

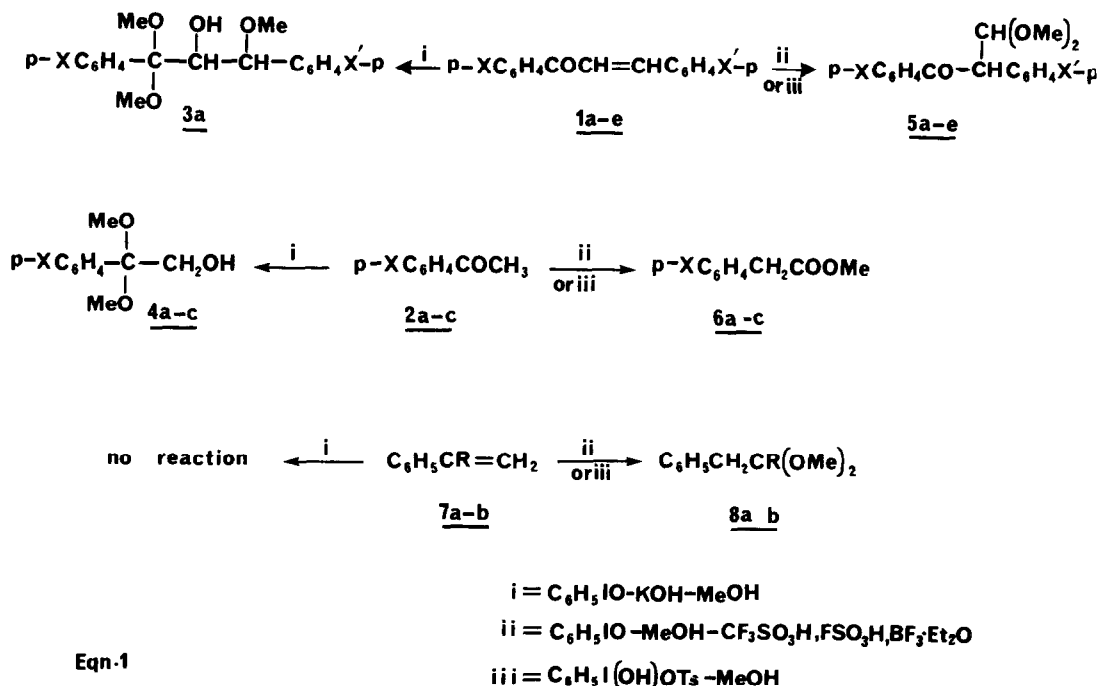
SOLVOHYPERIODINATION. A COMPARISON WITH SOLVOTHALLATION

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Summary. C_6H_5IO/CH_3OH and a catalyst such as FSO_3H , CF_3SO_3H or $BF_3 \cdot Et_2O$ as well as $C_6H_5(OH)OTs \cdot CH_3OH$, react with chalcones, acetophenones and styrenes to yield rearranged products. The overall course of these reactions is analogous to that of $Tl(NO_3)_3 \cdot CH_3OH$ in reaction with the same compounds.

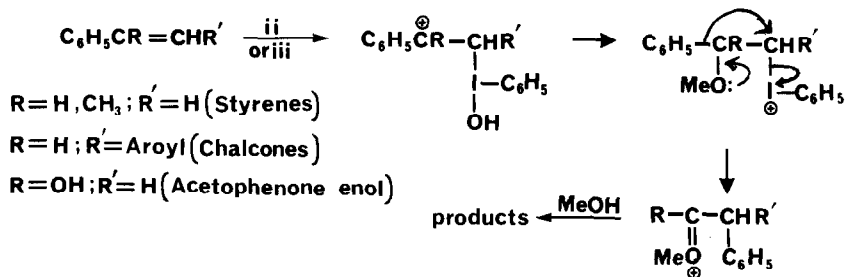
Oxythallation and solvothallation are now a well established part of synthetic methodology.¹ We now report that analogous rearranged products are formed in the system $C_6H_5IO \cdot CH_3OH$ -proton acid or Lewis acid relative to $Tl(NO_3)_3 \cdot CH_3OH$ in reaction with chalcones (1a-e), acetophenones (2a-c) and styrenes (7a-b). A further point is that within the context of hypervalent iodine chemistry, two distinct reaction pathways may be followed depending upon whether $C_6H_5IO \cdot CH_3OH \cdot KOH$ (conditions i)² or electrophilic conditions, viz. $C_6H_5IO \cdot CH_3OH$ -acid or $C_6H_5I(OH)OTs \cdot CH_3OH$ (conditions ii and iii, respectively) are used (Eqn 1):



Eqn-1

Non-rearrangement observed under conditions i has been verified by many examples.^{2,3} The rearrangement pathway, ii or iii, in the cases studied (Table 1), yields the same products as solvohallation.¹ Hence we propose the term solvohyperiodination, and, in fact, these reactions present a useful complement to organothallium methods.¹

We propose the following mechanism for solvohyperiodination:



At present it is not known whether cation radicals may intervene at any stage in the above pathway.⁴ The electrophile $\text{C}_6\text{H}_5\overset{\oplus}{\text{I}}\text{OH}$ is either formed by protonation of $\text{C}_6\text{H}_5\text{IO}$, or in the case $\text{C}_6\text{H}_5\text{I}(\text{OH})\text{OTs}$, $\text{C}_6\text{H}_5\overset{\oplus}{\text{I}}\text{OH}$ is present due to simple dissociation.⁵ In fact, Koser and Rebrovic have shown that in the system $\text{C}_6\text{H}_5\text{I}(\text{OH})\text{OTs}$ oxidation of styrene leads to rearrangement to 1,1 bis(tosyloxy)-2 phenylethane probably via the above pathway with tosylate anion serving as the nucleophile in both coordination steps.⁶

Finally, the above mechanistic pathway is analogous to that proposed for the reaction of these compounds with $\text{Tl}(\text{NO}_3)_3$.¹ The reaction under basic conditions, i, involves as a key step attack of the enolate anion² upon $\text{C}_6\text{H}_5\text{I}(\text{OCH}_3)_2$ found in situ.⁷ Styrenes obviously are incapable of this type reaction and hence are unreactive (Eqn.1).

Additional analogies between $\text{Tl}(\text{NO}_3)_3\text{-CH}_3\text{OH}$ and $\text{C}_6\text{H}_5\text{IO}$ under acid conditions have been observed by others for arylethyl ketones⁸ and diarylacetylenes.⁹

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References

1. A. McKillop and E. C. Taylor "Comprehensive Organometallic Chemistry," Wilkinson, G., Abel, E. W., Stone, F. G. A., Eds.; Pergamon Press 1983; Vol. 7, p. 465; A. McKillop, B. P. Swann, and E. C. Taylor, J. Am. Chem. Soc. 1971, 93, 4919; A. McKillop, B. P. Swann

- and E. C. Taylor, J. Am. Chem. Soc. 1973, 95, 3340; E. C. Taylor, C.-S. Chiang, A. McKillop, and J. F. White, J. Am. Chem. Soc. 1976, 98, 6750; E. C. Taylor, R. L. Robey, K. T. Liu, B. Favre, H. T. Bozimo, R. A. Conley, C.-S. Chiang, A. McKillop and M. E. Ford, J. Am. Chem. Soc., 1976, 98, 3037; J. A. Walker and M. D. Pillia, Tetrahedron Lett. 1977, 3707; W. D. Ollis, K. L. Ormand and I. O. Sutherland J. Chem. Soc. (c) 1970, 119; W. D. Ollis, K. L. Ormand, B. T. Redman, R. J. Roberts, and I. O. Sutherland, J. Chem. Soc. (c) 1970, 125; L. Farkas, A. Gottsegen, M. Nogradi and S. Antus, J. Chem. Soc. Perkin I, 1974, 305.
2. R. M. Moriarty, H. Hu, and S. C. Gupta, Tetrahedron Lett., 1981, 22, 1283; R. M. Moriarty, L. S. John, and P. C. Du, J. Chem. Soc. Chem. Commun., 1981, 641; R. M. Moriarty, S. C. Gupta, H. Hu, D. R. Berenschot, and K. B. White J. Am. Chem. Soc., 1981, 103, 686; R. M. Moriarty and H. Hu, Tetrahedron Lett. 1981, 22, 2747; R. M. Moriarty, O. Prakash and W. A. Freeman, J. Chem. Soc. Chem. Commun., 1984, 927.
 3. Ring-contraction has been observed in the $C_6H_5IO-CH_3OH-KOH$ oxidation of 3-cholestanone (R.M. Moriarty and I. Prakash, Tetrahedron Lett., 1984, 25, 5867) and 17 β -hydroxy-5- α -androstane-3-one (S.J. Daum, Tetrahedron Lett., 1984, 25, 4725).
 4. A. J. Bard, A. Ledwith and H. J. Shine, Adv. Phys. Org. Chem., 1976, 13, 155.
 5. G.F. Koser, R.H. Wettach, J.M. Troup and B.A. Frenze, J. Org. Chem., (1976) 41, 3609.
 6. L. Rebrovic and G. F. Koser, J. Org. Chem., 1984, 49, 2462.
 7. B. C. Schardt and C. L. Hill, Inorg. Chem., 1983, 22, 1563.
 8. Y. Tamura, Y. Shirouchi, and J.-I. Haruta, Synthesis, 1984, 231.
 9. E. B. Merkushev, L. G. Karpitskaya, and G. I. Novosel'tseva, Dokl. Akad. Nauk SSSR, 1979, 245, 607.
 10. E. C. Taylor, R. A. Conley, D. K. Johnson, A. McKillop and M. E. Ford, J. Org. Chem., 1980, 45, 3433.
 11. S. R. Johns, and J. A. Lamberto, Aust. J. Chem., 1969, 22, 1315.
 12. K. Kinder, Ber., 1941, 74, 315.
 13. Y. Yamashita and T. Shimamura, Kogakuin Daigaku Hokoku, 1957, 4, 29; C.A. 1959, 53, 14065f.
 14. L. Nadon, M. Tardot, M. Zador, and S. Fliszar, Can. J. Chem., 1973, 51, 2366.
 15. H. G. Walker and C. R. Hauser, J. Am. Chem. Soc., 1946, 68, 1386.

Table 1. Solvohyperiodination of Chalcones, Acetophenones and Styrenes.

Compounds	Product	Conditions				
$p\text{-X-C}_6\text{H}_4\text{COCH=CHC}_6\text{H}_4\text{-X}'$	$p\text{-X-C}_6\text{H}_4\text{CO-CH-C}_6\text{H}_4\text{-X}'$	$\text{C}_6\text{H}_5\text{IO/CH}_3\text{OH}$	$\text{C}_6\text{H}_5\text{I(OH)OTs/CH}_3\text{OH}$	Yield(%) ^a	mp° (Lit.m.p.)	
	$\text{CH(OCH}_3)_2$	Catalyst	time(hr)	time(hr)		
<u>1a</u> =X=X'=H	<u>5a</u> =X=X'=H	FSO ₃ H	6		85(48)	94(94.5-96.5) ¹⁰
		CF ₃ SO ₃ H	12		85(20)	
		BF ₃ ·Et ₂ O	12		75(25)	
				40	(58)	
<u>1b</u> =X=OCH ₃ , X'=H	<u>5b</u> =X=OCH ₃ , X'=H	FSO ₃ H	1		90(43)	120(120-21) ¹⁰
		CF ₃ SO ₃ H	12		90(59)	
		BF ₃ ·Et ₂ O	12		95(67)	
				36	(65)	
<u>1c</u> =X=X'=OCH ₃	<u>5c</u> =X=X'=OCH ₃	FSO ₃ H	12		90(42)	73(74-75) ¹⁰
		CF ₃ SO ₃ H	12		90(42)	
<u>1d</u> =X=H, X'=OCH ₃	<u>5d</u> =X=H, X'=OCH ₃	FSO ₃ H	12		60(18)	84(83.5-84) ¹⁰
		CF ₃ SO ₃ H	12		60(18)	
		BF ₃ ·Et ₂ O	12		92(49)	
				48	(55)	
<u>1e</u> =X=H, X'=Cl	<u>5e</u> =X=H, X'=Cl	FSO ₃ H	12		90(64)	93(93-93.5) ¹⁰
<u>Acetophenones</u>						
$p\text{-X-C}_6\text{H}_4\text{COCH}_3$	$p\text{-X-C}_6\text{H}_4\text{CH}_2\text{CO}_2\text{CH}_3$					
<u>2a</u> =X=H	<u>6a</u> =X=H	FSO ₃ H	12		61	77-78(77-78.5) ¹
				36	(52) ^b	
<u>2b</u> =X=OCH ₃	<u>6b</u> =X=OCH ₃	FSO ₃ H	12		71	85-86(86-87) ¹²
					(55) ^b	
<u>2c</u> =X=Cl	<u>6c</u> =X=Cl	FSO ₃ H	12		50	103-105(103-105) ¹³
				36	(50) ^b	
<u>Styrenes</u>						
$\text{C}_6\text{H}_5\text{CH=CH}_2$	$\text{C}_6\text{H}_5\text{CH}_2\text{CH(OCH}_3)_2$	FSO ₃ H	15 min.		80	(b.p. 219-221°/754 mm) ¹⁴
<u>7a</u>	<u>8a</u>		1		(61) ^c	
$\text{C}_6\text{H}_5\text{C(CH}_3)=\text{CH}_2$	$\text{CH}_3(\text{CH}_3\text{O})_2\text{C-CH}_2\text{C}_6\text{H}_5$	FSO ₃ H	15 min.		(81) ^d	(b.p. 97°C/13 mm) ^{14,15}
<u>7b</u>	<u>8b</u>					

(a) The yield in parentheses are based on the isolated crystalline product whereas others are based on NMR.

(b) Product isolated as the free acid after alkaline hydrolysis.

(c) Separated by column chromatography.

(d) Isolated as phenylacetone.

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