

## Ozonation of Allenic Esters

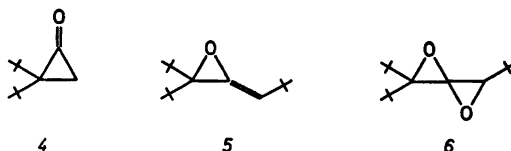
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The reaction between substituted allenic esters and ozone is described. When methyl 2-methyl-4,4-diphenylbutadienoate was ozonized, normal cleavage products, *viz.* carbon monoxide and the proper carbonyl compounds were formed, together with molecular oxygen and a compound having one oxygen atom more than the starting material. This compound was identified as 2,2-diphenyl-5-methoxy-4-methylfuranone. Analogous reactions took place when the parent butadienoic acid was ozonized. Several facts indicate that epoxides are precursors to the furanones. When methyl 2-methyl-4-phenylpentadien-2,3-oate and ethyl 2,4-dimethylpentadien-2,3-oate were ozonized only the expected carbonyl compounds and carbon monoxide were formed.

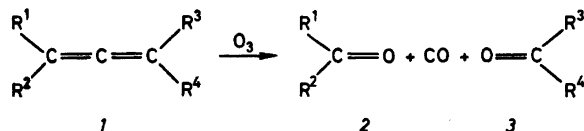
We have earlier reported on the ozonation of allenes *1a–d*.<sup>1</sup> The main products observed were carbonyl compounds *2* and *3* and carbon monoxide (Scheme 1).

Corresponding cleavage products were observed from *1g*, while from the more sterically hindered allenes *1e–f* compounds indicating only partial cleavage of the double bonds were found.<sup>2</sup> Thus *1e* gave the cyclopropanone *4* (27 %) in addition to normal cleavage products and *1f* gave the epoxide *5* and the spirobisepoxide *6* in various proportions depending upon the amount of ozone absorbed.



We now report on the reaction of ozone with some allenes carrying electronegative substituents (*1h–k*). The ozonation experiments were run in either methanol or dichloromethane using nitrogen as carrier gas, and the analytical results were essentially the same in both solvents. Thus if any Criegee-type zwitterion had been formed, it must have rearranged prior to reaction with methanol.<sup>1</sup> The analytical results from the ozonation (obtained as described in the experimental section) are given in Table 1.

The allenes did not react quantitatively with ozone under the experimental conditions used and the exit gases from the reaction of *1h* and *1i* contained both oxygen and carbon monoxide. The presence of the latter together with comparable amounts of the expected carbonyl compounds (benzophenone from both allenes, methyl pyruvate from *1h* and pyruvic acid from *1i*) indicates that normal ozonolysis ex-



Scheme 1. *a*,  $R^1 = \text{Me}$ ,  $R^2 = R^3 = R^4 = \text{H}$ ; *b*,  $R^1 = R^2 = \text{Me}$ ,  $R^3 = R^4 = \text{H}$ ; *c*,  $R^1 = R^2 = R^3 = \text{Me}$ ,  $R^4 = \text{H}$ ; *d*,  $R^1 = R^2 = R^3 = R^4 = \text{Me}$ ; *e*,  $R^1 = R^2 = t\text{-Bu}$ ,  $R^3 = R^4 = \text{H}$ ; *f*,  $R^1 = R^2 = R^3 = t\text{-Bu}$ ,  $R^4 = \text{H}$ ; *g*,  $R^1 = R^2 = t\text{-Bu}$ ,  $R^3 = R^4 = \text{H}$ ; *h*,  $R^1 = R^2 = \phi$ ,  $R^3 = \text{Me}$ ,  $R^4 = \text{CO}_2\text{Me}$ ; *i*,  $R^1 = R^2 = \phi$ ,  $R^3 = \text{Me}$ ,  $R^4 = \text{CO}_2\text{H}$ ; *j*,  $R^1 = \phi$ ,  $R^2 = R^3 = \text{Me}$ ,  $R^4 = \text{CO}_2\text{Me}$ ; *k*,  $R^1 = R^2 = R^3 = \text{Me}$ ,  $R^4 = \text{CO}_2\text{Et}$ .

Table 1. Analytical results from ozonation of allenes *1h-k*.<sup>a</sup>

	O <sub>3</sub> consumed	Allene reacted	O <sub>2</sub>	CO <sup>b</sup>	R <sub>1</sub> >R <sub>2</sub> CO	R <sub>3</sub> >R <sub>4</sub> CO	CO <sub>2</sub>	Active oxygen		Remarks
								with HClO <sub>4</sub>	without HClO <sub>4</sub>	
<i>1h</i>	3.6	3.4	1.5	1.5	1.3	1.3	0	1.5	0.5	<i>9b</i> formed
<i>1i</i>	3.6	3.0	2.0	0.9	1.2	<sup>c</sup>	0.2	1.1	0.1	<i>9a</i> formed
<i>1j</i>	3.9	5.0 <sup>d</sup>	0	3.0	3.3	3.1	0	0.3	0.2	
<i>1k</i>	4.2	4.3	0	2.8	3.0	2.8	0	0.9	0.5	

<sup>a</sup> All yields in mmol. <sup>b</sup> Averaged values from iodine and carbon dioxide estimation (Experimental). <sup>c</sup> Quantitative analyses (GLC) of pyruvic acid not possible under the experimental conditions, but estimation by NMR showed equimolar amounts of pyruvic acid and benzophenone. <sup>d</sup> Some allene polymerized, possibly catalyzed by ozone.

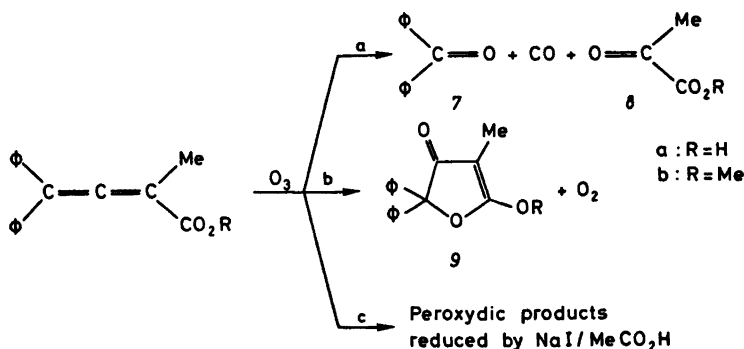
pected for allenes<sup>1</sup> takes place to an extent of 40–45% (Scheme 2, Route a).

The formation of molecular oxygen from ozone reaction with carbon-carbon double bonds is indicative of partial bond cleavage to give epoxides.<sup>3</sup> Contrary to the results from ozonation of the sterically hindered allenic hydrocarbons,<sup>2</sup> such oxides were not the ultimate products in the present work. Instead, tetric acid *9a* and 2,2-diphenyl-5-methoxy-4-methylfuranone *9b* were found as ultimate products from *1i* and *1h*, respectively. The structure of *9a* was proven by syntheses described in the experimental section.<sup>4</sup> Treatment of *9a* with diazomethane gave a mixture of *9b* and 2,2-diphenyl-3-methoxy-4-methylfuranone *10*.<sup>5</sup> Acid hydrolysis of *9b* gave a quantitative yield of *9a*.<sup>6</sup>

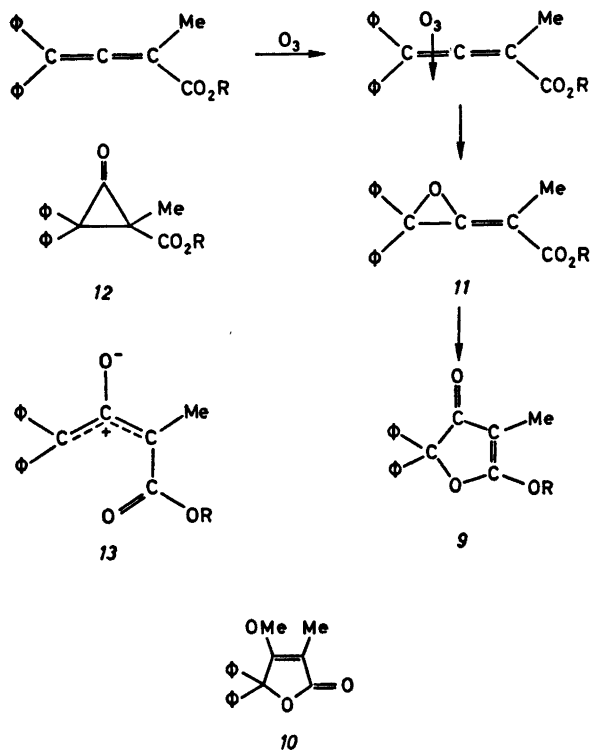
Several experimental facts indicate that the tetric acid *9a* and furanone *9b* are formed during work-up of the ozonation mixture. Firstly, the furanone *9b* reacts quantitatively

and much faster with ozone than does the starting material *1h*. Secondly, the amount of *9b* was reduced and triphenylphosphine oxide was found when triphenylphosphine was added to the cold ozonation solution immediately after excess ozone was purged out with nitrogen. Thirdly, the great difference in iodine formation by using perchloric acid in active oxygen estimation (Table 1) indicates the presence of a precursor to the furanone *9b* able to oxidize iodide in strong acid solution (possibly an epoxide). Furanone *9b* does not react with triphenylphosphine or with iodide in strong acid. Finally, when the allenic acid *1i* was ozonized in dichloromethane the reaction solution was clear and homogeneous as long as it was kept at low temperature. Upon warming up to room temperature *9a* precipitated.

Three different compounds could be regarded as possible precursors to *9a* or *9b*, viz. the epoxide *11*, the cyclopropanone *12* or the oxyallyl species *13* (Scheme 3).



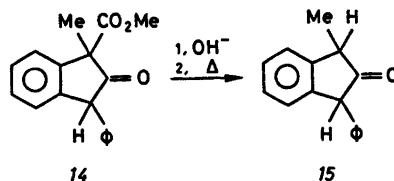
Scheme 2.



Scheme 3.

Bond-additivity schemes indicate that oxyallyl intermediates are from 120 to 200  $\text{kJ mol}^{-1}$  (depending upon substitution) less stable than the corresponding cyclopropanones.<sup>7</sup> Deoxygenation of epoxides by triphenylphosphine is quite common,<sup>8</sup> and it seems reasonable that some epoxides in strong acid solution may be able to oxidize iodide ions. Analogous reactions with cyclopropanones are probably less likely. For these reasons, and also due to analogy with the ozonation of the simple allenes<sup>2</sup> and of the sterically hindered olefines,<sup>3</sup> it seems likely that epoxides are the first formed real products from the ozonation of the allenic compounds *1h* and *1i*. Additional evidence for an epoxide intermediate is obtained by the isolation of reasonable yields of furanone *9b* by reaction of allene *1h* with monopero-phthalic acid.<sup>2</sup> The structural similarity is obvious between epoxide *11* and the bromonium ion suggested to explain the stereospecificity in the formation of bromo-lactones from reaction of allenic acids with bromine.<sup>9</sup>

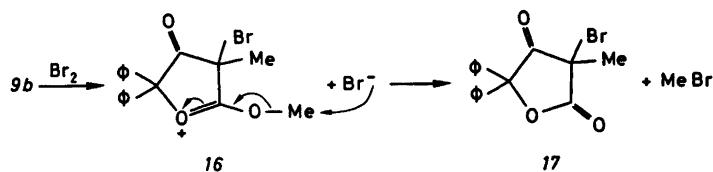
Quantitative analyses of *9b* in the reaction solution presented a problem not surmounted. Qualitative detection could be effected by column chromatography on silica gel. In GLC *9b* underwent rearrangement to indanone *14*, its structure being verified by hydrolysis and decarboxylation to *15* (Scheme 4).



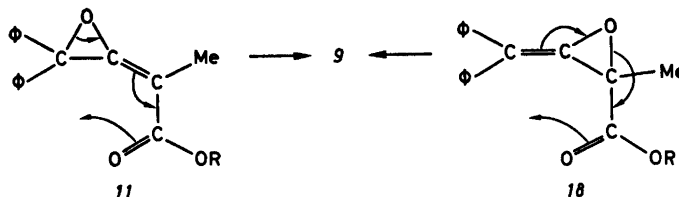
Scheme 4.

Therefore the oxygen analyses have been used as quantitative measure for *9* (Scheme 2, Route b) with systematic errors of about 10%.<sup>10</sup>

An interesting reaction was observed when tetronic ester *9b* was treated with bromine in carbon tetrachloride. The monobromo derivative *17* was formed together with methyl bromide (identified both by GLC and <sup>1</sup>H NMR).



Scheme 5.



Scheme 6.

The reaction may be formulated as an attack of bromine on the carbon atom  $\alpha$  to the carbonyl group forming the intermediate cation 16 which reacts very easily with the bromide nucleophile due to good leaving group ability of 17 (Scheme 5).

The IR spectrum of 17 (KBr) shows two carbonyl absorptions, one at 1800  $\text{cm}^{-1}$  (probably the  $\gamma$ -lactone shifted to higher frequency due to the carbonyl group in  $\beta$ -position) and one at 1760  $\text{cm}^{-1}$  (five-membered cyclic ketone with increased ring strain).<sup>11</sup>

The point and mode of attack of ozone on unsymmetric allenes deserves some comment. In Scheme 2, Route *a* would give the same results whichever double bond is attacked.<sup>1</sup> Reasonable rearrangement paths leading to compounds 9 from both oxide 10 and its analogue 18 could be envisaged (Scheme 6).

Thus, none of the facts produced so far indicate where ozone has attacked. However, some arguments may be presented to support the proposed direction of attack. Epoxides are known to be formed only when sterically hindered double bonds are attacked.<sup>2,3</sup> Consequently molecular oxygen was not a reaction product from ozonation of allenes 1*j* and 1*k* indicating only normal ozonolyses.<sup>1</sup> It may be added that an acidic rearrangement of 3-methoxycarbonyl 1,1-diphenylallene to diphenylcrotonolactone must have been initiated by proton addition to the 1,2-double bond in the allene.<sup>12</sup>

The possibility exists that Routes *a* and *b* are initiated through attack on different

double bonds. Allenes may be regarded as having two separate  $\pi$  systems due to the geometry of the  $\pi$  orbitals being perpendicular to each other. This is well demonstrated by the fact that the first UV absorption bands of tetraphenylallene and of 1,1-diphenylethylene coincide.<sup>13</sup> Thus, mostly inductive effects are operating to mutually influence the electron density of the double bonds. To get a qualitative measure of the relative electron density of the two double bonds, 1,1-diphenylethylene and methyl methacrylate were subjected to competitive ozone attack (see the experimental section) showing that only the former was attacked.

The analogy to olefin ozonation seems even more clear now that epoxides have been detected, either as such<sup>2</sup> or as shown in this work, to be highly probable intermediates rearranging to stable products whose structure are confirmed by synthesis. As allenes most likely behave as two separate olefin systems in electrophilic reactions it seems natural to conclude that they react with ozone in the same manner as olefins, *viz.* through initial  $\pi$  complex formation, rearranging to  $\sigma$  complexes.<sup>14</sup>

## EXPERIMENTAL

*General.* The ozone source was a Welsbach T 23 Ozone Generator giving 0.77–0.80 mmol of O<sub>3</sub>/min. Oxygen analyses were run using a Beckman F3 Oxygen Analyzer as described in the literature.<sup>10</sup>

Gas liquid chromatography (GLC) analyses were performed on Varian Aerograph model

200 and on Hewlett-Packard 5700A. IR spectra were recorded on a Perkin Elmer model 457 spectrophotometer and  $^1\text{H}$  NMR spectra on Varian A60A and Varian HA-100-15D (operating at 98 MHz) spectrometers.

**Materials.** The allenes were synthesized according to literature procedures.<sup>15</sup> Solvents were carefully dried prior to ozonation.

**Ozonation procedure.** In a typical run 10 mmol of the allene was dissolved in dichloromethane (35 ml) and ozonized with 5 mmol of ozone in nitrogen<sup>10</sup> at  $-78^\circ\text{C}$ . The exit gases were analyzed for oxygen<sup>10</sup> and for carbon monoxide.<sup>1</sup> The ozonation solution was diluted to 50 ml and examined for organic products by GLC. Results, see Table 1.

**2,2-Diphenyl-3-hydroxy-4-methylfuranone (9a).**<sup>4</sup> Methyl benzilate, sodium propionate and zinc, 0.1 mol of each, were heated for 5 h in propionic anhydride (200 ml). After cooling, filtering and washing with water the solution was evaporated leaving an oil which readily crystallized and was recrystallized from MeOH, m.p.  $90-91^\circ\text{C}$  (90%). This propionyl derivative (0.1 mol) dissolved in toluene (50 ml) was added dropwise to a dispersion of 15 g of basic aluminium oxide (impregnated with sodium (0.1 mol)) in toluene (200 ml). After 8 h at  $50^\circ\text{C}$  (vibromixer) the solution was cooled, filtered and thoroughly washed with dilute hydrochloric acid. **9a** separated upon partial evaporation of the solvent and was recrystallized from acetonitrile. M.p.  $245-246^\circ\text{C}$ . (10%). Anal.  $\text{C}_{17}\text{H}_{14}\text{O}_3$ : C, H.  $^1\text{H}$  NMR (60 MHz,  $\text{CDCl}_3$ ):  $\delta$  1.80 (3 H, s), 7.2-7.6 (10 H, s). IR (KBr): 2200-3200 (broad), 1720 (s), 1660 (m), 1610 (s).

**2,2-Diphenyl-5-methoxy-4-methylfuranone (9b)** was isolated from the ozonation solution of **1h** by column chromatography on silica gel using dichloromethane as eluting solvent. M.p.  $117^\circ\text{C}$  (heptane). Anal.  $\text{C}_{18}\text{H}_{16}\text{O}_3$ : C, H.  $^1\text{H}$  NMR (60 MHz,  $\text{CDCl}_3$ ):  $\delta$  1.67 (3 H, s), 4.15 (3 H, s) 7.2-7.7 (10 H, m). IR (KBr): 1695 (w), 1600 (s).

**Bromination of 9b.** **9b** (0.5 g) was dissolved in tetrachloromethane (20 ml) and bromine was added at  $-10^\circ\text{C}$ . The methyl bromide evolved was collected and examined by GLC and  $^1\text{H}$  NMR. Evaporation of solvent left **17** as a solid, m.p.  $90-91^\circ\text{C}$  (hexane). Anal.  $\text{C}_{17}\text{H}_{13}\text{BrO}_3$ : C, H, Br.  $^1\text{H}$  NMR (60 MHz,  $\text{CDCl}_3$ ):  $\delta$  1.80 (3 H, s), 7.3-7.4 (10 H, m). IR (KBr): 1800 (s), 1760 (s).

**Competitive ozonation.** 1,1-Diphenylethylene (5 mmol) and methyl methacrylate (5 mmol) were dissolved in dichloromethane and ozone (2.5 mmol) passed into the solution.

**Quantitative absorption.** GLC showed that only 1,1-diphenylethylene had reacted.

2. Crandall, J. K., Conover, W. W., Komin, J. B. and Machleder, W. H. *J. Org. Chem.* **39** (1974) 1723.
3. Bailey, P. S. and Lane, A. G. *J. Am. Chem. Soc.* **92** (1970) 230, and references therein.
4. Haynes, L. J. and Stanners, A. H. *J. Chem. Soc.* (1956) 4103.
5. Pelizzoni, F. and Jommi, G. *Gazz. Chim. Ital.* **89** (1959) 1894.
6. Kende, A. S. *Chem. Ind. London* (1956) 1053.
7. Liebman, J. F. and Greenberg, A. *J. Org. Chem.* **39** (1974) 123.
8. Boskin, M. J. and Denney, D. B. *Chem. Ind. London* (1959) 330; Bissing, D. E. and Speziale, A. J. *J. Am. Chem. Soc.* **87** (1965) 2683.
9. Kresze, G., Klomstein, L. and Runge, W. *Justus Liebigs Ann. Chem.* (1976) 979.
10. Bailey, P. S. and Reader, A. M. *Chem. Ind. London* (1961) 1063.
11. Bellamy, L. J. *The Infrared Spectra of Complex Molecules*, Chapman & Hall, London 1975, pp. 213, 368.
12. Aksnes, G. and Frøyen, P. *Acta Chem. Scand.* **22** (1968) 2347; See also Ref. 9.
13. Fischer, H. In Patai, S., Ed., *The Chemistry of Alkenes*, Interscience, London 1964, p. 1133.
14. Bailey, P. S., Ward, J. W., Hornish, R. E. and Potts, F. E., III. *Adv. Chem. Ser.* **112** (1972) 1.
15. Bestman, H. J. and Hartung, H. *Chem. Ber.* **99** (1966) 1198.

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## REFERENCES

1. Kolsaker, P. and Teige, B. *Acta Chem. Scand.* **24** (1970) 2101.