Tetrahedron Letters No.27, pp. 3111-3114, 1968. Pergamon Press. Printed in Great Britain.

REACTIONS OF EXCITED MOLECULES IV.

THERMAL ISOMERISATION OF THE XYLENES.

by W. D. Crow and C. Wentrup

Chemistry Department, Australian National University,

Canberra, A. C. T. 2600, Australia.

(Received in UK 25 March 1968; accepted for publication 5 April 1968)

As part of a comparative study of aromatic rearrangement (1,2) mechanisms under different conditions of activation, we were interested in the possible production of valence-bond isomerisation of benzene derivatives through vibrationally excited states arising from purely thermal activation. As an adjunct to photochemical isomerisation of o-xylene at 1600-2100 Å, Ward (3) reports the absence of any thermal isomerisation at 550°. This, coupled with the recent work of Lahmani et al.(4), who have induced photochemical isomerisation of pyrazines, prompts us to report the results we have obtained on vapour-phase pyrolysis of substituted benzenes.

Photochemical exchange of ring carbon atoms in substituted benzenes has been well demonstrated by labelling involving 1,3,5-$^{14}C_3$-mesitylene (5), or inferred from the isolation of valence-bond isomers corresponding to Dewar benzene(6), benzvalene (7) and prismane (7). It is clear that the concept of aromatic stability (in its usual laboratory sense of "unreactive") requires some revision in the light of the "reagents" currently in use, i.e. the aromatic ring is certainly not stable to electron or photon impact, and it may prove less stable to high temperature than has been thought --- particularly when the symmetry of its π-cloud is distorted by electronic or steric (8) effects of substituents.

The isomerisation of the xylenes is a known commercial process, employing either surface catalysis (9) or electrophilic equilibration (10). Photochemical isomerisation at 2537 Å has been reported (11), involving apparent 1,2-methyl shifts by a non-radical process; it is logical to assume that this involves ring-carbon exchange as in the case of mesitylene (5).

Ward (3) has reported essentially the same observations for the vapour-phase photolysis of o-xylene at 1600-2100 Å, and proposes that the isomerisation proceeds via a vibrationally excited ground state intermediate rather than directly from an upper electronic state - an argument which we feel could with profit be applied to other reactions involving photon or electron absorption. It was further proposed that the vibrational state giving rise to isomerisation lay above that leading to some radical decomposition routes (and is thus more efficiently populated by internal conversion from an upper electronic state than by thermal processes from lower vibrational ground states).

We have pyrolysed the three xylenes in a packed silica tube (12) at 1270°K under 4-5.5 m.m., collecting the products in a series of liquid N_2 traps prior to analysis by GLC. The results, presented in Table I, show that the xylenes interconvert to the extent of a few per cent., coupled with fairly extensive decomposition. The range over which isomerisation was observed was quite narrow; at lower temperatures and/or lower pressures (i.e. lower residence time) insufficient activation was achieved, while at higher pressures yields were decreased by secondary decompositions.

TABLE I.

Xylene Pyrolysis at 1270° K. (Yield % of Pyrolysate)*

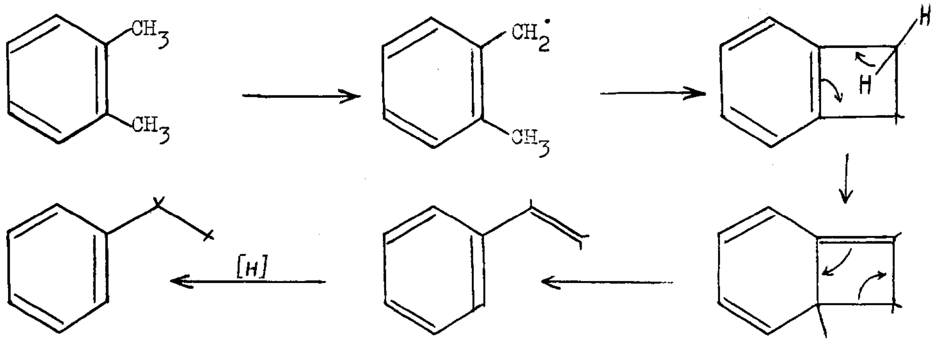
	P(mm)	ϕH	ϕCH_3	ϕC_2H_5	Styrene	o-Xylene	m-Xylene	p-Xylene
o-	4.0	2.7	15.6	0.2	14.0	(26)	1.6	0.4
o-	4.5	2.2	10.5	0.1	9.8	(3)	0.8	0.2
m-	4.5	0.0	3.8	-	2.4	0.25	(48)	Trace
m-	5.0	6.2	29.0	-	7.5	1.6	(23)	1.0
p-	4.3	5.3	17.5	-	3.8	0.6	3.5	(25)
p-	4.5	0.1	5.0	Trace	5.2	0.5	3.0	(14)
p-	5.5	1.0	6.6	-	4.0	0.2	1.3	(42)

* Analysed on 12'x ¼" column of 20% Carbowax 20M on Embacel. Gases and higher hydrocarbons were not estimated. Xylenes were analysed on a 50'x 0.02" Perkin-Elmer support-coated (MBMA) open tubular column. Figures in brackets refer to recovery of the starting material.

These observations are consistent with the proposal of Ward, and suggest that the vibrational levels involved are not too widely spaced, since it is evidently possible to populate the upper level, at least to some extent, by thermal means. It seems probable that the rate at which molecules are "pumped up" by collision may be critical, since it determines the time available for decomposition at any particular energy level. Similar effects were observed in the case of phenylnitrene isomerisation (1), in which the nature of the product was largely determined by the rate of sample introduction.

The predominant mode of isomerisation is seen to be a 1,2-methyl shift, whether it be by ring isomerisation or otherwise. o-Xylene forms four times as much m-xylene as p-xylene, while p-xylene forms six times as much m-xylene as o-xylene. Rather surprisingly, m-xylene produces more of the sterically crowded o-xylene than it does of the p-isomer, but this may possibly be due to polymer formation by p-xylene (about 1% of such a polymer was isolated in this case, and identified by IR. It does not occur in the case of o-xylene).

The relatively high yields of benzene and toluene are indicative of the radical pathway which is the major process; the similarly high yields of styrene from pyrolysis of o-xylene probably arise from a pathway similar to the photolytic production (3) of benzcyclobutene. Such a compound is unlikely to survive the reaction conditions, and the formation of styrene and ethylbenzene can be readily rationalised; since such products are not common to all the xylenes, they evidently arise from such a precursor. Formation



of ethylbenzene from benzyl radicals must also be considered as a possibility, and for this reason the presence of this compound is not regarded as of great significance. Production of xylenes by the attack of methyl radicals on toluene can be safely ignored, since it is known (13) that this reaction leads to the formation of benzyl radicals. Subsequent reactions should then lead to a fixed xylene ratio, regardless of the starting product, which is not in fact observed.

REFERENCES

1. W. D. Crow and C. Wentrup, Tetrahedron Letters, **44**, 4379 (1967)
2. R. F. C. Brown, W. D. Crow and R. K. Solly, Chemy. Ind., 343, (1966)
3. H. R. Ward, J. Amer. Chem. Soc., **89**, 2367,(1967)
4. F. Lahmani, N. Ivanoff and M. Magot, Compt. rend.(C), 1005 (1966)
   Tetrahedron Letters, **44**.3913 (1967)
5. L. Kaplan, K. E. Wilzbach, N. G. Brown and S. S. Yang,
   J. Amer. Chem. Soc., **87**, 675 (1965)
6. E. E. van Tamelen and S. P. Pappas, J. Amer. Chem. Soc., **84**, 3789 (1962)
7. K. E. Wilzbach and L. Kaplan, J. Amer. Chem. Soc., **87**, 4004 (1965)
   88, 1031 (1967)
8. E. M. Arnett and J, M. Bollinger, Tetrahedron Letters, **41**, 3803 (1964)
9. C. A., **55**, P8838 (1961)
10. C. A., **45**, P2503 (1951)
11. K. E. Wilzbach and L. Kaplan, J. Amer. Chem. Soc., **86**, 2307 (1964)
12. W. D. Crow and R. K. Solly, Aust. J. Chem., **19**, 2119 (1966)
13. A. F. Trotman-Dickenson and E. W. R. Steacie, J. Chem. Phys., **19**, 329 (1951)