

AN UNEXPECTED ISOMERISATION OF 1,4-DIARYLOXY-2-BUTYNES
TO Z,Z-1,4-DIARYLOXY-1,3-BUTADIENES-POTENTIAL DIENES
FOR DIELS-ALDER REACTION

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Abstract: 1,4-Diaryloxy-2-butyne 1 were converted to 1,4-diaryloxy-z,z-1,3-butadienes 2 in refluxing HMPA in presence of potassium carbonate.

In recent years there has been a great interest in the synthesis of functionalised 1,3-butadienes from simple 2-butyne derivatives, in view of the simplicity and easy availability of the latter compounds. These transformations involve either two S_N2 substitutions¹, or 2,3-addition of (pseudo) halogens across the triple bond followed by 1,4-elimination² or catalytic isomerisation of triple bond using ruthenium hydride complexes³ or base catalysts⁴. These reports prompted us to disclose our findings in this area. We encountered an unexpected isomerisation of 1,4-diaryloxy-2-butyne 1 to 1,4-diaryloxy-z,z-1,3-butadienes 2, when the former compounds were heated in hexamethylphosphorotriamide (HMPA) in presence of potassium carbonate. Even though the yields are only 25% - 30% (Table 1), the route is simple and straightforward and is significant in view of the resistance of 2-butyne to isomerise to 1,3-butadienes⁵ and in the light of several interesting thermal and acid catalysed transformations undergone by 1 in refluxing N,N-diethylaniline⁶.

In connection with our work in the area of Claisen rearrangements in oxygen heterocycles, we were interested in the study of synthesis and rearrangement of 2-methyl-3-aryloxymethylbenzofuran 3⁷, potential systems for Claisen rearrangement. The rearrangement of easily available 1 in refluxing HMPA in presence of potassium carbonate appeared to be the shortest route to the required compound 3, as analogous reactions of phenyl propargyl ethers are known to furnish 2-methylbenzofurans⁸. However, there was no evidence for the formation of 3, the expected product, when the crude reaction mixtures were analysed by NMR. Instead, 1,3-butadienes 2 are the only isolated products from the reaction of 1 in presence of HMPA/ K_2CO_3 . A typical isomerisation procedure is as follows: A mixture of 1g of 1a and 1.5g of K_2CO_3 in 10ml of HMPA is heated to reflux for 45 mts. Work-up of the reaction mixture and chromatography of the crude product over alumina with hexane elution afforded 280mg of 2a. The structure of 2 is based on NMR⁹ coupling constants, mass spectra and

hydrogenation experiments¹⁰. We have tried several other conditions to optimise the transformation for better yields. The conditions employed are HMPA/DBU, N,N-diethylaniline/ K_2CO_3 , DMSO/KOH, DMSO/ K^+ t-butoxide¹¹ etc. In all these cases no characterisable material could be isolated. Only HMPA/ K_2CO_3 seems to be best suited for the present transformation. We are currently investigating the utility of these dienes as 4π components in Diels-Alder reaction.

Acknowledgement: One of us (SRK) wishes to thank DAE, Govt. of India, for the award of a JRF-B fellowship.

Scheme 1

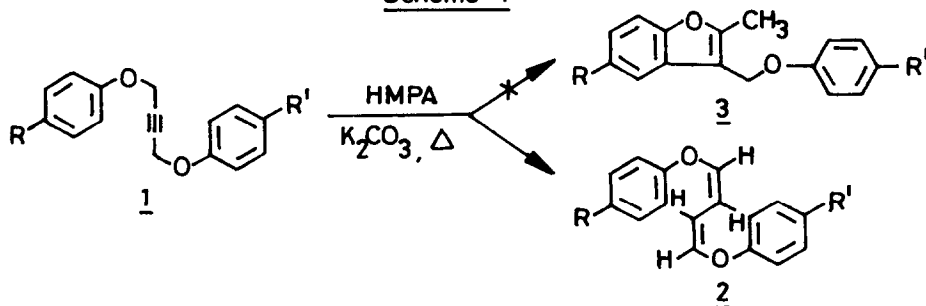


Table 1

2-butyne <u>1</u>	R	R'	Yield of <u>2</u>	m.p. of <u>2</u>
1a	CH ₃	CH ₃	28%	128°C
1b	H	H	25%	liquid
1c	CH ₃	Cl	26%	118°C
1d	Cl	Cl	30%	135°C

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 - ¹H-NMR spectrum of 2a, in CDCl₃, TMS, δ Scale, 2.3 (s, 6H), 5.9(dd, J=3.5Hz, 2H), 6.4 (dd, J=3.5 Hz, 2H), 6.8-7.2 (m, 8H).
 - The hydrogenation of 2d and 1d yielded the known 1,4-bis(p-chlorophenoxy)-butane. See Ref. M. Kulka, *J.Org.Chem.*, 22, 1957, 241.
 - This condition is reported to bring about isomerisation of 1,4-dimethoxy-2-butyne to a mixture of z,z:z,e:e,e, isomers of 1,4-dimethoxy-1,3-butadienes, in the ratio of 62:30:8 respectively (ref.4b). But use of similar reaction conditions in our case failed to furnish the z,z isomer. The structure of the product formed is under investigation.