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PURPLE BENZENE: PERMANGANATE OXIDATIONS USING QUATERNARY AMMONIUM IONS

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Anionic reagents in organic reactions can be greatly activated by modification of the counter ion. Crown ethers[1] and cryptates[2] are novel catalysts which function by solubilizing alkali metal salts in organic solvents: a striking example is "purple benzene" in which crown ethers can dissolve up to 0.06 M potassium permanganate in benzene.[3] We wish to report that "purple benzene" can be more readily obtained using quaternary ammonium ions with potassium permanganate, and that such solutions are very convenient for effecting oxidations.

When equal volumes of benzene and 0.02 M aqueous potassium permanganate were shaken in a separatory funnel, the benzene layer remained completely colorless. Addition of tetrabutylammonium bromide immediately brought color to the organic phase. As the data in Table I indicate, the extraction is quantitative at low concentrations of ammonium ion; with an excess of the quaternary ammonium ion, the permanganate is almost completely transported into the organic phase. Similar effects with other ammonium ions are indicated in Table II.

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TABLE I Extraction of MnO_4^- by NBu_4Br

mmoles MnO_4	mmoles NBu_4Br	mmoles of MnO_4 in benzene
1.000	0.298	0.30
1.000	0.796	0.71
1.000	1.54	0.95
1.000	3.12	0.97

TABLE II Extraction of 1.000 mmoles of MnO_4^- by Quaternary Salts

Salt	mmoles salt	mmoles in benzene
Me_4NCl	1.51	0.00
TEBACl[a]	1.63	0.84
Bu_4NBr	1.54	0.95
Bu_4PCl	1.54	0.96
CTA Br[b]	1.53	0.86
Aliquot 336[c]	1.52	0.93
SDS[d]	1.50	0.00

a. triethylbenzylammonium chloride
b. cetyltrimethylammonium bromide
c. General Foods -- trioctylmethylammonium chloride
d. sodium dodecyl sulfate

The benzene solutions can be separated and used for oxidations under anhydrous conditions. These solutions are rather stable; the permanganate titer had decreased only 17% after 45 hours. More conveniently, the two phase system can be used directly, requiring only a catalytic amount of ammonium ion to maintain a concentration of permanganate in the organic phase. Yields, ranging from fair to excellent and given in Table III, are comparable to those obtained with the crown ether procedures, but the procedure obviates need of a ball mill or expensive reagents.

TABLE III Oxidations with $KMnO_4$ using tricaprylmethyl ammonium chloride

Starting Material	Product	% Yield (isolated)
phenylacetonitrile	benzoic acid	86
benzyl alcohol	benzoic acid	92
trans-stilbene	benzoic acid	95
1 - octanol	octanoic acid	47
1 - octene	heptanoic acid	81

In a typical procedure, 4.8g of potassium permanganate and 50 ml of water were stirred vigorously for 10 minutes and then cooled in a water bath while 30 ml of benzene, 0.5g of tetrabutylammonium bromide, and 2g of stilbene were added. The mixture was stirred 3 hours at ambient temperature and worked up by addition of sodium bisulfite, acidification, separation and drying of the organic layer, and removal of the benzene on a rotary evaporator.

The convenience of the phase transfer procedure suggests that this should be the method of choice for permanganate oxidations.[4,5] The relative efficiencies of quaternary ammonium ions for extraction of permanganate may prove to be general for phase transfer catalysts; for example, we have noted a close parallel in their ability to catalyze reactions involving alkoxide and thiophenoxide ions.[6] The list of catalysts will be expanded in a future publication along with solvent and inert salt effects.

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