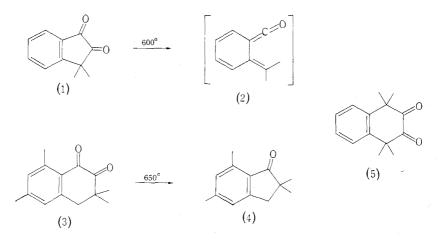
# THE PYROLYSIS OF POLYCARBONYL COMPOUNDS

## V.\* PYROLYSIS OF 3,3,6,8-TETRAMETHYLTETRALIN-1,2-DIONE AT 650°

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The pyrolytic decarbonylation<sup>1</sup> of the dione (1) at  $600^{\circ}/0.6$  mm gave a mixture of products formed by hydrogen transfer and recyclization reactions of an intermediate (2). To study the effect of a change of ring size on such reactions we have examined the pyrolysis of the tetralindione (3).<sup>2</sup> Pyrolysis of compound (3) at  $650^{\circ}/0.1$  mm with contact time 0.3 s over a silica packing gave the indanone (4)<sup>3</sup> (59%), the balance being starting material with traces of other products. This



smooth decarbonylation and recyclization parallels that previously observed with 1,1,4,4-tetramethyltetralin-2,3-dione  $(5)^4$  at  $600^\circ$ ; in both cases a higher temperature  $(c. 800^\circ)$  is needed to bring about further decarbonylation and other transformations. Pyrolysis of the dione (3) at  $800^\circ/0.5$  mm deposited much carbon in the tube, and gave a pyrolysate containing at least 19 components as shown by gas chromatography.

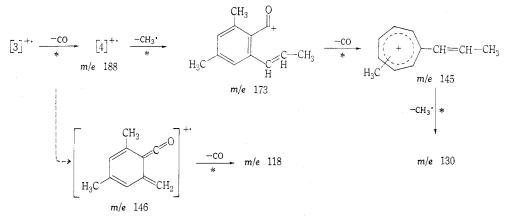
- \* Part IV, Aust. J. Chem., 1969, 22, 1457.
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- <sup>1</sup> Brown, R. F. C., and Butcher, M., Aust. J. Chem., 1969, 22, 1457.
- <sup>2</sup> Franck H.-G., Turowski, J., Erünlü, R. K., Storch, G., Zander, M., and Lemke, R., *Liebigs Ann.*, 1969, **724**, 94.
- <sup>3</sup> Dugan, J. J., de Mayo, P., Nisbet, M., Robinson, J. R., and Anchel, M., *J. Am. chem. Soc.*, 1966, **88**, 2838.
- <sup>4</sup> Brown, R. F. C., Gream, G. E., Peters, D. E., and Solly, R. K., Aust. J. Chem., 1968, 21, 2223.

Aust. J. Chem., 1970, 23, 1907-9

SHORT COMMUNICATIONS

Because of complications introduced by probable loss or migration of ring methyl groups this was not investigated further.

Not unexpectedly the 70-eV mass spectra of the dione (3) and of its pyrolysis product (4) were very similar from m/e 188 down. The major pathway of fragmentation of  $[3]^+$ , confirmed by the observation of metastable transitions and checked by accurate mass measurements at m/e 145 and 146, is shown in Scheme 1. Following



Scheme 1.—Mass spectral fragmentation of dione (3). Observed metastable transitions are marked with an asterisk.

the work of Occolowitz and White<sup>5</sup> on the energetics of formation and structure of the ion of m/e 115 from indene or o-tolylacetylene, we represent the present ion of m/e 145 as a tropylium cation. The ion of m/e 146 had the composition  $C_{10}H_{10}O$ and was of moderate intensity (19% of the base peak, m/e 173) in the spectrum of the dione (3), but was less intense (9%) in that of the indanone (4). There appeared to be no metastable transition to indicate its origin. The indanone (4) was prepared with deuteromethyl groups at C 2; the spectrum of this sample (4- $d_6$ ) confirmed the undeuterated sequence  $188 \rightarrow 173 \rightarrow 145$ , but gave no further information as to the formation of the ion of m/e 146.

#### Experimental

For general experimental directions and for pyrolytic and spectroscopic methods see Parts  $III^4$  and  $IV^1$  of this series.

#### Pyrolysis of the Dione (3) at $650^{\circ}$

3,3,6,8-Tetramethyltetralin-1,2-dione (3), prepared in 89% yield by oxidation of 3,3,6,8-tetramethyltetral-1-one (Aldrich Chemical Co.) with selenium dioxide in acetic anhydride,<sup>6</sup> was obtained as lemon yellow prisms from light petroleum, m.p.  $80-81^{\circ}$  (lit.<sup>2</sup> 78-79°).  $\nu_{\rm max}$  (CCl<sub>4</sub>) 1733, 1685, and 1610 cm<sup>-1</sup>. Condensation with *o*-phenylenediamine gave the corresponding quinoxaline, m.p.  $116-117^{\circ}$  (lit.<sup>2</sup> 116-116·6°).

The dione (3)  $(1 \cdot 0 \text{ g})$  was sublimed at  $0 \cdot 1 \text{ mm}$  during 90 min into a silica pyrolysis tube (40 by  $2 \cdot 6 \text{ cm}$  i.d.) packed with 5-mm lengths of silica tubing and heated at  $650 \pm 20^{\circ}$  over the central 30 cm. A liquid pyrolysate (920 mg) collected in the exit elbow and cold trap. Analysis

<sup>5</sup> Occolowitz, J. L., and White, G. L., Aust. J. Chem., 1968, 21, 997.

<sup>6</sup> Eistert, B., Greiber, D., and Caspari, I., Liebigs Ann., 1962, 659, 64.

of this by gas chromatography on a 12 ft QF-1 fluorosilicone column, and by integration of the n.m.r. spectrum run in CCl<sub>4</sub>, showed that it contained 2,2,5,7-tetramethylindan-1-one  $(4)^3$  (estimated yield 540 mg, 59%), small traces of three unidentified components of retention time slightly longer than this indanone, and starting material (3) (370 mg).

A sample of the tetramethylindanone was obtained pure by preparative gas chromatography, and was identified on the basis of comparison of spectral data with those previously reported.<sup>3</sup> Mass spectrum: m/e 188 (M<sup>+</sup>, 23%); 173 (100%).  $\nu_{max}$  (film) 1703 cm<sup>-1</sup>.  $\lambda_{max}$  (MeOH) 259 and 292–299 (broad) nm ( $\epsilon$  14700 and 2100) (lit. 260 and 292 nm, 14100 and 2200). N.m.r. spectrum (CDCl<sub>3</sub>):  $\delta$  1·22, s, 6H (2-Me<sub>2</sub>); 2·40, s, 3H (5-Me); 2·62, s, 3H (7-Me); 2·92, s, 2H (3-CH<sub>2</sub>); 6·98, s, 1H and 7·08, s, 1H (aromatic).

The 2,4-dinitrophenylhydrazone was obtained as deep red leaflets from chloroform-methanol, m.p. 254° (evac. capillary) (Found: C, 61.8; H, 5.6; N, 15.2.  $C_{19}H_{20}O_4N_4$  requires C, 61.9; H, 5.6; N, 15.2%).  $\lambda_{max}$  (MeOH) 392 nm ( $\epsilon$  28000). This derivative was originally reported<sup>3</sup> as having m.p. 222-224°, but Professor de Mayo (London, Ontario) has very kindly re-examined this sample and finds that it contained an impurity, revealed by thin-layer chromatography. After repurification the original sample also has m.p. 254° (evac. capillary), undepressed by the present sample.

#### Mass Spectra of Tetralindione (3) and Indanone (4)

The 70-eV mass spectra of these compounds were very similar from m/e 188 down, though there were some differences in intensities. The spectra are compared, in terms of intensities of peaks greater than 5% of the base peak, in the following list which gives m/e (intensity of ion from 3,3,6,8-tetramethyltetralin-1,2-dione, intensity of ion from 2,2,5,7-tetramethylindan-1-one): 216 (5, —); 188 (15, 23); 174 (15, 15); 173 (100, 100); 146 (19, 9); 145 (15, 15); 130 (10, 10); 129 (15, 15); 128 (17, 17); 118 (7, 3); 117 (10, 8); 115 (19, 17); 105 (10, 7); 103 (10, 8); 91 (16, 14); 77 (17, 13); 51 (14, 9); 41 (16, 9); 39 (20, 16).

Accurate mass measurements were made on the spectrum of the dione (3) (Found: 146.0726.  $C_{10}H_{10}O$  requires 146.073161. Found: 145.1013.  $C_{11}H_{13}$  requires 145.101720).

Methylation<sup>3</sup> of 5,7-dimethylindanone<sup>3</sup> (200 mg) in t-butanol (17 ml) containing potassium t-butoxide (from 150 mg of potassium) with methyl iodide (1 ml) gave a mixture estimated by gas chromatography to contain about 50% of 2,2,5,7-tetramethylindanone (4). Repetition of this alkylation using trideuteromethyl iodide and isolation of the 2,2-bis(trideuteromethyl) compound (4- $d_6$ ) by preparative gas chromatography gave an oil,  $\nu_{max}$  2225 (C–D str), 1700, and 1610 cm<sup>-1</sup>. The principal peaks in the high-mass region of the mass spectrum were as follows: m/e 195 (6%); 194 (M<sup>+</sup>, 32); 177 (21); 176 (100); 149 (3); 148 (9); 147 (3); 146 (3); 145 (1); 133 (6); 132 (7); 131 (6); 130 (4); 129 (3); 128 (2); 120 (2); 119 (2); 118 (4); 117 (4); 116 (3); 115 (3). Peaks at lower mass numbers were weak ( $\leq 3\%$ ).

#### **Acknowledgments**

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