Tetrahedron Letters,Vol.24,No.24,pp 2509-2512,1983 0040-4039/83 $3.00 + .00
Printed in Great Britain ©1983 Pergamon Press Ltd.

STUDIES IN CLAISEN REARRANGEMENTS

A NOVEL OXIDATIVE REARRANGEMENT OF 3-ARYLOXYMETHYL-(4H)-BENZOPYRANS

S.Selvaraj, K.G.Sanjeevi Babu and K.K.Balasubramanian*
Department of Chemistry
Indian Institute of Technology, Madras-600036, India

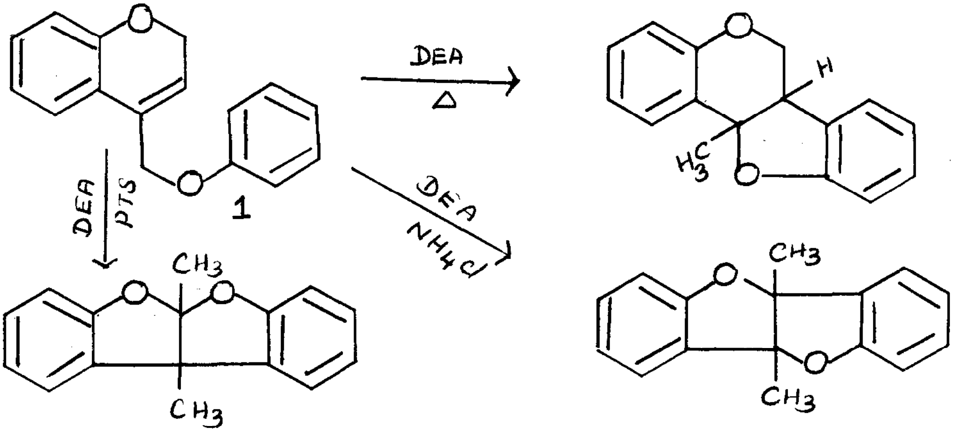
and

K.Rajagopalan
Department of Organic Chemistry,
University of Madras, A.C.College, Madras 600 025, India.

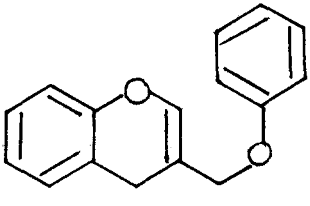
Abstract:

3-Aryloxymethyl-(4H)-benzopyrans 2 have been found to undergo a novel Oxidative Claisen rearrangement. In contrast, the Claisen rearrangement of 3-aryloxymethyl-(2H)-benzopyrans afforded only the normal products 8 .

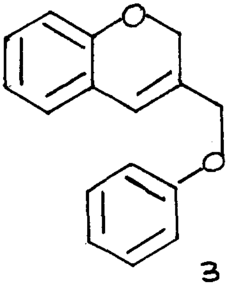
Several interesting transformations have been reported from the study of the thermal[1] and charge induced[2] Claisen rearrangement of 4-aryloxymethyl-(2H)-benzopyrans 1 .



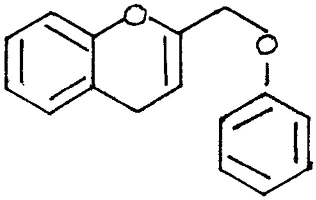
Prompted by these reports, we undertook the synthesis and a comparative study of the Claisen rearrangement of the hitherto unknown isomeric systems 2, 3 and 4 depicted below:



2



3



4

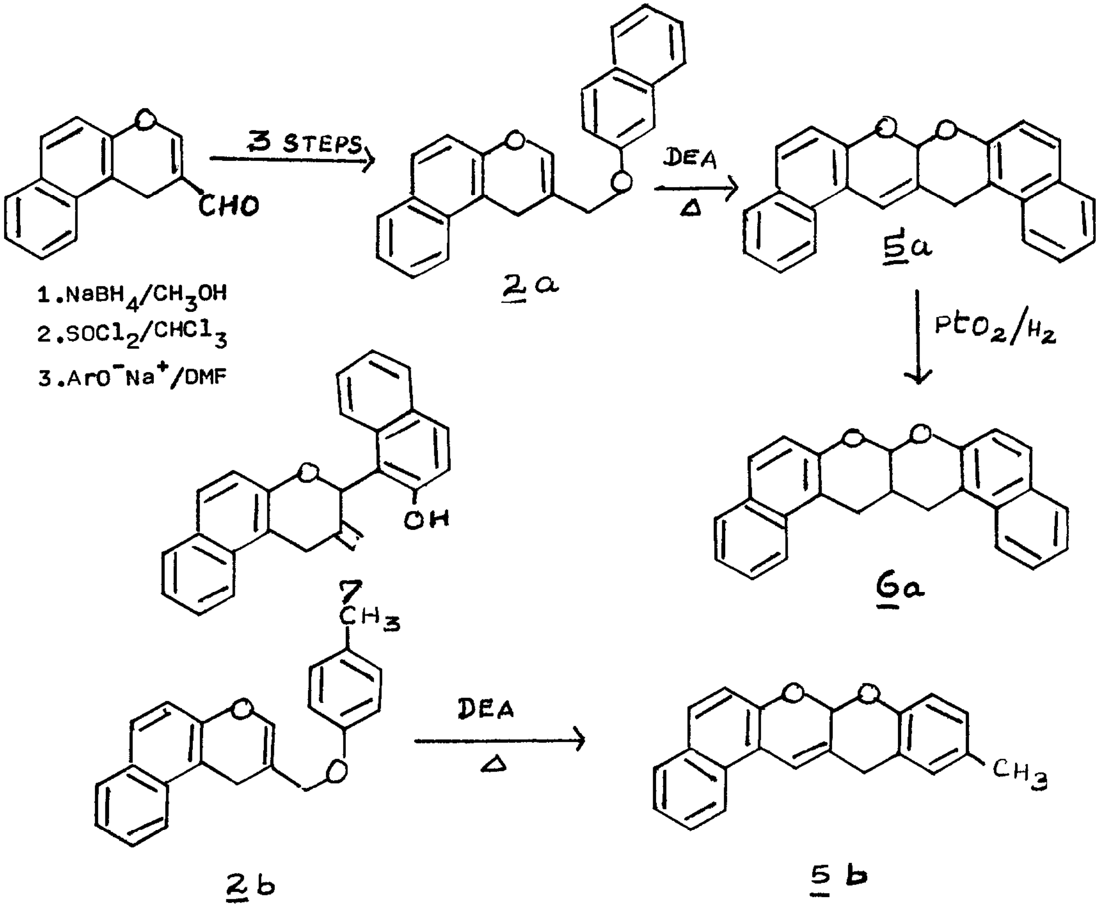
In this communication, we wish to describe a novel oxidative rearrangement of the ethers 2 to benzopyrano(2,3-b)benzopyrans 5 and emphasise the remarkable contrast in the thermal behaviour of the three isomeric systems, viz., 1, 2 and 3.

The starting ethers 2 and 3 were prepared from the respective aldehydes[3,4] by the standard sequence of reactions (vide schemes I and II). Refluxing a solution of the ether 2a in N,N-diethylaniline in a nitrogen atmosphere for 8 hrs, afforded, after work up and column chromatography of the crude product, a white solid, m.p.194°C in 35% yield. Elemental analysis and mass spectrum of this product (M^+ 336) indicated the molecular formula to be $C_{24}H_{16}O_2$, two units less in hydrogen than that of the starting compound. Its PMR spectrum showed signals at δ 4.1(q, 2H, J = 18 Hz), 6.7(s, 1H), 7.1-8.2(m, 12H). The ^{13}C NMR spectrum displayed signals at 150.94, 148.31, 132.30, 130.00, 129.51, 128.67, 128.22, 128.13, 126.84, 125.70, 124.10, 123.97, 121.97, 121.73, 121.00, 119.16, 117.35, 115.63, 114.49, 111.29, 96.02 and 31.23. The spectral data clearly eliminate all the structural possibilities that can be envisaged from the product 7 of normal Claisen rearrangement of the ether 2a and are consistent with the assigned structure 5a[5] . Catalytic reduction of the rearranged product 5a over PtO_2 yielded the dihydroderivative 6a, m.p.184-86°C (89%) (M^+ 338). Its PMR spectrum showed signals at δ 2.6-3.4(m,5H), 5.85(d, 1H, J=2Hz) and 7.1-7.8(m,12H). The ^{13}C spectrum of the dihydroderivative 6a exhibited only 13 signals;at δ 148.81(s, aromatic), 132.80(s,aromatic), 129.67(s,aromatic); 128.55(d,aromatic) 128.37(d,aromatic), 126.55(d,aromatic), 123.78(d,aromatic), 121.94(d, aromatic), 118.74(d,aromatic), 112.29(s,aromatic),95.06(d,C-8), 28.46(d,C-20), 24.80(t,C-19 and C-21). The spectral data thus further confirmed the assigned structures. Rearrangement of the ether 2b likewise, afforded the product 5b , m.p.74-76°C. Under the conditions of these rearrangements, the dihydrocompound 6a was found to be stable and did not lead to the formation of the compound 5a, indicating that this oxidative rearrangement does not proceed through the intermediacy of the dihydroproduct 6a . Oxidation must have occured at one of the early or intermediate steps and not in the final step of this transformation. Exposure of the ether 2a to trifluoroacetic acid in dichloromethane[6] or anhydrous aluminium chloride in dry carbontetra chloride[2] gave rise to products different from 5a.

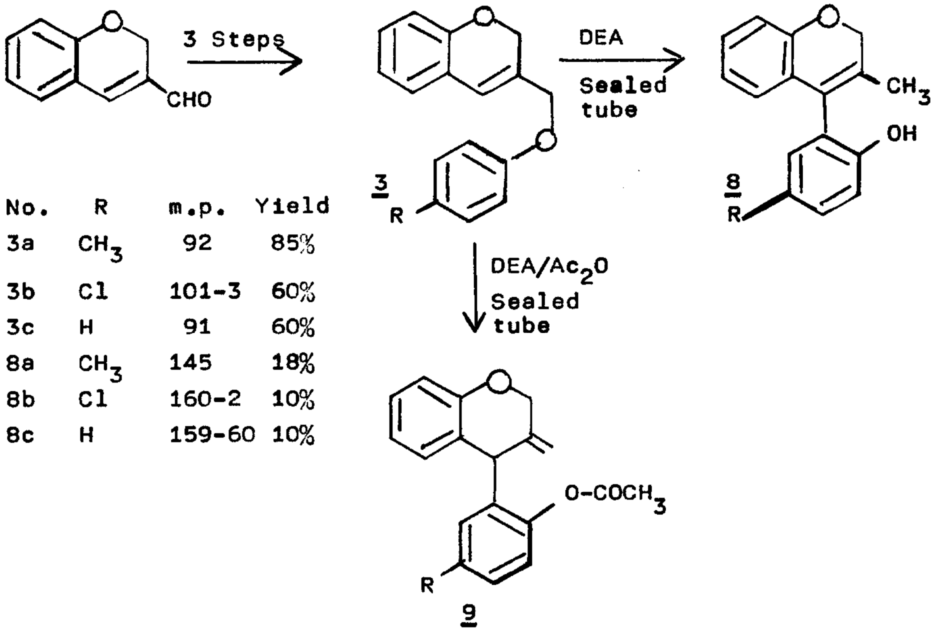
In contrast to the interesting rearrangements undergone by the ethers 1 and 2, the rearrangement of the 3-aryloxymethyl-(2H)-benzopyrans 3 was quite slow[8] (heating in N,N-diethylaniline in a sealed tube at 220°C for 80 hrs) and gave rise to normal products 8 but in poor yields. The reactions were considerably cleaner when the rearrangements were conducted in the presence of acetic anhydride. In the event, the acetate derivatives 9 were obtained in better yields (~60%).

Oxidative rearrangements of the type 2 → 5 have not been reported in any of the Claisen rearrangement studies so far[9-12]. The remarkable difference in the behaviour of these three isomeric systems viz., 1, 2 and 3 merits further investigations, particularly, a study of the Claisen rearrangement of the hitherto unknown 2-aryloxymethyl-(4H)-benzopyrans 4. We are currently working on this aspect.

SCHEME - 1



SCHEME II



No.	R	m.p.	Yield
3a	CH_3	92	85%
3b	Cl	101-3	60%
3c	H	91	60%
8a	CH_3	145	18%
8b	Cl	160-2	10%
8c	H	159-60	10%

Acknowledgement: Our thanks are due to Dr.K.Nagarajan, CIBA-GEIGY Research Centre, Bombay, for the analytical and mass spectral data. We thank Prof.A.J.Boulton, Univ. of East Anglia, U.K., for the ^{13}C NMR data and for useful discussions. We thank also Prof.C.A.Grob Univ. of Basle, Switzerland and Messrs.BASF, West Germany for the generous gift of propargyl alcohol.

References:

1. B.S.Thyagarajan, K.K.Balasubramanian, K.C.Majumdar, J.Heterocyclic Chem., 10, 159-64 (1973) and references cited therein.
2. D.K.Bates, Michael,C.Jones, J.Org.Chem., 3856 (1978).
3. K.K.Balasubramanian and S.Selvaraj, Tetrahedron Lett., 851 (1980).
4. Loic Rene and Edna Royer, Eur.J.Med.Chem. Chemical Therapeutica, 10, 72 (1975).
5. To our knowledge, this ring system, viz.,Benzopyrano(2,3-b)benzopyran is not known in literature.
6. U.Svanholm, V.D.Parker, J.Chem.Soc.,Chem.Comm., 645 (1972) and ibid., J.Chem.Soc., Perkin Trans., 11, 169 (1974).
7. The characterisation of products obtained from these reactions are under investigation.
8. Cinnamyl phenyl ether which have the same structural array rearrange much faster on refluxing in N,N-diethylaniline (3 to 14 hrs.). See W.N.White and W.K.Fift, J.Am.Chem.Soc., 83, 3846 (1961) The corresponding 4-chloro-3-aryloxymethylchromenes was found to undergo cleavage and dimerisation. See K.K.Balasubramanian, C.Devakumar, Mridula Nair and B.Venugopalan, Chemistry and Industry, 611, (1976).
9. D.S.Tarbell, 'Organic Reactions' , R.Adams, Ed., J.Wiley, New York, Vol.II (1944).
10. S.J.Rhoads, N.R.Raulins, Organic Reactions, 22, 1 (1975).
11. F.E.Ziegler, Accts.Chem.Res., 10, 227 (1977)
12. Gregory B.Bennett, Synthesis, 589 (1977).

(Received in UK 25 March 1983)