Tetrahedron Letters,Vol.23,No.46,pp 4821-4822,1982 0040-4039/82/464821-02$03.00/0
Printed in Great Britain

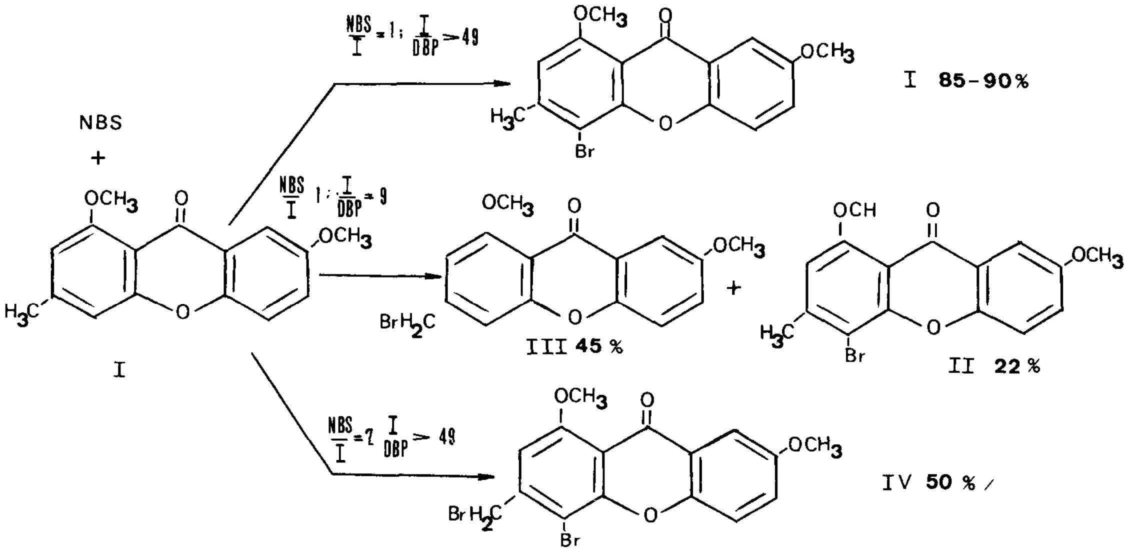
BROMINATION OF 1,7-DIMETHOXY-3-METHYLXANTHONE WITH N-BROMOSUCCINIMIDE

Gilberto Goissis

Departamento de Química e Física Molecular
Instituto de Física e Química de São Carlos-USP

It has been shown for this reaction that ring vs. side chain bromination is dependent on the concentration of free radical initiators.

The versatility of N-bromosuccinimide (NBS) as a brominating agent is a well documented fact. Non-polar solvents, with free radical initiators, promote allylic bromination in olefins[1,2] and side chain bromination of alkyl aromatic compounds[2,3]. Highly activated aromatic ethers and amines react with NBS alone giving in most cases ring bromination[2], selectivity towards mononuclear bromination being achieved in non-polar solvents[4,5]. In the case of heterocycles ring or side chain bromination can be controlled by the presence or absence of free radical initiators[2] but so far no results have been reported as to the effect of initiator concentration on the relative distribution of products, specially in the case of non-heterocyclic compounds, wich have been studied in this work with 1,7-dimethoxy-3-methylxanthone and dibenzoylperoxide (DBP). The products



observed are those of SCHEME I and their proton magnetic ressonance values are shown in TABLE I.

TABLE I: Chemical shift (δ) for the isolated products

Compound	Functional Group							
					Aromatic Protons			
	CH_3-	CH_3O-(1)	CH_3O-(7)	-CH_2-	H (2)	H (4)	H (5,6)	H (8)
I	2.41	3.99	3.88	-	6.51	6.78	7.23	7.63
II	2.53	3.98	3.88	-	6.66		7.34	7.65
III	-	3.98	3.88	4.45	6.55	7.66	7.28	7.65
IV	-	4.03	3.90	4.66	6.90		7.34	7.65

The nmr data show that only one bromine atom is introduced under the conditions used and most likely at position 2 or 4[2,6,7]. Product distribution as measured by nmr show that at a NBS/I ratio of one there is a progressive increase of compound III as the ratio of I/DBP drops down to 9 and its concentration is twice that of compound II. At I/DBP ratios > 49 compound II is the only product formed in 85-90% yelds. At NBS/I ratio of two compound IV is formed even at low DBP concentrations, complete convertion of I to II being observed within 5 min., one equivalent of NBS being consumed. Side chain bromination takes place at a slower rate (50 % yeld after 5 hrs.). No reaction is observed between compound I and NBS in the absence of DBP.

The results above show that under controlled peroxide concentration 1,7-dimethoxy-3-methylxanthone undergoes NBS bromination either on the ring or side chain. Although no generalization may be done as to the general behavior of activated aromatic compounds these results may be of use in this respect. Reaction of NBS with mono and dimethoxy alkylaromatic compounds under controlled peroxide concentration are present under way.

Acknowledgements: This work was supported by Fundação de Amparo à Pesquisa do Estado de São Paulo (FAPESP)

REFERENCES:

1. R.A. Barnes, J. Am. Chem. Soc., 70, 145 (1948).
2. L. Horner and E.H. Winkelmann in " Newer Methods of Preparative Organic Chemistry" Academic Press, Vol. III, p. 151 (1964).
3. Ng.Ph.Buu. Hoi, Ann. Chem., 556, 1 (1944).
4. R.H. Mitchel, Y.H. Lai and R.W. Willians, J. Org. Chem., 44, 4733 (1979).
5. S.Sivakamasundari and R. Ganesn, Intern. J. Chem. Kin., 12, 837 (1980).
6. M.M. Pinto and J. Polonia , Helv. Chim. Acta, 57, 2613 (1974)
7. T. Arunachalan, M. Anchel and M.S. Nair, J. Org. Chem., 37, 1262 (1972).

(Received in UK 14 September 1982)