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AUTOXIDATION REACTIONS OF DIARYLENMETHANES AND RELATED COMPOUNDS IN THE PRESENCE OF PHASE-TRANSFER CATALYSTS

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Investigations employing phase-transfer catalysts have resulted in a new method for oxidation of aromatic substrates containing active methylenic groups and of partially hydrogenated aromatic and heterocyclic systems.
The reaction, which is carried out in the presence of catalytic amounts of quaternary ammonium compounds in a benzene-concentrated aqueous alkali double phase, with oxygen or air as oxidant, at atmospheric pressure and at nearly room temperature or slightly higher, leads to high, and in some cases almost quantitative yields.

Oxidations of this kind are already known, but they require either extremely severe conditions in aqueous alkaline medium (1), or strong basic systems in anhydrous, exotic and expensive solvents, e.g. aprotic dipolar media (2,3).
The new oxidation technique confirms and occasionally improves the reported yields, takes advantage of usual and cheaper catalysts and solvents and needs very mild operative conditions.

The effect of the kind of catalyst can be illustrated by the following scale of activity :

$$Et_4N^+OH^- \approx BzMe_3N^+OH^- > (C_{16}H_{33})_2Et_2N^+Cl^- \gg BzEt_3N^+Cl^- \gg Et_4N^+Cl^- > Et_4N^+Br^-$$

The autoxidation reaction can therefore be related to the phase-transfer reactions well known in the literature (4): an interface reaction probably occurs, in accordance with the mechanism proposed by Makosza (5). When an oxidative dehydrogenation occurs the anomalous oxygen consumption can be explicated by H_2O_2 formation, in agreement with the mechanism already reported by Russell(3) relative to the dihydroanthracene oxidation in aprotic dipolar solvents.

Some significative results are reported in the following table.

Substrate	Time	Temp.	Reacted O_2 (moles/mole substrate)	Products (molar conversion %)
fluorene	24'	30°C	0.91	fluorenone (100)
xanthene	120'	30°C	0.54	xanthone (63)
xanthene	120'	50°C	0.76	xanthone (84)
thioxanthene	40'	50°C	0.98	thioxanthone (99)
acridane	60'	50°C	0.63	acridine (97)
9,10-dihydro-anthracene	160'	50°C	1.90	anthraquinone (75) + anthracene (9)
1,4,4a,9a-tetrahydroanthraquinone	45'	50°C	1.80	anthraquinone (100)
1,4,4a,5,8,8a,9a,10a-octahydro-anthraquinone	45'	50°C	3.58	anthraquinone (100)

Conditions: 50% aqueous sodium hydroxide 1.7 moles/mole substrate
dicetyldiethylammonium chloride 0.03 moles/mole substrate
oxygen partial pressure 1 atm.

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