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SIDE-CHAIN MONOCHLORINATION OF TOLUENES WITH SULFURYL CHLORIDE CATALYZED BY TETRAKIS(TRIPHENYLPHOSPHINE)PALLADIUM(0)[1]

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In the presence of tetrakis(triphenylphosphine)palladium(0), sulfuryl chloride chlorination of toluenes resulted almost exclusively in monochlorination to afford the corresponding benzyl chlorides in good yields.

Sulfuryl chloride is known to chlorinate side-chains of aralkyl hydrocarbons in the presence of benzoyl peroxide.[2,3] This usual free-radical chlorination, however, is not entirely satisfactory to the preparation of benzyl chlorides, since the reaction is often complicated by consecutive chlorinations, i.e., polychlorinations. Attempts for the monochlorination are generally unsuccessful except for chlorination with low conversion.[2] We report herein that side-chain monochlorination of toluenes proceeded smoothly in the presence of tetrakis(triphenylphosphine)palladium(0) to afford the corresponding benzyl chlorides in good yields.

$$XC_6H_4CH_3 \quad + \quad SO_2Cl_2 \xrightarrow{Pd(PPh_3)_4} XC_6H_4CH_2Cl \quad + \quad HCl \quad + \quad SO_2 \qquad (1)$$

Typically, sulfuryl chloride (9.8g, 73 mmol) in benzene (10 ml) was added dropwise to a stirred mixture of toluene (3.69g, 40 mmol), the palladium(0) catalyst (0.089g, 0.08 mmol) and benzene (10 ml) under reflux for 2 h. GLC analysis showed that the resulting mixture contained benzyl chloride and benzal chloride in a ratio of 98:2 with 82% consumption of toluene.

The results of the chlorination of other substituted toluenes are summarized in Table 1. It is seen from the Table that, in all cases, the corresponding benzyl chlorides were produced almost exclusively in good yields with satisfactory conversions.

For comparison purposes, benzoyl peroxide-catalyzed chlorination of toluene with sulfuryl chloride was carried out in benzene under reflux using a 1:1.5:0.005 mixture of toluene, sulfuryl chloride and the peroxide. It was thus found that the reaction gave a 73:27 mixture of benzyl chloride and benzal chloride.

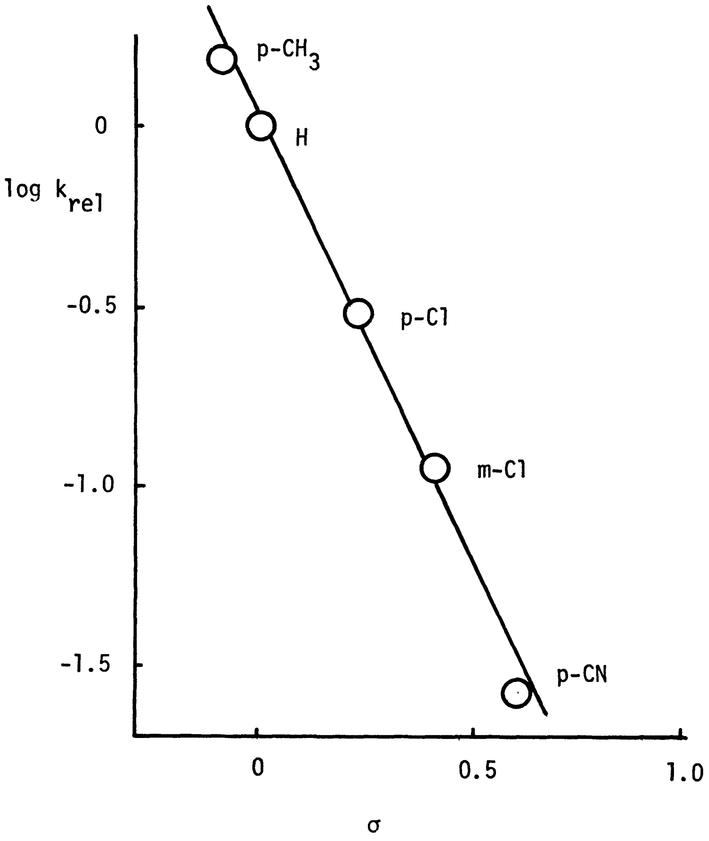
Table 1. Composition of Side-Chain Monochlorinated Product in Sulfuryl Chloride Chlorination of Toluenes in the Presence of Tetrakis(triphenylphosphine)palladium(0)[a]

Toluene	Product[b]	Composition,%[c]	Conversion,%[d]
$C_6H_5CH_3$	$C_6H_5CH_2Cl$	98[e]	82
p-$ClC_6H_4CH_3$	p-$ClC_6H_4CH_2Cl$	100	87
m-$ClC_6H_4CH_3$	m-$ClC_6H_4CH_2Cl$	96[f]	45
p-$CNC_6H_4CH_3$	p-$CNC_6H_4CH_2Cl$	100	50
p-$CH_3C_6H_4CH_3$	p-$CH_3C_6H_4CH_2Cl$	99[g]	85
p-$CH_2ClC_6H_4CH_3$	p-$CH_2ClC_6H_4CH_2Cl$	100	46

[a] Reactions were carried out under reflux for 2-5 h using a 1:2:0.002-1:4:0.002 mixture of a toluene, sulfuryl chloride and the palladium(0) catalyst. [b] Structural assignment for these products was based on a comparison of their NMR and IR spectra and GLC retention times with those of authentic samples after isolation by GLC. [c] Determined by GLC. [d] Conversion is meant by 100 X (moles of the toluene consumed)/(moles of the toluene charged). [e] Benzal chloride was also formed in 2% yield. [f] Ring chlorinated products were also produced in 4% yield. [g] α,α'-Dichloro-p-xylene was also produced in 1% yield.

Experiments to determine relative reactivities of toluenes toward the chlorination were carried out in order to obtain informations as to controlling factors in this particular system. Thus, two toluenes were allowed to react with a deficiency of sulfuryl chloride in benzene at 80°C in the presence of 0.2 mol% of the palladium(0) catalyst. The relative rates were calculated with the equation of Ingold and Shaw[4] from initial and final concentrations of the substrates as determined by GLC. The relative reactivities of toluenes were found to fall in the order p-$CH_3C_6H_4CH_3$ (1.36) $>$ $C_6H_5CH_3$ (1.00) $>$ p-$ClC_6H_4CH_3$ (0.29) $>$ m-$ClC_6H_4CH_3$ (0.15) $>$ p-$CNC_6H_4CH_3$ (0.03). It is immediately observable that introduction of electron-withdrawing group on the aromatic ring substantially decreases the rate of the chlorination. Plot for the relative reactivities versus Hammett σ values for the substituents[5] gave an excellent straight line with a slope of -2.17 and a correlation coefficient of 0.990 (See Figure 1). The ρ value is significantly more negative than that found for usual free-radical chlorination [ρ = -0.75 (80°C in benzene)[6], -0.80 (70°C in benzene)[6] or -0.83 (40°C in benzene)[7]], suggesting that highly electron-seeking species must participate in the present system. The highly electrophilic character observed for the present reaction seems to be responsible for the selective monochlorination.

Figure 1. A Plot of Relative Reactivities versus σ for Toluenes



Other common group VIII metal-phosphine complexes such as dichlorobis(triphenylphosphine)-nickel(II), dichlorobis(triphenylphosphine)palladium(II), dichlorotris(triphenylphosphine)-ruthenium(II) and chlorotris(triphenylphosphine)rhodium(I) also effected the chlorination of toluene with sulfuryl chloride, but the reactions were found to be accompanied by 5-44% of ring chlorination (See Table 2) upon refluxing a benzene solution of the hydrocarbon, sulfuryl chloride and the catalyst (molar ratio 1:2:0.002).

In conclusion, tetrakis(triphenylphosphine)palladium(0)-catalyzed sulfuryl chloride chlorination thus provides a novel and convenient method for selective chlorination of toluenes to benzyl chlorides.

Table 2. Product Distribution in Sulfuryl Chloride Chlorination of Toluene in the Presence of Phosphine-Complexes of Ni(II), Pd(II), Ru(II) and Rh(I)[a]

Catalyst	Product Distribution,%[b]			Conversion,%[c]
	$C_6H_5CH_2Cl$	$C_6H_5CHCl_2$	$CH_3C_6H_4Cl$	
$NiCl_2(PPh_3)_2$	94	1	5	71
$PdCl_2(PPh_3)_2$	86	1	13	62
$RuCl_2(PPh_3)_3$	57	1	42	78
$RhCl(PPh_3)_3$	55	1	44	66

[a] Reactions were carried out under reflux for 2-3 h using a 1:2:0.002 mixture of toluene, sulfuryl chloride and a catalyst. [b] Determined by GLC. [c] Conversion is meant by 100 X (moles of toluene consumed)/(moles of toluene charged).

References

1. Radical reactions in the coordination sphere. VI. For part V, see H. Matsumoto, T. Nakano, T. Nikaido and Y. Nagai, Chem. Lett., in press.
2. M. S. Kharasch and H. C. Brown, J. Am. Chem. Soc., 61, 2142 (1939).
3. For reviews, see (a) M. L. Poutsma, "Methods in Free-Radical Chemistry", Vol. 1, ed. by E. S. Huyser, Marcel Dekker, New York., (1969) p. 79; (b) G. Sosnovsky, "Free Radical Reactions in Preparative Organic Chemistry", MacMillan, New York, N. Y., (1964) p. 282.
4. C. K. Ingold and F. R. Shaw, J. Chem. Soc., 1927, 2918.
5. H. H. Jaffé, Chem. Revs., 53, 191 (1953).
6. T. Yamamoto, Nippon Kagaku Zasshi, 88, 889 (1967).
7. K. H. Lee and T. O. Teo, J. Chem. Soc. Parkin II, 1973, 689.

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