Predominant *ortho*- Substitution in the Gas-phase Attack of the t-Butyl Cation on *m*-Xylene

By Pierluigi Giacomello* and Fulvio Cacace
(*University of Rome,* 00100 *Rome, Italy*)

Summary The gas-phase attack of radiolytically formed t-butyl cation on *m*-xylene yields over 65% of the 1,3-dimethyl-4-t-butyl isomer under conditions favouring kinetic control of products, while a significant proportion of 1,3-dimethyl-5-t-butylbenzene is formed as the pressure is lowered from 760 to 20 Torr.

A study of the gas-phase attack of radiolytically formed t-butyl ion on toluene[1] has recently demonstrated the high substrate and positional selectivity of the gaseous electrophile [$k(\text{PhMe}):k(C_6H_6) > 55$; *para*:1/2 *meta* = 35:1]. Significantly, no *ortho* t-butylation was observed in toluene, even under conditions, *i.e.* high pressure gas and appreciable concentration of a gaseous base, which tend to minimize the isomerization of the arenium ions formed in the primary step.

Extension of the investigation to polymethylbenzenes has now shown that gas-phase t-butylation with the unsolvated Bu^{t+} cation can indeed occur at the ring positions *ortho* to a methyl group, provided they are sufficiently activated, a result which finds no parallel in the Friedel–Crafts t-butylation of the same substrate carried out in the liquid phase.[2]

The reaction was investigated by a technique described in detail elsewhere,[1,3] by irradiating (^{60}Co source; 37·5 °C) homogeneous gaseous systems containing neopentane as the bulk constituent at pressures ranging from 20 to 760 Torr, in the presence of 0·1—1·0 mol % of the gaseous substrate, a radical scavenger (O_2), and a gaseous base (EtOH or NH_3).

The t-butyl cation, formed with an ion-pair yield[4] of over 0·75 *via* process (1), and thermalised by a large number of

$$\text{neopentane} \rightsquigarrow \text{Bu}^{t+} + \text{Me} + \text{e} \tag{1}$$

unreactive[5,6] collisions with neopentane molecules, attacks the arene, forming gaseous arenium ions that eventually loose a proton to the base, giving t-butylxylenes as the final product.

The yields of the isomers formed, measured by g.l.c. with a flame ionization detector, and determined on at least two columns using individual calibration factors for each product, are given in the Table. In addition, competition experiments have been carried out, using toluene–*m*-xylene mixtures with molar ratios from 0·1 to 9·8, leading to a *k*(*m*-xylene) : *k*(toluene) ratio from 0·7 ± 0·1 in the presence of EtOH to 1·8 ± 0·2 in the presence of NH_3.

Table. Isomeric composition of products from the gas-phase attack of Bu^{t+} on *m*-xylene.[a]

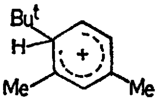
System composition Pressure/Torr			Relative yields[c] (%)	
Neopentane	*m*-Xylene	O_2	(III)	(IV)
733[b]	0·90	7	65	35
725	1·25	1	65	35
500	0·39	3	56	44
400	0·69	2	50	50
300	0·64	2	40	60
200	0·71	2	28	72
100	0·64	2	9	91
40	0·55	5	8	92
20	0·63	1	8	92

[a] Radiation dose from 5·8 to 11·5 MRad. [b] With 1·10 Torr EtOH. [c] Standard deviations *ca.* 5%.

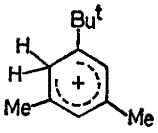
The isomeric composition of products, and its dependence on the pressure, suggest that attack of the gaseous t-butyl cation occurs predominantly at the two ring positions *ortho* to one methyl group of *m*-xylene, leading to the formation of (I) as the major primary intermediate. The change of the isomeric composition of products with pressure can be rationalized assuming either reversible de-t-butylation of the *ortho*-substituted intermediate (I), excited by the (limited) exothermicity of the attack,[1] or the isomerization of (I) to a thermodynamically more stable 'symmetrical' ion, *e.g.* (II), *via* intramolecular shift of the t-butyl group.

In any event, the extent of the de-t-butylation and/or intramolecular isomerization depends on the pressure, which affects collisional stabilization of (I), and on the concentration of gaseous base(s), which determines the rate of deprotonation, and therefore the lifetime of the arenium ions.

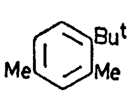
It should be underlined that the products composition measured at the highest neopentane pressure and EtOH concentration can be regarded only as a lower limit of *ortho*-substitution, since secondary isomerization is still likely to occur. Indeed, when a base like NH_3 is present in the gaseous system at concentrations sufficiently large to ensure efficient deprotonation of (I), the product contains larger proportions, up to 89%, of the 1,3-dimethyl-4-t-butyl isomer.



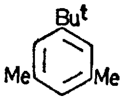
(I)



(II)



(III)



(IV)

The present results indicate that, while activation by one methyl group, as in the case of toluene, is insufficient to overcome the steric factors hindering *ortho* t-butylation, the combined effects of two methyl groups can sufficiently activate an *ortho* position to make its t-butylation significant.

Furthermore, the results obtained in the gas phase, where the interplay of steric and electronic factors regulating orientation can be studied in the absence of the complicating effects of solvent, suggest that the lack of *ortho* orientation in conventional Friedel–Crafts t-butylation of *m*-xylene does not represent an intrinsic feature of the reaction, but is rather to be traced to the influence of a specific liquid environment, and/or to the fast[7] isomerization of the primary substitution products promoted by the catalyst employed.

The authors acknowledge C.N.R. for a research grant.

(*Received*, 6*th February* 1975; *Com.* 134.)

[1] F. Cacace and P. Giacomello, *J. Amer. Chem. Soc.*, 1973, **95**, 5851.
[2] *Cf.* G. A. Olah, S. H. Flood, and M. E. Moffat, *J. Amer. Chem. Soc.*, 1964, **86**, 1060.
[3] P. Ausloos, *Progr. Reaction Kinetics*, 1969, **5**, 113.
[4] P. Ausloos and S. G. Lias, *J. Amer. Chem. Soc.*, 1970, **92**, 5037.
[5] S. G. Lias and P. Ausloos, *J. Chem. Phys.*, 1965, **43**, 2748.
[6] L. W. Sieck, S. K. Searles, and P. Ausloos, *J. Res. Natl. Bur. Std.*, 1971, **A 75**, 147.
[7] G. A. Olah, M. W. Meyer, and N. A. Overchuck, *J. Org. Chem.*, 1964, **29**, 2310.