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DEHYDRATION AND ALKYLATION REACTIONS BY THE USE OF PERCHLORATE SALTS

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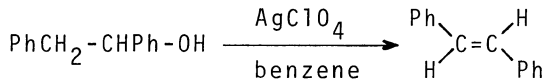
By the treatment of secondary and tertiary benzylic alcohols or tertiary aliphatic alcohols with $AgClO_4$ in benzene at refluxing temperature for 20 to 420 min, olefins were obtained as dehydrated products in good yields. Further, a new procedure for generating tin perchlorate was devised, and the application of this reagent to alkylation reactions of aromatic compounds from alcohols or paraformaldehyde was investigated.

Recently, perchlorate salt catalyzed reactions such as isomerization of epoxy compounds to ketones by lithium salt[1] and rearrangement of compounds with hindered σ-bond by silver salt[2] have been reported. This communication reports silver perchlorate catalyzed dehydration of alcohols to olefins and tin perchlorate catalyzed alkylation of aromatic compounds by use of alcohols and paraformaldehyde as alkylating reagents.

Treatment of 1,2-diphenylethanol with an equimolar amount of anhydrous silver perchlorate in refluxing benzene for 45 min, washing with water and isolation by silica gel chromatography afforded trans-stilbene in 91% yield. Stereoisomeric purity of stilbene was determined by GLPC to be 99%. Bis(1,2-diphenylethyl) ether, produced by an intermolecular dehydration, was obtained in 8% yield as a sole by-product. When a catalytic amount (0.006 equiv) of anhydrous silver perchlorate was used, stilbene and the ether were obtained in 7 and 4% yields, respectively. Thus, the use of more than 1 equiv of the reagent was demanded for quantitative conversion and exclusive olefin formation.



Of various organic solvents examined, benzene proved to be most suitable. Nitrobenzene gave a similar result, but reaction rate was reduced remarkably in toluene. A predominant or competitive ether-formation was observed in dichloromethane and nitromethane.

As is shown in Table 1, various tertiary alcohols and benzylic secondary alcohols were dehydrated to give the corresponding olefins by refluxing in benzene for the period shown in the Table. Exceptionally, 1-phenylethanol gave exclusively the corresponding ether. In the case of 1-methyl-1-cyclohexanol, 1-methylcyclohexene, an endo olefin, was obtained in high yield with isomeric purity of above 99%.

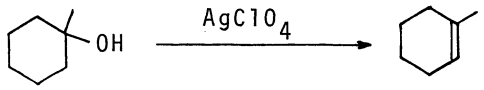
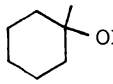


Table 1 Dehydration of Alcohols by the Use of Silver Perchlorate[a]

Alcohol	Refluxing time	Alkene	Yield, %	Ether Yield, %
$PhCH(OH)CH_2Ph$	45 min	$PhCH=CHPh$	91	8
$PhCH(OH)CH_3$	20 min	——		81
$PhCH(OH)C_2H_5$	1 hr	$PhCH=CHCH_3$	16	53
$PhCH(OH)(n\text{-}C_4H_9)$	50 min	$PhCH=CH(n\text{-}C_3H_7)$	45	41
$PhC(OH)(CH_3)_2$	1 hr	$PhC(CH_3)=CH_2$	81	—
$Ph_2C(OH)CH_3$	1 hr	$Ph_2C=CH_2$	95	—
	7 hr	 91	 1	—
$(CH_3CH_2)_3COH$	5 hr	$(CH_3CH_2)_2C=CHCH_3$	100	—
$(CH_3)_2C(OH)(CH_2)_2C(OH)(CH_3)_2$	5 hr	$(CH_3)_2C=CHCH=C(CH_3)_2$	8	63[b]

a. Reactions were carried out by the use of equimolar amount of silver perchlorate in benzene. b. 2,2,4,4-tetramethyltetrahydrofuran

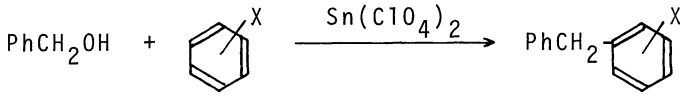
To ascertain the mode of this dehydration, reactions of two diastereoisomeric 1,2-diphenyl-1-propanol were compared. Threo isomer was dehydrated slightly more easily than erythro isomer. Cis-trans ratios of obtained α-methylstilbene from both isomers were almost the same indicating the intermediate formation of carbonium ion[3]. On the other hand, primary and aliphatic secondary alcohols do not participate in the reaction under the above mentioned conditions. From these results, it is reasonable to assume that the reaction would proceed through an intermediate formation of complex of alcohol with silver perchlorate. In refluxing benzene, this complex decomposes to form tertiary or benzylic carbonium ion, which in turn changes into olefin. In the cases of primary and secondary alcohols other that benzyl alcohols, dissociation of the complex to the starting alcohol and silver salt would be predominant to the formation of unstable carbonium ion.

By the next experiments, tin perchlorate, temporarily generated from tin fine powder and silver perchlorate, was found to be more effective for the above reaction. Schmidt reported the preparation of tin (II) perchlorate-acetonitrile complex by electrolysis of silver perchlorate in acetonitrile by using tin electrode[4]. On

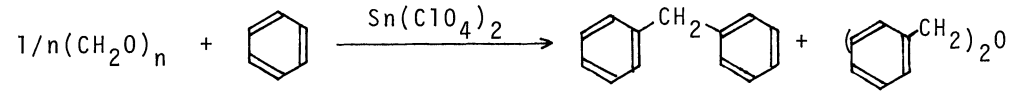
Table 2 Dehydration of threo- and erythro-1,2-Diphenyl-1-propanol by the Use of Silver Perchlorate

Alcohol	Solvent	Condition	α-Methylstilbene		
			Yield %	cis %	trans %
threo	benzene	reflux 3 hr	87	53	47
erythro	benzene	reflux 3 hr	43	55	45

this findings, conversion of silver perchlorate to tin perchlorate by use of tin metal was tried in benzene. When finely powdered tin metal was vigorously stirred in benzene solution of silver perchlorate, surface of tin turned lusterless indicating silver metal formation. This mixture was then heated at refluxing temperature and 1,2-diphenyl-1-propanol was added drop by drop. After usual treatment, α-methylstilbene was obtained in 84% yield. Contrary to the case of silver perchlorate, the reaction was completed even at room temperature within 4 hr to give α-methylstilbene and the ether in 10 and 26% yields, respectively. In addition, unexpected 1,1,2-triphenylpropane, alkylation product of benzene, was obtained in 33% yield. The result suggests that the complex of tin perchlorate and alcohol is effective in the Friedel-Crafts type alkylation of aromatic compounds. Several diphenylmethane derivatives were synthesized by this new procedure by the use of benzyl alcohol. Benzene, toluene and mesitylene reacted at room temperature to afford the corresponding diphenylmethanes in good yields. Anisole also afforded methoxydiphenylmethane, but its yield is reduced probably by competitive donation of anisole to tin ion. A higher temperature was required for less reactive chlorobenzene.

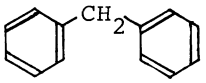
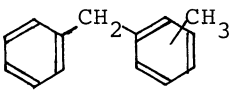
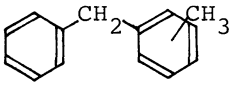
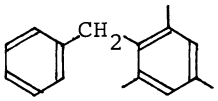
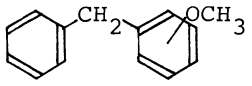
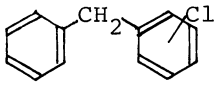
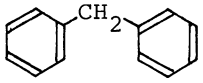
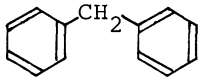


The synthetic utility of tin perchlorate as Lewis acid was further exemplified by the next experiment. Paraformaldehyde was added at room temperature to the tin perchlorate in benzene prepared as described above and the mixture was stirred for 4 hr. After an usula treatment, diphenylmethane and dibenzyl ether were obtained in 33 and 19% yields, respectively.



Further improvement of this reaction and development of the reactions by the use of tin perchlorate as a Lewis acid are now in progress.

Table 3 Preparation of Diarylmethanes by the Use of Tin Perchlorate

Compound	Solvent	Temperature	Time, hr	Diarylmethane	Yield %
$PhCH_2OH$	benzene	room temp.	4		63
	toluene	"	4		57
	"	"	18		84
	mesitylene	"	20		79
	anisole	"	40		46
	chlorobenzene	60°C	3		66
$(CH_2O)_n$	benzene	room temp.	4		33
$(CH_2O)_3$	"	"	4.5		27

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2) M. Sakai, H. Yamaguchi, H. H. Westberg, S. Masamune, ibid., 93, 1043 (1971).
3) Cis/trans ratio is nearly the same with that of α-methylstilbene obtained by the dehydration of 1,2-diphenyl-1-propanol in dimethyl sulfoxide: V. J. Traynelis, W. L. Hergenrother, J. R. Livingston, and J. A. Valicenti, J. Org. Chem., 27, 2377 (1962).
4) H. Schmidt, Z. anorg. allgem. Chem., 271, 305 (1953).

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