Tetrahedron Letters,Vol.27,No.48,pp 5883-5884,1986 0040-4039/86 $3.00 + .00
Printed in Great Britain Pergamon Journals Ltd.

A FACILE SYNTHESIS OF 3-METHYL-2H-1-BENZOPYRANS VIA CLAISEN REARRANGEMENT

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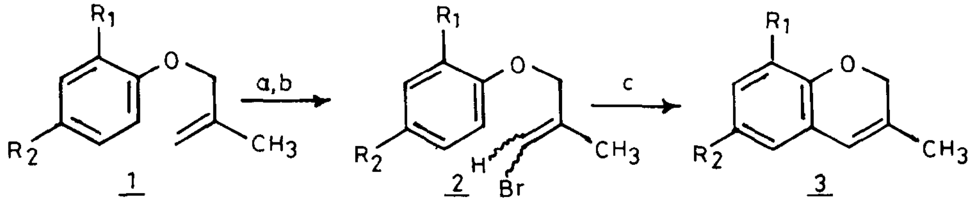
Summary : Several aryl-1(3-bromo-2-methyl-prop-2-ene) ethers 2 have been prepared and their thermal rearrangements in PEG-400 in the presence of N,N-diethylaniline were found to yield the title compounds.

The 2H-1-benzopyran ring system is an important heterocycle present in a number of naturally occuring molecules endowed with a variety of biological activities[1]. In our endeavour to synthesize substrates capable of undergoing Tandem-Claisen-oxyCope-Claisen rearrangement, ethers 2 figured as one of the starting materials. Though 3-methyl-2H-1-benzopyrans (bearing no substituent in the homocyclic ring) have been synthesized via Wittig reaction[2,3], investigation of the Claisen rearrangement of the ethers 2 as a possible route to substituted 3-methyl-2H-1-benzopyrans looked worthwhile. Claisen rearrangement of the ethers of type 2 have been reported to be either unsuccessful[4] or very sluggish requiring several days for completion of the reaction[5].

The methallyl ethers 1 were brominated carefully under controlled conditions to furnish the dibromo compounds. They were subjected to dehydrobromination in refluxing KOH-CH_3OH, without further purification, to yield the expected vinyl bromides 2 as a mixture of E and Z isomers.



a. Br_2- CCl_4, 5-10°C b.KOH-CH_3OH c.PEG-400·DEA,Δ

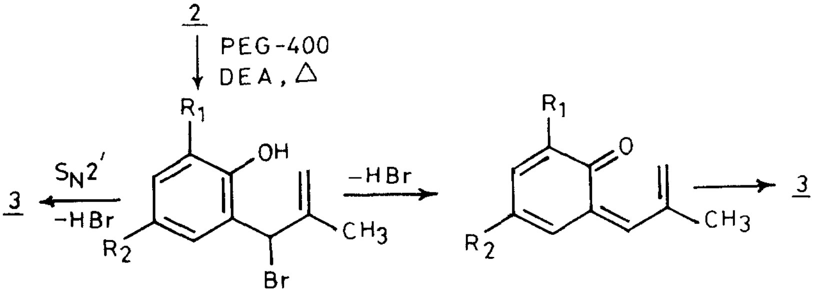
Refluxing ethers 2a in N,N-diethylaniline (DEA) for 10 h gave a mixture of starting material and 3-methyl-2H-1-benzopyran. The successful use of polyethylene glycol (PEG) in Claisen rearrangements[6] prompted us to use this solvent for the present study. Use of PEG-200 with added DEA (3 equivalents to 1 of ether 2a) did not result in a clean rearrangement. However, when ether 2a was refluxed in PEG-400 in the presence of DEA for 4-5 h it gave the pyran 3a in 85% yield. ^1H NMR spectrum confirmed its structure[7]. Similarly, ethers 2b-f were rearranged to the corresponding benzopyrans 3b-f in good yields (table).

Table[c]

Substrate	R_1	R_2	Yield of 2 %	M.p. or B.p.[a] of 2 in °C	Yield of 3 %	M.p. or B.p.[a] of 3 in °C
a	H	H	70	82-85/0.2 mm	85	65-66/0.2 mm
b	H	CH_3	70	96-100/0.2 mm	75	81-82/0.1 mm
c	H	Cl	85	105-110/0.5 mm	80	42-43
d	Cl	Cl	80	122-128/0.5 mm	76	70-72
e	OCH_3	H	80	100-105/0.5 mm	65	-[b]
f	H	C_6H_5	75	73-76	85	138-140

(a) M.p. and b.p. are uncorrected; (b) Attempts to distill this compound failed; (c) All new compounds (3a is a known compound) reported in this paper had satisfactory elemental analysis and spectral data.

The formation of these benzopyrans can be rationalised as follows:



We are currently investigating the scope of this rearrangement towards the synthesis of some complex skeletal frame works.

Acknowledgement

D.G. thanks University Grants Commission, Government of India for the financial assistance.

References

1. The Chemistry of Heterocyclic Compounds : Chromenes, chromanones and chromones, G.P.Ellis Ed., Interscience publications,pp.81 (1977).
2. E.E.Schweizer, A.T.Wehman and D.M.Nycz, J. Org. Chem. 38, 1583 (1973).
3. B.Begasse and M.Le Corre, Tetrahedron 36, 3409 (1980).
4. C.D.Hurd and C.N.Webb, J. Am. Chem. Soc. 58, 2190 (1936).
5. W.K.Anderson, E.J.Lavoie and J.C.Bottaro, J. Chem. Soc. Perk. Trans.I 1976, 1.
6. Usha Rao and K.K.Balasubramanian, Tetrahedron Letters, 1983, 5023.
7. A.T.Broune and R.H.Levin, Tetrahedron Letters, 1974, 2043.

(Received in UK 1 October 1986)