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$AgClO_4$-$SnCl_4$ AS AN EFFECTIVE CATALYST IN THE FRIEDEL-CRAFTS ALKYLATION

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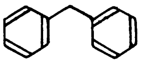
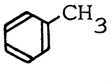
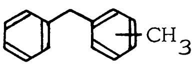
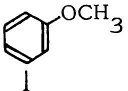
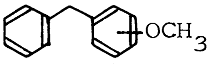
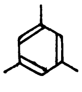
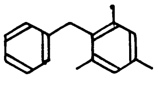
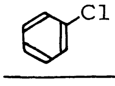
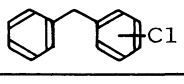
The Friedel-Crafts alkylation of aromatic compounds with benzyl alcohol or trioxane in the presence of $AgClO_4$-$SnCl_4$ was investigated. By this modified procedure various aromatic compounds including chlorobenzene were alkylated at room temperature in high yields. When trioxane was used as alkylating source, diphenylmethane was obtained in excellent yield without accompanying the formation of dibenzyl ether. Based on this finding, it was shown that C-O bond of the benzyl ether was cleaved under the very mild conditions by this couple.

Recently it was reported that the Friedel-Crafts alkylation reactions of aromatic compounds with benzyl alcohol or trioxane proceed successfully in the presence of $AgClO_4$-Sn$^{1)}$. Since no reaction was observed when benzene and benzyl alcohol were allowed to react in the filtered solution, it was shown that the reaction occurred on the surface of the solid mass. Then, a development of a new procedure for the preparation of the accelerator of the alkylation in a homogeneous phase was tried by adopting tin tetrachloride*, soluble in many organic solvents, instead of tin metal. When benzene solution of tin tetrachloride (1.4 mmol) was

Table. Reactions of Benzyl Alcohol with Various Aromatic Compounds in the Presence of $AgClO_4$-$SnCl_4$

Compound (Solvent)	Temperature,	Time, hr	Product	Yield, %	$AgClO_4$-Sn Yield, %
	room temp.	1.5		88	63
	room temp.	1.5		96	74
	room temp.	4.5		97 (*o*-34, *p*-63)	46 (*o*-18, *p*-28)
	room temp.	2.0		96	79
	room temp.	2.5		95	66

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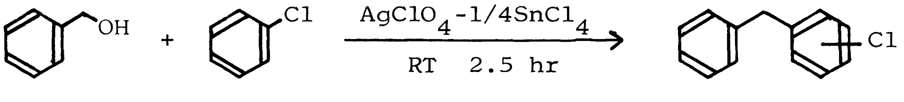
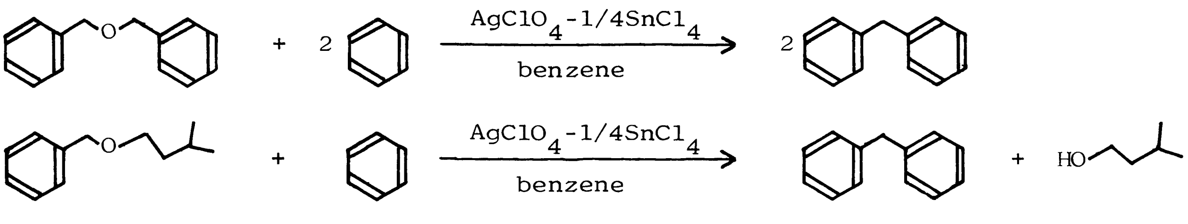
* Tin tetrachloride alone did not give a successful result.

added slowly to the silver perchlorate (5 mmol) in benzene, immediate separation of silver chloride occurred. To this stirred mixture, benzyl alcohol (5 mmol) in benzene was added and stirring was continued for additional 1.5 hr. After washing off of the metallic compounds by water, diphenylmethane was obtained in 88% yield. Anisole, which gave the alkylation product in a low yield by the use of $AgClO_4$-Sn, afforded benzylanisole in 97% yield. In all cases shown in the table yields are very much increased as compared with those obtained by the reaction using $AgClO_4$-Sn. In general, the Friedel-Crafts reaction of chlorobenzene requires an elevated temperature of about 60°[2]. However, by the present procedure chlorobenzene was benzylated with benzyl alcohol and $AgClO_4$-$SnCl_4$ within 2.5 hr at room temperature to give chlorodiphenylmethane in high yield.



On the next stage, reaction of trioxane with benzene was reinvestigated with use of $AgClO_4$-$SnCl_4$. Diphenylmethane was obtained in 76% yield without accompanying the formation of dibenzyl ether in contrast with the result that the ether formation in nearly the same ammount by the $AgClO_4$-Sn reaction. Based on this finding, it was expected that the present $AgClO_4$-$SnCl_4$ method was effective for the cleavage of the C-O bond of the benzyl ether. When dibenzyl ether was treated for 3.5 hr at room temperature with $AgClO_4$-$SnCl_4$, diphenylmethane was obtained in 83% yield, expectedly. In a similar way, reaction of isoamyl benzyl ether was tried and diphenylmethane was obtained in 73% yield. Isoamylbenzene was not isolated and isoamyl alcohol was detected by GLPC analysis.



REFERENCES

1) T. Mukaiyama, M. Kuwahara, T. Izawa, and M. Ueki, Chem. Lett., 287 (1972).
2) C. C. Price, "Organic Reactions", Vol.3, ed. by R. Adams, John Wiley & Sons, Inc., New York, N. Y. (1946), p. 1.

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