## THE ACID CATALYZED REARRANGEMENT OF A CYCLOPENTENONE OXIDE

## Albert Padwa Department of Chemistry, The Ohio State University Columbus, Ohio. (Received 12 February 1965)

A recent investigation of the products formed on irradiation of 2,6dimethyl-4-pyrone at high dilution revealed that the 4-pyrone had undergone an extraordinary rearrangement to 4,5-dimethyl-2-furaldehyde (1). Yates has suggested that the mechanism of this transformation involves the initial formation of 3,4-dimethyl-4,5-epoxy-2-cyclopenten-l-one. which further rearranges under the reaction conditions (1). In order to confirm the role of a substituted epoxyketone as an intermediate, the photolysis of a related cyclopentenone oxide was examined.

At an earlier date (2) we reported that brief irradiation of 3.4diphenyl-4,5-epoxy-2-cyclopenten-1-one (I) lead to the exclusive formation of 4,5-diphenyl-2-pyrone. At that time it was pointed out that this particular epoxyketone does not photochemically rearrange to a furan derivative, but instead gave a complex mixture of products (3). The failure to isolate the corresponding 2-furaldehyde from the photolysis of I suggested that another mechanism might pertain. One such possibility is that the rearrangement proceeded via a non-photochemical route. We now wish to report new evidence which supports the role of an epoxy-

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P. Yates and I. W. J. Still, J. Am. Chem. Soc., <u>85</u>, 1208 (1963).
 A. Padwa, <u>Tetrahedron Letters</u>, <u>No. 15</u>, 813 (1964).

<sup>(3)</sup> A. Padwa and R. Hartman, J. Am. Chem. Soc., 86, 4212 (1964).

ketone in this unusual transformation.

Treatment of I with aqueous acidic methanol resulted in a mixture of two major products. Separation by alumina chromatography gave, in addition to 4,5-diphenyl-2-pyrone (15%), an unsaturated aldehyde (53%), m.p. 128-129°, which was identified as 2,3-diphenylcrotonaldehyde (II). The structure of II was assigned on the basis of its elemental composition, Anal. Calcd. for C16H140: C, 86.45; H, 6.35. Found: C, 86.53: H, 6.33; 2,4-dinitrophenylhydrazone, orange needles, m.p. 227-228°, Anal. Calcd. for C22H1804N4: C, 65.66; H, 4.51; N, 13.92. Found: C. 65.57; H, 4.66; N, 13.78; spectral peaks appeared at: infrared spectrum:  $\lambda_{max}$  (KBr) 3.67  $\mu$  (aldehyde CH) and 5.96  $\mu$  (conjugated carbonyl); ultraviolet spectrum:  $\lambda_{max}$  277 mµ (e, 10,000); 60 Mc. n.m.r. (Deuterochloroform): singlet at 0.38  $\tau$ , singlet at 2.67  $\tau$ , singlet at 7.85  $\tau$ . The peak areas are in the ratio of 1:10:3. The physical constants of this material are in excellent agreement with those reported (4). Final verification was obtained by comparison of an infrared spectrum with an authentic sample (5).

A reasonable mechanism for the formation of II is presented below. When the reaction was carried out using anhydrous methanol (containing gaseous hydrochloric acid), there was obtained a complex mixture of proudcts (6), from which was isolated an approximately 10% yield of

<sup>(4)</sup> R. Breslow, J. Lockhart and A. Small, <u>J. Am. Chem. Soc.</u>, <u>84</u>, 2793 (1962).

<sup>(5)</sup> A highly purified sample was kindly provided by Professor R. Breslow.
(6) Thin-Layer Chromatography of the crude reaction mixture suggested the presence of between eight and ten other products among which were small amounts of 2,3-diphenylcrotonaldehyde and 4,5-diphenyl-2-pyrone.



a new unsaturated aldehyde, 4,5-diphenyl-2-furaldehyde (III), m.p. 77-78°. Anal. Calcd for  $C_{17H_{12}O_2}$ : C, 82.24; H, 4.87; Found: C, 82.08; H, 4.99. Spectral peaks appeared at: ultraviolet spectrum:  $\lambda \lambda_{max}$  (95% ethanol) 329, 256, 234 m<sub>µ</sub> (e, 19,500 e, 13,900, e, 21,00); infrared spectrum:  $\lambda_{max}$ (KBr): 3.64 µ and 6.03 µ; 60 Mc. n.m.r. (Deuterochloroform): singlet at 0.41  $\tau$ , multiplet at 2.69  $\tau$ , singlet at 2.81  $\tau$ . The peak areas are in the ratio of 1:10:1. Proof of structure III was obtained by comparison with an authentic sample synthesized by an application of the Vilsmeier reaction in which 2,3-diphenylfuran was treated with a 1:1 complex of dimethylforamide and phosphorus oxychloride. The previously unreported 2,3-diphenylfuran, m.p. 17-18°; b.p. 173-174° (8 mm.); n<sup>26</sup> 1.6426;  $\lambda_{max}$ (carbon tetrachloride) 11.24 µ; 60 Mc. n.m.r.: doublet at 2.57  $\tau$ , multiplet at 2.84  $\tau$ , doublet at 3.63  $\tau$  (J = 2 c.p.s.), (intensities 1:10:1), was in turn prepared by hydrolysis of dimethyl-4,5-diphenylfuran-2,3dicarboxylate (7) followed by a two step decarboxylation of the diacid.

This result is consistent with and supports the interpretation that an epoxyketone functions as the initial intermediate in the rearrangement of 2,6-dimethyl-h-pyrone to 4,5-dimethyl-2-furaldehyde. It is tempting to hypothesize that the dimethyl and diphenyl epoxyketones are in fact behaving analogously, the final step occurring via an acid catalyzed rearrangement rather than a photochemical path. A likely route for the formation of the 2-furaldehyde is then:



Further work is in progress on the scope of this novel acid catalyzed rearrangement; we are also investigating other cyclopentenone oxides to determine the generality of our observation.

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(7) J. B. Hendrickson, R. Rees, and J. F. Templeton, <u>J. Am. Chem. Soc.</u>, <u>86</u>, 107 (1964).