Asian Journal of Chemistry Vol. 12, No. 1 (2000), 324–326

NOTE

Synthetic and Structural Studies on Some New Butenolactones

R.P. CHAMOLI*, SHAILENDRA PRAKASH† and D.P. KOTHIYAL‡
Government Degree College, Chamba (Tehri-Garhwal), India

A series of new butenolactones has been synthesised by condensing a γ-oxoacid, β-(4-phenylbenzoyl) acrylic acid with various mono-, di- and trihydroxyphenols.

The substituted butenolactones are five membered unsaturated γ-lactones and some of them have received a wide attention due to their significant biological activity[1]. In this communication we report synthesis of some new butenolactones from a γ-oxoacid, β-(4-phenylbenzoyl)acrylic acid.

β-(4-Phenylbenzoyl)acrylic acid has been condensed with various phenolic compounds using concentrated sulphuric acid as condensing agent. The condensation products are butenolactones in which γ-carbon atom is attached to two different phenyl rings. Their structures have been established by elemental analysis, chemical reactions and spectral studies.

Melting points of the compounds were determined in open capillary tubes and are uncorrected. Compounds were checked for their purity by TLC. β-(4-Phenylbenzoyl)acrylic acid was prepared by literature procedure[2]. The various phenols used were phenol, resorcinol, catechol, quinol, phloroglucinol and pyrogallol.

General procedure for the synthesis of butenolactones (IV–IX)

β-(4-Phenylbenzoyl)acrylic acid (0.02 mol) was intimately mixed with appropriate phenolic compound (0.025 mol) and heated at 110–120°C until the contents become homogeneous. Concentrated sulphuric acid (4–5 drops) was added and heating was continued between 124–135°C for 2 to 6 h. On cooling a hard and brittle mass was obtained. It was crushed and washed well with water to remove excess of phenol. The residue was dissolved in 2% aq. NaOH and filtered. Acidification of the filtrate afforded the precipitate of butenolactones (IV-IX) which were purified by repeated crystallisation from ethanol. Physical data of the prepared compounds are presented in Table-1.

Acetylation of the butenolactone (V)

A mixture of butenolactone (V) (1.0 g), fused sodium acetate (3.0 g) and redistilled acetic anhydride (15 mL) was refluxed at 130–140°C for 3 h to give

---

†Department of Chemistry, Govt. P.G. College, Kotdwara (Garhwal), India.
‡Department of Chemistry, Govt. P.G. College, Gopeshwar (Chamoli), India.

a diacetyl compound (X) (1.0 g), m.p. 154–156°C (from ethanol). Found (%): C, 72.35; H, 4.71. $C_{22}H_{20}O_6$ required (%): C, 72.88; H, 4.67. IR (KBr): 1770, 1760, 1740, 1610 cm^{-1}. UV (MeOH): 208, 250, 296 nm.

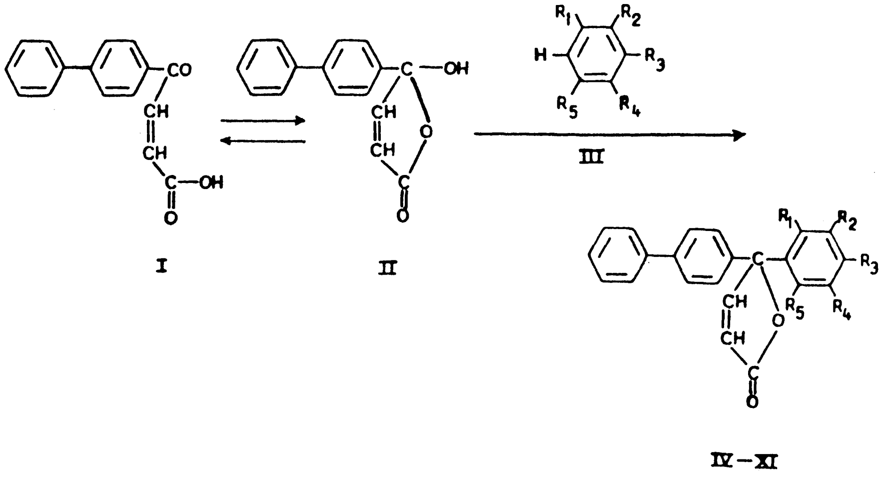
TABLE-1
PHYSICAL DATA OF VARIOUS BUTENOLACTIONES

Butenolactone	m.p. (°C)	Yield (%)	m.f.*
IV	150–152	64.5	$C_{22}H_{16}O_3$
V	170–172	72.1	$C_{22}H_{16}O_4$
VI	220–222	63.1	$C_{22}H_{16}O_4$
VII	215–217	70.1	$C_{22}H_{16}O_4$
VIII	220–222	56.2	$C_{22}H_{16}O_5$
IX	231–233	68.3	$C_{22}H_{16}O_5$

†All the compounds gave satisfactory elemental analysis

Bromination of the butenolactone (V)

Butenolactone (V) (1.0 g) was dissolved in glacial acetic acid (15 mL) and the resulting solution was cooled. A solution of bromine (1 mL) in glacial acetic acid (10 mL) was added drop by drop with stirring and cooling. On dilution with water, a pinkish brown dibromo compound (XI) (1.2 g) was obtained; m.p. 110–112°C



IV: $R_1 = R_2 = R_4 = R_5 = H$; $R_3 = OH$

V: $R_2 = R_4 = R_5 = H$; $R_1 = R_3 = OH$

VI: $R_1 = R_4 = R_5 = H$; $R_2 = R_3 = OH$

VII: $R_2 = R_3 = R_5 = H$; $R_1 = R_4 = OH$

VIII: $R_2 = R_4 = H$; $R_1 = R_3 = R_5 = OH$

IX: $R_4 = R_5 = H$; $R_1 = R_2 = R_3 = OH$

X: $R_2 = R_4 = R_5 = H$; $R_1 = R_3 = OCOCH_3$

XI: $R_5 = H$; $R_2 = R_4 = Br$; $R_1 = R_3 = OH$

Scheme-1

(from aqueous acetic acid). Found (%): C, 52.47; H, 2.82; Br, 31.77. $C_{22}H_{14}O_4Br_2$ requires (%): C, 52.58; H, 2.78; Br, 31.87. IR (KBr): 3450, 1795, 1730, 1705, 1685, 1620 cm^{-1}; UV (MeOH): 207, 256, 290 nm.

β-(4-Phenylbenzoyl) acrylic acid (I) reacted with phenols (III) in presence of concentrated sulphuric acid to give new butenolactones (IV–XI) in which γ-carbon atom is attached to two different phenyl rings. The acid (I) reacted with phenols through its lactol tautomeric form (II) as shown in the scheme. The occurrence of ring-chain tautomerism in γ-oxoacids is well known[3, 4] and in many chemical reactions, these acids participate through their cyclic lactol form[5, 6].

The IR spectra (in KBr, ν_{max} in cm^{-1}) of butenolactones (IV to IX and XI) showed a broad and strong absorption band around 3350 to 3450 cm^{-1} (bonded OH). The diacetyl compound (X) exhibited a band at 1760 cm^{-1} due to carbonyl stretching in phenolic acetate. All the butenolactones (IV–XI) displayed a sharp and strong band at 1760–1800 cm^{-1} assignable to lactonic carbonyl and the presence of this band supports the existence of a five-membered α,β-unsaturated γ-lactone ring in the proposed structures. All the compounds gave a sharp peak near 1620 cm^{-1} due to >C=C<stretching. The UV spectra of the butenolactones (IV–XI) showed two absorption bands at 204–216 nm and 248–292 nm in methanol due to lactonic structure[7].

ACKNOWLEDGEMENTS

The authors are thankful to Professor P.C. Gupta, former Head of Chemistry Department, Allahabad University for constant encouragement; the Director, CDRI, Lucknow, and the Head, RSIC, IIT, Madras for providing analytical and spectral data; and UGC, new Delhi for financial assistance to one of them (RPC).

REFERENCES

1. R.C. Larock, B. Refeling and C.A. Fellows, *J. Org. Chem.*, **43**, 131 (1978); D. Caine, F. Stephen and V.C. Ukachukawa, *J. Org. Chem.*, **48**, 740 (1983); Y.S. Rao, *Chem. Rev.*, **64**, 353 (1964).
2. H.G. Oddy, *J. Am. Chem. Soc.*, **45**, 2156 (1923).
3. P.R. Jones, *Chem. Rev.*, **63**, 461 (1963).
4. R.E. Valter, *Russ. Chem. Rev.*, **42**, 464 (1973).
5. C. Cauqill, H. Barrera and R. Barrera, *Bull. Soc. Chim. Fr.*, 173 (1951).
6. H. Burton and D.A. Munday, *J. Chem. Soc.*, 1727 (1959).
7. S.T. Vijayraghavan and T.R. Balasubramanian, *Indian J. Chem.*, **25B**, 760 (1986).

(*Received*: 26 August 1999; *Accepted:* 21 October 1999) AJC-1903