Synthesis of Chloromethoxybenzenes by Catalytic Decarbonylation of Phenoxyacetyl Chlorides with Chlorotris(triphenylphosphine)rhodium(I)

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Thiophenols are selectively chloromethylated on the sulfur atom whereas phenols react with the chloromethylating reagent preferentially in the nucleus. *O*-Chloromethylation of phenols can be achieved, however, by a somewhat inconvenient and laborious method which involves preparation of sodium phenoxymethane sulfonates under drastic conditions with subsequent chlorination and desulfonylation.[1] Anisole and anisoles carrying electron attracting groups, *e.g.* 4-chloroanisole, can be selectively chlorinated in the methoxy function under free radial conditions.[2,3] Decarbonylation of phenoxyacetyl chlorides under Friedel-Crafts conditions appears to be limited to phenoxyacetyl chlorides having at least one electron attracting substituent in the 2- or 4-position.[4] Thermal decarbonylation has been reported for phenoxyacetyl chlorides with two or more halogen atoms in the nucleus.[5]

We needed ready access to chloromethyl aryl ethers and as a method for their preparation we decided to study decarbonylation reaction of acid chlorides, in particular since certain transition metal compounds are known to promote decarbonylation of acyl halides, *e.g.* aromatic acyl halides.[6-8] Thus, when phenoxyacetyl chlorides were heated with chlorotris(triphenylphosphine)rhodium(I) as catalyst they were readily decarbonylated to the corresponding chloromethyl ethers. Whereas aromatic acyl halides in general have to be heated above 200 °C for the decarbonylative halogenation, the aryloxyacetyl chlorides were readily decarbonylated in the range 150 – 180 °C at atmospheric pressure; decrease in pressure also decreased the temperature required and also the rate of decarbonylation (Table 1).

The reaction is simple to carry out, the product being distilled directly from the reaction mixture.

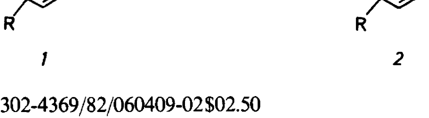

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Table 1. Decarbonylation of phenoxyacetyl chlorides.

	Substituent R	Temp. (°C)	Time (min)	Yield[a] (%)
2a	H	170	30	78
2a	H	130[b]	360	75
2b	2-Me	160	30	75
2c	2-MeO	170	30	79
2d	4-Cl	170	30	83
2e	2,4-Cl_2[c]	180	5	75
2f	4-MeCO[d]	150	20	71

Reactants *1* 28 mmol and catalyst 0.36 mol.%. [a] Isolated. [b] At 30 mm Hg. [c] Thermal decarbonylation requires reflux temperature (*i.e. ca.* 280 °C) for 0.5 – 3 h. [d] 3.8 mmol.

Moreover, the method can be used for aryl ethers containing both electron-donating and -attracting substituents (Table 1). Since the boiling point of the product lies well below that of the acid chloride reactant, the latter will not co-distill with the product.

2-Nitrophenoxyacetyl chloride could not be decarbonylated by this method because of extensive decomposition of the acetyl chloride at elevated temperature.

When the compounds of Table 1 were heated without the catalyst in the same temperature range, no significant decarbonylation was observed.

Experimental. Phenoxyacetyl chlorides 1 were prepared as described in the literature: *1a* b.p. 110 – 112 °C/10 mmHg;[9] *1b* b.p. 120 – 121 °C/10 mmHg;[10] *1c* b.p. 76 – 79 °C/0.02 mmHg;[11] *1d* b.p. 78 °C/0.05 mmHg;[12] *1e* b.p. 102 – 104 °C/0.5 mmHg;[12] *1f* b.p. 126 – 128 °C/0.01 mmHg.[13] ^1H NMR ($CDCl_3$): δ for CH_2 were in the above order 4.88, 4.90, 4.89, 4.82, 4.90, 4.97.

General procedure for decarbonylation of phenoxyacetyl chlorides. Chlorotris(triphenylphosphine)-rhodium(I) (100 mg) was added to the freshly distilled phenoxyacetyl chloride (28 mmol) and the mixture heated until evolution of carbon monoxide had ceased; the conditions are given in Table 1. The chloromethyl phenyl ethers were distilled off from the reaction mixture at reduced pressure: *2a* b.p. 71 – 72 °C/10 mmHg;[14] *2b* 96 – 98 °C/10 mmHg; *2c* 60 – 62 °C/0.02 mmHg;[1] *2d* 39 – 41 °C/0.01 mmHg;[14] *2e* 57 – 62 °C/0.01 mmHg;[1] *2f* 89 – 91 °C/0.01 mmHg. ^1H NMR ($CDCl_3$): δ for CH_2 were in the above order 5.82, 5.77, 5.86, 5.80, 5.80, 5.85.

Decarbonylation of phenoxyacetyl chlorides at reduced pressure. Chlorotris(triphenylphosphine)-rhodium(I) (100 mg) was added to freshly distilled phenoxyacetyl chloride (28 mmol) and the mixture heated at 130 °C and at 30 mmHg. The decarbonylated product was distilled off as formed; the reaction required *ca.* 6 h to go to completion.

1. Barber, H. J., Fuller, R. F., Green, M. B. and Zwartouw, H. T. *J. Appl. Chem. 3* (1953) 266.
2. Louw, R. and Franken, P. W. *Chem. Ind. London* (1977) 127.
3. Gross, H. and Bürger, W. *Org. Synth. 49* (1969) 16.
4. Palmer, M. H. and McVie, G. J. *Tetrahedron Lett.* (1966) 6405.
5. Lashua, S. C. and Ranck, D. E. *U.S.* 3.280.197 (1966); *Chem. Abstr. 66* (1967) P 2350b.
6. Blum, J. *Tetrahedron Lett.* (1966) 1605.
7. Tsuji, J. and Ohno, K. *Synthesis* (1969) 157 and previous publications.
8. Lau, K. S. Y., Becker, Y., Huang, F., Baenziger, N. and Stille, J. K. *J. Am. Chem. Soc. 99* (1977) 5664.
9. McElvain, S. M. and Carney, T. P. *J. Am. Chem. Soc. 68* (1946) 2592.
10. Higginbotham, L. and Stephen, H. *J. Chem. Soc. 117* (1920) 1534.
11. Fridman, S. G. *Zh. Obshch. Khim. 24* (1954) 642.
12. Krewson, C. F., Saggese, E. J., Carmichael, J. F., Ard, J. S. and Drake, T. F. *J. Agric. Food Chem. 7* (1959) 118.
13. Rüchardt, C. and Böck, H. *Chem. Ber. 104* (1971) 577.
14. Hayami, J., Tanaka, N., Kurabayashi, S., Kotani, Y. and Kaji, A. *Bull. Chem. Soc. Jpn. 44* (1971) 3091.

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