of an authentic sample of *trans*-hept-4-en-3-one (6),¹¹ one of the products from the photolysis of the diazo-ketone (2), produced mainly the corresponding *cis*-isomer (7), together with some of the



SCHEME 2

be minimal. Subsequently the diazo-ketones (12), (13), and (20) were also examined.



Photolysis of 3-diazoheptan-4-one (2) in anhydrous ether led to its rapid disappearance with formation of several unsaturated ketones (Scheme 2). Unexpected products included hexan-3-one, which must form by aerial oxidation, during isolation, of the keten produced in the competing Wolff rearrangement; this type of oxidation is well known.¹⁰ Traces of heptane-3,4-dione (5), formed by oxidation, and of heptan-4-one, formed by hydrogen abstraction from the solvent, were also detected. When the photolysis was carried out in aqueous dioxan only a small amount of homogeneous acid fraction could be

$\beta\gamma$ -isomers (8) and (9), formed by photoenolization.¹² No trace of hept-1-en-4-one, expected from the comparable photoenolization of the ketone (10), was detected amongst the photochemical reaction products of the diazo-ketone (2). It has been reported that this $\beta\gamma$ -isomer is unstable with respect to the conjugated ketone (10).¹³ Suitable control experiments showed that there was no overall loss of unsaturated ketones under the conditions of the photolysis. The results of the photodecompositions of the ketone (2), together with those of some thermal and metal-catalysed decompositions are presented in Table 1. The percentage ratio of oxygen-rearranged enone formation to the total amount of enones produced is included as a measure of oxiren participation. For complete equilibration, in the absence of substituent effects, a figure of 50% would be

⁸ V. Franzen, *Annalen*, 1957, **602**, 199.

⁹ M. Regitz and F. Menz, *Chem. Ber.*, 1968, **101**, 2622.

¹⁰ K. Dyckerhoff, H. W. Klever, H. Staudinger, and L. Ruzicka, *Ber.*, 1925, **58**, 1079.

¹¹ M. Andrac, *Ann. Chim. (France)*, 1964, **9**, 287.

¹² M. J. Jorgenson and N. C. Yang, *Tetrahedron Letters*, 1964, 1203; N. C. Yang and C. Rivas, *J. Amer. Chem. Soc.*, 1961, **83**, 2213.

¹³ E. E. Blaise, *Bull. Soc. chim. France*, 1905, **33**, 39.

expected. The results of a series of vapour-phase pyrolyses of the diazo-ketone (2) are expressed graphically in the Figure.

These results categorically show oxygen migration and hence oxiren participation during both the photochemical and the thermal decomposition of the diazo-ketone (2). In contrast, no oxiren participation was detected in the silver oxide or copper oxide catalysed reactions. The thermal and photochemical reactions require the production of a free oxocarbene intermediate in order to account

different properties in the catalytic decomposition of diazo-ketones. Copper usually inhibits the Wolff rearrangement completely¹⁵ and leads to reactions such as 'carbene' coupling,^{16,17} insertion into double bonds,^{17,18} and insertion into carbon-carbon and carbon-hydrogen single bonds.¹⁹ In contrast, silver catalysts promote Wolff rearrangements at higher temperatures but, at room temperature, catalyse the formation of enones.⁸ Newman²⁰ has proposed a radical-chain process for the silver oxide-triethylamine-catalysed

TABLE I
Decompositions of 3-diazoheptan-4-one (2)

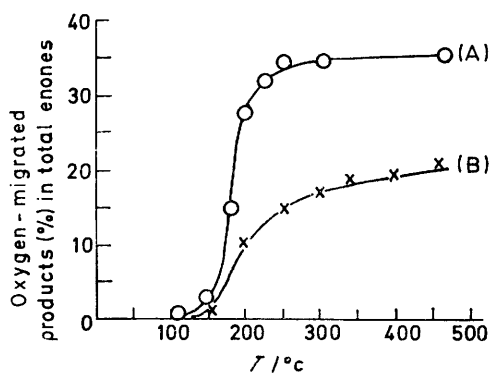
Expt. no.	mmol	Conditions	Solvent *	Volume (ml)	Temp. (°C)	Time (h)	Hepten-3-ones All heptenones (%)	Absolute yield (%) all enones
1	2.15	$h\nu$	Et ₂ O	40	20	1.5	44	30
2	12.5	$h\nu$	Et ₂ O	40	20	3.5	43	a
3	1.09	$h\nu + \text{Ph}_2\text{CO}$	Et ₂ O	40	20	1.5	Trace	a
4	1.57	Reflux	Ch	3	80	24	18	a
5	2.18	Ag ₂ O	(w-D) (15:85)	6	20	5	0	65
6	2.15	Cu ₂ O	Ch	5	80	1.0	0	60
7		Vapour phase pyrolysis			465		36	a

* Ch = Cyclohexane; w-D = water-dioxan.

• Not estimated.

for the oxygen migration. The degree of oxiren participation increases with temperature (Figure) and, in this instance, is even more favoured in the photochemical reaction.

The results of the metal-catalysed decompositions of 3-diazoheptan-4-one (2) are of interest. That no oxiren



Vapour-phase pyrolyses of diazo-ketones: (A) compound (2); (B) compound (14)

participation was observed implies no formation of free oxocarbenes. There is good evidence in the literature that copper forms complexes with oxocarbenes,¹⁴ and the intermediacy of such complexes would inhibit oxiren formation. The role of the silver catalyst is more ambiguous since silver and copper display markedly

Wolff rearrangement; however, more recent studies²¹ argue against this view and in favour of a triethylamine-silver complex of an intermediate carbene. Franzen's work⁸ also supports the latter view. The effect of temperature on the outcome of the silver-catalysed decompositions suggests a larger activation energy for Wolff rearrangement than for hydrogen migration to give an enone, the reactions diverging from a common intermediate.

The results on the photochemical and thermal decompositions of the diazo-ketone (2) completely support those of Strausz⁴ and also suggest a possible explanation for the discrepancies mentioned in the literature. Huggett and his co-workers⁵ searched for oxiren participation in a Wolff-rearrangement reaction under conditions of the Arndt-Eistert synthesis, which implies use of silver oxide as catalyst and which has now been shown not to involve oxiren participation. Franzen carried out his reactions with a long-wavelength light source ('Sunlamp'; 24 h photolysis) whereas Strausz used a higher energy medium-pressure mercury lamp similar to that used in the present studies. It is possible, therefore, that the Wolff rearrangement observed by Franzen was proceeding by a low-energy reaction profile, or by concerted migration-nitrogen elimination, thus by-passing oxiren intermediates.⁶

Several alternatives to the oxiren explanation for oxygen migration may be dismissed. Thus, the enones produced are stable, with respect to oxygen migration,

¹⁴ (a) T. Iyata, M. Takebayashi, and K. Ueda, *Bull. Chem. Soc. Japan*, 1970, **43**, 1500; (b) W. R. Moser, *J. Amer. Chem. Soc.*, 1969, **91**, 1135.

¹⁵ P. Yates, *J. Amer. Chem. Soc.*, 1952, **74**, 5376.

¹⁶ C. Grundmann, *Annalen*, 1938, **536**, 29.

¹⁷ J. Quintana and F. Sarratosa, *Tetrahedron Letters*, 1967, 2245.

¹⁸ J. Ficini and G. Stork, *J. Amer. Chem. Soc.*, 1961, **83**, 4678.

¹⁹ J. G. Colson and P. T. Lansbury, *Chem. and Ind.*, 1962, 821.

²⁰ P. F. Beal and M. S. Newman, *J. Amer. Chem. Soc.*, 1950, **72**, 5163.

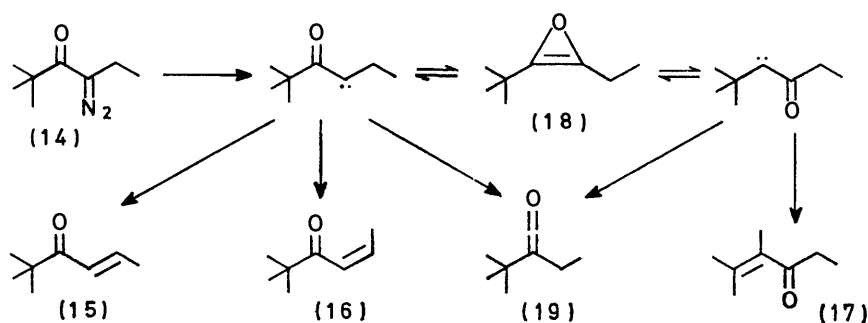
²¹ T. Iyata, Y. Tsuno, and Y. Yukawa, *Bull. Chem. Soc. Japan*, 1967, **40**, 2613.

under the photochemical conditions used. Intermolecular oxygen exchange is ruled out by the results of dilution studies (Table 1); neither in the photochemical nor in the thermal decompositions is there any significant change in the amount of 1,2-oxygen migration with concentration. Reversal of the Wolff rearrangement can also be discarded as a possible explanation since this cannot explain the label-scrambling results obtained by Strausz.⁴ Moreover, studies by Rowland and Russell indicate that this process, at best, is very inefficient during the photolysis of ketenes.²²

The possible intervention of triplet state intermediates has also been studied. Photolysis of the diazo-ketone (2) in the presence of benzophenone, such that the photosensitizer absorbed >95% of the light present, yielded only traces of the enones obtained by direct excitation. Control experiments showed that the enones were not unduly reactive under these conditions of decomposition. Thus, it can be assumed that triplet

hyde. The low yield of oxygen migration products from the ketones (12) and (13) reflects the preponderance of Wolff rearrangement in reactions of such terminal diazo-ketones. This effect has been attributed to conformational factors.^{25*}

It was of interest to examine whether groups other than hydrogen could be induced to migrate following the oxiren rearrangement. Since there is good precedent for methyl migration to a carbenoid centre,²⁵ 4-diazo-2,2-dimethylhexan-3-one (14), prepared by condensation of diazopropane with pivaloyl chloride in the presence of triethylamine (in the absence of the tertiary base only decomposition products were obtained), was studied. This model is also of interest since steric pressure of the *t*-butyl group should favour oxygen migration. Photolysis of the diazo-ketone (14) in anhydrous ether produced a mixture containing the unsaturated ketones (15)–(17) (Scheme 3). The *trans*- and *cis*-enones (15) and (16) are produced as a consequence of hydrogen migration



SCHEME 3

species do not rearrange *via* oxiren intermediates. It has similarly been demonstrated that the Wolff rearrangement requires a singlet state oxocarbene and is prevented by photosensitization.²³

In order to test the generality of oxiren participation in diazo-ketone decompositions several different substrates were investigated. Photolysis of 1-diazoheptan-2-one (12) in ether gave a mixture containing a 4% yield of the expected oxygen migration product, hept-2-enal, identical with an authentic sample.²⁴ The thermal decomposition of the diazo-ketone (12), in refluxing cyclohexane, also afforded the hept-2-enal (*ca.* 3%). The effect of a distant phenyl group on the migration was also examined, by photolysis of the diazo-ketone (13). The product of oxygen migration, *viz.* cinnamaldehyde, was detected, albeit in low yields (<5%), but the major product, obtained by photolysis in aqueous dioxan, was that of Wolff rearrangement, *viz.* 3-phenylpropionic acid (76%). Heating the diazo-ketone (13) in refluxing cyclohexane gave only traces of cinnamaldehyde.

without an oxygen shift. The 2,3-dimethylhex-2-en-4-one (17), however, can only arise *via* the oxiren intermediate (18). Traces of a ketene, assigned structure (19), were observed in the crude reaction product (weak i.r. band at 2120 cm^{-1}), but it was not isolated. The results of a series of photochemical and thermal decompositions of the diazo-ketone (14) are given in Table 2 and the results of the vapour-phase pyrolysis of this diazo-ketone are shown in the Figure. The enone product (17) was shown to be completely stable to the conditions of the photolysis both in the presence and in the absence of benzophenone. With the diazo-ketone (14), photolysis in anhydrous ether gave 14% of the rearranged enone (17) arising from oxiren intervention. An interesting effect of increasing solvent polarity was noted. As the dielectric constant of the reaction medium increased so did the amount of oxiren participation. With 2 : 3 water-dioxan, over 40% of the enone fraction consisted of the rearranged isomer (17).

The results show that oxiren participation is generally favoured in the photochemical reactions in comparison with analogous thermal reactions.† The degree of oxiren

* Conformational factors must also be pertinent in the results obtained by Z. Majerski and C. S. Redvanly, *J.C.S. Chem. Comm.*, 1972, 694.

† Similar results have been obtained by H. Kolshorn, H. Meier, E. Müller, and K. P. Zeller, *Chem. Ber.*, 1972, **105**, 1875.

²² F. S. Rowland and R. L. Russell, *J. Amer. Chem. Soc.*, 1970, **92**, 7508.

²³ W. Ando and M. Jones, *J. Amer. Chem. Soc.*, 1968, **90**, 2200.

²⁴ B. F. Daubert, C. J. Martin, and A. I. Schepartz, *J. Amer. Chem. Soc.*, 1948, **70**, 2601.

²⁵ F. Kaplan and G. K. Melloy, *J. Amer. Chem. Soc.*, 1966, **88**, 950.

involvement also increases with the polarity of the solvent. Furthermore, the oxygen migration increases, in the thermal reactions, as the temperature is increased. There are two principal explanations for these observations. Firstly, two competing processes could exist, one involving hydrogen migration concerted with nitrogen loss, which by-passes oxiren formation, and the other

actions gave the same products, (22)—(25), but in notably different ratios: the oxidation gave mainly the bicyclic ketones and the thermolysis of the diazo-ketone (20) gave largely the enone (23).

In terms of the foregoing two mechanistic hypotheses it could be reasoned that the thermal decomposition of the diazo-ketone (20) should involve a considerable

TABLE 2
Decompositions of 4-diazo-2,2-dimethylhexan-3-one (14)

Expt. no.	mmol	Conditions	Solvent *	Volume (ml)	Temp. (°C)	Time (h)	(1)	Absolute yield (%) all enones
							(17) + (1) + (1) (%)	
8	2.27	$h\nu$	Et ₂ O	40	25	1.0	14	35
9	1.36	$h\nu$	Et ₂ O	40	25	1.0	14	<i>a</i>
10	1.03	$h\nu$	w-D (1:9)	40	25	1.0	18	<i>a</i>
11	0.84	$h\nu$	w-D (1:4)	40	25	1.0	33	35
12	1.00	$h\nu$	w-D (1:4)	40	25	2.0	38	<i>a</i>
13	1.06	$h\nu$	w-D (2:3)	40	25	1.0	41	<i>a</i>
14	0.96	$h\nu$ + Ph ₂ CO	Et ₂ O	40	25	1.0	Trace	<i>a</i>
15	1.46	Reflux	Ch	2.50	80	24	9	45
16	0.99	Reflux	Ch	2.50	80	24	12	41
17	1.00	Ag ₂ O	Et ₂ O	10	25	24	0	61
18		Vapour phase pyrolysis			465		21	<i>a</i>

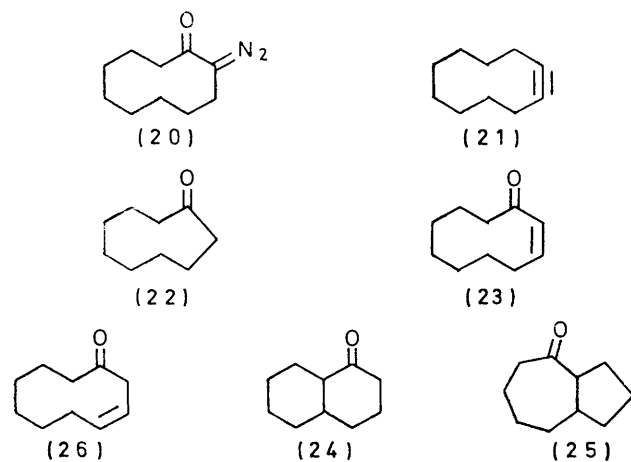
* Not estimated.

* See Table 1.

involving a non-concerted nitrogen loss to give a free oxocarbene intermediate which is in rapid equilibrium with the oxiren intermediate. Alternatively, in all cases a free oxocarbene is produced in which there is a significant activation energy difference between hydrogen migration and oxiren formation such that higher energy conditions favour the latter process. Our results do not distinguish between these two possibilities although it is interesting that an increased dielectric

amount of the concerted nitrogen loss-hydrogen migration leading to the enone (23), whereas, for the oxidation of the acetylene (21) an oxocarbene (or oxiren) is formed, which principally reacts by transannular carbon-hydrogen insertion reactions to give mainly the bicyclic ketones (24) and (25). In view of our previous results this leads to the prediction that photolysis of the diazo-ketone (20) should result in a greatly increased amount of the insertion products (24) and (25) compared to that obtained from the thermal decomposition. This prediction was substantiated by the appropriate experiments (Table 3). The products from the reactions were initially identified by their g.l.c.-mass spectral properties and relative yields were estimated from g.l.c. peak areas. Photolysis of a pure sample of the cyclodecenone (23) afforded a large amount of the deconjugated isomers (26).²⁸

Photolysis of the diazo-ketone (20) produces a considerable increase in the ratio between the bicyclic ketones (24) and (25) and the cyclodecenones (23) and (26), although the ratio is still below that obtained in the peroxy-acid oxidation of cyclodecyne. Comparison of the results of the photolyses in different solvents indicates a strong dependence on the polarity of the medium, and that the trend is opposite to that observed in the photolysis of the acyclic diazo-ketone (14) (see Table 2). This difference probably reflects the importance of conformational effects in determining the reaction course, a possibility which Ciabattoni also recognized.²⁵ A comparison of the direct photolysis with the sensitized decomposition of the diazo-ketone (20) was also informative. Padwa and Leyton²⁹ have pointed out that triplet-state oxocarbenes are very good hydrogen abstractors.



constant favours both an increased rate of nitrogen loss²⁶ and formation of oxiren intermediates (see Table 2), which supports the former explanation, *i.e.* the presence of two competing processes.

Recently Ciabattoni *et al.*²⁷ have compared the thermal decomposition of 2-diazocyclodecanone (20) with the peroxy-acid oxidation of cyclodecyne (21). Both re-

²⁶ W. Jugelt and D. Schmidt, *Tetrahedron*, 1969, **25**, 969.

²⁷ R. A. Campbell, J. Ciabattoni, P. W. Concannon, and C. A. Renner, *J. Amer. Chem. Soc.*, 1970, **92**, 3826.

²⁸ R. G. Carlson and J. H. Bateman, *Tetrahedron Letters*, 1967, 4151.

²⁹ A. Padwa and R. Layton, *Tetrahedron Letters*, 1965, 2167.

TABLE 3
 Decompositions of 2-diazocyclodecanone

Expt. no.	Conditions	Solvent *	Temp. (°C)	Time (h)	Ratio (%) ^a			Ratio (%) ^b		Cyclodecenone products
					(22)	(23) + (26)	(24) + (25)	(24) + (25)	(23) + (26)	
19	Reflux	PhH	80	15	38	53	9	14	86	(23) only
20		Ag ₂ O	25	24	1	93	6	6	94	(23) only
21		Ag ₂ O	25	24	Trace	95	5	5	95	(23) only
22		Cu ₂ O	80	1	57	26	17	39	61	(23) only
23	<i>hν</i>	Ch	25	1	40	39	21	36	64	(23) : (26) = 19 : 81
24	<i>hν</i>	Et ₂ O	25	1	60	27	13	33	67	Mainly (26)
25	<i>hν</i>	w-D (1 : 4)	25	1	3	70	26	27	73	Mainly (26)
26	Vapour-phase pyrolysis		500		0	62	38	38	62	

^a (22) + (23) + (24) + (25) + (26) assumed to equal 100%. ^b (23) + (24) + (25) + (26) assumed to equal 100%.

* See Table 1.

Furthermore, since 1,2-migrations are inhibited in the triplet state the sensitized photolysis should give mainly the bicyclic ketones (24) and (25), as was found. No trace of cyclononanone (22), produced from the keten as a result of the Wolff rearrangement, was observed, indicating the inhibition of this reaction under the photosensitization conditions.

EXPERIMENTAL

I.r. spectra were recorded with a Unicam SP 200 spectrometer and u.v. spectra with a Unicam SP 800 spectrometer for ethanolic solutions. Mass spectra were determined with an A.E.I. MS9 machine. G.l.c. analyses were routinely carried out with a Perkin-Elmer F11 gas chromatograph and the following columns: 2 m 15—85 PEGS on Chromosorb P (o.d. $\frac{1}{8}$ in); 2 m 15—85 Carbowax on Chromosorb W (o.d. $\frac{1}{8}$ in); and 4 m 2.5 : 97.5 Silicone gum on AW DMCS on Chromosorb G (o.d. $\frac{1}{8}$ in). Combined g.l.c.—mass spectral analyses were performed with a Perkin-Elmer 270 mass spectrometer and one of the foregoing columns. Absolute yields of products were determined by calibration of the g.l.c. system with an internal reference, generally *o*-methyl-anisole, and comparison of the peak areas with calibration graphs constructed by use of pure enones. Unless otherwise stated, all photolyses were carried out with a Pyrex filter and a 450 W medium-pressure mercury lamp. Solutions were degassed with dry, oxygen-free nitrogen for 10 min or more before photolyses. ¹H N.m.r. spectra were generally determined with a Varian A60 or T60 spectrometer, with deuteriochloroform as solvent and tetramethylsilane as internal reference.

3-Diazoheptane-4-one (2).—This was prepared according to the method of Regitz and Menz,⁹ and had ν_{\max} (film) 2070 and 1640 cm⁻¹ (lit.,⁹ 2075 cm⁻¹); τ 7.60 (4H, m), 8.3 (2H, m), 8.9 (3H, t, *J* 7 Hz), and 9.05 (3H, t, *J* 7 Hz).

cis-(11) and trans-Hept-2-en-4-one (10).—3-Diazoheptan-4-one (0.31 g) in dioxan (5 ml) was stirred with a suspension of silver oxide (20 mg) in water (1 ml) at room temperature for 3 h. Combined g.l.c.—mass spectral analysis on the PEGS column showed the formation of four products with *cis*-hept-2-en-4-one (11) (30%) and the *trans*-isomer (10) (33%) as major products together with traces of heptan-4-one (1%) and heptane-3,4-dione (2%). Carrying out the reaction on a larger scale in ether followed by preparative g.l.c. (15% E30 on diatomite C) gave authentic samples of the *cis*- and *trans*-enones. The latter isomer³⁰ had ν_{\max} .

³⁰ R. Heilmann, G. de Gaudemar, and P. Arnaud, *Compt. rend.*, 1955, **240**, 1542.

(CHCl₃) 1690s and 1625m cm⁻¹, τ 9.1 (3H, t, *J* 7 Hz), 8.4 (2H, m), 8.1 (3H, dd, *J* 1.5 and 6 Hz), 7.6 (2H, t, *J* 7 Hz), 4.0 (1H, dq, *J* 1.5 and 16 Hz), and 3.3 (1H, dq, *J* 6 and 16 Hz); *m/e* 112 (*M*⁺, 2%), 97 (20), 83 (8), 71 (5), 69 (100), 55 (5), 43 (15), 41 (45), and 39 (20). *cis*-Hept-2-en-4-one showed ν_{\max} (CHCl₃) 1690sh, 1665s, 1635s, and 985s cm⁻¹, τ 9.1 (3H, m), 8.4 (2H, m), 8.0 (3H, m), 7.6 (2H, m), and 3.9 (2H, m) (irradiation at τ 3.9 caused collapse of the multiplet at 8.0 to a singlet; INDOR experiments showed that the multiplets at τ 9.1, 8.4, and 7.6 were due to the propyl group); *m/e* 112 (*M*⁺, 15%), 97 (8), 83 (5), 71 (5), 69 (100), 55 (5), 43 (15), 41 (45), and 39 (20).

trans-Hept-4-en-3-one (6).—Ethyl methyl ketone (21.6 g) in anhydrous ether (50 ml) was added to a suspension of freshly prepared sodamide [from sodium (15.2 g)] in anhydrous ether (300 ml) over 10 min. The mixture was heated under reflux for 5 min, then ethyl propionate (61.2 g) in anhydrous ether (50 ml) was added. The mixture was heated, with stirring, under reflux for a further 2 h, poured on to ice-water (300 ml), acidified, and extracted with ether. The extract was evaporated to afford a brown oil (60 g), which was dissolved in hot methanol (75 ml) and added to copper acetate (40 g) in water (350 ml). After cooling, the blue precipitate was collected, washed with light petroleum (100 ml) and dried *in vacuo* to give dipropionylmethanato-copper(II) (25 g, 52%), m.p. (from ethanol) 209° (subl.) (lit.,³¹ m.p. 209—210°). The copper complex (20 g) was shaken with dil. sulphuric acid (400 ml) and ether (200 ml) and the ether solution was dried (Na₂SO₄) and evaporated to give, after distillation, dipropionylmethane (12.4 g, 77%), b.p. 78—80° at 30 mmHg, n_D^{23} 1.4563 (lit.,³⁰ b.p. 78—80° at 30 mmHg).

To a suspension of lithium aluminium hydride in anhydrous ether (75 ml) was added a solution of dipropionylmethane (100 g) in ether (25 ml) during 1 h at room temperature. The mixture was heated under reflux for a further 1 h to give, after work-up, hept-4-en-3-ol (6.75 g, 76%), b.p. 76—77° at 30 mmHg, n_D^{24} 1.4355. Oxidation of the allylic alcohol (3.43 g) in ether (100 ml) with manganese dioxide at room temperature for 24 h gave, after work-up, pure *trans*-hept-4-en-3-one (6)¹¹ (1.65 g, 50%), b.p. 56—59° at 30 mmHg, ν_{\max} (film) 1690s and 1635s cm⁻¹, τ 8.9 (6H, m), 7.6 (4H, m), 3.9 (1H, broadened, *J* 16 Hz), and 3.1 (1H, m); *m/e* 112 (*M*⁺, 15%), 83 (100), 69 (10), 55 (50), 43 (10), 41 (10), and 39 (15).

Photolysis of a sample of the *trans*-hept-4-en-3-one, under standard conditions, gave a rapid photoequilibration with

³¹ J. T. Adams and C. R. Hauser, *J. Amer. Chem. Soc.*, 1944, **66**, 1220.

the corresponding *cis*-isomer (7). The latter showed *m/e* 112 (M^+ , 35%), 83 (100), 57 (20), 55 (50), 43 (20), 41 (10), and 39 (15).

Hept-1-en-4-one.¹²—A sample was prepared by reaction of diallylcadmium with butanoyl chloride. The product was unstable and readily isomerized to *trans*-hept-2-en-4-one (10).

Decomposition of 3-Diazoheptan-4-one (2).—(a) *Photolysis*. The ketone (0.30 g) in anhydrous ether (40 ml) was photolysed for 90 min, the reaction being followed by observing the disappearance of the i.r. band at 2070 cm^{-1} . *o*-Methylanisole (0.300 g) was added as an internal reference and the solution was concentrated by removal of the excess of ether at room temperature. Products were analysed in the first instance by g.l.c.-mass spectrometry (both PEGS and Silicone gum columns). Products were hexan-3-one, *m/e* 100 (M^+), 71, 57, and 43, identical with an authentic sample; heptane-3,4-dione (5), *m/e* 128 (M^+), 71, 57, and 43 [the bis-2,4-dinitrophenylhydrazone of this diketone was isolated by preparative t.l.c. from the crude reaction mixture; m.p. 263–264° (lit.,³² m.p. 264°), the brick-red solid went purple on treatment with alcoholic KOH]; hept-2-en-4-ones (10) and (11), identical in their g.l.c.-mass spectral behaviour with authentic samples; hept-5-en-3-ones (8) and (9), as a mixture, *m/e* 112 (M^+ , 15%), 83 (5), 69 (10), 57 (100), 55 (30), 43 (15), 41 (10), and 39 (15), also identical with a minor fraction obtained by photolysis of *trans*-hept-4-en-3-one; and heptan-4-one, identical with an authentic sample. Yields are tabulated (Scheme 2 and Table 1).

(b) *Thermal*. These were carried out in an inert solvent, and vapour-phase pyrolyses were carried out in the injection port of the F11 analytical g.l.c. instrument by varying the inlet temperature and maintaining the column temperature constant (90°); both PEGS and silicone gum columns were used for analyses. Results for the PEGS column are given in the Figure.

1-Diazoheptan-2-one ³³ (12).—*n*-Hexanoyl chloride (2.80 g) in anhydrous ether (25 ml) was added dropwise to a solution of diazomethane (ca. 0.1M) in ether (100 ml) at 0°. Evaporation afforded the diazo-ketone as a yellow oil (2.9 g), ν_{max} 3100m, 2150s, and 1640s cm^{-1} , τ 9.1–8.7 (9H, m), 7.6 (2H, m), and 4.7 (1H, s). Photolysis of the diazo-ketone under standard conditions in ether (40 ml) for 60 min was followed by addition of *o*-methylanisole (0.051 g), evaporation to small bulk, and g.l.c.-mass spectral analysis on the PEGS and silicone gum columns. This showed the presence of hept-2-enal (4%), identical with an authentic sample;²⁴ ν_{max} 2705w, 1690s, and 1640m cm^{-1} ; 2,4-dinitrophenylhydrazones, m.p. 130° (lit.,²⁴ 131–132°). A small amount of heptan-2-one was also detected from the photolysis, *m/e* 114 (M^+), 99, 85, 71, 68, and 43.

Photolyses of 1-Diazo-3-phenylpropan-2-one (13).—The diazo-ketone (2.0 g), m.p. 46–47° (lit.,³⁴ 48–49°) was irradiated in 1 : 9 water-dioxan (40 ml) for 3 h. Extraction of the mixture, diluted with ether, with 10% (w/v) aqueous sodium carbonate solution (3 × 25 ml) and acidification of the latter gave 3-phenylpropionic acid (1.43 g 76%) as a low-melting solid, τ 7.2 (4H, m), 2.80 (5H, m), and -0.2 (1H, s). G.l.c. analysis of the neutral fraction from the ether extract confirmed the presence of cinnamaldehyde

(ca. 3%), identical with an authentic sample (g.l.c.-mass spectral analyses and preparation of its 2,4-dinitrophenylhydrazone). A pyrolysis, in refluxing cyclohexane, of the diazo-ketone (13) only gave traces of cinnamaldehyde.

4-Diazo-2,2-dimethylhexan-3-one (14).—Pivaloyl chloride (4.82 g) in anhydrous ether (25 ml) was added dropwise, during 1 h with stirring, to a solution of diazopropane (0.086M) and triethylamine (0.08M) in ether (600 ml) at -20°. After a further 3 h the solution was warmed to room temperature, washed with water, sodium carbonate solution, and finally water. The dried (Na_2SO_4) solution was evaporated to give a pale orange oil. Preparative t.l.c. (silica gel G; 1 : 9 acetone-light petroleum) gave the *diazoketone* (3.08 g, 50%), ν_{max} (film) 2100s and 1635s cm^{-1} , τ 8.8 (3H, t, J 8 Hz), 8.7 (9H, s), and 7.6 (2H, q, J 8 Hz) (Found: C, 62.6; H, 9.1; N, 17.8. $\text{C}_8\text{H}_{14}\text{N}_2\text{O}$ requires C, 62.3; H, 9.1; N, 18.2%).

2,3-Dimethylhex-2-en-4-one (17).—Propionyl chloride (18.5 g) and 2-methylbut-2-ene (21.0 g) were slowly treated with tin(IV) chloride (2.5 g) with cooling to 0°. The mixture was then allowed to warm to room temperature, left for 10 min, and treated with dilute hydrochloric acid (4N; 100 ml). The organic phase was re-washed with acid, then water, dried (Na_2SO_4), and distilled to give 2,3-dimethylhex-1-en-4-one ³⁵ (3.9 g, 15%), b.p. 80–90° at 50 mmHg. The residue, which was mainly 2-chloro-2,3-dimethylhexan-3-one (30 g) was treated with potassium hydroxide (25 g) in ethanol (250 ml). The mixture was left at room temperature for 15 min before extraction with water and ether. The organic extract was washed with water before drying (Na_2SO_4) and removal of ether. Distillation afforded 2,3-dimethylhex-2-en-4-one (12 g), b.p. 161–165° at 770 mmHg, ν_{max} 1690, 1620, and 980 cm^{-1} , characterized as its *semicarbazone*, m.p. (from ethanol) 189–190°, ν_{max} 3400, 3300, 1685, and 1630 cm^{-1} , τ 9.0 (3H, t, J 8 Hz), 8.3br (9H, s), 7.70 (2H, q, J 8 Hz), 4.40br (2H, s), and 2.0br (1H, s), *m/e* 183 (M^+) (Found: C, 58.65; H, 9.5; N, 23.2. $\text{C}_9\text{H}_{17}\text{N}_3\text{O}$ requires C, 58.95; H, 9.4; N, 22.9%).

Photolysis of 4-Diazo-2,2-dimethylhexan-3-one (14).—The photolyses (Table 2) were carried out by the standard procedure, the product being washed with aqueous sodium carbonate solution and water before drying (Na_2SO_4) and careful evaporation to small bulk. G.l.c.-mass spectral analysis of the photolyses showed the presence of three main products, identified by comparison with authentic samples. One of these was 2,3-dimethylhex-2-en-4-one (17), *m/e* 126 (M^+ , 20%), 97 (73), 69 (100), 57 (15), and 41 (90). The two other major components were identical with the *cis*- and *trans*-2,2-dimethylhex-4-en-3-ones produced in the silver oxide-catalysed decomposition of the starting material.

Photolysis of 2-Diazocyclodecanone.³⁶—2-Diazocyclodecanone (70) (0.14 g) (m.p. 56–57°; lit.,^{36a} 56–57°), prepared by the method of Regitz and Rüter,^{36b} in anhydrous ether (40 ml) was photolysed under the standard conditions. After evaporation to small bulk, g.l.c. on the Carbowax and PEGS columns and g.l.c.-mass spectroscopy on the Carbowax column, showed the presence of cyclononane, cyclodec-3-enone, and a mixture of two bicyclic ketones. Relative yields were estimated from the appropriate peak areas.

Cyclodec-2-enone (23).—2-Diazocyclodecanone (0.27 g)

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³⁴ L. Canonica and A. M. Moderna, *Gazzetta*, 1950, **80**, 412.

and silver oxide (0.25 g) in dry ether (20 ml) were stirred together in the dark for 24 h before filtration and evaporation. The residue was chromatographed (silica; 1:9 acetone–light petroleum) to give cyclodec-2-enone³⁷ (0.18 g, 79%), ν_{\max} 1690s and 1635m cm^{-1} , τ 8.7 (8H, m), 8.1 (2H, m), 7.6 (4H, m), 4.30 (1H, dt, J 8 and 12 Hz), and 3.60 (1H, d, J 12 Hz), m/e 152 (M^+ , 6%), 133 (9), 125 (7), 109 (18), 98 (52), 97 (14), 95 (36), 82 (41), 81 (100), 68 (63), 67 (29), 55 (46), 54 (21), 53 (23), 41 (44), and 39 (31).

Cyclodec-3-en-1-one (26).—The enone (23) (0.17 g) in dry ether (40 ml) was photolysed for 75 min under the standard conditions. Evaporation gave an oil which was purified

by preparative t.l.c. to give the cyclodec-3-enone³⁸ (0.14 g), ν_{\max} 1700s and 1635w cm^{-1} , τ 9.0–7.1 (12H, m), 6.8 (2H, m), and 4.3 (2H, m) (irradiation at τ 6.8 caused the multiplet at 4.3 to simplify), m/e 152 (M^+ , 28%), 109 (21), 98 (74), 95 (26), 84 (23), 83 (21), 81 (33), 79 (16), 70 (17), 68 (26), 67 (60), 56 (67), 55 (100), 54 (18), 45 (15), 42 (20), 41 (65), and 39 (38).

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³⁷ R. G. Carlson and J. H. Bateman, *J. Org. Chem.*, 1967, **32**, 1608.