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CLAISEN REARRANGEMENT OF ARYL PROPARGYL ETHERS IN POLY(ETHYLENE GLYCOL)- A REMARKABLE SUBSTITUENT AND SOLVENT EFFECT[§]

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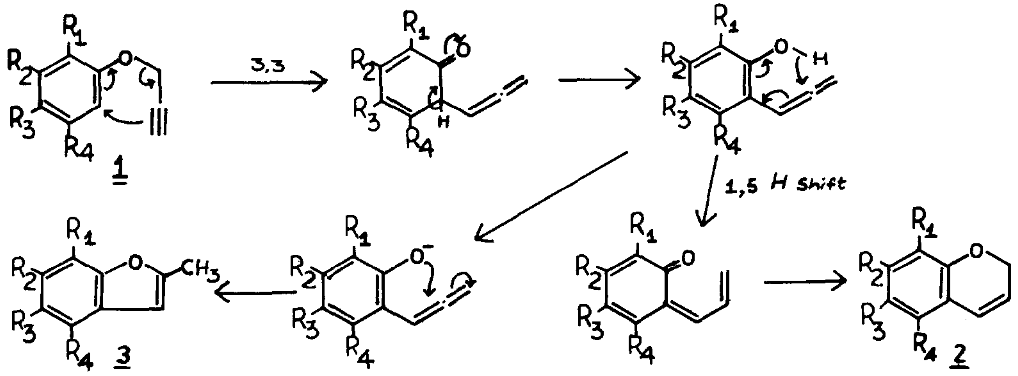
Abstract:
The Claisen rearrangement of aryl propargyl ethers in poly(ethylene glycol) - 200 at 220°C affords products in good yields. Aryl propargyl ethers containing electron donating groups yield (2H)-benzopyrans and those containing electron withdrawing groups yield 2-methylbenzofurans.

Thermal rearrangement of aryl propargyl ethers has been recognised as one of the general methods for the synthesis of (2H)-benzopyrans[1]. This rearrangement requires the use of high boiling solvents which will provide the high temperature necessary for the rearrangement[2]. Recent reports on the utility of poly(ethylene glycol)-200 (PEG) in organic synthesis prompted us to investigate the rearrangement of aryl propargyl ethers in PEG.

Aryl propargyl ethers[3] rearranged cleanly on heating in PEG-200 at 220°C to afford products in good yields. The reaction has been found to be 2 to 2.5 times faster in PEG when compared to in N,N-diethylaniline. When the substituent in the aryl group of the propargyl ether 1 is electron donating the product obtained is exclusively the (2H)-benzopyran 2 (Table I). On the other hand, ethers listed in Table III which contain electron withdrawing groups gave rise to 2-methylbenzofurans 3 as the only isolable product in moderate yields.



Interestingly a mixture of (2H)-benzopyrans 2 and 2-methylbenzofurans 3 were obtained from the rearrangement of ethers 1m-1p (see Table II).

TABLE I

Yields of (2H)-benzopyrans from the rearrangement of substituted aryl propargyl ethers.[4]

Compd No.	R_1	R_3	Yield %
1a	H	CH_3	88
1b	H	Cl	64
1c	H	OCH_3	90
1d	$-C_4H_4-$		65

TABLE II

Yields and ratios of 2:3 from the rearrangement of substituted aryl propargyl ethers[5].

Compd No.	R_1	R_3	Rxn. time in h	Yield %	Ratio 2:3
1m	Cl	H	1	50	43:57
1n	Cl	Cl	1	60	27:73
1o	H	CHO	1.5	40	75:25
1p	$COCH_3$	H	1	52	25:75

In order to rationalise the products obtained, we recognise the acidity of the phenol as well as the nucleophilic susceptibility of the central allenic carbon play a vital role. The formation of benzofurans from the rearrangement of ethers 1e to 1l in PEG is apparently due to the enhanced acidity of the phenolic intermediates compared to those of 1a-1d and also due to greater dissociation of these allenyl phenols in this solvent thereby leading to internal nucleophilic attack by the alleny phenoxide at the central allenic carbon. Thus, as could be anticipated when 1e was heated in PEG in the presence of p-toluenesulphonic acid at 220°C for 3 hours only the corresponding (2H)-benzopyran was obtained.

TABLE III

Yields of 2-methylbenzofurans from the rearrangement of substituted aryl propargyl ethers.

Compound No.	R_1	R_2	R_3	R_4	Rxn. time in h	Yield %
1e	H	H	NO_2	H	3.0	34 [6,10]
1f	H	NO_2	H	H	1.0	23
1g	NO_2	H	H	H	1:5	56
1h	H	H	$COCH_3$	H	0.75	57 [7]
1i	CHO	H	H	H	0.75	40
1j	H	CHO	H	H	0.75	46
1k	OCH_3	H	NO_2	H	2.0	46 [8]
1l	OCH_3	H	H	NO_2	2.0	45

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2. S.J. Rhoads and N.R. Raulins in Organic Reactions, Vol. 22, Chapter 1 Wiley, 1975.
3. Compounds 1a-1p were prepared according to the general procedure outlined by I. Iwai and J. Ide, Chem. Pharm. Bull. (Japan), 10, 926 (1962) and were characterised by IR and NMR spectra only. No elemental analysis was thought necessary.
4. The reaction time for the rearrangement of ethers 1a-1d is 30 minutes.
5. The relative ratios of 2:3 were determined by NMR analysis.
6. M. Harfnest and E. Thom, J. Org. Chem., 37, 841 (1972). In our hands p-nitrophenyl propargyl ether 1e did not give rise to any rearrangement product when refluxed in o-dichlorobenzene for 42 hours, only starting material was recovered.
7. p-acetylphenyl propargyl ether 1h yielded the corresponding 2-methylbenzofuran in PEG whereas Anderson et al reported the formation of (2H)-benzopyran in N,N-diethylaniline. W.K. Anderson and E.J. LaVoie, J. Org. Chem., 38, 3832, (1973).
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