Oxygenation of Toluene with Dialkyl Peroxydicarbonate–Ferric Chloride

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IN 1964 Razuvaev and his co-workers[1] reported the production of tolyl cyclohexyl carbonates from interaction of toluene and dicyclohexyl peroxydicarbonate in the presence of ferric chloride. They postulated that the ester arises from ferric chloride-induced heterolytic breakdown of the peroxide affording the cyclohexyloxycarboxy-cation as the electrophile. At the same time recognition was given to the presence of products characteristic of radical-type reactions. Because certain aspects of this work were at odds with related results[2] from studies of Friedel–Crafts oxygenation in this laboratory, we felt impelled to subject the area to a more detailed scrutiny.

A re-investigation of the dicyclohexyl peroxydicarbonate decomposition was undertaken under conditions similar to those reported by the Russian workers. The results are tabulated in comparison with the earlier disclosure.

TABLE *Toluene oxygenation with dicyclohexyl peroxydicarbonate and ferric chloride*

	$C_6H_{11}\cdot O\cdot CO_2\cdot C_6H_4\cdot Me$	
Metal halide	Yield, %[a]	*o* : *m* : *p*
$FeCl_3$[b]	23	63 : 4 : 33
$FeCl_3$[c]	40	85 : 0 : 15

[a]Based on one mole of product per mole of peroxide.
[b]Toluene : peroxide : $FeCl_3$ = 16·4 : 1 : 0·13, 60°, 2 hr.
[c]Peroxide : $FeCl_3$ = 1 : 0·13, 40—60°, see ref. 1.

Although our findings are qualitatively similar to those previously reported, there exists an appreciable difference in the isomer distributions. In addition products arising from competing radical processes were present: cyclohexanol, cyclohexanone, benzyl chloride, and carbon dioxide (in agreement with Razuvaev *et al.*), along with smaller amounts of previously unreported substances (dicyclohexyl carbonate, benzaldehyde, and bibenzyl). In a control experiment (peroxide alone in toluene at 60°), decomposition resulted in $<1\%$ of nuclear oxygenation.

Studies were also made with the more readily available di-isopropyl peroxydicarbonate under conditions simulating those of the Russian investigators. With this peroxide and ferric chloride in ratios of 1 : 0·1—0·5 in toluene (heterogeneous) at 60°, we obtained tolyl isopropyl carbonates ($o:m:p.$ = 64 : 4 : 32) in 29—35% yield. Products typical of the routes involving radicals were also formed. Modifying to a homogeneous system by incorporation of acetonitrile with the ferric chloride did not appreciably alter the results, although a higher metal halide : peroxide ratio was necessary in order to procure comparable yields. In the absence of metal halide, less than 1% of aromatic ester ($o:m:p$ = 51 : 13 : 36) was formed. It is quite significant that when the peroxide–ferric chloride–toluene combination was studied at somewhat lower temperatures, *e.g.*, 22—24°, conditions making for very slow homolysis of the oxygen–oxygen bond, unchanged peroxide was recovered in 99% yield after six hours. One would not expect Friedel–Crafts catalysis, as suggested by the previous investigators,[2] to display a high degree of sensitivity to relatively small variations in temperature. It should be pointed out that the present isomer distribution is markedly different from that ($o:m:p$ = 34 : 11 : 55) reported for the product from toluene–di-isopropyl peroxydicarbonate–aluminium chloride.[2]

Such a drastic temperature effect for aromatic oxygenation is more consonant with the participation of alkoxycarboxy-radicals initially formed from homolysis of the peroxide. Subsequent oxidative conversion into product occurs through the agency of ferric salt (*cf.* ref. 4) followed by an induced decomposition.

As expected the breakdown of both dialkyl peroxydicarbonates in the presence of ferric chloride was faster than the uncatalyzed reaction. Ferric ion regenerated in the induced decomposition can function as the oxidant, thus setting up a chain process. The oxidation aspect can be portrayed in two ways. One possibility would be direct conversion of the oxy-radical into an oxonium-type ion which then effects electrophilic substitution.

Alternatively, the transformation may entail aromatic complex formation involving the oxy-radical with subsequent oxidation by ferric chloride. Oxidation of carbon radicals by cupric salts as part of a chain process is a well established transformation.[3] We deem it advisable to defer a more detailed treatment of the theoretical aspects until a broader base of experimental data is available.

The analogous cupric chloride system is treated elsewhere.[4]

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