THE THERMAL [3, 3] CLAISEN REARRANGEMENT OF THE 3-SUBSTITUTED PHENYL ALLYL AND PROPARGYL ETHERS. THE SYNTHESIS OF 4-HALOBENZO[*b*]FURANS

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Abstract - **The thermal [3, 3] Claisen rearrangement of the 3-substituted phenyl allyl and propargyl ethers is regioselective. The major product of the reaction incorporates a 1, 2, 3-trisubstituted benzene ring. The 2-allenylphenol intermediates can be manipulated into the preparation of 4-substituted benzo[*b*]furans. The observed regioselectivity supports the biradicaloid mechanism of the Claisen rearrangement.**

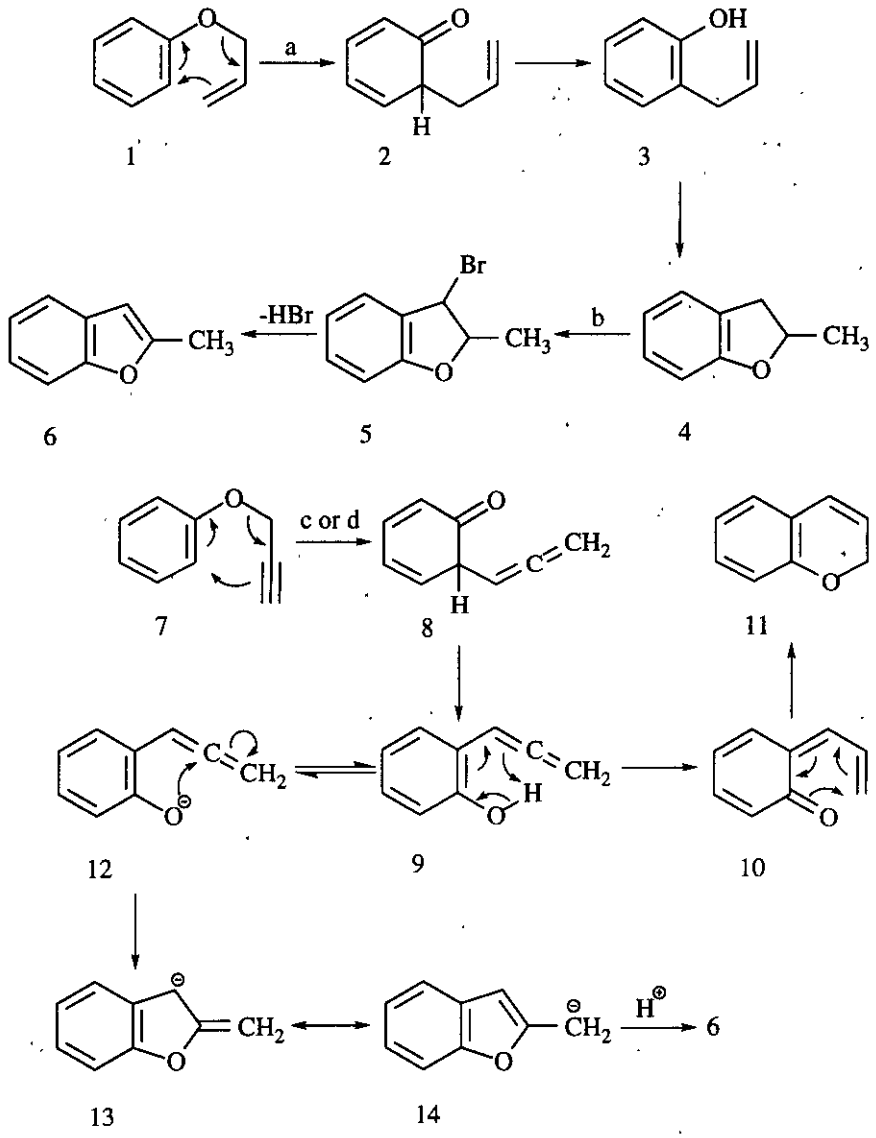
The preparation of 4-halobenzo[*b*]furans was a key part in our efforts towards the synthesis of benzo[*b*] furanyl C-glycosides. The 4-halobenzo[*b*]furans that we needed were not commercially available and they are also relatively unavailable by the traditional[1] synthetic methods. The thermal [3, 3] Claisen rearrangement[2-8] of suitable 3-substituted phenyl allyl and propargyl ethers, followed by cyclisation of the initially obtained products, presented an attractive synthetic route to these 4-halobenzo[*b*]furans. Here, we shall discuss both the synthetic route and the mechanism of the thermal [3, 3] Claisen rearrangement.

The Thermal[3, 3] Claisen Rearrangement of the Aryl Allyl and Aryl Propargyl Ethers

The allyl phenyl ether (**1**) undergoes thermal [3, 3] Claisen rearrangement to produce the allyl cyclohexadienone[2-7] (**2**). The rearrangement is followed by the enolization of the compound (**2**) to reestablish the aromatic ring and form the 2-allylphenol (**3**). The allylphenol (**3**) undergoes another intramolecular transformation, under the reaction conditions, to furnish the 2, 3-dihydro-2-methyl-benzo[*b*]furan[9] (**4**) (Scheme 1).

The conversion of the 2,3-dihydrobenzo[*b*]furan (**4**), into the corresponding benzo[*b*]furan (**6**) can be achieved in very high yield by the benzylic bromination of **4,** to produce the intermediate 3-bromo-2, 3-dihydro-2-methyl benzo[*b*]furan (**5**). The dehydrobromination of **5** is spontaneous under the reaction conditions and the final product is the 2-methylbenzo[*b*]furan (**6**) (Scheme 1).

The thermal [3, 3]-Claisen rearrangement of the aryl propargyl ether (**7**) produces the allenylcyclohexa-dienone (**8**). Rearomatization of **8** through enolization produces the allenylphenol (**9**).



Scheme 1 Reagents and conditions: a, 160-170° C, under nitrogen; b, NBS, hν, CCl_4; c, diethylaniline, 217° C, under nitrogen; d, diethylaniline, 217° C, K_2CO_3, under nitrogen.

We have shown[2] that the reactions of **9** can be greatly influenced by selecting the reaction conditions. The allenylphenol (**9**) can undergo a [1, 5] H-shift to form the dienylcyclohexadienone (**10**), under neutral environment, which then rearranges[2-8] electrocyclically into the benzopyran (**11**) (Scheme 1).
This pathway to the benzopyran (**11**) is favored in non-polar and non-basic solvents such as decalin. However, if the medium is polar and basic, such as diethylaniline, and especially in the presence of a basic salt, potassium carbonate, the outcome of the reaction is altered and the 2-methylbenzo[*b*]furan (**6**), becomes the favored product.[2] In this process, under the basic and polar conditions, the allenylphenol (**9**) is converted into the phenoxide (**12**). The phenoxide (**12**) undergoes an electrocyclic rearrangement into

the anion (**14**), which by recovering the proton from the solvent, becomes the 2-methylbenzo[*b*]furan (**6**), (Scheme 1).

The Thermal [3, 3] Claisen Rearrangement of the 3-Halophenyl Allyl Ethers

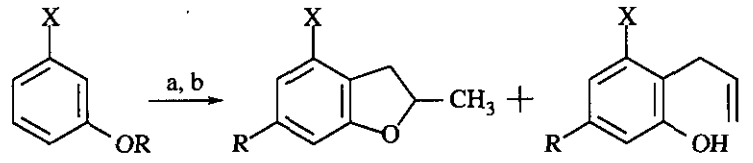
The 3-chloro- (**15**), and the 3-bromophenol (**16**) were easily converted to the allyl 3-chlorophenyl (**17**) and 3-bromophenyl (**18**) ethers,[9] in boiling acetone by allyl bromide in the presence of potassium carbonate at high yields (93% and 90% respectively).

Table 1 Product yields (%) of the thermal [3, 3] Claisen rearrangement

Entry	Ether	Product[10]	Yield* (%)
1	17	19	12
		20	6
		23	49
		24	28
2	18	21	11
		22	8
		25	48
		26	23
3	36	39	24
		40	16
4	37	41	33
		42	17
5	36	31	32
		32	16
6	37	33	32
		34	16
7	38	43	30
		44	2

* by ^{1}H NMR

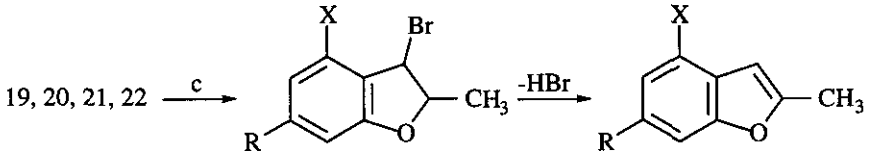
The allyl 3-chlorophenyl ether (**17**) was rearranged by heating under nitrogen at 160-170°C. The reaction product was a mixture of the chloro-2, 3-dihydrobenzo[*b*]furans[8,9] (**19**) and (**20**), and the allylchlorophenols (**23**) and (**24**). Similarly, the allyl 3-bromophenyl ether (**18**), under the same reaction conditions, yielded a mixture of the bromo-2, 3-dihydrobenzo[*b*]furans (**21**) and (**22**), and the allylbromophenols (**25**, **26**). In both reactions the predominant regiochemical outcome was the formation of 1, 2, 3-trisubstituted compounds (**19**, **21**, **23**, **25**) (Table 1, Scheme 2).



15 X = Cl, R = H
16 X = Br, R = H
17 X = Cl, R = Allyl
18 X = Br, R = Allyl

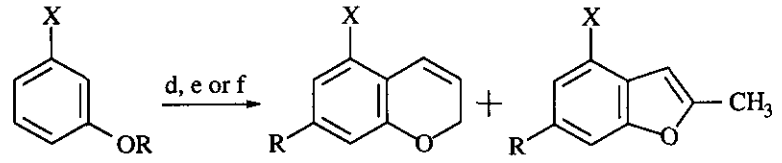
19 X = Cl, R = H
20 X = H, R = Cl
21 X = Br, R = H
22 X = H, R = Br

23 X = Cl, R = H
24 X = H, R = Cl
25 X = Br, R = H
26 X = H, R = Br



27 X = Cl, R = H
28 X = H, R = Cl
29 X = Br, R = H
30 X = H, R = Br

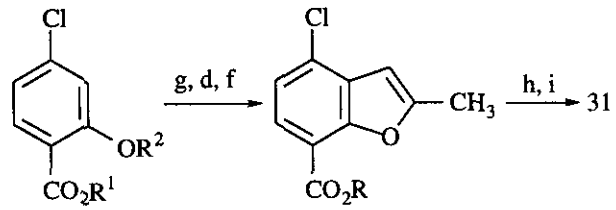
31 X = Cl, R = H
32 X = H, R = Cl
33 X = Br, R = H
34 X = H, R = Br



15, 16
35 X = NO_2, R = H
36 X = Cl, R = C_3H_3
37 X = Br, R = C_3H_3
38 X = NO_2, R = C_3H_3

39 X = Cl, R = H
40 X = H, R = Cl
41 X = Br, R = H
42 X = H, R = Br

31, 32, 33, 34
43 X = NO_2, R = H
44 X = H, R = NO_2



45 R^1 = R^2 = H
46 R^1 = CH_3, R^2 = H
47 R^1 = CH_3, R^2 = C_3H_3

48 R = CH_3
49 R = H

Scheme 2 Reagents and conditions: a, allyl bromide, K_2CO_3, acetone, 56° C; b, 160-170° C, under nitrogen; c, NBS, hv, CCl_4; d, bromopropyne, K_2CO_3, acetone, 56° C; e, diethylaniline, 217° C, under nitrogen, 3 h; f, diethylaniline, 217° C, K_2CO_3, under nitrogen, 3 h; g, methanol, H_2SO_4, 56° C; h, NaOH, ethanol 95 %, 78° C; i, isoquinoline, Cu_2O, 242° C.

Benzylic bromination of the mixture of the chloro-2, 3-dihydrobenzo[*b*]furans (**19**, **20**) with *N* -bromo-succinimide produced the corresponding mixture of the 3-bromodihydrobenzo[*b*]furan derivatives (**27**) and (**28**), which were efficiently dehydrobrominated during the reaction to yield the corresponding mixture of the 4-chloro- and 6-chloro-2-methylbenzo[*b*]furans (**31**) and (**32**). The mixture of the 4-bromo- and 6-bromo-2-methylbenzo[*b*]furans (**33**) and (**34**) was similarly obtained from the benzylic bromination and dehydrobromination of the mixture of the bromo-2, 3-dihydrobenzo[*b*]furans (**21**) and (**22**) (Scheme 2).

The Thermal [3, 3] Claisen Rearrangement of the Aryl Propargyl Ethers

The rearrangement of the propargyl ethers (**36**, **37** and **39**) followed the same regiochemical pattern. The more hindered compounds were the major reaction products (Table 1, Scheme 2). The propargyl ethers (**36**, **37** and **38**) were prepared in high yields (93 %, 98 %, 93 % respectively) by reacting the 3-chloro- (**15**), the 3-bromo- (**16**) and the 3-nitrophenol (**35**) with 3-bromopropyne and potassium carbonate in boiling acetone. The thermal rearrangement of the 3-nitrophenyl propargyl ethers was investigated because of the easy conversion of the aromatic nitro derivatives to aromatic halides *via* reduction to the corresponding aromatic amine followed by the Sandmeyer reaction.

Thermal rearrangement[5-7] of the 3-chlorophenyl propargyl ether (**36**) in boiling diethylaniline under nitrogen produced a mixture of products consisting of the 5-chlorobenzopyran (**39**) and the 7-chloro-benzopyran (**40**). The 3-bromophenyl propargyl ether (**37**) under the same reaction conditions yielded a similar mixture of products made of the 5-bromobenzopyran (**41**) and the 7-bromobenzopyran (**42**). In each case the 5-halobenzopyrans (**39**) and (**41**) were the major reaction products (Table 1).

The rearrangements of the propargyl ethers (**36**, **37** and **38**) in boiling diethylaniline, under nitrogen, in the presence of potassium carbonate, produced the corresponding mixtures of 2-methylbenzo[*b*]furans. The mixture of the 4-chloro-2-methylbenzo[*b*]furan (**31**) and the 6-chloro-2-methylbenzo[*b*]furan (**32**) was obtained from the 3-chlorophenyl propargyl ether (**36**), the mixture of the 4-bromo-2-methylbenzo-[*b*]furan (**33**) and the 6-bromo-2-methylbenzo[*b*]furan (**34**), from the 3-bromophenyl propargyl ether (**37**), while the 4-nitro-2-methylbenzo[*b*]furan (**43**) and the 6-nitro-2-methylbenzo[*b*]furan (**44**) from the 3-nitrophenyl propargyl ether (**38**) (Scheme 2). The 4-substituted 2-methylbenzo[*b*]furans (**31**, **33** and **43**) were again the major regioisomers (Table 1). The mixtures of the regioisomeric halobenzo[*b*]furans were not easily separable, as were the regioisomers of the halobenzopyrans. The halobenzo[*b*]furans were contaminated by traces of the corresponding benzopyrans as shown from the respective ^{1}H-NMR spectra of the mixtures. The nitrobenzo[*b*]furans were separated by column chromatography.

The regioselectivity of the thermal [3, 3] Claisen rearrangement of the 3-halophenyl propargyl ethers therefore offers a short and direct access to the 4-halobenzo[*b*]furans and the 5-halobenzopyrans, although the final mixture of the products, for simply substituted compounds, might not be easily separated by column chromatography.

The Synthesis of the 4-Chloro-2-methylbenzo[*b*]furan (31)

The difficult if not impossible separation of the mixtures of the halobenzo[*b*]furans produced from the rearrangements of the 3-halophenyl propargyl ethers and the lower overall yield of the 4-halobenzo[*b*]-furan because of the competing regioisomer, forced us to investigate an alternate synthetic approach. The commercially available 4-chlorosalicylic acid (**45**) was converted to the methyl ester (**46**), in boiling methanol with catalytic amount of concentrated sulfuric acid. The propargyl ether (**47**) was prepared from the ester (**46**), under the standard reaction with the bromopropyne. Thermal rearrangement of the propargyl ether (**47**), in boiling diethylaniline in the presence of potassium carbonate, yielded only the methyl 4-chlorobenzo[*b*]furanoate ester (**48**), because the site of the competing cyclisation is blocked by the ester group. Hydrolysis of the benzo[*b*]furanoate ester (**48**), with sodium hydroxide in ethanol (95 %) yielded the 4-chloro-2-methyl-7-benzo[*b*]furanoic acid (**49**). Decarboxylation of the acid (**49**), in boiling isoquinoline in the presence of copper(I) oxide, yielded the 4-chloro-2-methylbenzo[*b*]furan (**31**) in 46 % overall yield from the acid (**45**) (Scheme 2).

Table 2 Product distribution of the thermal [3, 3] Claisen rearrangement of allyl and propargyl aryl ethers

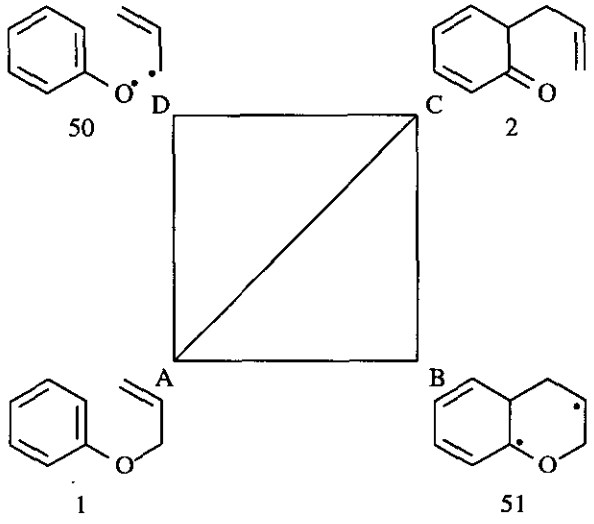
X	Ether	Product Yield (%)		Reference
		[1, 2, 3]*	[1, 2, 5]*	
OMe	Propargyl	54	46	6, 7
OBz	Propargyl	63	-	6
Cl	Propargyl	32	16	#
Br	Propargyl	32	16	#
NO_2	Propargyl	30	2	#
Me	Allyl	56	44	8, 9
F_3C	Allyl	63	37	8
Br	Allyl	64	36	8, 9
C_4H_9	Allyl	74	26	8
NHAc	Allyl	46	40	9
Cl	Allyl	65	35	9
OBz	Allyl	77	23	9
CN	Allyl	70	30	9
Cl	Allyl	24	16	#
Br	Allyl	33	17	#

*Substitution pattern on the benzene ring of the product. Carbon-1 is the carbon atom bearing the oxygen. # From this work.

The Regioselectivity of the Thermal [3, 3] Claisen Rearrangement. Mechanistic Considerations

The consistent regioselectivity exhibited by the rearrangement, an almost constant 2:1 preference for the "1, 2, 3-trisubstituted benzene" product regardless of the nature of the phenyl substituents was quite remarkable (Tables 1, 2).

The observed regioselectivity must be attributed to some dominant mechanistic features of the reaction mechanism which allowed both electron withdrawing and electron donating substituents to exert the same influence. It is also evident that steric hindrance was relatively unimportant and was clearly dominated by the other factors. Undoubtedly, the highest yield products are formed *via* the lowest in energy, steric and electronic, reaction pathways. Hence, these Claisen rearrangements are controlled by very dominant electronic/bonding factors, since these factors consistently outweigh the steric factors. Thus, the regioselectivity of these Claisen reactions can be used to indicate and support the operating mechanism.



Scheme 3 The More-O'Ferrall-Jencks diagram.

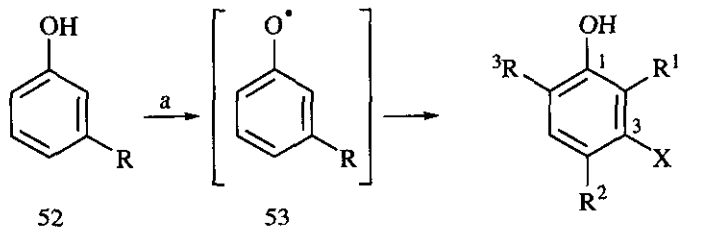
The entire spectrum of the possible events is best described by a More-O'Ferrall-Jencks diagram[11] (Scheme 3). The diagonal pathway, AC, corresponds to the concerted synchronous mechanism.[12, 13] However, the concerted synchronous mechanism has been criticized[10, 11, 14-20] since it is recognized that the bond breaking and the bond forming processes can occur consecutively, albeit almost concurrently, rather than simultaneously.

The ADC pathway, in which the cleavage of the allylic or propargylic bond precedes any new bond formation, has been explored and eliminated from consideration by crossover experiments.[21] This mechanism is regarded as highly unlikely in most circumstances.

Kinetic isotope effect studies,[10, 11, 14-18] experimental as well as theoretical HMO calculations, carried on simple allyl vinyl and allyl phenyl ethers, point to a concerted aromatic mechanism with the bond

breaking preceding the bond forming process. However semiempirical[19, 20] calculations predicted a biradicaloid mechanism, supporting the ABC pathway (Scheme 3).

Additional experimental evidence against the ADC pathway can be gathered from the regiochemistry of the free radical nitration[22] of the 3-substituted phenols (**52**), *via* their phenoxyl radicals (**53**) (Scheme 4). The calculated unpaired electron density distribution in the phenoxyl radicals (**53**), and the eventual regiochemistry of the nitration reaction, are shown in Table 3.



52 53

54 $R^1 = NO_2$, $R^2 = R^3 = H$
55 $R^2 = NO_2$, $R^1 = R^3 = H$
56 $R^3 = NO_2$, $R^1 = R^2 = H$

Scheme 4 Free radical nitration of 3-substituted phenols; a, $NaNO_3$, 3M H_2SO_4, CH_2Cl_2, catalyst $NaNO_2$, room temperature, 48 h.

Table 3 Unpaired electron density on the phenoxyl radicals (**53**) and nitration product distribution

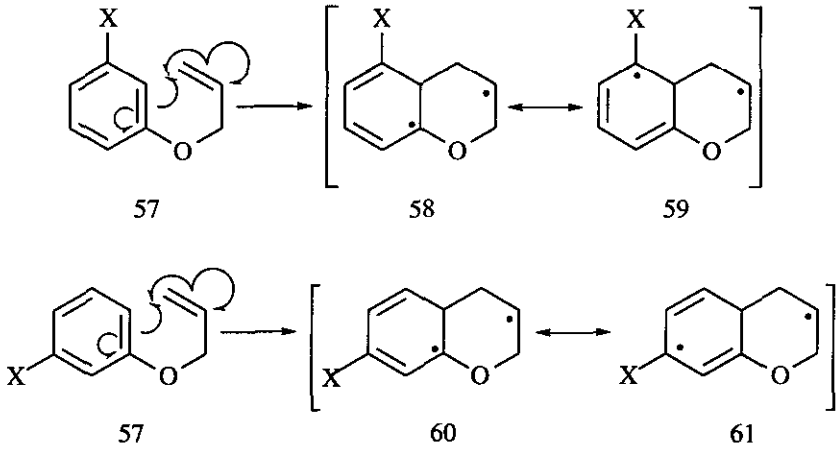
Entry	X	Unpaired electron density			Nitration product (%)		
		2-C	4-C	6-C	54	55	56
1	MeO	0.1639	0.3959	0.2697	18.9	45.8	31.2
2	Cl	0.1680	0.3971	0.2607	19.5	45.9	30.2
3	CN	0.1939	0.3853	0.2432	22.4	44.6	28.1
4	NO_2	0.2133	0.3733	0.2339	24.7	43.3	27.1
5	CHO	0.2028	0.3852	0.2297	23.4	44.5	26.5
6	COMe	0.1993	0.3877	0.2304	23.0	44.8	26.6

Reference 22b

These data clearly show that the regiochemistry of these nitrations closely adhere to the unpaired electron densities in the phenoxyl radical. The major product in all the reactions is the 4-nitro substituted (**55**) (43.3-45.8 %), corresponding to the higher electronic density at C-4. The 6-nitro substituted (**56**) (26.6-31 %) is the next higher yield product leaving the 2-nitro substituted (**54**) (18.9-24.7 %) to be the minor corresponding to the lower electron density at C-2. Thus, if the ADC pathway of the More O'Ferral

diagram (Scheme 3) represented a viable pathway for the Claisen rearrangement, then the regioselectivity of the thermal rearrangement reactions ought to parallel those of the free radical nitrations, since similar phenoxyl radicals would have been involved. However, the regiochemistry observed in our thermal Claisen rearrangements and those from other investigators[2-8] have clearly favored substitution at the 2-position (Table 3).

The ABC diradicaloid pathway introduces the 1, 4-diradical set of intermediates for consideration (Scheme 5). Experimental evidence[23] for the formation and lifetime of similar 1, 4-diradical intermediates have convincingly been generated.



Scheme 5. Diradical intermediates for the thermal [3, 3] Claisen rearrangement of the allyl 3-substituted phenyl ethers.

The diradicaloid ABC pathway also ought to respond to the greater unpaired electron density at C-6 than at C-2, since these electron densities should be in proportion to the frontier orbital electron densities. Hence, one would have expected a greater rate of "new" bond formation at C-6 than at C-2 both because of the greater steric availability of C-6 and it's greater transition state electron density.

The 1, 4-diradical structure (**58**) with the resonance structure (**59**) and the isomeric 1, 4-diradical structure (**60**) with the resonance structure (**61**) are the expected intermediates from the isomeric transition states of the rearrangement of the allyl 3-substituted phenyl ether (**57**). The 1, 2, 3-trisubstituted phenyl 1, 4-diradicals (**58**) and (**59**) are leading to the major regioisomer. The relative stability of the diradicals (**58**, **59**) and (**60**, **61**) should be the controlling factor for the observed reaction regioselectivity. The substituents of the aromatic ring, whether an electron donating or withdrawing group, stabilize[24-26] the dienyl radicals. The radicals are more stable when the substituent X is an electron withdrawing group due to the synergistic captodative effects[24-26] of the oxygen and the X. The linearly conjugated dienyl radicals (**58**) and (**59**) are also more stable[24] than the cross conjugated dienyl radicals (**60**) and (**61**), becoming the favored intermediates yielding the major product for the reaction. The 1, 4-diradical mechanism was also

employed to explain the stereoselectivity of the Claisen rearrangement of monosaccharide based allyl vinyl ethers.[27]

CONCLUSION

The 4-halobenzo[*b*]furans and other 4-substituted benzo[*b*]furan derivatives are the major products of the thermal [3, 3] Claisen rearrangement of suitably 3-substituted phenyl propargyl ethers. Separation difficulties by column chromatography may be encountered for simple benzo[*b*]furan derivatives. The minor regioisomers can be eliminated by temporarily blocking the competing cyclisation site. The regioselectivity of the cyclisation, favoring the 4-substituted benzo[*b*]furans, which is independent of the nature of the phenyl substituent, is best rationalized by considering the biradicaloid mechanism, suggested from semiempirical calculations.

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