Tetrahedron Letters No. 48, pp 4167 - 4170, 1977. Pergamon Press. Printed in Great Britain.

ORANGE BENZENE. NEUTRAL DICHROMATE OXIDATIONS IN ORGANIC SOLVENTS

Robert O. Hutchins*, Nicholas R. Natale, William J. Cook
Department of Chemistry, Drexel University, Philadelphia, Pa. 19104

Jack Ohr
Aero Materials Laboratory, Naval Research Center, Warminster, Pa.

(Received in USA 15 June 1977; received in UK for publication 11 October 1977)

The use of phase transfer reagents to facilitate the solution of monovalent inorganic ions in organic solvents of low solvating ability has recently accorded increasing attention primarily because the resulting "naked" anions often provide enhanced, superior or divergent reactivity relative to that under traditional conditions[1,2]. Conspicuously absent, however, are examples of successful solubilization and utilization of dianions[2c]. Presumably, this absence reflects the difficulty in overcoming the strong crystal coulombic attractions, the strong solvating power of water and/or a geometrical problem of clustering two bulky crown ether molecules of tetraalkylammonium ions in close proximity of dianions. Indeed, an encompassing search for a suitable phase-transfer reagent for dichromate anion ($Cr_2O_7^=$) revealed that this ubiquitous species strongly resisted solubilization in typical organic solvents using a wide variety of available crown ethers (i.e., 18-crown-6, 15-crown-5)[2], tetraalkylammonium[1] and tetraalkylphosphonium[1] salts. In fact, the only successful reagent was found to be Adogen 464[3], a liquid, commercial mixture of methyl trialkyl (C_8-C_{10}) ammonium chlorides. Although the rationale for this uniqueness is not obvious, as illustrated in the Figure and Table 1, fascile solubilization of potassium dichromate was effected in several solvents including: CH_2Cl_2, $CHCl_3$, CCl_4, and benzene (and benzene-hexane mixture) using a 2:1 ratio of adogen 464 to dichromate; of the solvents tried, only hexane remained unreceptive. Solid potassium dichromate can be dissolved directly in solvents without prior solution in water simply by vigorously stirring the crushed salt in the appropriate solvent containing two equivalents of adogen 464. The resulting orange solutions are fairly stable at ambient temperature, but slowly darken after several days.

Figure 1. Extraction of Dichromate Anion with Benzene and Adogen 464.

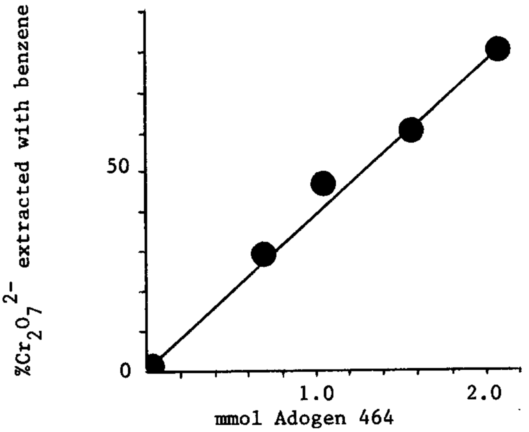

Table 1. Extraction of Dichromate Anion with Various Solvents.[a]

Solvent	Equivalent Adogen 464[2] / Equivalent Dichromate	%$Cr_2O_7^{2-}$ in organic solvent
Benzene	2.01	92
Methylene chloride	2.02	88
Chloroform	2.02	85
Carbon Tetrachloride	2.04	98
Hexane	1.72	0[b]

a. Extracted from an aqueous solution of dichromate. b. Adogen 464 is insoluble in hexane.

Preliminary investigation of the oxidative utility of dichromate in benzene without added acid reveals the reagent to be very mild, effective and discriminate in the oxidation of conjugated alcohols to the corresponding aldehyde or ketone at 55°. As indicated in Table 2, aliphatic alcohols are oxidized sluggishly under the same conditions. Thus, the system should be useful for neutral oxidations of activated alcohols especially where acid or base would be detrimental.

In a typical procedure, the alcohol (5 mmole) and an internal standard was added to a slurry of potassium dichromate (1.5 g, ca. 5 mmole) and Adogen 464 (2.5 g, ca. 5 mmole) in 25 ml of benzene. The reaction mixture was stirred under nitrogen at 55° for the prescribed time (Table 2). The benzene was then removed on a rotary evaporator and the residue flash disstilled at reduced pressure in a Kugelrohr apparatus. The mixture was then analyzed by gas chromatography (Carbowax column), and the spectra (ir and nmr) of products were compared to those of authentic materials.

We are continuing to explore the scope and chemoselectivity of this unique reagent system.[5]

Table 2. Oxidation of Alcohols with Potassium Dichromate in Benzene at 55°C.

Entry	Alcohol	Product	Time(hours)	Yield[a]
1.	Benzyl alcohol	Benzaldehyde	15	82
2.	1-Phenyl-ethanol	Acetophenone	15	80
3.	Cinnamyl alcohol	Cinnamaldehyde	18	91
4.	Decanol	Decanal	17	6
5.	2-Octanol	2-Octanone	24	33
6.	Cyclododecanol	Cyclododecanone	24	45

A. Yields determined by glpc using internal standards and are corrected for detector response.

References

1. For general reviews of phase transfer reagents see, a) E. V. Dehmlov, Angew. Chem. Int. Ed. Engl., 13, 170 (1974); b) J. Dockx, Synthesis, 441 (1973); c) R. A. Jones, Aldrichimica Acta, 9, 35 (1976).

2. For a review of the utility of crown ethers as phase transfer agents see, a) G. W. Gokel and H. D. Durst, Synthesis, 168 (1976); b) D. J. Cram and J. M. Cram, Science, 183, 803 (1974); c) Solubilization of alkaline earth dications has been accomplished using the related cryptand ligands; see for example V. M. Loyola, R. G. Wilkains and R. Pizer, J. Amer. Chem. Soc., 97, 7382 (1975) and cited references.

3. Adogen 464 is a product of Ashland Chemical Company.

4. Examples of other oxidations utilizing phase-transfer reagents include; a) "purple benzene," (potassium permanganate) D. J. Sam and H. E. Simmons, J. Amer. Chem. Soc., 94, 4024 (1972); A. W. Herriott and D. Picker, Tetrahedron Lett., 1511 (1974); b) hypochlorite, G. A. Lee and H. H. Freedman, Tetrahedron Lett. 1641 (1976); c) perchlorates A. K. Qureshi, and

B. Sklarz, J. Chem. Soc., C, 412 (1966), d) RuO4, T. A. Foglia, F. A. Barn and A. J. Malloy, private communication.

5. Several other solvents are also useful for solubilizing dichromate: diethyl ether, ethyl acetate and toluene all successfully formed orange solutions. For certain applications such media may be preferable to benzene and chlorinated hydrocarbons. In addition, observations indicate that several other di- and polyanions can also be brought into solution using Adogen 464; thus CrO_4^{2-} and $Ce(NO_3)_6^{2-}$ form yellow and orange benzene solutions, respectively, and potassium nitrodisulfonate dimer can be solubilized without dissociation in the absence of moisture and air, leading to yellow-orange solutions of $[ON(SO_3)_2]_2^{4-}$. In contrast, the purple monomer, $ON(SO_3)_2^{2-}$ can be extracted from aqueous media to form a new "purple benzene." The utility of these intriguing new reagent systems is currently being evaluated.