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A SIMPLE ROUTE FOR THE SYNTHESIS OF 4-CHLOROCHROMENES AND CHROMAN-4-ONES

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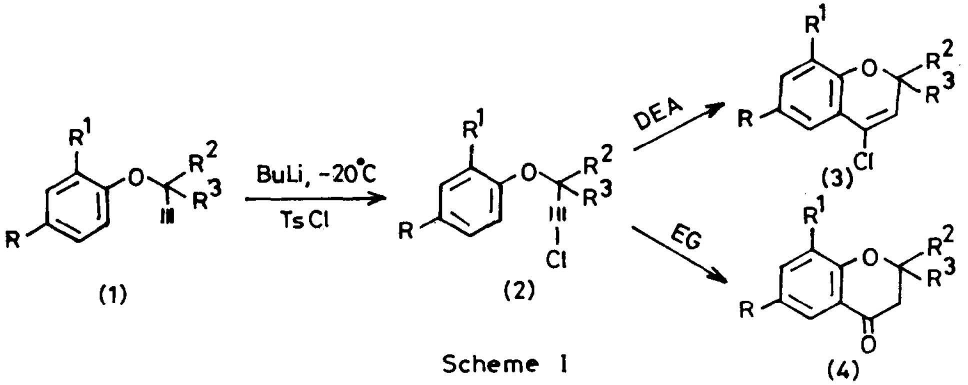
Abstract - A one pot synthesis of a number of 4-chlorochromenes and chroman-4-ones was achieved from γ-chloropropargyl aryl ethers proceeding through Claisen rearrangement, depending upon the solvent of choice.

Benzopyran compounds[1] are attracting continued attention due to their biological and insecticidal properties. The synthesis of chroman-4-one, the synthetic intermediate for this class of compounds, has therefore been the subject of our study[2]. Recent reports[3] on the synthetic utility of 4-chlorochromenes has prompted us to communicate our new synthesis of 4-chlorochromenes and chroman-4-ones from γ-chloropropargyl aryl ethers (2)[4].

When (2a) was refluxed in N, N-diethylaniline for 2h. the product obtained after usual work up was found to be 4-chlorochromene(3a) in 80% yield [5] (Scheme I). This was further confirmed by comparison with the authentic sample[6] by HPLC, IR, NMR and mass spectra. This was found to be general when extended to other substituents (2a-g)[7] (see Table I). When α-methyl- γ-chloropropargyl aryl ethers (2h-j) were subjected to rearrangement in refluxing DEA, the corresponding 4-chloro-2-methylchromenes (3h-j) were formed within 15 min. When extended to α, α-dimethyl cases (2k & 2l), the rearrangement was found to be even more rapid and the reaction was complete in 5 min.[8] at 180°C (Table I).

To our surprise, when ethers (2a-g) were refluxed in ethylene glycol a clean transformation to the corresponding chroman-4-ones (4a-g) was observed. γ-chloro- α -



Scheme I

Table I: Synthesis of 4-chlorochromenes(3) and chroman-4-ones(4)

Entry	R	R^1	R^2	R^3	Reaction temp. & time in DEA	Yield of (3) %	Reaction time at 180°C in EG	Yield of (4) %
a	OCH_3	H	H	H	215°C, 2h	80	4h	75
b	CH_3	H	H	H	215°C, 2h	75	4h	72
c	H	OCH_3	H	H	215°C, 2h	60	4h	74
d	H	CH_3	H	H	215°C, 2h	76	4h	60
e	Cl	H	H	H	215°C, 2h	72	4h	68
f	H	Cl	H	H	215°C, 2h	60	4h	60
g	H	H	H	H	215°C, 2h	60	4h	72
h	CH_3	H	CH_3	H	215°C, 15 min	70	40 min	65
i	Cl	H	CH_3	H	215°C, 15 min	67	40 min	70
j	OCH_3	H	CH_3	H	215°C, 15 min	78	40 min	76
k	Cl	H	CH_3	CH_3	180°C, 5 min	72	5 min	70
l	OCH_3	H	CH_3	CH_3	180°C, 5 min	80	5 min	72

methyl and α , α -dimethylpropargyl aryl ethers (2h-l) also afforded 2-methyl and 2,2-dimethylchroman-4-ones (4h-l) in good yields (see Table I). It is evident that (4) resulted from the hydrolysis of 4-chlorochromenes (3) under the reaction conditions[9]. This was established by refluxing (3a) in ethylene glycol for 2h. which gave rise to (4a) in 80% yield. Thus, the easy availability of the starting material, inexpensive and nontoxic solvent employed, simple work up and fairly high yield make this method more advantageous than the existing methods[10].

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References and Notes:

1. G.P. Ellis, 'Chromenes, Chromanones and Chromones', Wiley, New York, 1977.
2. G. Ariamala and K.K. Balasubramanian, J.Chem.Soc.,Chem.Commun., 1988, 34.
3. P.E. Brown and Q. Islam, Tetrahedron Lett., 1987, 3047; P. Anastasis, P.E. Brown and W.Y. Marcus, J.Chem.Soc., Perkin Trans I, 1986, 1127.
4. γ-chloropropargyl aryl ethers(2) could be prepared from the corresponding lithium salts of aryl propargyl ethers (1) with p-toluenesulfonylchloride.
5. Structural assignments were based on the spectral data and by comparison with those of authentic material wherever they are known.
6. H. Hofmann and G. Salbeck, Chem.Ber. 1971, 104, 168.
7. In the case of ethers 2e, 2f and 2g minor amount (~10%) of cis-2,3-dichloroallyl aryl ethers were also formed.
8. M. Harfenist and E.J. Thom, J.Org.Chem., 1972, 37, 841.
9. The mechanism probably involves the intermediate 4-chloro-4-(β -hydroxyethoxy) chroman (or) ethylene ketal of (4),which in the presence of the acid generated undergoes hydrolysis to afford (4).
10. H.J. Kobbe and A. Widdig, Angew.Chem.Int.Edn.Engl., 1982, 21, 247; S.T. Saengachantara and T.W. Wallace, J.Chem.Soc.,Chem.Commun., 1986, 1692, also see Ref.1.

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