Tetrahedron Letters,Vol.29,No.40,pp 5099-5100,1988
Printed in Great Britain

0040-4039/88 $3.00 + .00
Pergamon Press plc

THE BROMOKETONE - PHENOL REARRANGEMENT

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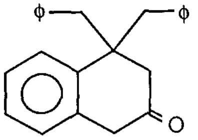
Summary: Reaction of ketone 1 with phosphorus pentabromide or bromine results in bromination (or dibromination) at C-4. The resulting α-bromoketones rearrange rapidly in acid solutions to yield phenols 2 and 3.

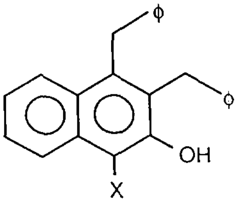
Dienone - phenol rearrangements are probably the best known rearrangement processes which result in aromatization of previously alicyclic rings.[1] They have been employed in syntheses of steroid carcinogens.[2] In these reaction the migrating groups originate at positions *ortho* or *para* to the original carbonyl functions.

We now report the first example of an "aromatizing" rearrangement in which the migrating group originates at a position *meta* to the carbonyl function of a cyclohexanone derivative.

Reaction of ketone 1[3] with two moles of phosphorus pentabromide (in an attempt to convert it to a vinyl bromide) yielded as the sole product 3,4-dibenzyl-1-bromo-2-naphthol (2), m.p. 141-142°C (ethanol).



1

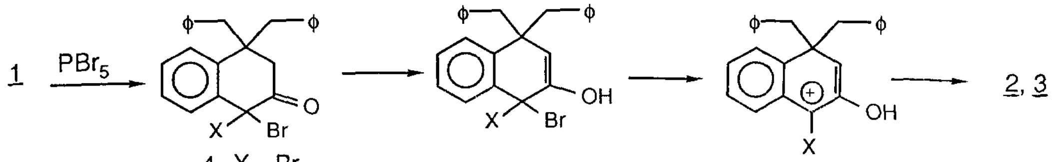


2, X = Br

3, X = H

Reaction of ketone 1 with one mole of phosphorus pentabromide yielded unreacted 1, phenol 2, and a third component, assumed to be 3,4-dibenzyl-2-naphthol (3) since its ^{1}H NMR spectrum showed singlets ($-\underline{CH_2}Ar$) at δ 4.21 and 4.41 (compared to δ 4.29 and 4.43 for phenol 2). Since 2 and 3 could not readily be separated, phenol 3 was prepared as a pale brown oil by debromination of 2 with zinc in acetic acid, and shown to be the third component in the reaction mixture by comparison of spectra and tlc retention times.

Formation of 2 and 3 from 1 was hypothesized to result from a mechanism such as that shown below:[4]



4, X = Br
5, X = H

To confirm this mechanism, ketone 1 was reacted with bromine in carbon tetrachloride at -10^{0}C. Reaction with two moles of bromine, followed quickly by washing with sodium bicarbonate to remove hydrogen bromide, yielded the expected dibromide 4 as a pale yellow oil which was stable for several days at room temperature (or several weeks at 0^{0}C). However, samples of 4 invariably rearranged to 2 on prolonged storage. If the hydrogen bromide produced by the bromination were not rapidly neutralized, rearrangement of 4 was complete in 2-3 hours at room temperature. Reaction of 1 with one mole of bromine yielded a mixture containing both 4 and the monobromoketone 5 (identified by a signal at δ 4.72). On standing this mixture rearranged to yield both 2 and 3, thus confirming most details of the mechanism

Acknowledgements: We thank the donors of the Petroleum Research Fund, administered by the American Chemical Society, for a grant which supported this work.

REFERENCES AND FOOTNOTES

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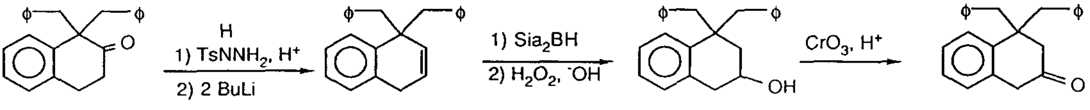
1. For reviews, see A. J. Waring in "Advances in Alicyclic Chemistry," H. Hart and G. J. Karabatsos, Eds., p. 207, Academic Press, New York, 1966; B. Miller in "Mechanims of Molecular Migrations," Vol. 1, B. S. Thyagarajan, Ed., p. 247, Interscience Publishers, New York, 1968; B. Miller, *Acc. Chem. Res.*, *1975*, 8, 245.
2. H. H. Inhoffen in "Progress in Organic Chemistry," Vol. 2, J. W. Cook, Ed., p. 146, Buttersworth Scientific Publications, London, 1953.
3. Ketone 1 (oil) was prepared from 1,1-dibenzyl-2-tetralone as shown below:



4. Phosphorus pentabromide can react as an electrophilic brominating agent at high temperatures (B. M. Mikhailov and M. S. Promyslov, *Zhur. Obsheh. Khim*, *1950*, 20, 338), but we are not aware of any other example of such reactions with ketones.

(Received in USA 22 July 1988)