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STUDIES IN CLAISEN REARRANGEMENT - NOVEL THERMAL AND MERCURIC TRIFLUROACETATE INDUCED TRANSFORMATIONS OF 2,4-DI(N-ARYL)AMINO-1,3,5-TRIAZIN-6YL-PROP-2-YNYL ETHERS+

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Abstract - The thermal rearrangement of 2,4-di(N-aryl)amino-1,3,5-triazin-6yl-prop-2-ynyl ethers **1** yield a mixture of 6-methyleneimidazo(1,2-a)-1,3,5-triazine-4-one **6** and 6-methylimidazo(1,2-a)-1,3,5-triazine-4-one **7**, whereas under the influence of mercuric trifluroacetate the ethers **1** yield only **6**, at room temperature. Mechanisms invoking [3,3] sigmatropic rearrangement of ethers **1** were proposed to account for the product formation.

Introduction:

While there are a number of reports on oxy-allylic Claisen rearrangement in nitrogen heterocycles[1], only a few are known on analogous oxy-propargylic Claisen rearrangement. The known examples are uracil propargyl ether[2], 4-pyridyl propargyl ether[3], 3-pyridyl propargyl ether[4]. While [3,3]-sigmatropic rearrangement, of allyl imidates has been well documented[1], similar transformation of propargyl imidates or the like systems[5] have not been investigated in detail. The first example of successful thermolysis of propargyl trichloroacetimidates was reported only in recent years[6,7,8].

The paucity of reports on the rearrangement of propargyl imidates and earlier observations in our laboratory on facile thermal rearrangement of bis-propargyl ethers of various dihydroxynaphthalenes[9] and propargylthiobenzimidazoles[10], prompted investigations on thermal and Lewis acid-catalysed[11,12] rearrangements of s-triazinyl propargyl ethers **1**. Our initial studies on thermal rearrangement have been published[13]. In the present paper the details of these investigations will be discussed.

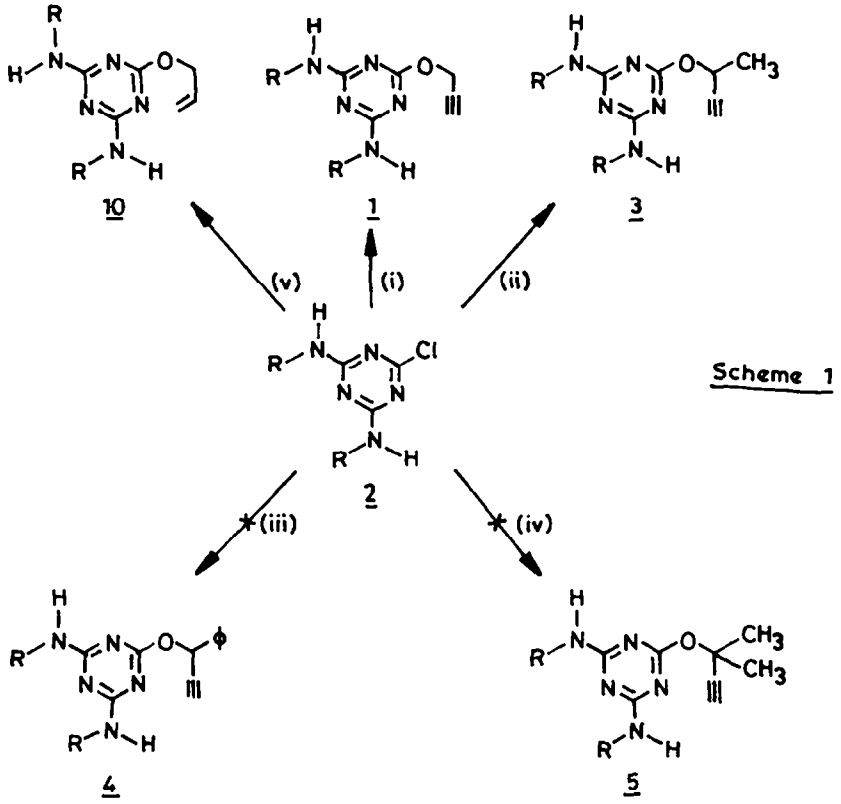
Results and Discussion

The s-triazinyl ethers **1a-e** were prepared in near quantitative yields by the reaction of the known[14] 2,4-bis(arylamino)-6-chloro-1,3,5-triazines **2a-e** with one equivalent of sodium hydroxide and 1.5 equivalents of propargyl alcohol in DMF or DMSO medium at room temperature.

The preparation of substituted propargyl ethers **3a** and **3b** posed some problem. These could not be prepared by any of the described methods. When 3-butyn-2-ol was treated with the 2,4-bis(anilino)-6-chloro-1,3,5-triazine **2a** in presence of sodium hydroxide with DMF as solvent, only the known[15] 2,4-bis(anilino)-6-(N,N-dimethylamino)-1,3,5-triazine was obtained in 80% yield. With a slight

+ Dedicated to Prof.S.Swaminathan, on the occasion of his 60th birthday.

modification in the conditions, the synthesis of 3a and 3b could be accomplished. Refluxing a solution of the 3-butyn-2-ol in dry benzene with sodium hydride or sodium metal followed by treatment with the chloro triazines 2b and 2c furnished the desired ethers 3a and 3b respectively in 85% yield. Neither phenylethynyl carbinol nor 2-methyl-3-butyn-2-ol underwent any reaction with the chlorotriazine 2a and ethers 4 and 5 could not be prepared.



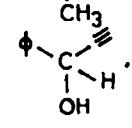
Scheme 1

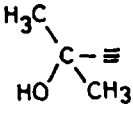
R

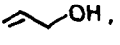
a C_6H_5
b p-CH_3-C_6H_4
c p-OCH_3-C_6H_4
d p-Cl-C_6H_4
e p-NO_2-C_6H_4

(i) $\equiv -CH_2OH$, NaOH, DMF/DMSO, RT

(ii) $\equiv -CH(CH_3)-OH$, Na/NaH, benzene, Δ

(iii)  , Na/NaH, benzene, Δ

(iv)  , Na/NaH, benzene, Δ

(v)  , NaOH, DMF/DMSO, RT

Rearrangement studies:

After a detailed study of the thermal behaviour of the above ethers 1a-e, 2 and 3 in various solvents like benzene, DMF, HMPT and o-dichlorobenzene (o-DClB), o-DClB has been found to be best solvent for the study. It is of interest to note that for phenyl propargyl ethers also, o-DClB was found to be best solvent to transform them into chromenes[16].

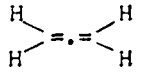
The rearrangement of 1a in o-DClB for shorter duration i.e., 2 hrs, led to a product 6a which was faster moving (0.9 Rf in benzene) compared to the starting material 1a (Rf 0.8 in benzene). This product crystallised out, on cooling in a freezer. The recrystallisation of the solid, yielded a pure

material, which showed the following properties. It analysed for $C_{20}H_{19}N_5O$ and mass spectrum showed it to be isomeric (M^+ 345) with the starting material 1a. The IR spectrum showed peaks at 3400 cm^{-1}, 1670 cm^{-1} and 1630 cm^{-1} and ^{1}H-NMR spectrum δ 2.25 (s, 3H), 2.40 (s, 3H), 4.84-4.96 (broad, singlet, 1H), 5.11-5.22 (a closely spaced triplet, 2H, J = 0.2Hz), 6.47-6.62 (broad singlet, 1H), 6.97-7.51 (m, 8H) and 6.85-6.96 (broad singlet, 1H exchangeable with D_2O).

When the rearrangement was carried out for longer duration (4 hrs) in o-DClB, it resulted in the formation of a more polar product (Rf 0.3 in benzene) compared to starting material 1b (Rf 0.8 in benzene). This product was also isolated as in the previous case. The elemental analysis and mass spectra indicated it to be isomeric with the starting material 1b. The mass spectrum exhibited a totally different fragmentation pattern compared to either fast moving product 6a or the starting material 1b. Its ir spectrum showed peaks at 3380 cm^{-1} and 1680 cm^{-1} and the NMR spectrum exhibited signals at δ 2.25 (s, 3H), 2.40 (s,3H), 2.6(s,3H) and 7.05-7.77 (m, 8H), 7.18-7.20 (broad singlet, 1H, disappears on D_2O exchange). The details of the other ethers prepared is given in Table 1.

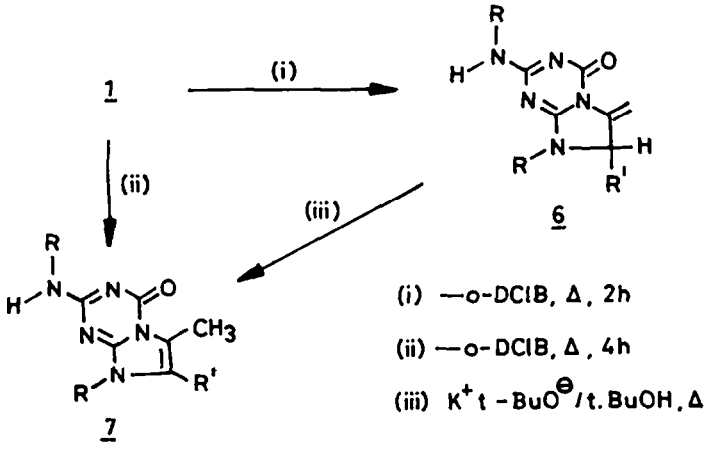
Of the substituted propargyl ethers 3a, 3b and 4 only the ethers 3a and 3b were observed to undergo reaction when refluxed in o-DClB (1.5-2.0 hrs). No reaction was observed in the case of ether 4, which was recovered even after refluxing for 10 hrs. in o-DClB. The ethers 3a and 3b afforded products in 70% yield. These products showed similar structural features as the faster moving product 6a-6c, of earlier propargyl ethers 1. It is interesting to note that the prolonged heating of 3a and 3b does not lead to the formation of slower moving product.

Structure of the rearrangement products:

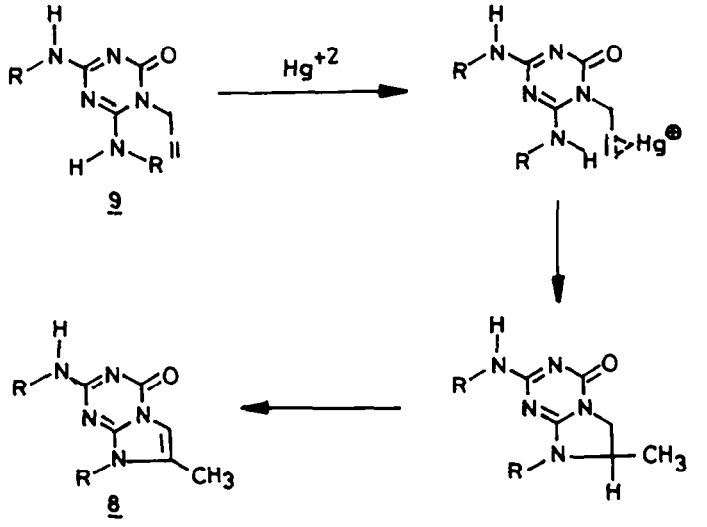
Elemental analysis and mass spectra of the products 6a-6e indicated that they are isomeric with their starting ethers, 1a-d, 3a and 3b respectively. The IR spectra of the above products showed clearly the absence of bands due to C≡C-H and  but exhibited peaks at 1670 cm^{-1} and due to C = C and amide type carbonyl groups. Deuterium exchange studies on these products revealed only one exchangeable -NH. From the NMR spectra of these compounds the presence of exomethylene group can be inferred [δ 4.85 (broad singlet, 1H) and δ 6.5 (broad singlet, 1H)]. This is further revealed by the facile isomerisation of these compounds by potassium t-butoxide in refluxing t-butanol to the respective slower moving spots 7a-7d, whose nmr spectra are characterised by clear absence of signals in the region δ 4.8-6.5 and presence of a sharp signal at δ 2.60 due to vinyl methyl group. Bases such as sodium ethoxide and sodium hydroxide did not bring about the above isomerisation. When the product 6b was subjected to catalytic hydrogenation using PtO_2 or 10% Pd-$BaSO_4$ employing ethanol or ethyl acetate as solvents, only complex mixtures, as evidenced by tlc, were obtained and no tractable material could be isolated. Based on the spectroscopic evidence various possibilities were ruled out and the following structures were assigned to (6) and (7) (Scheme 2).

It was hoped that an independent synthesis of the imidazo[1,2-a]-1,3,5-triazin-4-one 8 involving oxymercuration and demercuration followed by an oxidation of hitherto unknown N-allyl derivative 9 would provide some information regarding the structures 6 and 7 (Scheme 2). The Claisen rearrangement of 2,4-diamino-s-triazinylallyl ethers 10a-d seemed to be simple and attractive method for preparing the required N-allyl derivative 9 (Scheme 3).

Surprisingly, the allylethers 10a-d did not undergo any reaction when refluxed in o-DClB. Even after 15 hrs of refluxing o-DClB, there was no indication of any reaction taking place. When higher boiling solvents like



Scheme 2



Scheme 3

N,N-diethylaniline (bp 216°c) and HMPT (bp 238°c) were employed, these ethers gave a complicated mixture, within one hour of the start of the reaction, from which no pure product could be separated. It has been reported[17] that copper brings about the conversion of 2,4,6-triallyloxy-1,3,5-triazine to the 1,3,5-triallyl derivative at room temperature itself. When the triazinyl allyl ethers 10a-d were refluxed in chloroform or methylene chloride containing catalytic to molar equivalent of powdered copper for 3 hrs no reaction was observed and starting ethers 10a-d were recovered in major amounts (more than 80%) along with an insoluble material; refluxing in chloroform for 12 hrs led duly to an infusible material, which was insoluble in solvents like chloroform, benzene, hexane and methanol.

Since hard and soft Lewis acids have been found to bring about the Claisen and hetero Cope rearrangements under remarkably milder conditions, the rearrangement of s-triazinyl allyl ethers 10a-d was investigated under some of the literature described conditions. Treatment of allyl ether 10b with catalytic quantity of trifluroacetic acid (TFA) in dry benzene at room temperature or under

reflux in pure TFA led to the recovery of starting ether 10b only. Reaction of the allyl ether 10b in dry methylene chloride at 0°c with even catalytic amount of $TiCl_4$ or $AlCl_3$ led only to infusible material. When a solution of the allyl ether 10b in dry methylene chloride was treated with an equivalent quantity (catalytic quantity did not have any effect) of mercuric trifluroacetate at room temperature, no homogenous product could be obtained as the reaction was found to be very complex. It may be mentioned here that under the above reaction conditions, Overman et al. have reported[18] that the allyl imidates undergo a facile formal Claisen rearrangement.

The reluctance of the s-triazinyl allyl ethers 10a-d to undergo any rearrangement under conditions under which the s-triazinyl propargyl ethers 1a-d have been found to suffer smooth rearrangement is rather unexpected since the Claisen rearrangement of allyl ethers are known to occur more readily than that of the corresponding propargyl ethers. For example, it was reported that while aryl allyl ethers rearrange in about 3 hrs the analogous aryl propargyl ethers require longer hours of heating in the same solvents. When there is a competition between propargylic and allylic groups for the one and the same vinylic moiety in the substrate it was observed that the allylic group is the one that preferentially participated in the rearrangement as was seen from the product isolated[19].

The single crystal x-ray diffraction studies[13] on the trifluroacetic salt $[C_{20}H_{20}N_5O_3]^+ [CF_3COO]^-$ of the slower moving product 7c confirmed the structure assigned to it thus establishing also structures 6a-d for the faster moving products.

Reactions of 2,4-di-(N-aryl)-amino-1,3,5-triazin-6-yl prop-2-ynyl ethers induced by mercuric trifluroacetate

Charge induced sigmatropic rearrangements have been the subject of several investigations in recent times. Various hard acids[20], soft acids[21] and inorganic complexes[22] have been employed with considerable success as well as with limitations to bring about the charge induced transformations. Overman et al[22c] reported a facile 3,3-sigmatropic rearrangement of allylic trichloroacetimidates catalysed by mercury(II) trifluoroacetate and palladium salts. These reactions were cleaner compared to the protic and Lewis acid catalysed reactions and afforded the contra-thermodynamic products. However, there are no reports on charge induced sigmatropic rearrangements of propargylic imidates and related systems. It has now been observed that mercuric trifluoroacetate brings about the selective conversion of ethers 1 to the thermodynamically less stable 6-methyleneimidazo(1,2,-a)1,3,5-triazin-4-ones 6 under mild conditions.

The reaction of ethers 1 with equimolar amount of mercuric trifluoroacetate in dichloromethane for 2 hrs yielded the exo methylene products 6 in 35% to 60%, depending on the substituent in the aromatic ring (Table 7). There was no evidence for the formation of the isomeric products in these reactions. The products were isolated after alkaline sodium borohydride work up. The reactions were found to be clean and devoid of any side reactions.

Reactions of ethers 1 with mercuric oxide in acetic acid in the presence of a catalytic amount of sulphuric acid led only to the corresponding hydrated products. This observation is in contrast to the reported reaction of 1,6-diaryloxy-2,4-hexadiynes[21b] and of 1,4-diaryloxy-2-butynes[12] which were found to yield the respective chromenes, via 3,3-sigmatropic rearrangements.

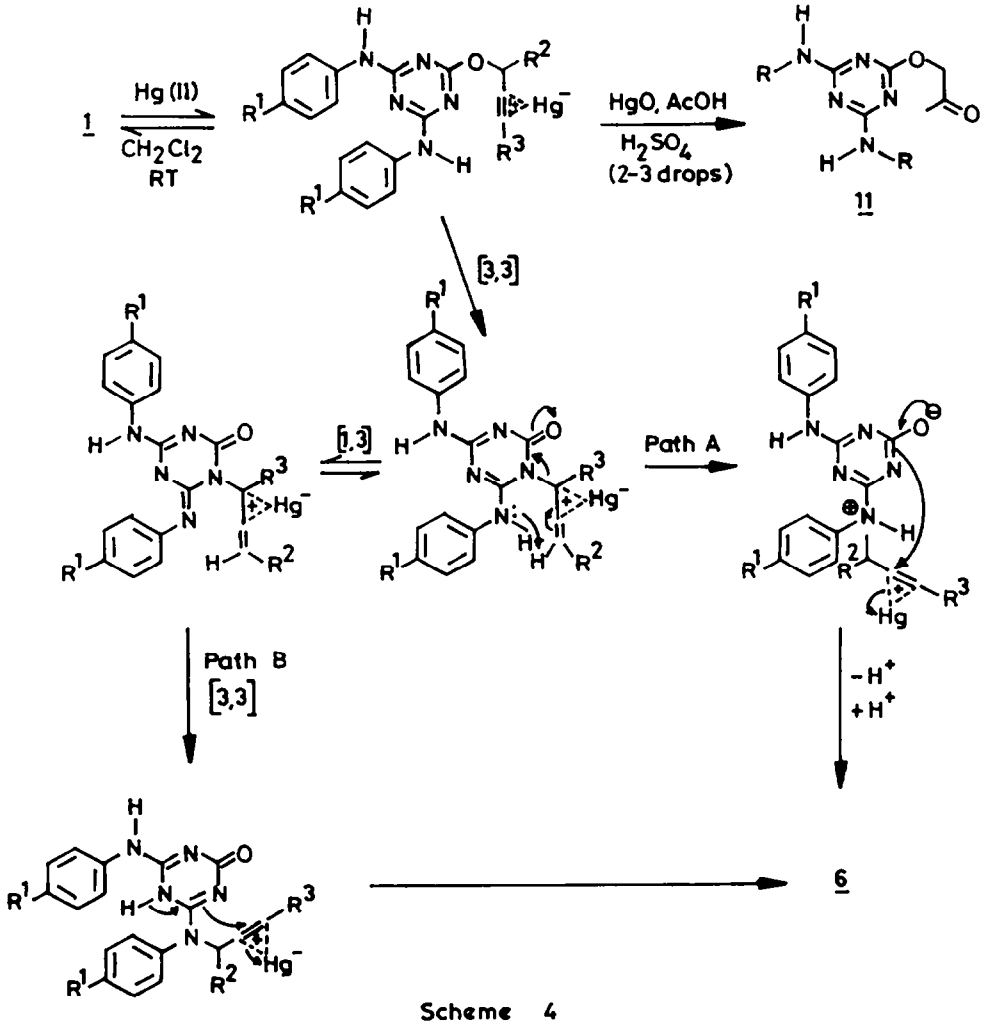
The reaction of ethers 1 with hard Lewis acids like $AlCl_3$ and $TiCl_4$ were found to result in extensive decomposition. In view of the reported tremendous rate acceleration of Claisen rearrangement of phenyl allyl ethers in trifluoroacetic acids[23], the reaction of ether 1 in the presence of trifluoroacetic acid

as a catalyst and as a solvent were examined. In both the cases, the starting material was isolated unchanged.

Interestingly, the bis propargyl ethers[12] did not undergo any reaction when exposed to mercuric trifluoroacetate in dichloromethane, indicating a significant role for the dianilino functionality present in ethers 1.

Mechanistic proposals:

The thermal rearrangement of ethers 1 to product 6 or 7 was rationalised by invoking nucleophilic assistance in the initial [3,3] sigmatropic rearrangement. A closely analogous mechanism is proposed to account for mercuric trifluoroacetate catalysed transformation 1-6. This is based on a few reported Hg(II) salt catalysed Claisen rearrangements which envisage Hg(II) ion complexation with the triple bond and subsequent 3,3-sigmatropic rearrangement of the mercuric complex. The resulting intermediate can either by path A or by path B lead to the final product. The two pathways differ only with regard to the mode of formation of the N-propargyl intermediate. While pathway A visualises a migration of the allenyl moiety from ring nitrogen to one of the aniline nitrogens, pathway B envisages a 1,3-hydrogen shift and a subsequent diaza Cope rearrangement (Scheme 4).



Scheme 4

Careful monitoring of this reaction did not reveal any intermediates. Lowering of temperature of the reaction also failed to indicate any intermediate. These observations clearly indicate that mercuric trifluoroacetate not only accelerates the initial step but also the subsequent steps. In this, the behaviour of the s-triazinyl propargyl ethers 1 is in contrast to that of 2-propargyl-thiobenzimidazoles which give rise to 3-methylthiazolo-(3,2-a)-benzimidazoles without skeletal rearrangements[24].

It is significant to note that no bis-triazinyl mercurials are formed in the reaction of ethers 1 with mercuric trifluoroacetate, whereas reaction of phenyl propargyl ethers, under similar conditions, affords only the 4,4'-bis chromenyl mercurials, which could not be demercurated[25].

To our knowledge this is the first example of mercuric trifluoroacetate induced rearrangement of a propargyl imidate like system and the first of its kind in the chemistry of s-triazines. The transformation described above provides a simple annulation method of entry to the imidazo(1,2-a)-1,3,5-triazine ring system which is not at all well studied[26]. We are currently investigating the mechanism and synthetic potential of this transformation.

Experimental Section

General Considerations: Melting points are uncorrected. UV spectra are recorded in methanol using a Beckman DGBT model spectrometer. Infra red spectra were recorded on a Perkin-Elmer-257 instrument. NMR spectra were taken on a Varian A-60 D, T-60, XL-100 and Bruker WH-90 instruments with $CDCl_3$ and trifluoroacetic acid (TFA) as solvents and TMS as an internal standard. Mass spectra are recorded on a Varian Mat CH-7 spectrometer. All the solvents employed in the present study were purified using literature reported procedures.

1. Synthesis of 2,4-bis(N-arylamino)-6-propargyloxy-1,3,5-triazines 1a-1e: General Procedure: Sodium hydroxide (0.03 m) was dissolved in hot propargyl alcohol (7 ml) and the solution added to the DMF/DMSO solution (1:1) (30 ml) of the known 2,4-bis(N-arylamino)-6-chloro-1,3,5-triazine 2[14] (0.02 m). After 3 hrs of stirring at room temperature, the above solution was poured onto crushed ice and the solid was filtered and dried. The above solid was extracted with chloroform and the solid got after the removal of the solvent was crystallised using benzene (Table 1).

Table 1

Preparation of 2,4-bis(N-arylamino)-6-propargyloxy-1,3,5-triazines 1

Entry No.	arylamino substituent	Compound No.	M.P.°C	Yield (%)
1.	H	1a	114	90
2.	4-CH_3	1b	148	95
3.	4-OCH_3	1c	132	90
4.	4-Cl	1d	169	90
5.	4-NO_2	1e	175	85

2. General Procedure for the preparation of 2,4-bis(N-arylamino)-6-butynyloxy-1,3,5-triazines 3a and 3b: Sodium (0.03 m) or sodium hydroxide (0.03 m) was dissolved in hot 3-butyn-2-ol (10 ml) in refluxing benzene (50 ml) and the 2,4-bis(N-arylamino)-6-chloro-1,3,5-triazine 2 (0.01 m) was then added and the solution refluxed while stirring for 3 hrs. The reaction mixture was then filtered and poured onto crushed ice, the benzene layer separated and removal of the solvent yielded pure 2,4-bis(N-bis(N-arylamine)-6-butynyloxy-1,3,5-triazines 3.

Table 2: Preparation of 2,4-bis(N-arylamino)-6-butynyloxy-1,3,5-triazines 3a 3b

Entry No.	Compound	M.P.°C	Yield (%)
1.	2,4-bis(4-methylamino)-6-butynyloxy-1,3,5-triazine 3a	140	85
2.	2,4-bis(4-methoxyanilino)-6-butynyloxy-1,3,5-triazine 3b	148	85

3. Rearrangement of 2,4-bis(N-arylamino)-6-properyloxy-1,3,5-triazine 1a-1e Synthesis of 6-methyleneimidazo(1,2-a)-1,3,5-triazin-4-one 6: The ether 1 (0.01 m) was refluxed in o-DCIB (30 ml) for 2 hrs then cooled to room temperature and left in the refrigerator for one to two hrs. The white crystalline product formed (70-75%) was filtered, dried and recrystallised (Table 3). These products were characterised by both spectral and elemental analysis.

Table 3: General Procedure for the synthesis of 6-methyleneimidazo(1,2-a)-1,3,5-triazine-4-one 6:

Entry No.	Compound No.	Yield(%)	M.P.°C
1.	6a	70	170
2.	6b	70	188
3.	6c	75	190
4.	6d	74	198
5.	6e	70	168

4. General Procedure for the synthesis of 6-methylamidazo(1,2-a)-1,3,5-trigzine-4-ones 7: The ether 1 (0.01 m) was pyrolysed in refluxing oDCIB (30 ml) for 4 hrs and on cooling, white crystals, crystallised out, which on further crystallisation from chloroform yielded the 6-methyl-imidazo-(1,2a)-1,3,5-triazine-4-ones 7.

Table 4: Synthesis of 6-methylimidazo(1,2-a)-1,3,5-triazine-4-one 7:

Entry No.	Compound No.	M.P.°C	Yield(%)
1.	7a	208	55
2.	7b	250	30
3.	7c	255	40

5. General Procedure for the isomerisation of 6 to 7: Potassium metal (0.02 m) was dissolved in refluxing anhydrous t-butanol (20 ml) and 6-methylene derivative 6 (0.01 m) was added. The refluxing was continued for another one hr the solvent was removed under vacuum (10 mm) and poured onto crushed ice. The solid 6-methyl derivative 7 was separated, filtered and dried. The yields varied from 90-95%. The nmr and mass spectra of the above isomerised products 7a-c were similar to those of the slower moving products obtained from the thermal rearrangement of the respective s-triazinyl ethers 1a-c.

6. General Procedure for the preparation of the 2,4-bis(N-arylamino)-1,3,5-triazin-6-allyloxy-10a-d: Sodium hydroxide (0.03 m) was dissolved in hot allyl alcohol (10 ml) and the above solution was added to the DMSO (30 ml) solution of 2 (0.02 m). After 3 hrs stirring at room temperature the reaction mixture was worked-up as in previous cases. The products were characterised by IR, NMR, Mass spectra and analysis.

Table 5: Synthesis of 2,4-bis(N-arylamino)-6-allylo-y-1,3,5-triazine 10a-d:

Entry No.	Substituent in arylamino group		M.P.°c	Yield(%)
1.	H	10a	118	85
2.	4-CH_3	10b	130	83
3.	4-OCH_3	10c	140	80
4.	4-Cl	10d	155	70

7. General Procedure for the reaction of ethers 10b under various conditions: The allyl ether 10b (0.01 m) was dissolved in the appropriate solvent and the reactions was carried out under the conditions. The results are summarised in Table 6.

Table 6: Attempted rearrangement reactions on 2,4-bis(N-aryl-amino)-6-allyloxy-1,3,5-triazines 10b:

Entry No.	Reaction conditions	Reaction Time	Observations
1.	O-Dichlorobenzene/reflux	15 hrs	Starting Material recovered
2.	N,N-DEA/reflux	5 hrs	Complex mixture as indicated by tlc
3.	HMPA/reflux	5 hrs	-do-
4.	Cu-powder/$CHCl_3$/reflux	3 hrs	S.M.recovered
5.	$Hg(CF_3COO)_2/CH_2Cl_2$/RT	5 hrs	Complex Mixture
6.	TFA/reflux	5 hrs	S.M. recovered

8. General Procedure for the reaction of ethers 1 with mercuric trifluoroacetate: Equimolar amounts of 1 and $Hg(CF_3COO)_2$ (catalytic quantity of $Hg(CF_3COO)_2$ did not have any effect) were mixed in dry dichloromethane (5 ml/MMole) and stirred at room temperature for 2 hrs. The reaction was then quenched slowly with excess alkaline sodium borohydride solution. The mixture was filtered and the organic layer was washed with water. The dried organic layer was evaporated to yield the product whose IR spectra and melting point data along with nmr data tallied with the exo-methylene product 6 isolated from the thermal rearrangement.

Table 7: Synthesis of 6-methyleneimidazo(1,2-a)-1,3,5-triazine-4-one 6:

Entry No.	Product	M.P.°C	Yield(%)
1.	6a	170	60
2.	6b	188	50
3.	6c	190	55
4.	6d	198	40
5.	6e	168	35

9. General Procedure for the hydration of the ethers 1: The ether (0.005 m) was refluxed in glacial acetic acid (25 ml) with a catalytic amount of mercuric acetate (0.0005 m) in presence of con. sulphuric acid (2-3 drops) for a duration of 3 hrs. The mixture was cooled down to room temperature, poured onto crushed ice and neutralised with saturated sodium bicarbonate solution. The crude solid was filtered off, washed with water and dried. The melting points and yields obtained for various ketones 11a-d are given in Table 8. They are characterised by spectral and analytical data.

Table 8: Hydration of Ethers 1a-d:

Entry No.	Product No.	M.P.°C	Yield(%)
1.	11a	128	65
2.	11b	134	68
3.	11c	138	72
4.	11d	142	60

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