

A New Preparative Method for (*E*)-2,3-Diarylbut-2-enedials

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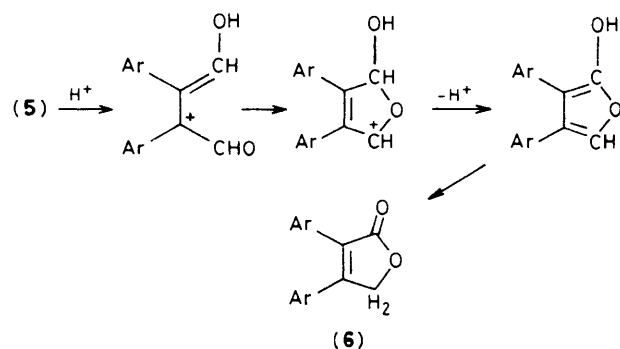
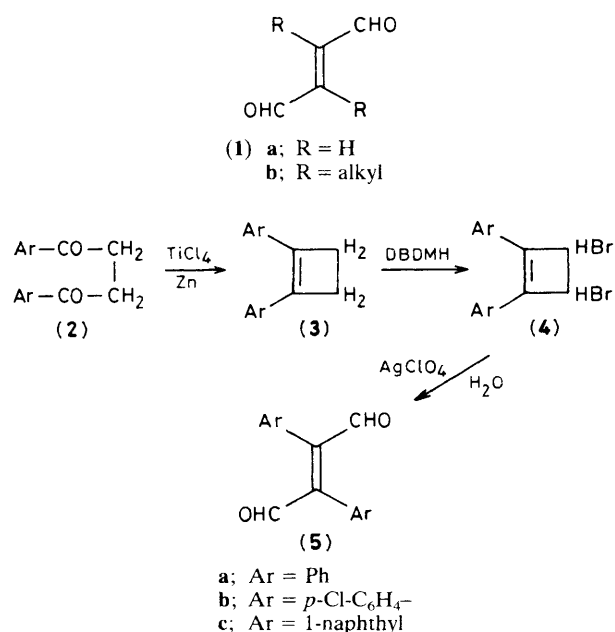
Reaction of 1,2-diaryl-3,4-dibromocyclobut-1-enes (**4**) with silver perchlorate in the presence of water gave (*E*)-2,3-diarylbut-2-enedials (**5**), which when treated with acid were converted into 2,3-diarylbut-2-en-4-olides (**6**).

Although but-2-enedial (**1a**)¹ and its 2,3-dialkyl derivative (**1b**)² are known, no 2,3-diarylbut-2-enedials (**5**) have been reported. We have prepared compounds (**5**) by treating the 1,2-diaryl-3,4-dibromocyclobut-1-enes (**4**) with silver perchlorate in the presence of water. The butenes (**4**) were easily obtained by reductive cyclisation of the 1,4-diarylbutane-1,4-diones (**2**) followed by bromination.

When 1,4-diphenylbutane-1,4-dione (**2a**) was treated with $\text{TiCl}_4\text{-Zn}^3$ in tetrahydrofuran (THF) under N_2 at 50–60 °C

for 24 h, 1,2-diphenylcyclobut-1-ene (**3a**) was obtained as colourless needles in 87% yield, m.p. 56 °C. By the same method, the 1,4-di(*p*-chlorophenyl) derivative (**2b**), m.p. 101–102 °C, and the 1,4-di(1-naphthyl) derivative (**2c**), m.p. 110–112 °C, were obtained in 71 and 88% yields, respectively. Treatment of (**3a**), (**3b**), and (**3c**) with 3 mol of *N,N'*-dibromodimethylhydantoin (DBDMH) in CCl_4 at 50–60 °C for 12 h gave their dibromo derivatives (**4a**), m.p. 120–121 °C, (**4b**), m.p. 140–142 °C, and (**4c**), m.p. 227–228 °C, in 89, 39, and 88% yields, respectively. The *trans*-structure of (**4a**) was determined by comparing its physical data with those of an authentic sample prepared by bromination of 3,4-dihydroxy-1,2-diphenylcyclobut-1-ene.⁴

Reaction of (**4a**) with silver perchlorate (practical grade of 90% purity, Wako Pure Chemical Industries Ltd., Japan) in THF containing water (10%) at room temperature for 10 min gave 2,3-diphenylbut-2-enedial (**5a**) as yellow needles in 80% yield, m.p. 221–222 °C, $\nu(\text{CO})$ 1680 cm^{-1} , λ_{max} 317 (ϵ 9700)



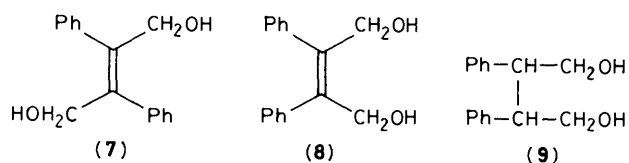
Scheme 1

and 408 nm (1700), $\delta(\text{CHO})$ 10.00.† Similar treatment of (4b) and (4c) with silver perchlorate gave (5b), m.p. 199–200 °C and (5c), m.p. 209–210 °C, in 80 and 95% yields, respectively. The mechanism of the reaction is not clear.

2,3-Diarylbut-2-enedials are useful materials for the preparation of various compounds because they contain two formyl groups and one double bond. For example, treatment of (5a) with HCl gas in CHCl_3 at room temperature for 1 h gave 2,3-diphenylbut-2-en-4-olide (6a)⁵ as colourless needles in 92% yield, m.p. 119–120 °C, $\nu(\text{CO})$ 1745, $\nu(\text{C}=\text{C})$ 1645 cm^{-1} , λ_{max} 288 nm (ϵ 13 500), $\delta(\text{CH}_2)$ 5.09. Similar treatment of (5b) and (5c) gave (6b), m.p. 119–120 °C, and (6c), m.p. 176–178 °C, in 75 and 78% yields, respectively. A plausible reaction mechanism for the formation of (6) is shown in Scheme 1.

The (*E*) structure of (5) was determined from the following experiments. Reduction of (5a) with sodium borohydride gave (*E*)-2,3-diphenylbut-2-ene-1,4-diol (7) as colourless prisms in 95% yield, m.p. 116–117 °C, $\delta(\text{Ph})$ 7.30, $\delta(\text{CH}_2)$ 4.12. On the other hand, reduction of (6a) with lithium aluminium hydride gave (8), the (*Z*)-isomer of (7),⁵ as colourless needles in 90% yield, m.p. 86.5–87.5 °C, $\delta(\text{Ph})$ 7.03, $\delta(\text{CH}_2)$ 4.40.

† The i.r., u.v., and n.m.r. spectra were measured in Nujol mull, CHCl_3 , and CDCl_3 , respectively.



The methylene protons of (7) which are shielded by the phenyl rings appear at higher magnetic field than do those of (8). Conversely, the phenyl protons of (8) which are shielded by the other phenyl ring appear at higher magnetic field than do those of (7). Catalytic reduction of (7) and (8) over Pd-C gave *rac*-(9), m.p. 125–127 °C, and *meso*-(9), m.p. 143–144 °C,⁵ respectively in almost quantitative yields.

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