β-Lactones as Kinetic Products in the Iodolactonization Reaction

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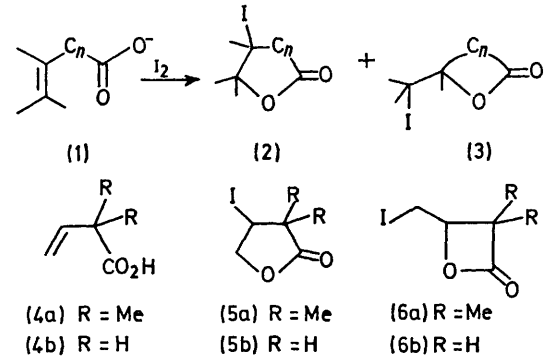
Summary β-Lactones are the kinetic products from the iodolactonization of certain βγ-unsaturated acids. These γ-iodo-β-lactones are readily isomerized to more stable β-iodo-γ-lactones.

UNSATURATED sodium carboxylate salts react with iodine to form lactones when the site of unsaturation is in a sterically accessible βγ-, γδ-, or δε-position, (**1**) → (**2**) and/or (**3**). Under a set of standard conditions for this reaction, the iodolactonization reaction,[1] δ-lactones are formed from δε-unsaturated acids and γ-lactones are formed from βγ- or γδ-unsaturated acids.[2] We have recently described a new method of iodolactonization which produces β-lactones from a variety of βγ-unsaturated acids.[3] In a systematic effort to compare this new method with the standard method,[2] we have discovered that the γ-iodo-β-lactones formed in the new procedure are often the initial products formed in the standard procedure.

The standard iodolactonization procedure as applied to 2,2-dimethylbut-3-enoic acid (**4a**) produces the expected γ-lactone (**5a**), whereas the new procedure[3] gives the β-lactone (**6a**). If the standard reaction mixture is modified by substituting pure (**6a**) for (**4a**), the characteristic β-lactone absorption at 1827 cm^{-1} is gradually replaced by γ-lactone absorption below 1800 cm^{-1} over the standard reaction period of 24 h. During this time, the β-lactone (**6a**) is rearranging to the γ-lactone (**5a**).

This result obviously implied, but certainly did not prove, that β-lactones are initial products in the standard iodolactonization method. In order to detect a possible β-lactone intermediate the standard procedure was interrupted at an early stage. After a reaction time of 15 min, (**4a**) gave the β-lactone (**6a**) as the major product. Fortunately, the rate of β-lactone formation is much faster than the rate of rearrangement to the γ-isomer so that the β-lactone is easily detected as the kinetic product in the standard procedure.

The standard method gives a poor yield of γ-iodolactone from (**4b**).[2,3] However, when the standard conditions are modified merely by shortening the reaction time, both γ and β-lactones, (**5b**) and (**6b**), can be detected by characteristic



i.r. bands at 1770 and 1833 cm^{-1}. Once again the β-lactone is the kinetic product as shown by a preponderance of the 1833 cm^{-1} carbonyl band after a reaction time of 2 min. Rearrangement of (**6b**) to (**5b**) is suggested by a diminishing intensity of this band at the expense of the 1770 cm^{-1} band, the two bands becoming approximately equal in intensity after 15 min. After 24 h the β-lactone band is considerably diminished.†

Even though the γ-iodo-β-lactones are formed as kinetic products in the standard method, the new procedure[3] is still the method of choice for preparing them.†

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† Yield of neutral material (**5b** + **6b**) from iodolactonization of (**4b**)/reaction time = 6·3%/30 sec; 7·0%/2 min; 7·6%/15 min; <0·7%/24 h. See ref. 3 for the preparation of pure (**6b**).

[1] H. O. House, 'Modern Synthetic Reactions,' Benjamin, New York, 1965, p. 143ff.
[2] E. E. Van Tamelen and M. Shamma, *J. Amer. Chem. Soc.*, 1954, **76**, 2315.
[3] W. E. Barnett and W. H. Sohn, *Tetrahedron Letters*, in the press.
[4] W. E. Barnett and J. C. McKenna, *Chem. Comm.*, 1971, 551; W. E. Barnett and J. C. McKenna, *Tetrahedron Letters*, 1971, 2595.