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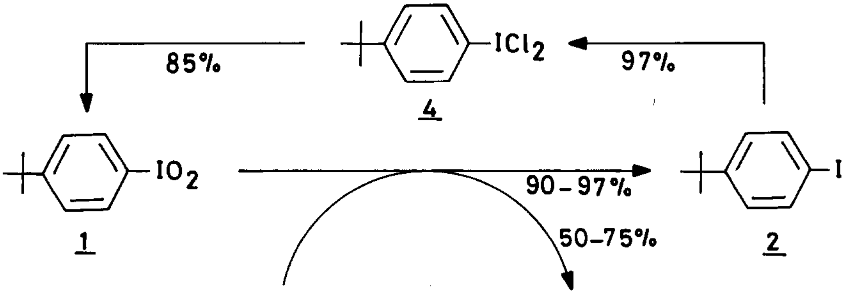
4-^{t}BUTYL IODOXYBENZENE : AN EFFECTIVE OZONE EQUIVALENT

S. Ranganathan*, D. Ranganathan and S.K. Singh

Department of Chemistry, Indian Institute of Technology
Kanpur 208016, India

Summary: The specifically designed reagent, 4-^{t}Butyl iodoxybenzene (1)-soluble in hot, benzene, chlorobenzene and nitrobenzene- cleaves a range of π bonds to carbonyl compounds in 50-75% isolated yields. In every case, the reagent 1 is transformed to 4-^{t}butyl iodobenzene (2) in 90-97% yields, which can be recycled.

Our extended search for an effective ozone equivalent led to the identification of iodoxybenzene (3) as a reagent of promise[1]. A severe limitation of 3 was its insolubility in most non-polar solvents. This problem has now been overcome with the novel reagent, 4-^{t}butyl iodoxybenzene (1), whose preparation and reaction profile are summarized below:



olefins	2 x carbonyl
acetylene	1,2-dicarbonyl
phenanthrene	phenanthraquinone
anthracene	anthraquinone
tetralin	α-tetralone

4-^{t}Butyl iodoxybenzene (1)[2] is a stable and crystalline compound mp 217-221 °C (CAUTION[3]). The estimated[4] solubility of 1 in hot, benzene, chlorobenzene and nitrobenzene are, respectively, 0.2%, 6% and 9%. Oxygen transfer to the substrates are accomplished in hot chlorobenzene or nitrobenzene[5]. TABLE I summarizes the results of the reaction 1 with a representative selection of acceptors. The transformations brought about with 1 and a range of substrates are clean[6], the products directly isolable and the resulting 2 effectively recycled. Therefore 4-^{t}butyl iodoxybenzene should turn out to be a reagent of promise and utility not only with reference to the oxidation of hydrocarbons but others as well.

TABLE I

substrate (mmol)	$4\text{-}{}^{t}BuC_6H_4IO_2$ mmol	solvent (ml)	time hr	product (% yield)[7]	$4\text{-}{}^{t}BuC_6H_4I$ % yield[7]
bis-cyclohexylidene[8] (2)	2.5	PhCl (10)	2	cyclohexanone (59)	91
E-stilbene (1)	2.0	PhCl (8)	6	benzaldehyde (67) + benzil (20)	94
9-benzylidene fluorene (0.5)	0.5	PhCl (8)	7	fluorenone (50) + benzaldehyde (45)	92
diphenylacetylene (2)	2.0	PhCl (8)	18	benzil (65)	91
diphenylacetylene (1)	1.5	$PhNO_2$ (2)	10	benzil (57)	-
phenanthrene (1)	2.0	PhCl (5)	10	phenanthra quinone (75)	97
anthracene (0.5)	1.0	$PhNO_2$ (4)	7	anthraquinone (59)	-
tetralin (6)	1.5	PhCl (10)	6	α-tetralone (60)[9]	97

REFERENCES AND NOTES

1. S. Ranganathan, D. Ranganathan and P V Ramachandran, Tetrahedron, 40, 3145 (1984).
2. $4\text{-}{}^{t}$Butyl iodoxybenzene (1): Compounds 1, 2, and 4 are novel. $4\text{-}{}^{t}$Butyl Iodobenzene (2): $4\text{-}{}^{t}BuPh$ (59 mmol)+I_2 (25 mmol) + HIO_3 (111 mmol) +AcOH (18 ml) + H_2O (3 ml) reflux 8 hr; decant, decanted portion admix with, H_2O (30 ml) + MeOH-KOH (20%, 30 ml); reflux 0.5 hr, cool; wash lower 2 with H_2O (x 3), dry ($MgSO_4$) and distil; yield 11 g (71%), bp 114°/ 0.05 torr; nmr :δ: CCl_4 : 1.3 (9H), 7.03 (d, J=8 Hz, 2H), 7.5 (d, J=8 Hz, 2H). $4\text{-}{}^{t}$Butyl iodobenzenedichloride (4): Pass dry Cl_2 through ice-salt cooled, stirred 2 (10 mmol) in dry hexane (15 ml) till excess; collect precipitated yellow 4, wash with chilled hexane, dry; yield 3.2 g (97%), mp 84°C; stable: cool and dry; soluble: $CHCl_3$, PhH. nmr:δ: $CDCl_3$: 1.36 (9H), 7.4 (d, J=8Hz, 2H), 8.06 (d, J=8Hz, 2H). $4\text{-}{}^{t}$Butyl iodoxybenzene (1): (the following procedure gives best results): A floating yellow suspension of 4 (30 mmol) on Aq NaOCl (75 ml; from 75 ml 5N NaOH+ 12 g Cl_2) + AcOH (0.2 ml) keep with intermittant shaking at rt 1.5 hr; heavy yellow precipitate formed (?); then keep mixture 60-70°C, with intermittant shaking 0.5 hr; yellow precipitate transformed to light, white, frothy 1; cool, filter, wash H_2O (x 5), air dry, wash $CHCl_3$ (x3), dry; yield 7.5 g (86%), mp 217-221°C (EXPLODES); calcd for $C_{10}H_{13}IO_2$: C, 41.09, H, 4.45; found: C, 40.8, H, 4.31%.
3. During numerous oxidations with 1 no exploision has occurred. However, we urge that caution be exercised and no reaction be done without solvent.
4. Very rough estimates since 1 decomposes slowly in hot solvents leading to 2.
5. All reactions at 130-140°C (TABLE I). Work-up: PhCl evaporated in vacuo; chromatograph silica gel column made in hexane; 2 eluted with hexane, products with PhH: hexane.
6. Product yields are not optimized; this would require a study of the extent of decomposition of 1 to 2 and consequent adjustment of the reagent needed.
7. All yields are of isolated pure compounds.
8. Very conveniently made by the procedure of, D.H.R. Barton and B.J.Willis, J. Chem. Soc., Perkin, I, 309 (1972).
9. Yield based on reagent.

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