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THERMAL BEHAVIOUR OF ARYL γ-HALOPROPARGYL ETHERS

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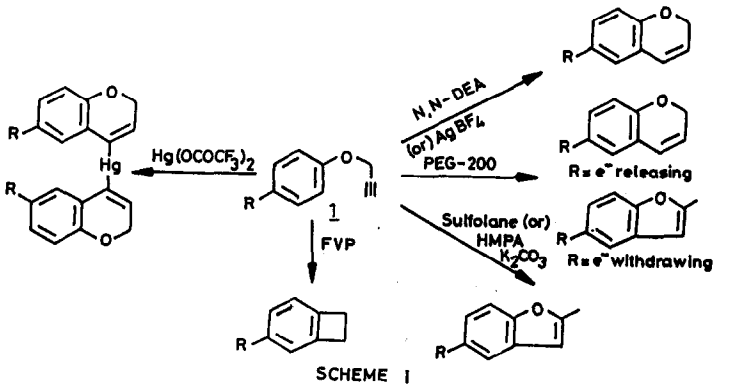
Abstract: A systematic study of the behaviour of aryl γ-halopropargyl ethers under thermal condition was undertaken. Aryl γ-bromopropargyl ethers 2 underwent unique transformation in N,N-diethylaniline (215°C, 6 h) giving rise to a mixture of products 3,4 and 5, whereas, under similar conditions aryl γ-chloropropargyl ethers 8, afforded 4-chlorochromenes, 9. A remarkable substituent and solvent effect has been observed in the thermolysis of these aryl γ-bromo and γ-chloropropargyl ethers, rendering this transformation as a method for the synthesis of a number of substituted 4-bromochromenes 3, 4-chlorochromenes 9 and chroman-4-ones 7. In contrast, solution thermolysis of aryl γ-iodopropargyl ether 11 afforded aryl propargyl ether 1 as the major product.

One of the important methods developed during the past several decades for C-C bond formation through highly ordered cyclic transition state involves the Claisen rearrangement[1]. The Claisen rearrangement of aryl propargyl ethers in high boiling solvents has found useful application as a method for the synthesis of 2H-1-benzopyrans[2]. The course of the rearrangement was observed to be markedly dependent upon the nature of the substituents, solvent[3] and the presence or absence of added bases[4]. No regioselectivity has been observed in the case of meta substituted aryl propargyl ethers[5]. Silver and mercuric ions have been



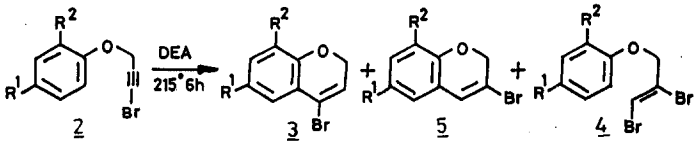
SCHEME I

found to catalyse this transformation[6] (Scheme-I).

Although the many facets of the aryl propargyl Claisen rearrangement have been well investigated, surprisingly there are only few reports [7], that too published only in recent times, on the thermal behaviour of aryl propargyl ether, functionally substituted at the γ-carbon of the propargyl moiety. In continuation of our on-going projects in the area of benzopyrans[8], we undertook a study of the synthesis and thermal rearrangement of aryl γ-halopropargyl ethers. Our objective in taking up this study was two-fold. To find out if these ethers would resemble aryl propargyl ether and afford 4-halochromenes or would behave like halogenoacetylenes, which are known for a wide range of thermal stability - explosive nature at one extreme to inertness even after several hours of heating at elevated temperatures[9].

RESULTS AND DISCUSSION

Aryl γ-bromopropargyl ethers:2 Aryl γ-bromopropargyl ethers 2 required for the study were prepared in quantitative yield from the corresponding aryl propargyl ethers 1[10]. The Claisen rearrangement of 2a was investigated in N,N-diethylaniline (DEA) at 215°C for 6 h. A dark viscous liquid was obtained in 46% yield upon work up of the neutral ether extract. The product was found to be highly nonpolar and its complexity could not be inferred from TLC. Its ^{1}H-NMR spectrum was more revealing, displaying signals at δ 4.4 (doublet, J: 8Hz), δ 4.65(doublet, J: 1.5Hz), δ 4.82 (doublet, J: 1.5Hz) and δ 5.75 (triplet, J: 8Hz) apart from the aromatic signals. Presence of 4-bromochromene 3a, the product expected in this reaction, could be inferred. Analysis of the integration and the chemical shifts indicated that the other products also contain $-OCH_2$ but without a vicinal partner in their structures. The weak doublet at δ 4.65 and the triplet at δ 7.1 with a relative integration of 2:1 suggested that this might be due to cis (or) trans-2,3-dibromoallyl aryl ether 4a (or) 6a, while the other product might well be the 3-bromochromene 5a, which would account for the doublet at δ 4.82 (Scheme-II).



SCHEME II

This surmise turned out to be true when the mixture was separated by column chromatography over alumina into pure components and their structures established by spectral data and also by comparison with the respective authentic samples[11] by HPLC. The mixture was analysed and separated using HPLC and the ratio of the products confirmed thereby (Table-I). The stereochemistry of the dibromoallyl aryl ether obtained in this rearrangement was fixed on the basis of the $^3J_{C-H}$ in ^{13}C-NMR gated spectrum of 4a and of the other isomer 6a synthesised independently. It is interesting to note that the other isomer, viz. trans-2,3-dibromoallyl aryl ether 6a was not formed in this reaction. This transformation was found to be a general one when extended to other aromatic ring substituents with the exception of ethers 2f and 2q[12]. As can be seen from the Table-I, the electron releasing substituents were found to have noticeable effect in changing the product ratio.

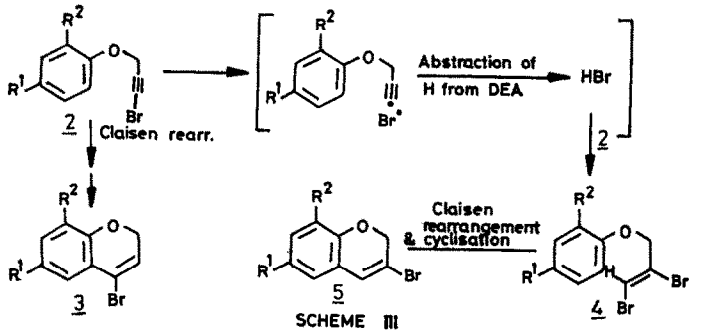
The occurrence of two competing reactions viz. aryl propargyl ether Claisen rearrangement and another reaction which probably involves the homolysis of the C≡C-Br was evident from the formation of 3a and 4a. While the formation of 3a was only anticipated, that of 4a was a surprise and lacks precedence in the

Table-I

Entry	R^1	R^2	Overall yield (%)	Ratio of 3:5:4
a	Cl	H	46	2:1:6.2
b	H	H	40	1:1.5:1.7
c	CH_3	H	50	3:4:1
d	OCH_3	H	55	6:1.2:1
e	Cl	Cl	45	0.5:1:1.2
f	$COCH_3$	H	-	-
g	NO_2	H	-	-
h	H	CH_3	40	2:1:1
i	H	OCH_3	52	2:1.5:1

literature. Viehe et al[9] have mentioned the formation of adducts of the type Ø(Br)C=C(Br)C≡CØ in the thermolysis of phenylbromoacetylene and the formation of HBr adduct was not observed. Analysis of the ratio of the products obtained indicates that the competing homolysis reaction is faster compared to the Claisen rearrangement. This is established by refluxing 2a in DEA for 1/2 h, wherein only 3a and 4a were formed in the ratio of 1:3,overall 60% yield. This indicates that the formation of 4a is faster than that of 3a (~ 3.1 times).

To have a probe into the mechanism, inter convertibility of products obtained was examined. While 3a and 5a were stable under the reaction conditions, 4a was smoothly transformed to 5a (75%) in 6 h. Formation of 5a from 4a could be rationalised as outlined in Scheme-III. The propargyl Claisen rearrangement was found to be totally suppressed in the presence of HBr. Thus, when 2a was refluxed in DEA in the presence of diethylanilinehydrobromide, 4a was the sole product (70%). Interestingly, heating 2a in DEA, in the presence of added bases like K_2CO_3 or $NaHCO_3$ for 6 h, led to debromination, resulting in the formation of aryl propargyl ether 1a.



SCHEME III

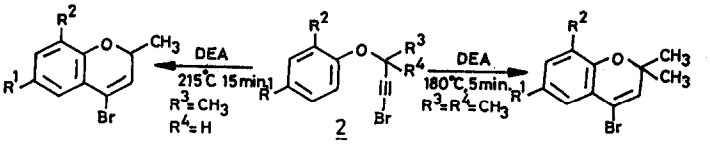
From the above observations, the mechanism of this transformation can be rationalised as in Scheme-III. Diethylaniline being a good free radical inhibitor[13] can lead to the formation of HBr by quenching the bromine radical. The liberated HBr could then add on to 2a leading to the formation of 4a. Our various attempts to trace the fate of the 3-aryloxyprop-1-ynyl radical were unsuccessful. Analysis of the reaction mixture at shorter or longer reaction time did not indicate any coupled product or aryl propargyl ether or chromene, products that could arise out of the radical. Reactions carried out with 1 equivalent of DEA at 215°C or with 1 equivalent of DEA in refluxing orthodichlorobenzene did not show the incorporation of 3-aryloxyprop-1-ynyl radical

into DEA, as revealed by the NMR analysis of the recovered DEA[14].

Phenyl(arylsulfonyl)acetylenes are reported[15] to add to alkenes like benznorbornadiene stereospecifically leading to trans products, which are formal adducts of the two fragments derived from homolytic cleavage of the C-S bond. In the light of this literature observation, a few attempts were made to trap the aryloxypropynyl radical. Reactions carried out with 2a in the presence of alkenes like benznorbornadiene, cyclohexene or anthracene as trapping agents in high boiling solvents or neat at 160-200°C failed to furnish any trapped adduct, but yielded only the same mixture of products.

α-substituent effect: From the above findings, it is clear that the competitive homolysis of C-Br bond was the predominant reaction compared to the aryl propargyl Claisen rearrangement, thereby lending little synthetic utility. α,α-dimethylpropargyl aryl ethers have been reported[16] to rearrange much faster compared to aryl propargyl ethers, while α-methylpropargyl aryl ether displayed moderate rate enhancement. This has been attributed to a conformational effect, which brings about an increase in the proportion of the rotamer best positioned for Claisen rearrangement. In the light of this report, it was of interest to examine the thermal behaviour of γ-halo-α-methylpropargyl aryl ethers wherein such α-methyl substituents could be expected to accelerate the Claisen rearrangement while their effect on the competing C-Br bond hololysis might not be very significant.

Reactions carried out on aryl γ-bromo-α-methylpropargyl ethers 2j,2k, 2l in DEA at 215°C for 15 min were highly encouraging, giving rise to a single product in each case viz. 4-bromo-2-methylchromenes (3j-l) in good yields (Scheme-IV and Table-II). As anticipated, the rearrangement of γ-bromo-α,α-dimethylpropargyl aryl ethers 2m-o was much faster, but the products formed were found to decompose at this temperature. Hence to attain a cleaner reaction, the reaction was carried out in DEA for 5 min at 180°C, wherein 4-bromo-2,2-dimethylchromenes 3m-o were obtained in very good yields (Scheme IV and Table-II). It was clear that α-methyl substituents did not have any effect on the C-Br bond homolysis, as none of the products arising from such homolysis was present even as the minor ones.



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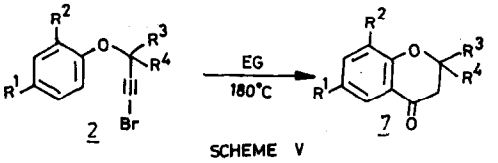
SCHEME IV

Table-II

Synthesis of 4-bromo-2-methyl and 2,2-dimethylchromenes and chroman-4-ones

Starting ether	R^1	R^2	R^3	R^4	Yield of 3 %	Yield of 7 %
2j	Cl	H	CH_3	H	85	65
2k	CH_3	H	CH_3	H	78	65
2l	OCH_3	H	CH_3	H	82	72
2m	Cl	H	CH_3	CH_3	80	70
2n	CH_3	H	CH_3	CH_3	70	75
2o	OCH_3	H	CH_3	CH_3	75	82

Solvent effect: With a view to bring about greater selectivity in this transformation and get more insight into the mechanism, the rearrangement was studied in various solvents. The rearrangement of 2a was carried out in neutral solvents like o-dichlorobenzene (180°C), decane (174°C) and diphenyl ether (259°C). In all these solvents when the reaction was performed for a shorter duration the starting ether was recovered, while at longer reaction time only intractable tarry material resulted. Solvents like dimethylformamide (150°C, 24 h), diglyme (162°C, 10 h) led to the recovery of starting ether, while heating in quinoline for 2 h at 180°C or 20 min at 180°C led to resnification. Recently, polyethylene glycol-200 has been shown to be an ideal solvent for propargyl and allyl Claisen rearrangement[3]. When 2a was heated in PEG-200 for 1/2 h at 220°C, interestingly, a mixture of four products resulted in a total yield of 55%. Chroman-4-one 7a was formed in addition to 3a, 4a and 5a. It was evident that 7a resulted from the hydrolysis of the 4-bromochromene 3a under the reaction condition[7]. This was established by heating 3a in PEG-200 at 220°C for 1 h. However, ethylene glycol was found to be a better solvent for this purpose. It brought about a cleaner and complete conversion of 3 to chroman-4-ones 7, whereas 3-bromochromene 5 was unaffected under this conditions. γ-bromo-α-methyl and α,α-dimethylpropargyl ethers 2j-l afforded 2-methyl and 2,2-dimethylchroman-4-ones 7j-o in good yields when heated in ethylene glycol (Scheme-V and Table-II).

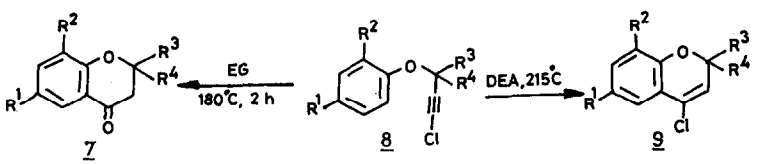


2 7

SCHEME V

Aryl γ-chloropropargyl ethers: 8 The behaviour of halogenoacetylene is highly dependent on the nature of the halogen attached, for the polarisability of -C≡C-X determines the reaction pathway accordingly. Hence, it was thought worthwhile to undertake a study of thermal behaviour of aryl γ-chloropropargyl ethers, wherein it was anticipated that the competing homolysis might be suppressed and a cleaner conversion to 4-chlorochromenes might be realised.

In contrast to γ-bromopropargyl aryl ethers 2, γ-chloropropargyl aryl ethers 8 could not be prepared by the action of sodium hypochlorite. Reaction of the appropriate lithium acetylide with p-toluenesulfonyl chloride furnished[10] γ-chloropropargyl aryl ethers 8 in 50-60% yield. Refluxing 8a in N,N-diethylaniline for 2 h afforded 4-chlorochromene 9a as the major product along with dichloroallylaryl ether 10a (3:1) in 72% total yield. The reaction when extended to other substituted cases 8c,d,f-l afforded the respective 4-chlorochromenes 9 (Table-III and Scheme-VI). Rearrangement of these γ-chloropropargyl aryl ethers in ethylene glycol led to the formation of chroman-4-ones 7 in good yields (Table - III).



7 8 9

SCHEME VI

Table-III

Synthesis of 4-chlorochromens 9 and chroman-4-ones 7

Starting ether	R^1	R^2	R^3	R^4	Reaction Temp. and time in DEA	Yield of 9 %	Reaction time in EG	Yield of 7 %
8a	Cl	H	H	H	215°C, 2 h	72	4 h	68
8b	H	H	H	H	215°C, 2 h	60	4 h	72
8c	CH_3	H	H	H	215°C, 2 h	75	4 h	72
8d	OCH_3	H	H	H	215°C, 2 h	80	4 h	75
8e	H	Cl	H	H	215°C, 2 h	60	4 h	60
8f	H	OCH_3	H	H	215°C, 2 h	60	4 h	74
8g	H	CH_3	H	H	215°C, 2 h	76	4 h	60
8h	CH_3	H	CH_3	H	215°C, 15 min	70	40 min	65
8i	Cl	H	CH_3	H	215°C, 15 min	67	40 min	70
8j	OCH_3	H	CH_3	H	215°C, 15 min	78	40 min	76
8k	Cl	H	CH_3	CH_3	180°C, 5 min	72	5 min	70
8l	OCH_3	H	CH_3	CH_3	180°C, 5 min	80	5 min	72

Aryl γ-iodopropargyl ethers: 11 The thermolysis of aryl γ-iodopropargyl ether[10] 11 was investigated in N,N-diethylaniline. It was anticipated that the major reaction in this case would be homolysis of iodine-carbon bond and aryl propargyl Claisen rearrangement might not be able to compete. As expected, when 11a was refluxed in DEA, 4-iodochromene was not formed. However, to our surprise, the major product formed under these conditions was found to be aryl propargyl ether 1a with minor amount of diiodoallyl aryl ether.

γ-halogen effect: In the case of Claisen rearrangement, the aromatic substituents are known to exert a moderate effect on the rate of rearrangement. For example, the relative rate for p-NO_2, p-H and p-OCH_3 aryl propargyl ethers, as reported in literature[16], are 1:3.8:4.5. In view of this it was felt worthwhile to investigate the effect of γ-halo group in the present study. To execute the same, the substrates of choice would be the ones wherein there is no competitive homolysis of C≡C-X bond. For this purpose, α-methylpropargyl p-chlorophenyl ether 1j, γ-bromo-α-methylpropargyl p-chlorophenyl ether 2j and γ-chloro-α-methylpropargyl p-chlorophenyl ether 8i where chosen, wherein there was no competing reactions observed.

Rearrangement of all these ethers was carried out in DEA at 180°C for 25 min. NMR spectral analysis of the crude product showed 50% conversion to 4-chloro and 4-bromo-2-methylchromenes in the case of bromo and chloro ethers 8i and 2j, whereas there was only 5% conversion in the case of γ-unsubstituted ether 1j under this condition. The above observations reveal beyond doubt that the γ-halo substituent in the aryl propargyl ethers brings about significant acceleration of the rate of rearrangement. However, there was not any noticeable difference in the rate of the reaction by changing the halogen from bromine to chlorine, as reflected by our experimental observation.

Results of synthetic utility: The utility of this work for the synthesis of 4-halochromenes depends on the substituents attached to the aromatic ring and at the α-position of the propargyl moiety as well as on the nature of the halogen at the γ-position. Our work has shown that this transformation can be a good method for the synthesis of 4-chlorochromenes, 4-bromo-2-methylchromenes and 4-bromo-2,2-dimethylchromene. The present work has also led to a novel, simple and one pot entry to the synthesis of variously substituted chroman-4-ones.

The existing routes for the synthesis[18] of 4-chromanones involve mostly the cyclisation of aryloxypropionic acids (or nitriles or chlorides), reduction of chromones and cyclisation of hydroxychalcones.

In conclusion, by modelling the halogen-ethynyl moiety and by choosing the appropriate solvent, the behaviour of γ-halopropargyl aryl ethers can be directed towards the chemistry of halogenoacetylene or towards the typical aryl propargyl Claisen rearrangement thereby making this transformation synthetically useful.

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EXPERIMENTAL

General considerations:

Melting points reported are uncorrected. Ultraviolet spectra were recorded in methanol using Shimadzu 240 instrument. IR spectra were recorded on Perkin-Elmer 1310 instrument and ^{1}H-NMR spectra were recorded on 60 MHz Hitachi (R-600) or 90 MHz, EM-390 instruments. N,N-diethylaniline (DEA) was purified by refluxing over potassium hydroxide and stored over the same. Ethylene glycol was dried by distillation from calcium oxide and stored over molecular sieves (4 A°). Commercial PEG-200 was used without further purification. All the compounds reported are unequivocally characterised by spectral data. No elemental analysis was thought necessary, due to their simple structures and instability.

General procedure for the preparation of aryl γ-bromopropargyl ether 2 : To 20 ml of 5 M sodium hydroxide solution was added with cooling between 5° and 20°C 50 mmol of bromine. Subsequently, 25 mmol of aryl propargyl ether[2] in 10 ml of dimethoxyethane was introduced. The air in the flask was replaced by nitrogen. The mixture was vigorously stirred for 4-5 h. The reaction mixture was poured into water and extracted with hexane. The combined hexane extracts was washed with water, dried and concentrated under vacuo. The product was chromatographed on silica gel or recrystallised prior to use from hexane.

γ-bromopropargyl p-chlorophenyl ether 2a: Yield : 85% m.p: 50°C (lit[9] m.p:51°C) IR : (neat): cm^{-1}: 3050-2900(s), 2200(s), 1480(s), 1220(s) and 880(s); NMR:(CCl_4):δ: 4.62(s,2H), 6.7-7.25(AB quartet, 4H); UV:nm: 280(3,200), 220(22,000). Anal.Calcd. for C_9H_6BrClO: C, 44.03; H, 2.46. Found C, 43.86; H, 2.67. The other ethers 2b-o were also obtained in 80-85% yield and characterised.

General procedure for the preparation of aryl γ-chloropropargyl ethers 8: To 10 mmol of aryl propargyl ether in 50 ml of ether was added at -10°C 12 mmol of butyl lithium. To this solution was added in 15 min. 12 mmol of p-toluene sulfonyl chloride, while the temperature was maintained between 0-5°C. A white suspension was formed. After an hour, the flask was heated for 1/2 h at 35°C. The mixture was poured into crushed ice and extracted with ether. The combined ether extracts was washed with water dried and concentrated. The product was chromatographed over silica gel.

p-chlorophenyl γ-chloropropargyl ether 8a: Yield: 60%. IR : (neat): cm^{-1}: 3000-2850(s), 2200(s), 1580(s), 1200(s), 990(s); NMR: (CCl_4):δ: 4.65(s,2H), 6.6-7.45(AB quartet, 4H); UV : nm: 285(1,400), 228(1,800). Anal.Calcd. for $C_9H_6Cl_2O$: C, 54.76; H, 3.01. Found C, 54.87; H, 3.38. The other ethers 8b-l were prepared similarly in 50-60% yield and characterised.

Preparation of γ-iodopropargyl (p-chlorophenyl) ether 11: 15 mmol of p-chlorophenyl propargyl ether in 30 c.c of methanol was vigorously stirred. To this added over 15 mins. 20 mmol of iodine and 20 ml of 10% aqueous sodium hydroxide solution, the reaction temperature kept at 20-5°C. After stirring for 1 h, it was poured into water and extracted with hexane. The combined ether extracts was washed with water, dried and concentrated. The product was recrystallised from hexane. Yield : 80%. m.p : 52°C(lit[9] m.p : 52-3°C). IR : ($CHCl_3$): cm^{-1}: 3000-2850(s), 2200(s), 1585(s), 1200(s); NMR:δ: 4.85(s,2H), 6.7-7.6(AB quartet, 4H); UV : nm : 285(1,600), 278(2,000).

Rearrangement in N,N-diethylaniline: A solution of 200 mg of aryl γ-halopropargyl ether in 10 ml of DEA was heated to 210-15°C under nitrogen atmosphere. The solvent was removed under vacuum and the residue was taken in hexane and last traces of DEA was washed away with 2N HCl. The organic layer

was washed with 10% sodium hydroxide and water. The hexane extract was dried and concentrated in vacuo. The crude product was chromatographed over neutral alumina.

Rearrangement of 2a: Rearrangement of 2a carried out as detailed above for 6 h gave a viscous liquid in 46% (after rapid filtration through a short column of alumina). The products isolated and their characteristics:

(i) Cis-2,3-dibromoallyl p-chlorophenyl ether 4a: IR : neat : cm^{-1}: 3100-2800(m), 1580(s), 1220(s), 810(s); NMR:(CCl_4):δ: 4.65(d,J:1.5 Hz, 2H), 7.1(t,J:1.5 Hz,1H) 6.9-7.2 (AB quartet, 4H); UV : nm : 285(1,400), 280(2,000); $M^{+\cdot}$, m/z 324(5).

(ii) 4-bromo-6-chlorochromene 3a: IR : ($CHCl_3$) : cm^{-1} : 3000-2800(m), 1620(s), 1500(m), 1200(s); NMR:(CCl_4):δ: 4.4(d,J:8 Hz,2H), 5.72(t,J:8Hz,1H), 6.2-6.8 (m,3H); UV : nm : 320(1,500), 285(1,400), 255(2,200).

(iii) 3-bromo-6-chlorochromene 5a: IR : ($CHCl_3$) : cm^{-1}: 2950-2850(m), 1620(s), 1480(s), 1200(s); NMR:(CCl_4):δ: 4.82(d,J:1.5 Hz, 2H), 6.5-7.2(m,4H); UV : nm : 320(3,200), 285(15,000), 230(16,500).

Rearrangement in ethylene glycol:

A solution of 200 mg of aryl γ-halopropargyl ether in 16 ml of ethylene glycol was heated to 180°C in an inert atmosphere. The reaction mixture was poured into water and extracted with dichloromethane. The combined extracts was washed thoroughly with water and by 10% sodium hydroxide solution. The dried organic layer was concentrated in vacuo. The crude product was chromatographed over silica gel.

Rearrangement of 2a: The rearrangement of 2a carried out as above for 4 h gave rise to a mixture of 5a, 4a and 7a in 40% yield.

6-chlorochroman-4-one 7a: m.p: 105°C(lit[18], m.p: 106°C). IR : ($CHCl_3$) : cm^{-1}: 3100-2850(m), 1685(s), 1610(s), 1200(s); NMR:(CCl_4):δ: 2.6(t,J:6 Hz,2H), 4.35(t,J:6 Hz,2H),6.5-7.6(m,3H); UV : nm : 300(9,000), 245(17,000).

Synthesis of 4-bromo-2-methyl and 2,2-dimethylchromenes 3 :

4-bromo-6-chloro-2-methylchromene 3i: Rearrangement of 2i in DEA at 215°C for 15 min afforded 3i in 85% yield. IR : (neat) : cm^{-1} : 3000-2800(m), 1620(s), 1450(s), 1200(s), 870(s); NMR:δ: 1.5(d,J:6 Hz,3H), 4.7-5.2(m, 1H), 5.7(d,J: 3 Hz, 1H), 6.6-7.2(m, 3H); UV : nm : 315(1,580), 285(1,800), 225(16,000).

4-bromo-2,6-dimethylchromene 3k: Yield : 78%. IR : (neat) : cm^{-1} : 3000-2850(m), 1620(s), 1450(s), 1200(s), 870(s); NMR:δ: 1.48(d, J: 6 Hz, 3H), 2.3(s, 3H), 4.7-5.2(m,1H), 5.7(d,J : 3 Hz, 1H),6.55-7.2(m,3H); UV : nm : 315(1,600), 285(2,000), 220(16,000).

4-bromo-6-methoxy-2-methylchromene 3l: Yield : 82%. IR : ($CHCl_3$) : cm^{-1} : 3000-2800(m), 1620(s), 1450(s), 1200(s), 870(s); NMR:δ: 1.48(d, J: 6 Hz,3H), 3.82(s,3H), 4.7-5.2(m,1H), 5.7(d, J: 3 Hz, 1H), 6.5-7.1(m, 3H); UV : nm : 315(1,600), 285(2,000), 225(16,000).

4-bromo-6-chloro-2,2-dimethylchromene 3m : Rearrangement of 2m in DEA at 180°C for 5 min afforded 3m. Yield : 80% IR : ($CHCl_3$): cm^{-1} : 3000-2800(m), 1620(s), 1450(s), 1200(s), 870(s); NMR:δ: 1.4(s,6H), 5.8(s,1H), 6.7-7.3(m,3H); UV : nm : 315(1,580), 285(2,600), 230(16,000).

4-bromo-2,2,6-trimethylchromene 3n : Yield : 70% IR : ($CHCl_3$) : cm^{-1} : 3000-2800(m), 1620(s), 1450(s), 1200(s), 870(s); NMR:δ: 1.4(s,6H), 2.3(s,3H), 5.8(s,1H), 6.7-7.1(m,3H); UV : nm : 315(1,600), 285(2,000), 230(16,000).

4-bromo-2,2-dimethyl-6-methoxychromene 3o: Yield : 75% IR : ($CHCl_3$) : cm^{-1} : 2800-3000(m), 1620(s), 1450(s), 1200(s), 870(s); NMR:δ: 1.4(s,6H), 3.8(s,1H), 6.5-7.3(m,3H); UV : nm : 315(1,600), 285(2,000), 230(16,000).

Synthesis of 4-chlorochromenes 9 :

4,6-dichlorochromene 9a : Rearrangement of 8a in DEA at 215°C for 2 h afforded 9a in 72% yield. IR : neat : cm^{-1} : 3000-2850(m), 1450(s), 1200(s), 870(s); NMR:δ: 4.85 (d,J:4 Hz, 2H), 5.9(t, J:4 Hz, 1H), 6.45-7.4(m,3H); UV : nm : 315(1,600), 255(2,200).

4-chlorochromene 9b: Yield : 60%; IR : (neat) : cm^{-1} : 3000-2850(m), 1620(s), 1220-1200(s), 870(s); NMR:(CCl_4):δ: 4.85(d,J: 4Hz, 2H), 5.8(t,J:4 Hz, 1H), 6.8-7.45(m,4H); UV : nm : 320(1,400), 285(2,000), 230(15,000).

4-chloro-6-methylchromene 9c: Yield : 75%; IR : ($CHCl_3$) : cm^{-1} : 3050-2850(m), 1615(s), 1450(s), 1200(s), 870(s): NMR:(CCl_4):δ: 2.3(s,3H),4.75(d,J:4 Hz,2H), 5.8(t,J:4 Hz,1H), 6.5-7.2(m,3H); UV : nm : 315(1,600),285(2,000), 230(16,000).

4-chloro-6-metyoxychromene 9d: Yield : 80% ; IR : ($CHCl_3$) : cm^{-1} : 3000-2800(m), 1620(s), 1450(s), 1200(s), 870(s) ; NMR:(CCl_4):δ: 3.75(s,3H), 4.75(d,J:4 Hz,2H), 5.9(t,J:4 Hz, 1H), 6.6-7.2(m,3H).

4,8-dichlorochromene 9e: Yield : 60% ; IR : ($CHCl_3$) : cm^{-1} : 3000-2850(m), 1620(s), 1220-1200(s), 870(s); NMR:($CDCl_3$):δ: 4.85(d,J:4 Hz, 2H), 5.8(t,J:4 Hz, 1H), 6.8-7.45(m,3H); UV : nm : 328(1,400), 285(2,000), 230(15,000).

4-chloro-8-methoxychromene 9f: Yield : 60% ; IR : ($CHCl_3$) : cm^{-1} : 300-2850(s), 1620(s), 1450(s), 1200(s); NMR:(CCl_4):δ: 3.75(s,3H), 4.75(d,J:4 Hz, 2H), 5.85(t,J:4 Hz, 1H), 6.6-7.3(m,3H); UV : nm : 315(1,600), 285(2,200), 230(16,000).

4-chloro-8-methylchromene 9g : Yield : 76% ; IR : ($CHCl_3$): cm^{-1} : 3000-2850(m), 1620(s), 1450(s), 1200(s), 870(s); NMR:(CCl_4):δ: 2.2(s,3H), 4.85(d,J:4 Hz, 2H), 5.8(t,J:4 Hz, 1H), 6.6-7.3(m,3H); UV : nm : 320(1,600), 285(2,000), 230(15,000).

4-chloro-2,6-dimethylchromene 9h: Rearrangement carried out in DEA at 215°C for 15 min afforded 9h in 70% yield. IR : (neat) : cm^{-1} : 3050-2850(m), 1620(s), 1450(s), 870(s) ; NMR:(CCl_4):δ: 1.47(d,J:6 Hz, 3H), 2.3(s,3H), 4.7-5.2(m,1H), 5.7(d,J:4 Hz, 1H), 6.55-7.2(m,3H); UV : nm : 315(1,600), 285(1,050), 230(16,000).

4,6-dichloro-2-methylchromene 9i : Yield : 67% ; IR : ($CHCl_3$): cm^{-1} : 3000-2850(m), 1620(s), 1450(s), 1200(s), 870(s) ; NMR:δ: 1.45(d, J:6 Hz,3H), 4.75-5.35(m,1H), 5.77(d,J:4 Hz, 1H), 6.6-7.4(m,3H); UV : nm : 315(1,580), 285(2,000), 220(16,000).

4-chloro-6-methoxy-2-methylchromene 9j : Yield : 78% ; IR : ($CHCl_3$) : cm^{-1} : 3000-2850(s), 1600(s), 1420(s), 1200-1210(s), 870(s); NMR:(CCl_4):δ: 1.5(d,J:6 Hz, 3H), 3.75(s,3H), 4.7-5.4(m,1H), 5.8(d,J:4 Hz, 1H), 6.6-7.1(m,3H).

4,6-dichloro-2,2-dimethylchromene 9k : Rearrangement of 8k in DEA at 215°C for 5 min afforded 9k in 62% yield. IR : ($CHCl_3$) : cm^{-1}: 2850-3000(m), 1620(s), 1450(s), 1200(s), 870(s); NMR:δ:1.45(s,6H), 5.75(s,1H), 6.4-7.5(m,3H); UV : nm : 315(1,580), 285(2,000).

4-chloro-2,2-dimethyl-6-methoxychromene 9l : Yield : 80% ; IR : ($CHCl_3$) : cm^{-1}: 3000-2800(s), 1620(s), 1450(s), 1200(s); NMR:(CCl_4):δ: 1.4(s,6H), 3.75(s,3H), 5.8(s,1H), 6.5-7.2(m,3H); UV : nm : 315(1,600),285(2,000), 230(16,000).

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