

A ONE STEP SYNTHESIS OF 2,2,3,4-TETRAPHENYL-3-BUTENO-4-LACTONE FROM BENZOIN

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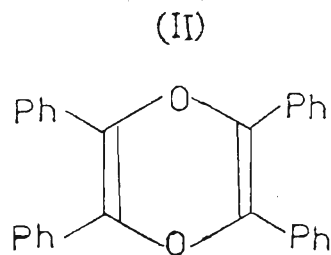
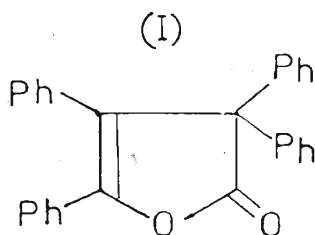
(Date of receipt : 06 October 1988)

(Date of acceptance : 19 May 1989)

Abstract: A one step synthesis of 2,2,3,4-tetraphenyl-3-buteno-4-lactone is described and a possible mechanism for its formation is presented.

1. Introduction

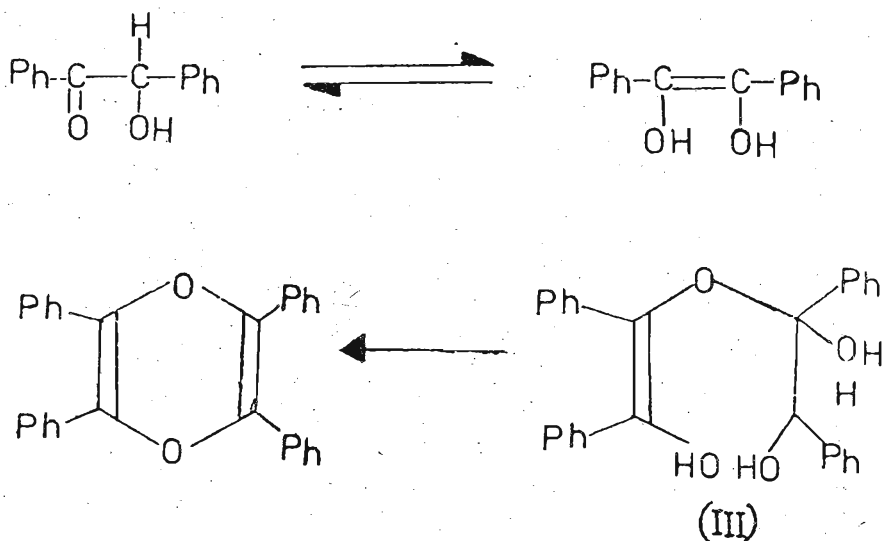
The title compound (I) was first reported⁷ over a century ago and some aspects of the chemistry of this compound has been reviewed by subsequent workers.² This lactone is generally prepared^{1,3,4} by the thermolysis of 2,3,5,6-tetraphenyl-1,4-dioxadiene (II). The latter compound is synthesised by acid catalysed (4-toluenesulphonic acid) self condensation of benzoïn.²



2. Results and Discussion

In view of the prominence achieved by polyphosphoric acid as a reagent in synthetic organic chemistry,⁶ we attempted to dimerise benzoïn in the presence of this reagent. When benzoïn was heated with polyphosphoric acid at 90–100°C, instead of the expected tetraphenyl-1,4-dioxadiene (II), almost quantitative yield of 2,2,3,4-tetraphenyl-3-buteno-4-lactone (I) was obtained. In the presence of acids, benzoïn undergoes self condensation to form (II) via the intermediate (III)³ as depicted in scheme-1.

Scheme — 1

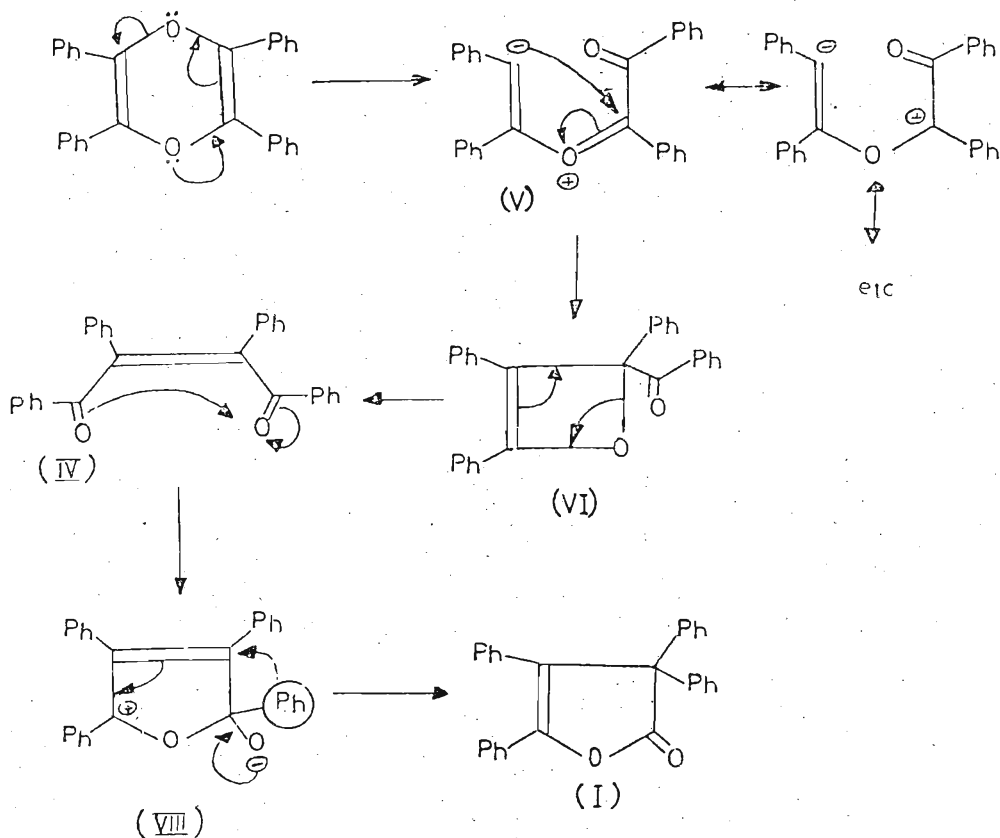


It has been well established² that rearrangement of (II) to give (I) is not acid catalysed and that the formation of (I) does not involve the prior formation and subsequent aerial oxidation of tetraphenyl furan.² Thermal rearrangement of (II) produces in addition to (I), varying quantities of cis-dibenzoyl stilbene (IV); benzil and desoxybenzoin.^{3,4} It is known that in the presence of (IV) higher yields of the lactone (I) is produced³ and the thermal transformation of (IV) gives (I).⁷ It has also been established that when the thermolysis of (II) is conducted at lower temperatures, in different solvents, under reflux, higher yields of compound (IV) are obtained.⁴

It is quite apparent from the above facts that in the thermal transformation of (II) to (I), cis-dibenzoyl stilbene (IV) may be a key intermediate. Various mechanistic pathways have been postulated for the intermediate formation of (IV),^{1,3,4} in the thermal rearrangement of (II) to (I). However, it is pertinent to note that the transformation of (II) to (I) takes place even when the reaction is carried out in an inert atmosphere of nitrogen.⁵ Moreover, high yields of (IV) are obtained when the reaction is carried out in polar solvents,⁴ suggesting that free radical pathways are unlikely.

Thus in view of the above observation, the most likely route for the transformation of (II) to (I) is depicted in scheme-2.

Scheme - 2



Thermal rearrangement of (II) would give the resonance stabilised intermediate (V) which can cyclise to the oxeten intermediate (VI). Subsequent rearrangement of (VI) should give a mixture of *cis*-dibenzoylstilbene (IV) and the *trans*-isomer, but appears to form the *cis*-isomer stereoselectively. Electrocyclic ring closure of (IV) would give rise to the zwitterionic intermediate (VII), which rearranges by phenyl group migration to form the lactone (I).

3. Experimental

Benzoin used was of reagent grade and was purified by recrystallisation. Solvents used were purified by distillation, immediately prior to use. Infrared spectra were recorded on a Perkin-Elmer (577) grating spectrophotometer, using capillary tubes and are uncorrected.

Synthesis of 2,2,3,4-tetraphenyl-3-butenol-4-lactone-

Benzoin (1.634g, 7.69×10^{-3} moles) was heated with polyphosphoric acid (75cm^3) in an oil bath maintained at 90° – 100° C for 12 hours. The mixture gradually darkened and a dark reddish brown tarry product was obtained. The mixture was carefully and cautiously diluted with water (200cm^3). An orange-red precipitate was separated by filtration, washed thoroughly with water and recrystallised several times from ethanolchloroform mixture (1:1) to give colourless plates (1.41g, 86%); mp 137.4° C (lite: 137.1° C– 137.6° C); mixed mp with benzoin (mp 137° C) depressed; elemental analysis, found C, 86.21; H, 5.03%; expected for $\text{C}_{28}\text{H}_{20}\text{O}_2$, C, 86.57; H, 5.19% NMR(CDCl_3) 7.8 – 7.2 (m, ring protons); IR(KBr), 3020, 1785, 1635, 1600, 1590, 1280, 1210, 1000, 750, 690 cm^{-1} .

References

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