

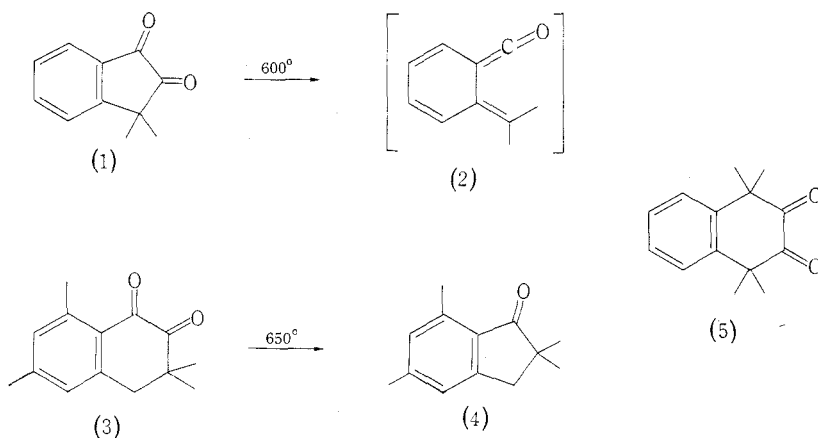
THE PYROLYSIS OF POLYCARBONYL COMPOUNDS

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

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The pyrolytic decarbonylation¹ of the dione (1) at 600°/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).² Pyrolysis of compound (3) at 650°/0.1 mm with contact time 0.3 s over a silica packing gave the indanone (4)³ (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°; in both cases a higher temperature (c. 800°) is needed to bring about further decarbonylation and other transformations. Pyrolysis of the dione (3) at 800°/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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¹ Brown, R. F. C., and Butcher, M., *Aust. J. Chem.*, 1969, **22**, 1457.

² Franck H.-G., Turowski, J., Erünlü, R. K., Storch, G., Zander, M., and Lemke, R., *Liebigs Ann.*, 1969, **724**, 94.

³ Dugan, J. J., de Mayo, P., Nisbet, M., Robinson, J. R., and Anchel, M., *J. Am. chem. Soc.*, 1966, **88**, 2838.

⁴ Brown, R. F. C., Gream, G. E., Peters, D. E., and Solly, R. K., *Aust. J. Chem.*, 1968, **21**, 2223.

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

⁶ 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_4 , 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.³ Mass spectrum: m/e 188 (M^+ , 23%); 173 (100%). ν_{max} (film) 1703 cm^{-1} . λ_{max} (MeOH) 259 and 292–299 (broad) nm (ϵ 14700 and 2100) (lit. 260 and 292 nm, 14100 and 2200). N.m.r. spectrum (CDCl_3): δ 1.22, s, 6H (2-Me₂); 2.40, s, 3H (5-Me); 2.62, s, 3H (7-Me); 2.92, s, 2H (3-CH₂); 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. $\text{C}_{19}\text{H}_{20}\text{O}_4\text{N}_4$ requires C, 61.9; H, 5.6; N, 15.2%). λ_{max} (MeOH) 392 nm (ϵ 28000). This derivative was originally reported³ 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. $\text{C}_{10}\text{H}_{10}\text{O}$ requires 146.073161. Found: 145.1013. $\text{C}_{11}\text{H}_{13}$ requires 145.101720).

Methylation³ of 5,7-dimethylindanone³ (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, ν_{max} 2225 (C–D str), 1700, and 1610 cm^{-1} . The principal peaks in the high-mass region of the mass spectrum were as follows: m/e 195 (6%); 194 (M^+ , 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 ($\leq 3\%$).

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