Tetrahedron Letters Vol. 21, pp 4731 - 4734 0040-4039/80/1201-4731$02.00/0
©Pergamon Press Ltd. 1980. Printed in Great Britain

A NOVEL THERMAL TRANSFORMATION OF 2,4-DI(N-ARYL)AMINO-1,3,5-TRIAZIN-6-YL PROP-2-YNYL ETHERS

K.K.Balasubramanian, G.V.Bindumadhavan, M.R.Udupa
Department of Chemistry, Indian Institute of Technology
Madras 600 036, India

and

B.Krebs
Anorganisch-chemisches Institut der Universität
Gievenbecker Weg 9, D-4400 Münster, F.R.G.

Summary: 2,4-Dianilino-1,3,5-triazin-6-yl propargyl ethers have been found to undergo a novel thermal transformation yielding the isomeric 6-methylene imidazo [1,2-a] -1,3,5-triazines.

Numerous reports have appeared in recent years on the Claisen rearrangement of aryl propargyl ethers, vinyl propargyl ethers and of related systems[1,2]. Many of these transformations have found useful applications in organic synthesis[3]. However, rearrangement of propargyl imidates and the like systems have not been investigated in detail[4]. The recent publication of Overman *et al*[5] on the Claisen rearrangement of propargyl trichloroimidates has prompted us to disclose our own findings on a novel thermal transformation of 2,4-di(N-aryl)amino-1,3,5-triazinyl propargyl ethers **1**a-d.

The starting ethers **1**a-d were prepared by reacting sodium propargyloxide with 6-chloro-2,4-di(N-aryl)amino-1,3,5-triazines in dry dimethylformamide or benzene. When the ether **1**a was refluxed in o-dichlorobenzene for 5 hours, and the reaction mixture cooled under ice, colourless crystals, m.p.198° (60%), homogeneous and slightly more polar than the starting ether on tlc, was obtained. Elemental analysis ($C_{18}H_{13}Cl_2N_3O$) and mass spectrum (M^+ 385) indicated it to be isomeric with the starting compound. The product showed the following spectral characteristics: IR C=O at 1680 and C=C at 1640 cm^{-1}; PMR signals at δ4.84-4.96(m, 1H), 5.11-5.22(m, 2H), 6.47-6.62(m, 1H), 6.97-7.51 (m, 8H) and 6.85-6.96 (broad singlet, 1H, exchangeable with D_2O).

The allenic intermediate arising from the Claisen rearrangement of the ether **1**a can lead to either product **4** or to a host of other cyclised products[7]. However, only structure **2**a is consistant with the observed difference in the chemical shifts of the two olefinic protons at δ

4.84-4.96 and 6.47-6.62 and other spectral data.

Rearrangement of the other di(N-aryl)amino-1,3,5-triazinyl propargyl ethers 1b-d also afforded the respective 6-methylene imidazo [1,2-a] -1,3,5-triazines 2b-d (Table 1) but along with the isomeric 6-methylimidazo [1,2-a] -s-triazines 3b-d which were separable. The methyleneimidazotriazines 2a-d undersent readily isomerisation quantitatively when treated with potassium t-butoxide in t-butanol to the respective 6-methyl derivatives 3a-d. Spectral characteristics of 3b; IR 1680 cm^{-1}; M^+ 377; PMR δ2.60(s, 3H). 3.50(s, 3H), 3.55(s, 3H), and 7.1-7.6(m, 10H). High resolution mass spectrum of 3c indicated that the peak at m/e 303 (50%) arises only by the loss of NCO moiety from the molecular ion. The base catalysed isomerisation of 2a-d to 3a-d clearly rules out the alternative structure 5. X-ray diffraction studies carried out on the trifluoroacetate salt $(C_{20}H_{20}N_5O_3)^+ (CF_3COO^-)$ of the base 3b confirmed the structure of the salt to be 3a, thereby suggesting the structure 3b for the free base.

The salt crystallises in the monoclinic system with space group $P2_1/c$ and the cell constants are a=10.404(3), b=12.997(3), c=16.511(3)Å, β=92.45(3)° and Z=4. The structure was solved by direct methods and refined to R=0.060 from 2387 reflections. The cationic part of the salt with bond distances (Å) is shown in fig.1. (Hydrogen atoms are omitted for clarity and standard deviations are 0.005 Å).

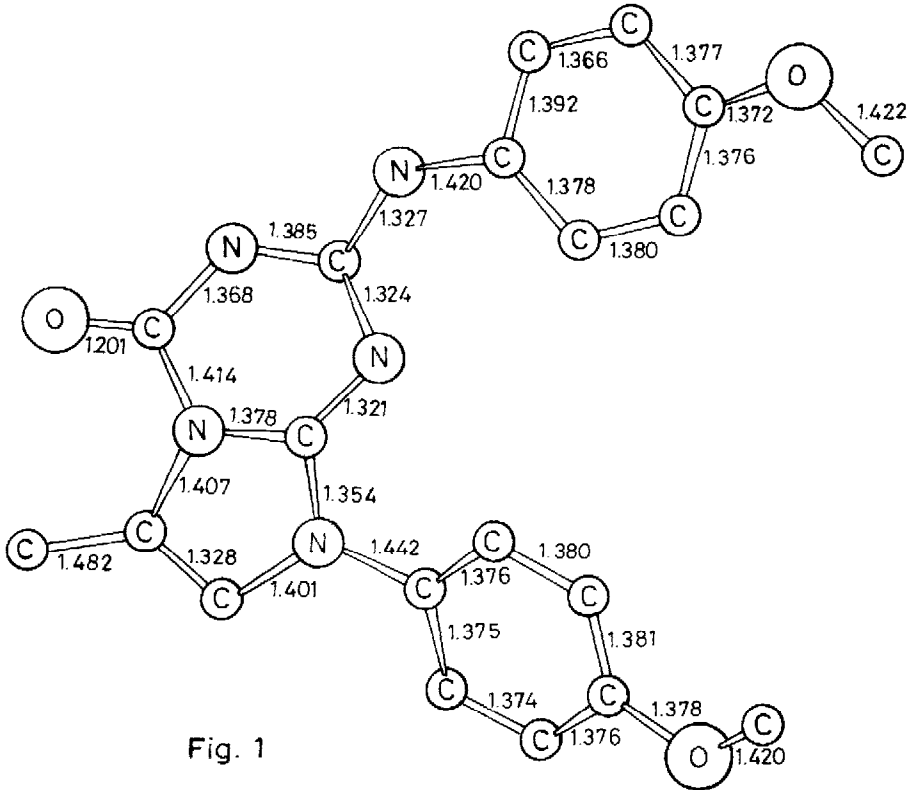
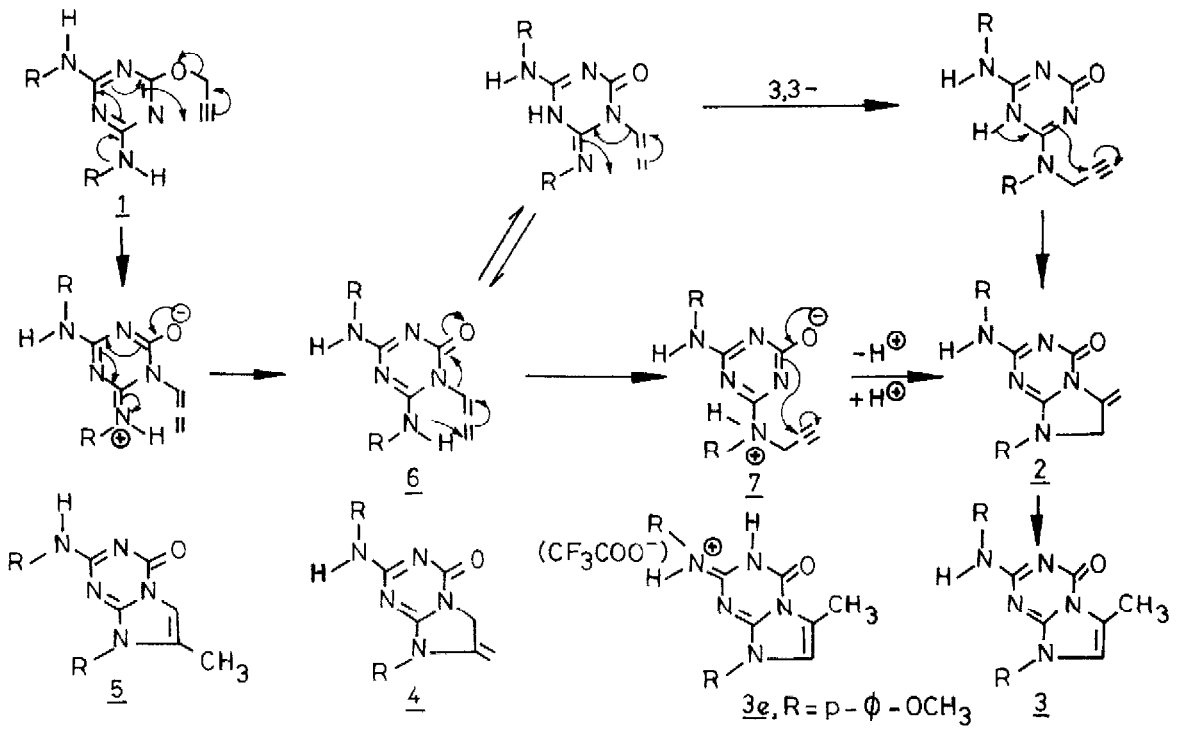


Fig. 1

Interestingly, the corresponding allyl triazinyl ethers, viz., 2,4-di(N-aryl)amino-1,3,5-triazin-6-yl allyl ethers, failed to undergo Claisen rearrangement when heated to o-dichlorobenzene indicating that the first step in the mechanism of the transformation of the ethers 1a-d to 2a-d may not be a simple 3,3-sigmatropic shift. However, work is underway to settle this point. Formation of the products 2 from 1 may be visualised as outlined below:



	R	1 mp°C	1 Yield %	2 mp°C	2 Yield %	3 mp°C	3 Yield %
a	p-ϕ-Cl	169	90	198	60	258°	-
b	p-ϕ-OCH_3	132	95	190	55	255	40
c	p-ϕ-CH_3	148	90	188	65	250	30
d	ϕ	114	90	170	40	208	55

All the new compounds described in this communication showed satisfactory elemental and spectral data.

It is likely that the gain of aromaticity in going from structure 6 to 7 and the reduced susceptibility of the central carbon of the allenic

system in 6 for nucleophilic attack may be the controlling factors in the formation of 2 in preference to 4.

In summary, 2,4-di(N-aryl)amino-1,3,5-triazin-6-yl propargyl ethers have been found to undergo a novel thermal transformation affording the 8-methylimidazo [1,2-a] -1,3,5-triazines and the isomeric 6-methylene derivatives. The mechanism of this transformation is visualised to involve a nucleophilically assisted migration of the propargyl group from O to N, followed by a further migration from ring N to aninino N and a final ring closure. This transformation provides a new and convenient entry into the synthesis of the imidazo [1,2-a] -1,3,5-triazine ring system 'which is not at all well studied'[9] and for which there are not many routes at present.

Acknowledgement: The financial aid from the Ministry of Defence and the Department of Atomic Energy, Government of India, is gratefully acknowledged. We thank Dr.K.Nagarajan, CIBA-GEIGY research centre, Bombay, Dr.Ramasamy, C.L.R.I., Madras, Dr.Balasubramanian, Department of Organic Chemistry, University of Madras, and Prof.Gossauer, Technical Universitat Berlin, for spectra and analytical data. Our thanks are due to BASF, West Germany for a generous gift of propargyl alcohol and to Dr.C.Georgoulis, Universite Pierre at Marie Curie, Paris for the high resolution mass spectrum.

REFERENCES:

1. S.J.Rhods and N.R.Raulins, Org.React.,22, 1 (1975)
2. G.B.Bennett, Synthesis, 589 (1977)
3. D.K.Bates and M.C.Jones, J.Org.Chem., 43, 3856 (1978)
4. A few examples of propargyl thiomimidate Claisen rearrangements are known. See K.K.Balasubramanian and B.Venugopalan, Tetrahedron Lett., 31, 2645 (1974)
5. L.E.Overmann, C.K.Marlowe and L.A.Clizbe, Tetrahedron Lett., 43, 599 (1979)
6. a) J.Thurston, J.Dudley, D.Kaiser, I.Mechnbleikner, F.Schaefer, D.Helm-Hamen, J.Am.Chem.Soc., 73 2981 (1951)
   b) F.Curd, J.Landguist and E.Rose, J.Chem.Soc., 159 (1947)
7. The N-allene intermediate 6 can suffer cyclisation through the anilino Nitrogen or through the ortho position of the aniline or through the oxygen of the triazinone. Alternatively, the N-allene 6 can undergo a hetero Cope rearrangement leading to the migration of the allene group from N at 1 position to the N at 5 position, followed by again cyclisation involving either the anilino N or the ortho position of the anilino groups.
8. The x-ray studies were carried out on the salt as no good crystal of the free base for diffractometer studies could be obtained.
9. E.J.Prisbe, J.P.H.Verheyden and J.G.Moffat, J.Org.Chem., 43, 4774 (1978) and references 8 and 9 cited therein.

(Received in UK 24 September 1980)