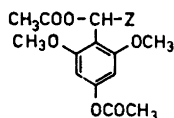
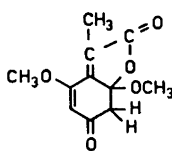


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11. Husebye, S. *Acta Chem. Scand.* **27** (1973). *In press.*
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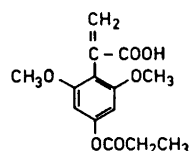
(2b) and (3a),** respectively, are formed. Moreover, small amounts of corresponding diesters of 2,6-dimethoxy-hydroquinone are produced.



- (1a) Z = H
(1b) Z = COOH

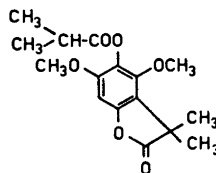


(2a)

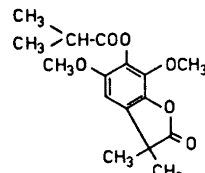


(2b)

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(3a)



(3b)

β -Lactones in the Perkin Reaction*

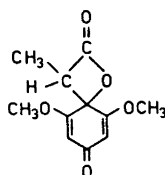
MAURI LOUNASMAA

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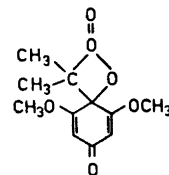
It is now well established that the Perkin reaction, which is generally applied for aromatic aldehydes,¹ readily takes place, utilizing a great variety of quinones.²⁻¹⁰ Due to the instability of the products formed, the reaction generally goes further, leading mostly to aromatic compounds. In the case of 2,6-dimethoxy-*p*-benzoquinone it has been shown^{4,6,8,10} that with acetic, propionic, and isobutyric acid anhydrides the products (1a), (1b), (2a),

By analogy with commonly accepted schemes, the mechanisms outlined in Refs. 2 to 8 can be presented for the formation of these compounds. However, as has been pointed out recently,^{9,10} at least some of these compounds may be formed through a β -lactone.

When the standard reaction procedure²⁻⁸ is modified by utilizing shorter reaction times and lower temperatures, it is possible in the cases of propionic and isobutyric acid anhydrides to isolate β -lactones from the reaction mixtures. For



(2c)



(3c)

* Part X. Sur les Réactions des Quinones. For Part IX, see Ref. 10.

** Analytical data presented for product (3a)⁸ do not exclude the structure (3b).

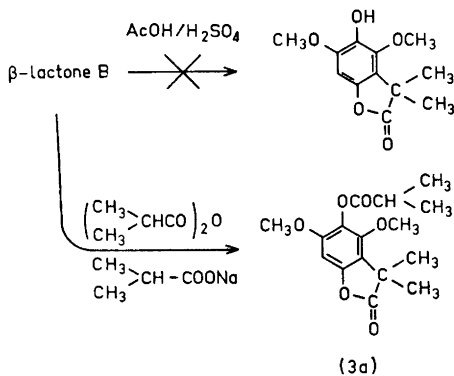
these β -lactones, characterized here by letters A and B, the structures (2c) and (3c), respectively, are proposed.

The following physical data were obtained for the isolated β -lactones:

β -Lactone A ($C_{11}H_{12}O_6$), m.p. 134–135°C d., IR. ν_{\max} 1840, 1665, 1635, and 1600 cm^{-1} , 1H NMR ($CDCl_3$) τ 4.36 (1H, d, J 1 cps), τ 4.46 (1H, d, J 1 cps), τ 5.76 (1H, quart., J 7 cps), τ 6.18 (6H, s), and τ 8.70 (3H, d, J 7 cps), mass. m/e 224 (M^+), 196, 180, 169, 165, 152, and 137.

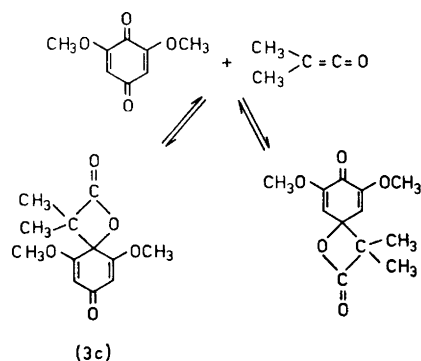
β -Lactone B ($C_{12}H_{14}O_6$), m.p. 154.5°C, IR. ν_{\max} 1840, 1660, 1650, 1635, and 1602 cm^{-1} , 1H NMR ($CDCl_3$) τ 4.46 (2H, s), τ 6.18 (6H, s), and τ 8.60 (6H, s), mass. m/e 238 (M^+), 210, 194, 179, 169, 166, and 151.

Transformation of β -lactone A to product (2a) and similarities in the 1H NMR spectra of β -lactones A and B favour the fact that the β -lactone ring in both cases is in the position 1. Moreover, the fact that β -lactone B is not transformed to a γ -lactone by an acidic treatment according to Chitwood *et al.*,¹¹ supports the position 1.



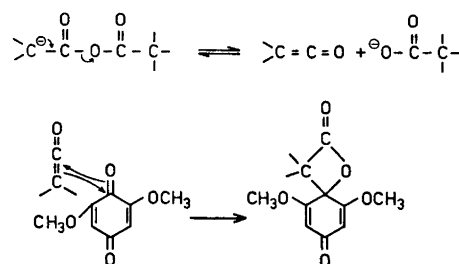
On the other hand, transformation of the β -lactone B to product (3a) by prolonged heating with isobutyric acid anhydride in the presence of sodium isobutyrate seems to support the position 4. However, this transformation can be explained by the equilibria between the β -lactones and the original quinone, presented below, followed by a rearrangement and an esterification.

The existence of an equilibrium between a β -lactone and the original quinone in the reaction mixture is supported by the fact



that the treatment of β -lactone B with propionic acid anhydride and sodium propionate leads to products (2a) and (2b). Due to the existence of this equilibrium, the isolation of β -lactones A and B does not prove with certainty that these β -lactones are intermediates in the formation of products (2a), (2b), and (3a). However, it proves that β -lactones can be formed in the Perkin reaction conditions.

The most plausible way for the formation of β -lactones A and B is presented in Scheme 1. It consists of the formation of a ketene from the corresponding carboxylic acid anhydride, followed by the addition of the ketene to the carbonyl group of the quinone.



By analogy, and taking into account the general reactivity of ketenes with aldehydes,¹² it seems reasonable to suppose that at least in some favourable cases, the normal Perkin reaction of aromatic aldehydes goes through a β -lactone. A more detailed discussion on this subject has been published recently.⁹

The long known failure of aliphatic aldehydes to undergo the Perkin reaction,¹³ and the fact that the reaction of ketene with aromatic aldehydes in the presence of anhydrous potassium acetate to produce α,β -unsaturated carboxylic acid anhydrides is not applicable to aliphatic aldehydes,¹⁴ are in agreement with the above presented conclusions.

Experimental. The IR spectra have been obtained from KBr-discs on a Perkin Elmer 237 instrument. The NMR spectra have been taken with a Varian T-60 instrument in CDCl_3 , using TMS as internal standard, and the mass spectra with an A.E.I. MS-9 instrument. The melting points have been determined on a Reichert micro hot stage and are uncorrected.

Reaction between 2,6-dimethoxy-p-benzoquinone and propionic acid anhydride. A mixture of 2,6-dimethoxy-p-benzoquinone (0.001 mol; 168 mg), sodium propionate (300 mg) and propionic acid anhydride (5 ml) was stirred at 95°C for 2 h. The crude mixture was separated in the normal way and successively fractionated by column and preparative layer chromatography (silica gel/chloroform). Among the fractions obtained two were analyzed more in details.

Fraction 1 (10 mg) (β -lactone A). Recrystallized from CCl_4 . M.p. 134–135°C d. Analytical data, given in the theoretical part, indicate that it is a compound of structure (2c).

Fraction 2 (130 mg). Recrystallized from CCl_4 . M.p. 127.5°C. Identified by m.p., IR and NMR as product (2a).

Reaction between 2,6-dimethoxy-p-benzoquinone and isobutyric acid anhydride. A mixture of 2,6-dimethoxy-p-benzoquinone (0.01 mol; 1.68 g), sodium isobutyrate (3 g), and isobutyric acid anhydride (50 ml) was stirred at 95°C for 6 h. The crude mixture was separated in the normal way and purified by column chromatography (silica gel/chloroform). Yield 1.5 g (β -lactone B). Recrystallized from CCl_4 . M.p. 154.5°C. Analytical data, given in the theoretical part, indicate, that it is a compound of structure (3c).

Reaction between β -lactone A and propionic acid anhydride. A mixture of β -lactone A (5 mg), sodium propionate (5 mg), and propionic acid anhydride (0.5 ml) was stirred at 100°C for 48 h. The reaction mixture worked up in the normal way contained *inter alia* compounds (2a) and (2b).

Reaction between β -lactone B and isobutyric acid anhydride. A mixture of β -lactone B (100 mg), sodium isobutyrate (100 mg), and isobutyric acid anhydride (10 ml), was

stirred at 150°C for 60 h. The reaction mixture worked up in the normal way consisted mainly of compound (3a).

Reaction between β -lactone B and propionic acid anhydride. A mixture of β -lactone B (100 mg), sodium propionate (100 mg), and propionic acid anhydride (10 ml) was stirred at 100°C for 72 h. The reaction mixture worked up in the normal way contained *inter alia* compounds (2a) and (2b).

Attempt to transpose the β -lactone B to a γ -lactone. To a stirred mixture of 200 mg of β -lactone B in 5 ml of glacial acetic acid was added 4 drops of conc. H_2SO_4 . The mixture was stirred for 18 h at room temperature. After work-up more than 80 % of β -lactone B was recovered. No γ -lactone could be detected.

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