

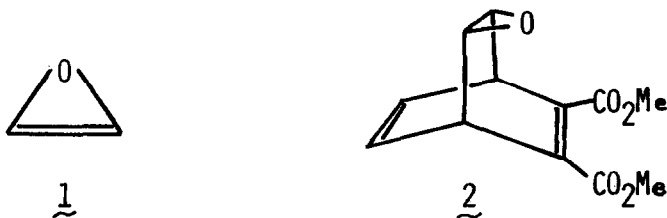
FLASH THERMOLYSIS OF A FORMAL OXIRENE-ARENE ADDUCT

E. Lewars\* and G. Morrison

Department of Chemistry, Trent University,  
Peterborough, Ontario K9J 7B8, Canada

(Received in USA 9 September 1976; received in UK for publication 10 January 1977)

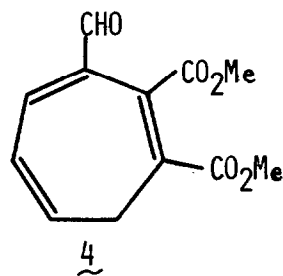
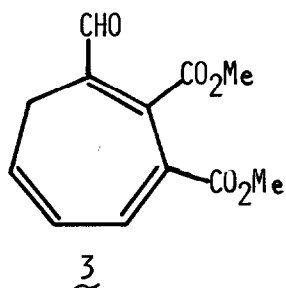
Because of the theoretical and experimental challenge attaching to oxirene (1)<sup>1</sup>, and the success shown by the technique of flash thermolysis in generating hitherto elusive molecules<sup>2</sup>, we subjected the formal oxirene-arene adduct 2<sup>3</sup> to flash thermolysis in the hope of obtaining oxirene. Thermal reverse Diels-Alder fragmentation<sup>4</sup> of 2 to oxirene and dimethyl phthalate is a priori a reasonable possibility, since the transition state for such a process should be favored by the aromaticity of the incipient arene. We have found that while there is



indeed some evidence that fragmentation of 2 to oxirene and dimethyl phthalate occurs, the main reaction pathway is more complex.

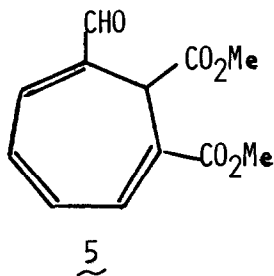
Sublimation of 2 through a quartz tube at 250° and ca. 10<sup>-3</sup> torr led to complete recovery of starting material, but at 300°/10<sup>-3</sup> torr a 65% yield of an aldehyde, m.p. 105-106°, was obtained. This compound, C<sub>12</sub>H<sub>12</sub>O<sub>5</sub><sup>†</sup>, was assigned structure 3 or 4 on the basis of its transformation to a second aldehyde 5 (see below) and the following spectroscopic evidence. The <sup>1</sup>H NMR spectrum showed an

<sup>†</sup> Formula by high-resolution mass spectrometry.



AMX pattern ( $\delta_A 7.50$ ,  $\delta_M 6.52$ ,  $\delta_X 5.97$ ,  $J_{AM} = 5.5$ ,  $J_{MX} = 9$  Hz) with  $H_X$  also coupled to a  $CH_2$  group at 2.67 ( $J = 7$  Hz), revealing a  $C=CH_A-CH_M=CH_X-CH_2$  grouping with  $H_A$  strongly deshielded. In addition, the spectrum displayed a CHO peak ( $\delta 9.48$ , s) and two  $CO_2Me$  methyls (3.77, 6H, giving way to two 3H singlets on addition of  $Eufod_3-d_{27}$  shift reagent). These data are almost uniquely compatible with structures 3 and 4.<sup>5</sup> Consonant with structure 3/4, the UV spectrum revealed extensive unsaturation,  $\lambda_{max}$  (MeOH) 242 nm ( $\epsilon$  15,600), 285 nm ( $\epsilon$  5,000), and the IR spectrum showed  $\lambda_{max}$  (K Br) 5.80 $\mu$  (conjugated ester) and 5.93 $\mu$  (conjugated aldehyde).

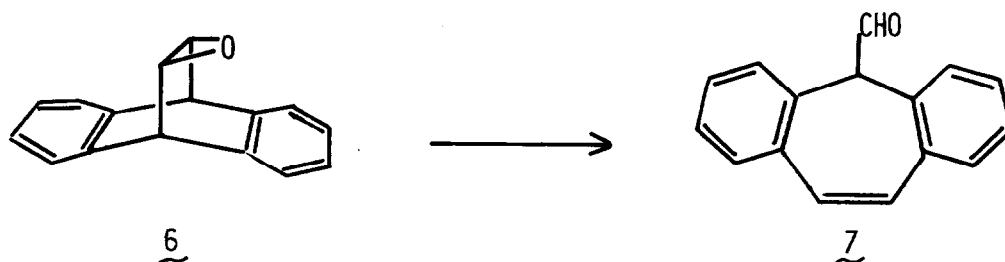
Thermolysis of 3/4 or of 2 at 400 /10<sup>-3</sup> torr gave a 72% yield of a second aldehyde,  $C_{12}H_{12}O_5$ <sup>†</sup>, m.p. 108-110°. The <sup>1</sup>H NMR spectrum of this compound displayed, besides a CHO peak ( $\delta 9.43$ , s) and two  $CO_2Me$  methyls ( $\delta 3.77$ , s and 3.45 s), an olefinic ABCD system ( $\delta 7.50-7.27$ , m, 1H; 7.13-6.93, m, 1H; 6.93-6.67, m, 2H) and a peak at 5.63 (s, 1H). These spectra suggest structure 5 for this second aldehyde, and this is further supported by its IR spectrum,  $\lambda_{max}$  (K Br)



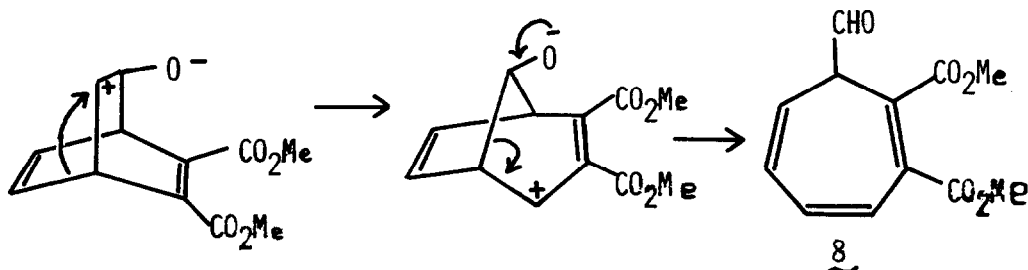
5.76 $\mu$  (saturated ester), 5.86 $\mu$  (conjugated ester), 5.94 $\mu$  (conjugated aldehyde), and the UV spectrum,  $\lambda_{max}$  (MeOH) 228 nm ( $\epsilon$  34,000), 313 nm ( $\epsilon$  6,500)<sup>6</sup>.

It should be pointed out that of the 18 possible bis(carbomethoxy)cycloheptatrienecarboxaldehydes with the carbomethoxy groups on adjacent carbons and the aldehyde group on another carbon, only structures 3 and 4 fit the spectroscopic data for the first (300° thermolysis) aldehyde, and only structure 5 that for the second (400° thermolysis) aldehyde. Further support for a bis(carbomethoxy)cycloheptatriene structure for the second aldehyde was provided by the fact that treatment of 2 with acidic alumina gave 5 in 50% yield. The alumina-catalyzed conversion of a barrellene oxide to a cycloheptatrienecarboxaldehyde finds precedence in the rearrangement of 6 to 7.<sup>7</sup>

<sup>†</sup>Formula by high-resolution mass spectrometry.



The formation of the aldehydes 3 or 4, and 5, can be rationalized in terms of C-O bond cleavage (heterolytic, as shown here, when promoted by alumina, possibly homolytic under flash thermolysis conditions) and Wagner-Meerwein rearrangement to give a bicyclo[3.2.1] system which undergoes another Wagner-Meerwein shift, yielding the cycloheptatrienecarboxaldehyde 8; this could be transformed into 3 or 4, or into 5, by sequential 1,5-sigmatropic shifts of hydrogen (thermolysis)<sup>8</sup> or by alumina-catalyzed double bond isomerization.



The thermolysis was also carried out at higher temperatures in the hope of detecting the desired reverse Diels-Alder reaction. In the range 600-800°, trapping of the thermolyzate at -140° on the sodium chloride disc of an infrared cryostat<sup>9</sup> gave a band at 4.63 $\mu$ , attributable to ketene. The simplest interpretation of this is that oxirene was extruded from 2 and isomerized to ketene<sup>10</sup>, although isomerization of 2 to the bicyclo[2.2.0]octadienone followed by extrusion of ketene cannot be ruled out. At the optimum temperature of ca. 700°, the yield of ketene was estimated from the intensity of the infrared band to be roughly 5%, and vapour phase chromatographic examination of the thermolysate showed a peak, comprising about 3% of the total thermolysate, with a retention time identical to that of dimethyl phthalate. This peak was also included in that portion of the thermolysate which on TLC had the same mobility as dimethyl phthalate, but because of the complexity of the mixture (at least 14 components) a pure sample for comparison with authentic dimethyl phthalate could not be obtained. At 800° the yield of ketene began to fall off, and at 900° there was extensive deposition of carbon in the thermolysis tube, and no ketene was observed.

### Acknowledgements

We thank the National Research Council of Canada and the Trent Research Council for support of this work, and Professor J. F. King of the University of Western Ontario for arranging to have the high-resolution mass spectra taken.

### References

1. (a) R. N. McDonald and P. A. Schwab, J. Amer. Chem. Soc., **86**, 4866 (1964); J. K. Stille and D. D. Whitehurst, ibid., **86**, 4871 (1964); A. Padwa, D. Crumrine, R. Hartman and R. Layton, ibid., **89**, 4435 (1967); J. Fenwick G. Frater, K. Ogi and O. P. Strausz, ibid., **95**, 124 (1973); P. W. Concannon and J. Ciabattoni, ibid., **95**, 3284 (1973). (b) S. A. Mathu and P. Sammes, Chem. Commun., 11 (1972); H. E. Avery and S. J. Heath, Trans. Faraday Soc., **68**, 512 (1972); I. G. Csizmadia, H. E. Gunning, R. K. Gosari and O. P. Strausz, J. Amer. Chem. Soc., **95**, 133 (1973).
2. (a) E. Hedaya, J. Amer. Chem. Soc., **89**, 4213, 4214 (1967); E. Hedaya, Da. W. McNeil, P. Schissel and D. J. McAdoo, ibid., **90**, 5284 (1968); J. F. King, P. de Mayo and D. J. Verdun, Can. J. Chem., **47**, 4509 (1969); J. F. King, P. de Mayo, C. L. McIntosh, K. Piers and D. J. H. Smith, ibid., **48**, 3704 (1970). (b) J. F. King, R. A. Marty, P. de Mayo and D. L. Verdun, J. Amer. Chem. Soc., **93**, 6304 (1971); R. Bloch, R. A. Marty and P. de Mayo, Bull. Soc. Chim. Fr., 2031 (1972).
3. E. Vogel, W. A. Böll and H. Günther, Tetrahedron Letters, 609 (1965).
4. H. Kwart and K. King, Chem. Rev., **68**, 415 (1968).
5. The  $^1\text{H}$  NMR spectrum of  $\frac{3}{4}$  is very similar to that of a compound assigned the same type of structure, but with a phenyl in place of a CHO: J. F. King, R. M. Enanoza and E. G. Lewars, Can. J. Chem., **52**, 2409 (1974).
6. This UV spectrum is very similar to that of dimethyl 1,3,5-cycloheptatriene-1,6-dicarboxylate: R. Darms, T. Threlfall, M. Pesaro and A. Eschenmoser, Helvetica Chimica Acta, **46**, 2893 (1963).
7. S. J. Cristol and R. L. Bly, J. Amer. Chem. Soc., **82**, 6155 (1960).
8. G. B. Gill, Quart. Rev., Chem. Soc., **22**, 338 (1968); A. P. Ter Borg and H. Kloosterziel, Recl. Trav. Chim. Pays-Bas, **88**, 266 (1969); K. W. Egger, J. Amer. Chem. Soc., **90**, 1 (1968).
9. We used a simplified version of the apparatus of de Mayo and coworkers, reference 2(b).
10. Cf. references 1(a).