Tetrahedron Letters No. 40, pp 3537 - 3538, 1974. Pergamon Press. Printed in Great Britain.

A NEW CARBON SKELETON REARRANGEMENT UNDER BASIC CONDITIONS : 2-HYDROXY[3,5-$^{2}H_{2}$]-BENZALDEHYDE FROM 2-QUINUCLIDINIO[3,5,7-$^{3}H_{2}$]TROPONE IN CONCENTRATED ALKALI[1]

Gino Biggi, Francesco Del Cima, and Francesco Pietra*
Department of Chemistry, Universita`di Pisa, 56100 Pisa, Italy

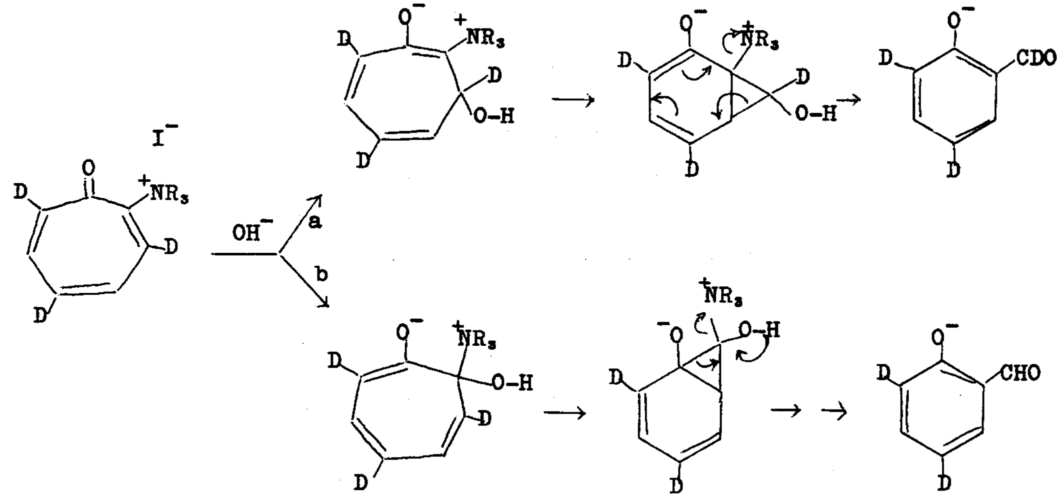
(Received in UK 6 June 1974; accepted for publication 19 June 1974)

Our knowledge of carbon skeleton rearrangements under basic conditions is very limited in comparison with carbonium ion rearrangements.[2] Therefore it was quite interesting recently to discover several new base-induced ring contractions of troponoids[3] leading to benzene derivatives.[4] We report here a novel such case which, besides adding to our general knowledge of base-induced carbon skeleton rearrangement, is of high specific interest in the area of pseudoaromatic compounds.[3]

It is known that 2-quinuclidiniotropone[4] in dilute alkali gives benzoic acid in nearly quantitative yield by expulsion of C_1 from the seven-membered ring whereas when the rearrangement is carried out in 5.8 M alkali, benzoic acid is accompanied by ca. 25% of salicylaldehyde, the aldehydic carbon arising from troponoidal C_3.[4b] We have now found that on raising sodium hydroxide concentration to 7.8-8 M,[5] 2-quinuclidinio[3,5,7-$^{3}H_{2}$]tropone gives a 1:2 to 1:1 mixture of 2-hydroxy[3,5-$^{2}H_{2}$]benzaldehyde and 2-hydroxy[3,5-$^{2}H_{2}$]α-deuteriobenzaldehyde.[4b]

Though exchange of the aldehydic proton under the above reaction conditions[5] was considered very unlikely,[6] it was safe to carry out experiments in order to exclude it rigorously. Thus, an aqueous solution of 2-hydroxy[3,5-$^{2}H_{2}$]α-deuteriobenzaldehyde, obtained by the treatment of 2-chloro[3,5,7-$^{3}H_{2}$]tropone with 1 M aqueous NaOH,[4b] was made strongly alkaline (8 M) with NaOH for 15 min whereby no exchange of the aldehydic deuterium for hydrogen was observed.

These findings are consistent with two parallel paths (Scheme) whereby the ''heavy'' aldehyde is formed by OH^- attack at C_3 (path a),[4b] whilst the ''light'' aldehyde arises from OH^- attack at C_2 (path b). This would then constitute the



SCHEME

the first case of the long proposed,[7] but subsequently disproved[8] benzenoid rearrangement of troponoids by C_2 expulsion, thus complementing benzenoid rearrangements undergone by troponoids with bases by expulsion of C_1,[4b,8] C_3,[4b,9] C_6,[4] and, perhaps, also C_4 or C_5.[10]

We acknowledge financial support from C.N.R., Roma.

REFERENCES AND NOTES

1)Pseudoaromatic Compounds. XVI. Part XV : F. Pietra, Chem. Comm., in the press.
2) J. D. Roberts and M. C. Caserio, ''Basic Principles of Organic Chemistry'', W. A. Benjamin, New York, N. Y., 1965, p 495.
3) F. Pietra, Chem. Rev., 73, 293 (1973).
4) (a) G. Biggi, F. Del Cima, and F. Pietra, Chem. Comm., 1627 (1971); (b) G. Biggi, A. J. de Hoog, F. Del Cima, and F. Pietra, J. Amer. Chem. Soc., 95, 7108 (1973).
5) To avoid heterogeneous conditions in aqueous medium, the experiment was performed on adding a solution of 2-quinuclidiniotropone iodide in the minimum amount of dimethyl sulfoxide to concentrated aqueous sodium hydroxide under vigorous stirring. After 15 min the mixture was acidified, dichloromethane extracted and the aldehyde recovered from the organic phase by chromatography on a silica gel column.
6) W. J. Bover, W. J. Scott, and P. Zuman, 165 ACS Meeting, April 1973, ORGN 25.
7) P. L. Pauson, Chem. Rev., 55, 9 (1955), p 83.
8) W. von E. Doering and D. B. Denny, J. Amer. Chem. Soc., 77, 4619 (1955).
9) E. J. Forbes, D.C. Warrell, and W. J. Fry, J. Chem. Soc. (C), 1693 (1967).
10) Y. Kitahara, Sci. Repts. Tohoku Univ., I 39, 255 (1956), referred to in T. Nozoe, T. Mukai, and T. Sakai, Tetrahedron Lett., 1041 (1965).