Isolation of a 1,2-Dihydrophenol Derivative During an Oxepin Synthesis

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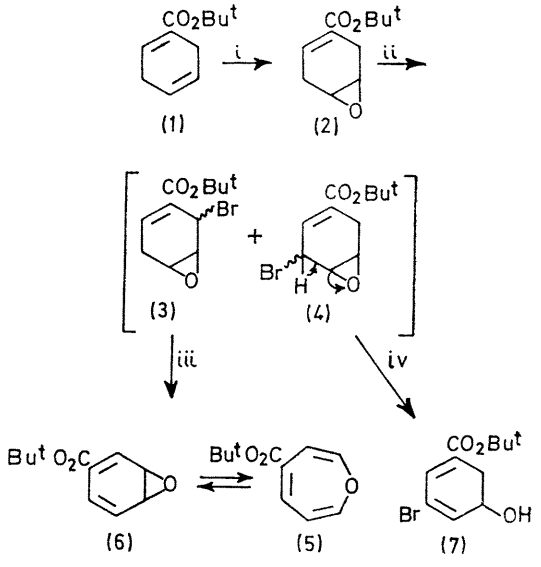
Summary The reaction of t-butyl 4,5-epoxycyclohex-1-enecarboxylate (**2**) with *N*-bromosuccinimide produces a mixture of two pairs of epimeric bromides, (**3**) and (**4**), which react with triethylamine to give t-butyl oxepin-4-carboxylate (**5**) [from (**3**)] and with potassium t-butoxide to give t-butyl 5-bromo-2,3-dihydro-3-hydroxybenzoate (**7**) [from (**4**)].

THE synthesis of oxepin-benzene oxide valence tautomers is usually achieved by elimination of HBr from 4,5-dibromocyclohexene oxide or 3-bromocyclohexa-1,4-diene monoxides with base.[1] We report an application of the latter procedure to isomeric bromides that leads to an oxepin or to a derivative of 1,2-dihydrophenol.

Diene (**1**)† (prepared in 70% yield from t-butyl propiolate and butadiene in benzene at 100°) was epoxidised with peracetic acid to produce (**2**) (80%). Epoxide (**2**) did not react with Br_2 in $CHCl_3$ or AcOH at room temperature for 18 h‡ but did react with *N*-bromosuccinimide to produce a mixture of allylic bromides consisting of almost equal amounts of the pairs of epimers (**3**) and (**4**) (estimated from the n.m.r. spectrum). Treatment of the bromide mixture with Et_3N at room temperature for 8 h resulted in 1,4-elimination of HBr from epimers (**3**) to produce t-butyl oxepin-4-carboxylate (**5**) (41%) (see Scheme). Excess of Et_3N did not improve the yield of (**5**). The unchanged epimers (**4**) were separated from (**5**) by distillation and on treatment with $KOBu^t$ were isomerised to (**7**) (84%). [Similar treatment of the mixture of (**3**) and (**4**) with $KOBu^t$ produced (**7**) in 49% yield based on the total bromide mixture but no (**5**) could be isolated nor was any (**3**) recovered.] Thus Et_3N reacts selectively with (**3**) to



SCHEME

Reagents: i, $CH_3{\cdot}CO_3H$–$CHCl_3$ (40%); ii, *N*-bromosuccinimide–CCl_4; iii, Et_3N–Et_2O; iv, Bu^tOK–Et_2O at −78°, 30 min.

† Satisfactory analytical data were obtained for all new compounds reported except for the mixture of (**3**) and (**4**) which was not analysed and (**7**) in which case the elemental composition was determined from the high resolution mass spectrum.

‡ Models indicate that axial attack of bromine appears to be hindered by 1,3-diaxial interactions involving the methylene hydrogen atoms.

give (**5**) while KOBu^t decomposes (**3**) (or a product thereof) and isomerises (**4**) to (**7**) by initial abstraction of the most acidic proton.

Orange needles of (**5**), m.p. 37—39°, [λ_{max} (MeOH) 300 nm (ϵ 1140) trailing to >400 nm; δ ($CDCl_3$) 1·50 (9H, s), 5·40 (1H, d, *J* 5 Hz), 5·45 (1H, d, *J* 5 Hz), 5·80 (1H, dd, *J* 7, 5 Hz), 6·24 (1H, d, *J* 5 Hz), and 7·02 p.p.m. (1H, d, *J* 7 Hz)] were obtained by distillation and low-temperature recrystallisation from light petroleum. Oxepin (**5**) formed a Diels–Alder adduct (m.p. 164·5—166°) with maleic anhydride in refluxing benzene *via* the benzene oxide valence tautomer (**6**). Hot aqueous acid converted (**5**) into *m*-hydroxybenzoic acid and a trace of *p*-hydroxybenzoic acid.

The dihydrophenol (**7**) [δ ($CDCl_3$) 1·5 (9H, s) 2·3—2·9 (3H, m), 4·4 (1H, m), 6·5 (1H, m), and 7·0 p.p.m. (1H, m), ν_{max} (neat) 3450, 1708, 1635, and 1575 cm^{-1}] was obtained as a liquid by short-path distillation and gave an acetate on treatment with acetic anhydride–pyridine. Thermal decomposition of (**7**) or its acetate yielded t-butyl *m*-bromobenzoate.

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[1] E. Vogel and H. Günther, *Angew. Chem. Internat. Edn.*, 1967, **6**, 385.