

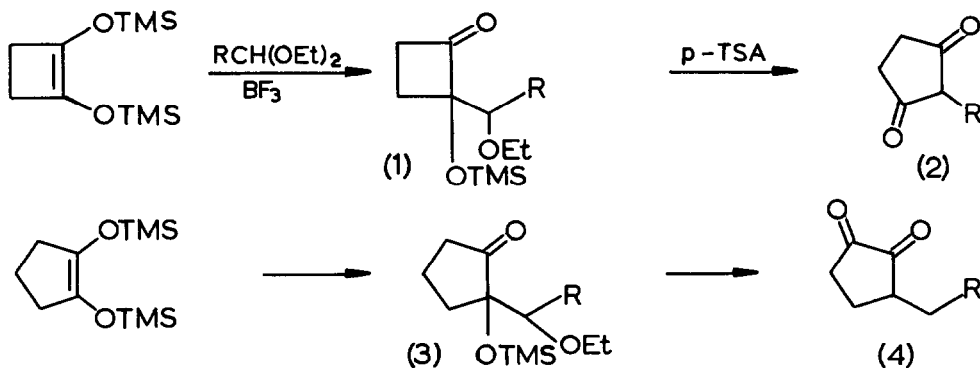
SYNTHESIS OF 3-ALKYLCYCLOPENTANE-1,2-DIONES BY
 ACID-CATALYSED REARRANGEMENTS OF α -KETOGLYCOL DERIVATIVES

Gerald Pattenden and Simon Teague

Chemistry Department, The University, Nottingham, NG7 2RD.

Summary: Treatment of the adducts(3) derived from 1,2-bis(trimethylsilyloxy)cyclopentene and acetals, with *p*-toluene sulphonic acid in hot benzene is shown to lead to the corresponding 3-alkylcyclopentane-1,2-diones(4).

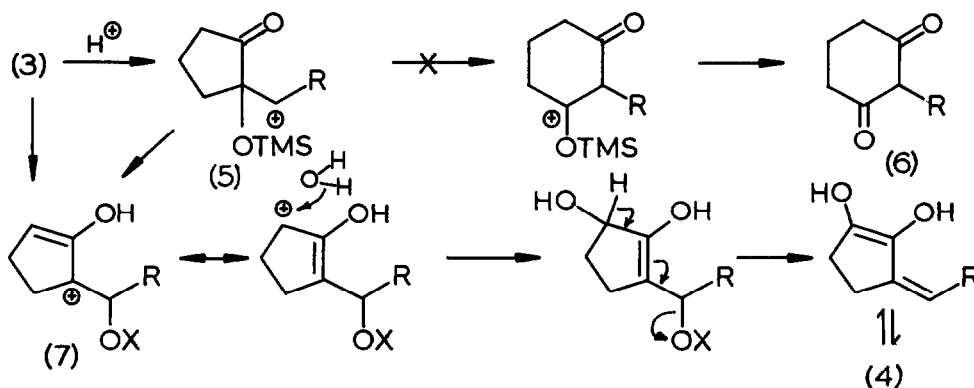
The pinacolonic rearrangement of adducts(1) derived from 1,2-bis(trimethylsilyloxy)cyclobutene and acetals, constitutes a useful synthetic route to 2-substituted cyclopentane-1,3-diones (2).¹ We now report that the corresponding sequence starting from 1,2-bis(trimethylsilyloxy)cyclopentene, instead leads to cyclopentane-1,2-dione derivatives (4). Several 3-alkyl substituted cyclopentane-1,2-diones occur naturally, and a number are used commercially as flavourants in various food items.²



Aldol reaction between 1,2-bis(trimethylsilyloxy)cyclopentene and isobutyraldehyde diethylacetal in the presence of boron trifluoride etherate at -78° , led to the cyclopentanone (3, $R=CHMe_2$) (65%), b.p. $124-6^\circ/12\text{ mm.}$, which on heating with *p*-toluenesulphonic acid in benzene rearranged giving the crystalline 1,2-dione (4, $R=CHMe_2$)³ (71%), m.p. $88-90^\circ$ (Lit.^{2b} m.p. $90-2^\circ$), ν_{max} (CCl_4) $1710, 1660\text{ cm}^{-1}$, δ 7.3 (OH), 2.4 ($-CH_2CH_2-$), 2.3 (d, J 6.2, CH_2CH), 2.0 (nonet, J \sim 6.5, CH_2CHMe_2), 9.52 (d, J 6.7, $CHMe_2$), δ_{carbon} 203.8, 149.7, 148.5, 38.0 t, 32.1 t, 27.0 d, 25.8 t, 22.8 q, p.p.m. In a similar manner, using the acetals/ketals derived from benzaldehyde, acetaldehyde and acetone, we obtained the 1,2-diones (4, $R=Ph$: 46% overall), (4, $R=CH_3$; 57% overall) and

(4, R=Me₂; 21% overall). In neither case did we obtain evidence for the co-formation of 2-alkylcyclohexane-1,3-diones (i.e. 6)³, resulting from ring expansion in (3).

The rearrangement of (3) to (4) at the expense of ring expansion (to 6) is interesting and the difference between the cyclobutanone [(1) + (2)] and cyclopentanone [(3) + (4)] acid catalysed rearrangements probably has its origin in release of ring strain in the former case. We envisage the rearrangement of (3) to (4) proceeding via the carbocation intermediate (5) through the enol (7). A closely similar rearrangement has been observed previously by Maignan and Rouessac during their studies of the acid-catalysed rearrangements of α,β -spiroepoxy- and 2-alkenyl-2-hydroxycyclopentanones.⁴



In a parallel series of reactions, the adducts derived from 1,2-bis-(trimethylsilyloxy)cyclohexene and several acetals [e.g. PhCH(OEt)₂, MeCH(OEt)₂, Me₂CHCH(OEt)₂] were found to undergo a similar rearrangement leading to the corresponding 3-alkylcyclohexane-1,2-diones.

We thank the S.E.R.C. for a studentship (to S.T.) and the Royal Society for an equipment grant.

References

1. E. Nakamura and I. Kuwajima, *J.Amer.Chem.Soc.*, 1977, **99**, 961; see also: I. Kuwajima and I. Azegami, *Tetrahedron Letters*, 1979, 2369, and W. Oppolzer and R.D. Wylie, *Helv.Chim.Acta*, 1980, **63**, 1198.
2. For other recent syntheses of cyclopentane-1,2-diones, see: (a) ref.3, (b) C.M. Leir, *J.Org.Chem.*, 1970, **35**, 3203; (c) R. Cookson and R.M. Lane, *J.Chem.Soc., Chem.Commun.*, 1976, 804, and refs. cited therein.
3. The 1,2- and 1,3-diones are drawn in the ketonic forms to show their similarity; they actually exist as enols.
4. C. Maignan and F. Rouessac, *Bull.Soc.Chim.France*, 1973, 1454; 1974, 2035; 1976, 550.