Preliminary communication

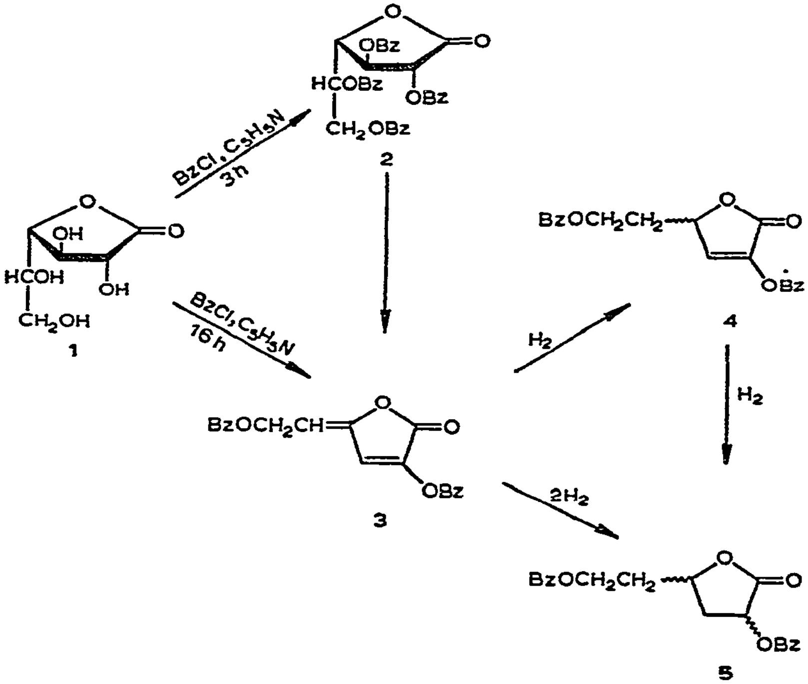
The formation of an unsaturated lactone derivative on benzoylation of D-galactonolactone

ROSA M. DE LEDERKREMER* and MARTA I. LITTER

Departamento de Química Orgánica, Facultad de Ciencias Exactas y Naturales, Universidad de Buenos Aires, Perú 222, Buenos Aires (Argentina)

(Received March 3rd, 1971; accepted in revised form October 4th, 1971)

Because of the effect of the carbonyl group, aldonolactone derivatives readily undergo β-elimination reactions to yield unsaturated lactones[1—3]. We now report the formation of 3-benzoyloxy-5-(2-benzoyloxyethylidene)-2(5*H*)furanone (3) by elimination under benzoylating conditions.



Benzoylation of D-galactono-1,4-lactone (1) with benzoyl chloride in pyridine for 3 h afforded tetra-*O*-benzoyl-D-galactono-1,4-lactone (2) as an amorphous,

---

*Research member of the Consejo Nacional de Investigaciones Científicas y Técnicas.

chromatographically homogeneous product; $[\alpha]_D$ + 22.3° (c 1, chloroform); ν_{max}^{Nujol} 1790 (1,4-lactone) and 1720 cm^{-1} (benzoate carbonyl). When the benzoylation reaction was conducted for 16 h at room temperature with an excess of benzoyl chloride and pyridine, and the reaction mixture processed as usual, the di-unsaturated lactone 3 crystallized from ether in 36% yield after removal of benzoic acid and benzoic anhydride by sublimation under diminished pressure. The same product was formed by treating 2 with benzoyl chloride and pyridine for 20 h.

The structure of compound 3 was assigned on the basis of chemical and spectral studies. It had m.p. 127–127.5°, was optically inactive, and it absorbed strongly in the u.v.; $\lambda_{max}^{CHCl_3}$ 283 (ϵ 37,500), 277 (sh) nm (35,000). The i.r. spectrum showed absorption at 1775 (α,β-unsaturated 1,4-lactone), 1730 (benzoate carbonyl), 1690 (s) and 1660 (w) cm^{-1} (C=C–C=O). The n.m.r. spectrum at 60 MHz (chloroform-*d*) showed the presence of two *O*-benzoyl groups which gave a multiplet at τ 1.6–2.6 that included the H-4 signal. A 1-proton quartet attributed to the exocyclic, olefinic proton was observed at τ 4.32 (J 6.2 and 8 Hz).

Reductive ozonolysis of 3 afforded glyoxylic acid, from C-4 and C-5 (furanone numbering), easily detected by a specific colorimetric reaction[4], and identified with an authentic sample as the dimedone derivative. Oxalic acid, derived from C-2 and C-3, was isolated as its calcium salt, after hydrolysis of the benzoic anhydride.

The unsaturated lactone 3 absorbed 2 mol of hydrogen (5% Pd on $BaSO_4$) to give a crystalline, 2,6-di-*O*-benzoyl-3,5-dideoxy-aldohexonolactone (5), m.p. 81–82°. The i.r. spectrum of 5 showed a shift in the lactone carbonyl band (1775 → 1790 cm^{-1}) ascribable to the loss of α,β unsaturation. The n.m.r. spectrum showed a 10-proton multiplet at τ 1.80–2.80. A 4-proton multiplet in the methylene region (τ 6.7–8.2) indicated that 5 was a dideoxy lactone. The H-2 signal resonated at τ 4.28 as a pair of doublets ($J_{2,3}$ 8 Hz, $J_{2,3'}$ 10 Hz). The H-4, H-6 and H-6' signals appeared as overlapping multiplets at τ 5.00–5.70. The second, diastereoisomeric product theoretically possible was not isolated.

When hydrogenation of 3 was stopped after the consumption of one mole of hydrogen, the mono-unsaturated lactone 4 crystallized from ethanol and was recrystallized from the same solvent; m.p. 138–139°; $\lambda_{max}^{CH_3OH}$ 232 nm (ϵ 23,500); ν_{max}^{Nujol} 1760 (α,β-unsaturated 1,4-lactone), 1730 (benzoate carbonyl) 1710 and 1640 cm^{-1} (C=C–C=O) The n.m.r. spectrum gave an 11-proton multiplet at τ 1.7–2.7 due to the aromatic protons and the olefinic hydrogen, and the H-4 signal appeared as a multiplet centered at τ 4.6. A 2-proton triplet (J 6 Hz) attributed to H-6,6' was observed at τ 5.4. The methylene protons resonated as a multiplet at τ 7.3–7.9. Compound 4 absorbed one mole of hydrogen to give the dideoxy lactone 5.

Treatment of 5 with 16% methanolic ammonia afforded a crystalline 3,5-dideoxy-aldohexonamide, m.p. 109°; ν_{max}^{Nujol} 3250 (OH), 3100 (NH), 1630, 1620 cm^{-1} (amide carbonyl). It did not consume periodate, in agreement with a 3,5-dideoxy structure. The relative configuration at C-2 and C-4 has not yet been determined.

ACKNOWLEDGMENTS

The authors thank Dr. B. B. de Deferrari for the microanalyses, Mr. J. J. Ferrer for measurement of i.r. and n.m.r. spectra, and the Consejo Nacional de Investigaciones

Científicas y Técnicas (Buenos Aires) for a graduate fellowship to M. I. L. and for financial support.

REFERENCES

1 N. Pravdić and H. G. Fletcher, Jr., *Carbohyd. Res.*, 12 (1970) 471.
2 K. Isono, K. Asahi, and S. Suzuki, *J. Amer. Chem. Soc.*, 91 (1969) 7490.
3 G. M. Cree, D. W. Mackie, and A. S. Perlin, *Can. J. Chem.*, 47 (1969) 511.
4 E. Eegriwe, *Z. Anal. Chem.*, 100 (1935) 34.