

Metal-catalysed Oxidation of Acetylenes and Diazo-ketones

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The molybdenum-catalysed oxidation of acetylenes and the metal-catalysed decompositions and oxidations of α -diazo-ketones appear to proceed *via* transient metal-oxocarbene complexes. The formation of oxirens as intermediates in these reactions is excluded. The initial product from these oxidations is the corresponding α -diketone.

It has been demonstrated recently that the thermal and photochemical decomposition of certain aliphatic diazo-ketones can proceed *via* an oxocarbene, which can equilibrate *via* oxiren species, as indicated by a net 1,2-oxygen migration.¹⁻³ The effect of metal salts on the decomposition of α -diazo-ketones has mainly been limited to studies with copper and silver catalysts.^{4,5} It has been found that these metals completely inhibit oxiren participation;¹ there are two possible explanations for this effect. It could be that a triplet oxocarbene species is formed by metal-promoted spin inversion from the initially produced singlet species. However, this is probably not responsible for the quenching of the oxygen-migrating step in the presence of silver or copper since studies on the photodecomposition of α -diazo-ketones in the presence of triplet sensitizers, such as benzophenone, afforded completely different products, resulting, for example, from hydrogen abstraction.⁶ An alternative explanation is that metal-oxocarbene complexes are involved in these decompositions. Evidence in support of this is that the rate of decomposition of diazo-ketones is enhanced by the presence of metal salts;^{4,5,7} this suggests a more intimate involvement of the metal ion than in simply spin-inverting an intermediate oxocar-

bene. Furthermore, evidence for the intermediacy of a metal-carbene-olefin complex has recently been obtained⁸ from the copper-catalysed decomposition of ethyl diazoacetate during its addition to olefins to produce cyclopropanes.

Although both silver and copper inhibit the formation of oxiren intermediates from oxocarbenes, it remained to investigate the effects of other metals. Oxirens, as members of the general class of 3-heteracyclopropenes, are 4 π -electron antiaromatic systems potentially capable of stabilisation by complexation to suitable transition metals. Typical examples of this effect are the well known stability of the tricarbonyliron-cyclobutadiene complex⁹ and the recent observations¹⁰ that decomposition of diaryl-thiadiazoles and -selenadiazoles in the presence of enneacarbonyliron(0) leads to the formation of heteracyclopropene intermediates. The generation of oxocarbenes in the presence of certain transition metal compounds was therefore undertaken in order to investigate the possibility of metal-oxiren complex formation.

Reaction of 3-diazoheptan-4-one with enneacarbonyliron(0) in anhydrous tetrahydrofuran gave the isomeric hept-2-en-4-ones as the major product (28%).

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² M. Kolshorn, H. Meier, E. Müller, and K. P. Zeller, *Chem. Ber.*, 1972, **105**, 1875.

³ J. Fenwick, G. Frater, K. Ogi, and O. P. Strausz, *J. Amer. Chem. Soc.*, 1973, **95**, 124.

⁴ P. Yates, *J. Amer. Chem. Soc.*, 1952, **74**, 5376; J. Ficini and G. Stork, *ibid.*, 1961, **83**, 4678.

⁵ V. Franzen, *Annalen*, 1957, **602**, 199.

⁶ A. Padwa and R. Leyton, *Tetrahedron Letters*, 1965, 2167.

⁷ C. Grundmann, *Annalen*, 1938, **536**, 29.

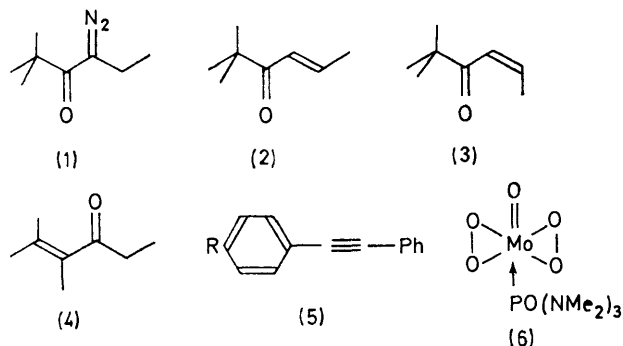
⁸ W. R. Moser, *J. Amer. Chem. Soc.*, 1969, **91**, 1135.

⁹ F. G. A. Stone, *Nature*, 1971, **232**, 534.

¹⁰ P. G. Mente and C. W. Rees, *J.C.S. Chem. Comm.*, 1972, 418.

Strikingly, the predominant isomer was the *cis*-enone (*cis-trans* ratio 4:1), which immediately indicated an iron-substrate complex as an intermediate. No products arising from migration of the oxygen atom (*e.g.* hept-4-en-3-one) were detected, which indicates an absence of oxiren participation in this case.¹ A similar decomposition of 2-diazo-2-phenylacetophenone in refluxing tetrahydrofuran catalysed a rapid decomposition of the substrate but no metal complex could be isolated and this reaction was not studied further.

A similar result was obtained with the decomposition of 3-diazoheptan-4-one in the presence of hexacarbonylmolybdenum in refluxing benzene; only a mixture of *cis*- and *trans*-hept-2-en-4-ones was obtained. The decomposition was faster in the presence of the hexacarbonylmolybdenum than in its absence. A final experiment with 4-diazo-2,2-dimethylhexan-3-one (1) and hexacarbonylmolybdenum gave only the unsaturated ketones (2) and (3), with complete absence of the oxiren-derived product (4); in the absence of the metal complex the ketone (4) was produced.¹



Oxidation of acetylenes by peroxy-acids has also been postulated to proceed *via* oxirens,^{11,12} or by direct formation of the more stable oxocarbenes.¹³ Final products from these oxidations include Wolff rearrangement products^{11,12} and, from dec-5-yne, unsaturated ketones.¹⁴ Relatively little work on the oxidation of acetylenes with metal oxidants has been recorded. Khan and Newman found that aqueous potassium permanganate solution converts acetylenes into α -diketones,¹⁵ and similar results have been reported for the action of thallium trinitrate¹⁶ and ruthenium tetraoxide¹⁷ on acetylenes.

Treatment of diphenylacetylene (5; R = H) with an excess of *t*-butyl hydroperoxide and a catalytic amount of hexacarbonylmolybdenum, a reagent known to effect the smooth transformation of olefins into epoxides,¹⁸ resulted in formation of benzil and a mixture of the benzoic acid derivatives indicated (Table). Treatment of benzil

under the same oxidising conditions produced a similar mixture of oxidation products (Table), confirming that benzil was the primary product. This was further substantiated by the reaction of diphenylacetylene with the molybdenum peroxy-complex (6),¹⁹ which gave a low yield of benzil as the only detectable product. None of the products of these oxidations (Table) had the Wolff-rearranged diphenylacetic acid structure, in contrast to the results observed for the peroxy-acid oxidation of diphenylacetylene.^{11,12} The lack of any tendency to

Products (%) of oxidations with molybdenum systems^a

Product	Substrate					
	(5; R = H)		PhCO-COPh		PhCO-PhCN ₂	
	A	B	A	B	A	B
Benzil	35	5	42	100	37	79
<i>t</i> -Butyl benzoate ^b	6 (1) ^c	0	11 (1) ^c	0	3	0
<i>t</i> -Butyl perbenzoate ^b	11 (1.8) ^c	0	20 (1.8) ^c	0	9	0
Benzoic acid ^b	31 (5.2) ^c	0	64 (5.7) ^c	0	19	0
Recovered starting material	41	92			0	0
Total material recovered	91	97	89	100	(37) ^d	(79) ^d

^a For reaction conditions see Experimental section; A, with *t*-butyl hydroperoxide and Mo(CO)₆; B, with the complex (6).
^b Two equiv. possible from starting material. ^c Amount of product relative to *t*-butyl benzoate. ^d Other products were not investigated. % Benzil quoted.

rearrange was also found for 1-(4-methoxyphenyl)-2-phenylacetylene (5; R = MeO), in which any predisposition for aryl migration would be enhanced by the presence of the methoxy-substituent. Treatment of this acetylene with the complex (6) gave 4-methoxybenzil as the only product. Use of *t*-butyl hydroperoxide and catalytic amounts of hexacarbonylmolybdenum also gave 4-methoxybenzil, as well as a complex mixture of oxidation products derived from the benzil. A careful examination of these products revealed no trace of aryl-migrated derivatives.

The failure to observe Wolff rearrangements in these oxidations, in contrast to the peroxy-acid oxidations, implicated the intermediacy of molybdenum-oxocarbene complexes. In support of this postulate, it was found that treatment of 2-diazo-2-phenylacetophenone with the molybdenum complex (6) afforded a high yield of benzil together with traces of benzoic acid. Reaction with *t*-butyl hydroperoxide and hexacarbonylmolybdenum gave, in 66% yield, a mixture of benzil, benzoic acid, and *t*-butyl benzoate and perbenzoate. Furthermore, the reaction of 3-diazoheptan-4-one with the molybdenum complex (6) gave mainly heptane-3,4-dione, accompanied by a mixture of *cis*- and *trans*-hept-2-en-4-ones (ratio 55:45). No trace of hepten-3-ones was detected.

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¹⁷ H. Gopal and A. J. Gordon, *Tetrahedron Letters*, 1971, 2941.

¹¹ A. N. McDonald and P. A. Schwab, *J. Amer. Chem. Soc.*, 1964, **86**, 4866.

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¹⁴ V. Franzen, *Chem. Ber.*, 1954, **87**, 1478.

¹⁵ N. A. Khan and M. S. Newman, *J. Org. Chem.*, 1952, **17**, 1063.

¹⁸ M. N. Sheng and J. G. Zajacek, A.C.S. Advances in Chemistry Series, 1968, vol. 76, p. 418; G. R. Howe and R. R. Hiatt, *J. Org. Chem.*, 1971, **36**, 2493; T. N. Baker, G. J. Mains, M. N. Sheng, and J. G. Zajacek, *ibid.*, 1973, **38**, 1145; J. Kaloustian, L. Lena, and J. Metzger, *Bull. Soc. chim. France*, 1971, 4415.

¹⁹ H. Mimoun, I. S. de Roch, and L. Sajus, *Tetrahedron*, 1970, **26**, 37.

To summarise, it appears that both the molybdenum-catalysed oxidations and decompositions of diazo-ketones and the catalysed oxidations of acetylenes proceed *via* the initial formation of molybdenum-oxocarbene complexes. It is well known that carbenes form complexes with the Group VI metals,²⁰ but so far it has not been possible to isolate the intermediate oxocarbene complexes. In all cases the formation of complexed oxiren intermediates can be ruled out, in contrast to the results obtained for thiirens and selenirens.

EXPERIMENTAL

M.p.s were determined on a Kofler hot-stage apparatus. I.r. spectra were recorded on a Unicam SP 200 spectrometer either for films or for Nujol mulls; u.v. spectra were obtained on a Unicam SP 800 instrument with ethanol as solvent. ¹H N.m.r. spectra were recorded on a Varian A60 instrument with deuteriochloroform as solvent and tetramethylsilane as internal reference. G.l.c. analyses were carried out as described previously.¹ Peak areas were used to estimate yields, by comparison with calibration graphs for the pure compounds.

Decomposition of 3-Diazoheptan-4-one.—(a) *With enneacarbonyldi-iron.* To the diazo-ketone¹ (0.141 g) in anhydrous tetrahydrofuran (2.5 ml) enneacarbonyldi-iron (0.267 g, 1.5 equiv.) was added, and the mixture was stirred in the dark at room temperature for 48 h to give a viscous solution. *o*-Methylanisole was added as an internal g.l.c. standard and the mixture was then examined by g.l.c. and g.l.c.–mass spectral analysis. The only identifiable products were *cis*- and *trans*-hept-2-en-4-ones (ratio *cis*–*trans* 82 : 18).

(b) *With hexacarbonylmolybdenum.* The diazo-ketone (0.100 g) and hexacarbonylmolybdenum (0.101 g, 0.4 equiv.) in benzene (2 ml) were refluxed with stirring for 4 h. G.l.c. analysis showed that only *cis*- and *trans*-hept-2-en-4-ones were formed.

Decomposition of 4-Diazo-2,2-dimethylhexan-3-one.—The

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diazo-ketone¹ (0.101 g) and hexacarbonylmolybdenum (0.096 g, 0.5 equiv.) in dry benzene (3 ml) were refluxed and stirred together for 2 h. G.l.c. and g.l.c.–mass spectral analysis showed that only *cis*- and *trans*-2,2-dimethylhex-4-en-3-ones were formed (49%).

A similar decomposition of 2-diazo-2-phenylacetophenone with the iron complex in refluxing tetrahydrofuran was rapid but no clean products were isolated, so this reaction was not studied further.

Oxidations of Diphenylacetylene and 2-Diazo-2-phenylacetophenone.—Oxidations were carried out on a 0.001 mol scale; the results are in the Table. Oxidations with hexamethylphosphoramide-oxidiperoxomolybdenum(vi) (6)¹⁹ were carried out in dichloromethane (5 ml) at room temperature for periods of 3 days. The products were recovered by preparative t.l.c. (silica gel G). The oxidations with *t*-butyl hydroperoxide were carried out on a 0.001 mol scale with hexacarbonyl molybdenum as catalyst (20 mg) and an excess (1.0–1.5 ml) of *t*-butyl hydroperoxide. The mixture was heated in refluxing benzene (2.5 ml) for 5 h before isolation of the products by preparative t.l.c. The products had the following properties: benzil, m.p. 92–94° (lit.,²¹ 95°); benzoic acid, m.p. 122°; *t*-butyl perbenzoate, *M*⁺ 194, *v*_{max} 1755 cm⁻¹, *λ*_{max} 230, 273, and 280sh nm; *t*-butyl benzoate *M*⁺ 178, *v*_{max} 1710 cm⁻¹, identical (i.r. spectrum) with an authentic sample.

*Oxidation of 1-(4-Methoxyphenyl)-2-phenylacetylene*²² (5; R = OMe).—The acetylene (0.208 g) and the molybdenum complex (6) (0.356 g, 1 equiv.) in dichloromethane (5 ml) were stirred at room temperature for 3 days. Preparative t.l.c. gave unchanged acetylene (0.158 g, 79%) and 4-methoxybenzil (0.038 g, 19%), m.p. 58° (lit.,²³ 58°), *v*_{max} 1670 cm⁻¹.

One of us (S. A. M.) thanks the Salters' Company for a scholarship.

[3/1071 Received, 24th May, 1973]

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²³ H. Kwart and M. M. Baevsky, *J. Amer. Chem. Soc.*, 1958, **80**, 580.