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AN INTERESTING RING CONTRACTION OF A CLASS OF BROMOHYDRINS AND TRANS-DIBROMIDES

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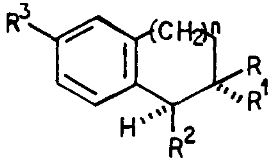
Abstract : An efficient ring contraction of stereoisomeric 1,2-benzo-4-bromo-3-hydroxycyclohept-1-ene and their derivatives (1a-e) to (2a-c) is reported, and a probable mechanism for this ring contraction has been suggested.

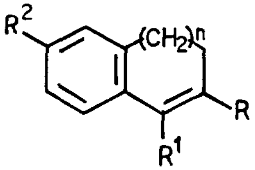
In connection with some other problems, we required the *trans*-bromohydrin (1a) in quantity. The crystalline *trans*-dibromide[1] (1b) showing benzylic hydrogen doublet at $\delta(CDCl_3)$ 5.48 (J=5Hz) was prepared from the styrene (4a), λ_{max}(EtOH) 262 nm (ϵ 17,490). Attempted preparation[2] of (1a) by heating under reflux (22h) a solution of the above *trans*-dibromide (1b) in a mixture of acetone and water (9:1) in presence of $MgCO_3$, afforded a product which after careful chromatography furnished, interestingly, the ring-contracted aldehyde (2a[3], 34%), ν_{max} 2735 (w) and 1720 (s) cm^{-1}, δ 9.38 (1H,d,J=2Hz,CHO); and a mixture (32%) of (2a) and its oxidation product (3) as the minor and major constituent in the mixture, ν_{max} 1720 (m) and 1670 (s) cm^{-1}. Crystallisation of this mixture provided 6-methoxy-1-tetralone (3) identical in all respects with an authentic sample. Similar treatment of (1b) under N_2 afforded only the aldehyde (2a) (from i.r. and ^{1}H n.m.r.). This aldehyde was directly oxidised to the ketone (3,67% based on 1b) by heating under reflux (22h) with aqueous alkaline tetrahydrofuran. Similar ring contraction of the crystalline *trans*-dibromide (1c), $\delta(CDCl_3)$ 5.33 (1H,s, benzylic), 3.75 (3H,s,OMe) and 2.10 (3H,s,Me), available through the styrene (4b), λ_{max} 264 nm (ϵ17,254), δ 6.10 (1H,s, olefinic proton) and 1.88 (3H,s), furnished in quantitative yield the stable aldehyde (2b)[4], ν_{max} 2700 (m) and 1710 (s) cm^{-1}, δ 9.27 (1H,s,CHO), 3.65 (3H,s,OMe) and 1.30 (3H,s,Me); and this furnished a crystalline 2,4-DNP in excellent yield.

Ring contraction of the *trans*-dibromides (1b-c)[5] probably proceeds through the intermediate *trans*-bromohydrins. With this idea in mind, the *trans*-bromohydrin (1a)[6], ν_{max} 3600 cm^{-1}, $\delta(CDCl_3)$ 4.86 (1H,d,J=7.5Hz, benzylic proton), prepared from (4a) following the stereospecific procedure of Dalton et al[7], was subjected to the above ring contraction procedure. The products after chromatography were the pure aldehyde (2a, 56%); and a mixture[8] (23%) of (2a) and the unsaturated aldehyde (4c), ν_{max} 1720 (s) and 1685 (s) cm^{-1}.



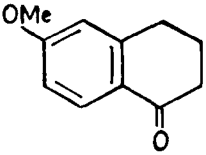
(1)

	R	R^1	R^2	R^3	n
a:	H	Br	OH	OMe	2
b:	H	Br	Br	OMe	2
c:	Me	Br	Br	OMe	2
d:	H	Br	OH	H	2
e:	Br	H	OH	OMe	2
f:	H	Br	OH	OMe	1

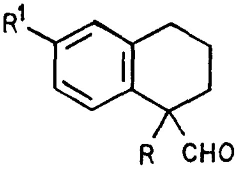


(4)

	R	R^1	R^2	n
a:	H	H	OMe	2
b:	Me	H	OMe	2
c:	H	CHO	OMe	1
d:	H	CHO	H	1
e:	Br	H	OMe	1



(3)



(2)

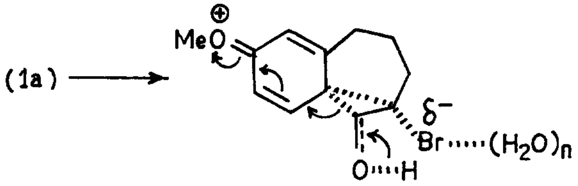
a: $R = H$, $R^1 = OMe$
b: $R = Me$, $R^1 = OMe$
c: $R = R^1 = H$

To study the role of the methoxyl group as in (1a-c) for the above ring contraction, the known *trans*-bromohydrin (1d)[9], lacking the methoxyl group, was treated under the above reaction condition to give only the unchanged material (1d). At higher temperature, i.e. refluxing (22h, N_2) a solution of (1d) in a mixture of dioxane-water (12:1) in presence of $MgCO_3$ afforded in good yield the ring-contracted aldehyde (2c, 69%), ν_{max} 2720 (m) and 1715 (s) cm^{-1}; δ 9.45 (1H,d,J=2Hz, CHO); and a mixture (19%) of (2c) and (4d), ν_{max} 1720 (m) and 1678 (s) cm^{-1}.

To investigate whether the stereochemistry of the bromohydrins is important for the above ring contraction, a solution of the crude *cis*-bromohydrin (1e)[10], δ 4.85 (1H,d,J=1Hz, benzylic proton), in aqueous acetone was refluxed (22h, N_2) as before to furnish mainly the recovered bromohydrin (1e). Under refluxing dioxane as before, the bromohydrin (1e) afforded in respectable yield the desired aldehyde (2a, 40%); and a mixture (20%) of (2a) and the unsaturated aldehyde (4c) as the major and minor product (from i.r.) respectively.

Ring contraction reaction was then extended to 6-membered trans-bromohydrin (1f)[11]. This bromohydrin under refluxing dioxane as before was completely recovered unchanged. Under forcing condition, i.e. heating under reflux (22h, N_2) in aqueous diglyme in presence of $MgCO_3$, the bromohydrin (1f) furnished the crystalline vinyl bromide (4e, 57%), δ 6.83-6.33 (4H,m, aromatic and vinyl protons), 3.70 (3H,s,OMe) and 2.90-2.60 (4H,m, benzylic and allylic protons), m/e 240 and 238 (M^+, doublet), as a result of dehydration. The failure of the 6-membered bromohydrin (1f) to ring contraction may possibly be due to high strain involved in attaining the transition state similar to (5).

We wish to propose the transition state (5)[12] (Scheme 1) involving Ar_1-3 type[13] participation for the above ring contraction. The conformation of the bromine atom (the leaving group) in the transition state seems to play an important role and this follows from the relative ease of ring contraction of the trans-bromohydrin (1a) when compared with its cis-isomer (1e).



(5)

SCHEME 1

The aerial oxidation of the reactive aldehyde (2a) to the ketone (3) through the intermediate hydroperoxide is not unusual particularly in acidic or alkaline medium which facilitates enolisation.

It may be mentioned in this connection that solvolysis of 3,4-dibromo-1:2,5:6-dibenzocyclooctatetraene was reported[14] earlier to afford ring contraction product.

The ring contraction reaction reported here seems to have synthetic importance, and further work is on progress.

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REFERENCES AND NOTES

1. All compounds described herein are racemic and provided the expected spectral data and elemental analyses. I.r. spectra reported are for solutions in $CHCl_3$ and n.m.r. spectra for solution in CCl_4 unless otherwise stated.
2. Cf.F.Straus and A. Rohrbacher, Chem.Ber., 54, 40 (1921); W.D. Cotterill, J.Cottam and R. Livingstone, J. Chem. Soc. (C), 1006 (1970).
3. This aldehyde having α-hydrogen is unstable. Attempted preparation of its 2,4-DNP gave a mixture. This aldehyde was prepared earlier by a different method (see ref.15) but no spectral data was reported.
4. This compound having gem-methyl-aldehydo function may serve as a potential intermediate for the synthesis of a class of terpenes.
5. Direct ring contraction of these dibromides can not be altogether ruled out at this stage.
6. Purification of this bromohydrin was difficult due to its partial transformation to ring-contracted product(s).
7. D.R. Dalton, V.P. Dutta and D.C. Jones, J. Am. Chem. Soc., 90, 5498 (1968).
8. The presence of 6-methoxy-1-naphthaldehyde in this mixture can not be ruled out altogether at this stage. Rechromatography of this mixture provided additional amount of (2a).
9. A. Chatterjee, D. Banerjee, B. Banerjee and R. Mallik, Tetrahedron, 39, 2965 (1983).
10. The stereochemistry of (1e) was established from comparison of its ^{1}H n.m.r. spectrum with that of its trans-isomer (1a).
11. A. Chatterjee, D. Banerjee and R. Mallik, Tetrahedron, 33, 85 (1977).
12. The participation of water molecules for the solvation of bromine atom is supported by the fact that attempted ring contraction of (1d) in the absence of water furnished recovered (1d; 75%), and a small amount of ring contraction product.
13. Cf. W.S. Murphy and S. Wattanasin, Chem.Soc.Rev., 12, 213 (1983).
14. M. Avram, I.G. Dinulescu, D. Dinu, G. Mateescu and C.D. Nenitzescu, Tetrahedron, 19, 309 (1963).
15. A. Kumar, R. Sing and A.K. Mandal, Synth. Commun., 12(8), 613, 1982.

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