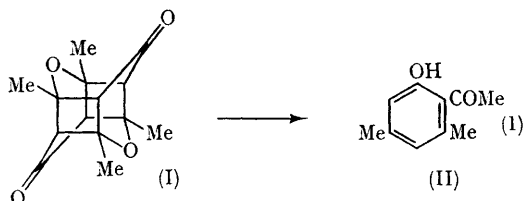


Pyrolysis of the Cage Photodimer of 2,6-Dimethyl-4-pyrone

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The cage photodimer of 2,6-dimethyl-4-pyrone (I),¹ has been found to undergo the remarkable transformation shown in equation (1) on being heated at 265–285°. The structure of the product (II)

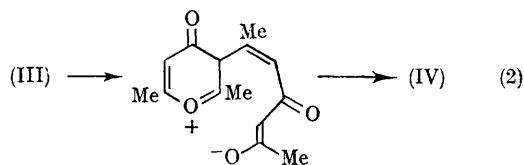


and spectroscopic data: λ_{\max} (CHCl₃) 6.05, 6.21 μ ; λ_{\max} (EtOH) (log ϵ) 256 (4.09), 278 (4.18), 310 (4.14) $m\mu$; λ_{\max} (EtOH-NH₄OH) (log ϵ) 246 (4.14), 280 (4.06), 340 (4.22) $m\mu$; δ (CDCl₃) 1.70 (s, 3H), 1.98 (s, 3H), 2.10 (d, $J \sim 1$ Hz., 3H), 2.17 (s, 3H), 3.18 (q, $J \sim 1$ Hz., 1H), 5.23 (s, 1H), 5.62 (s, 1H) p.p.m.; m/e (rel. abund.) 248 (9%), 164 (36%), 163 (26%), 149 (87%), 85 (20%), 77 (20%), 43 (100%).

The thermal conversion of (I) into (III) is unexceptional;² the conversion of (III) into (IV) is considered to involve ionic reactions in the melt as indicated in equation (2). This reaction sequence

was established by direct comparison (spectra, mixed m.p.) with an authentic sample.^{2†} The fate of three of the four carbon atoms lost from (I) in this process is illuminated by the observation that acetone is formed concurrently.

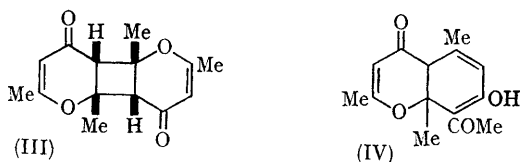
The course of the conversion has been elucidated by the demonstration that compounds (III) and (IV) are formed on pyrolysis of (I) at 220–260°, and that (III) on pyrolysis at 225–240° is converted to (IV), which in turn is converted into (II) at 265–270°.



is accompanied by conventional cleavage of the cyclobutane ring of (III) to give 2,6-dimethyl-4-pyrone, which is observed as a product in the pyrolysis of both (III) and (I) [but not (IV)]. The formation of (II) from (IV) could involve a retro-Diels-Alder reaction;[‡] reaction of acetylketen, formed concomitantly, with water, formed by more highly destructive pyrolytic pathways, could then account for the formation of acetone. Alternatively, compound (II) and acetone could be formed by direct attack of water on (IV).

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The formation of (III) and the establishment of its structure have been reported previously.¹ The structure of (IV), m.p. 105–107°, which gave a positive ferric chloride test in both methanol and water, was established by its elemental composition

† This sample was kindly supplied by Dr. E. Gosselink.

‡ Comparison of the mass spectra of compounds (IV) and (II) suggests that such a reaction is brought about by electron impact.

¹ P. Yates and M. J. Jorgenson, *J. Amer. Chem. Soc.*, **1963**, **85**, 2956.

² L. I. Smith and J. W. Opie, *J. Org. Chem.*, **1941**, **6**, 427.

³ Cf., A. Mustafa, *Chem. Rev.*, **1952**, **51**, 1.