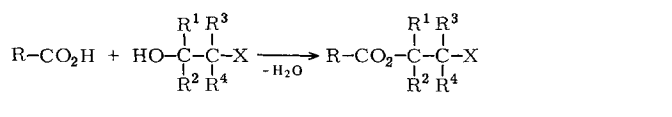
CAS Registry numbers:
(1), 60537-80-6; *(2)*, 60563-07-7; *(3)*, 60537-81-7; *(4)*, 60537-82-8; *(5)*, 60537-83-9; $(NH_4)_2MoS_4$, 15060-55-6; Cs_2MoOS_3, 14348-14-2; $(NH_4)_2MoO_2S_2$, 16150-60-0; $(NH_4)_2WS_4$, 13862-78-7; $CsWOS_3$, 14348-13-1

[1] *A. Müller* and *E. Diemann*, Chem. Commun. *1971*, 65; *E. Diemann* and *A. Müller*, Coord. Chem. Rev. *10*, 79 (1973).
[2] *K. H. Schmidt* and *A. Müller*, Coord. Chem. Rev. *14*, 115 (1974).
[3] *N. Mohan*, *A. Müller*, and *K. Nakamoto* in *R. J. H. Clark* and *R. E. Hester*: Advances in Infrared and Raman Spectroscopy, Vol. 1. Heyden, London 1975, p. 173; *I. Paulat-Böschen*, *B. Krebs*, *A. Müller*, *E. Königer-Ahlborn*, and *H. Dornfeld*, Inorg. Chem., in press.
[4] *G. Krüss*, Justus Liebigs Ann. Chem. *225*, 1 (1884).
[5] *A. Müller*, *E. Diemann*, and *U. Heidborn*, Z. Anorg. Allg. Chem. *371*, 136 (1969).
[6] *E. Corleis*, Justus Liebigs Ann. Chem. *232*, 244 (1886).

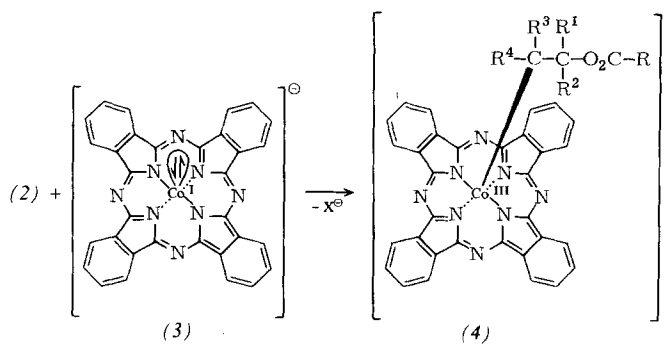
A New Technique of Protecting Groups—Cleavage of β-Halogenated Alkyl Esters with Supernucleophilic Cobalt(I)-phthalocyanine[1]

By *Heiner Eckert* and *Ivar Ugi*[*]

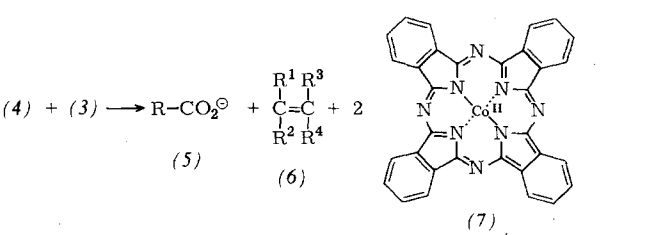
Carboxy groups of α-amino acids and peptides can be protected by esterification with β-halogenated alcohols *(1)* at the C terminus[2]. β-Halogenated alcohols of potential utility are 2-chloroethanol *(1a)* and 2-bromoethanol *(1b)*, 2,2-dibromopropanol *(1c)*, 2,2,2-trichloroethanol *(1d)*, and 2,2,2-trichloro-*tert*-butanol *(1e)* (chloretone).



(1) *(2)*



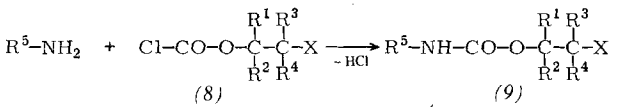
(3) *(4)*



(5) *(6)* *(7)*

$R^1 = R^2 = H, CH_3$; $R^3 = H, CH_3, Cl$; $R^4 = H, X$; $X = Br, Cl$

Amino groups can be provided with urethane protecting groups by reaction with the chloroformates *(8)* of the above alcohols.



(8) *(9)*

Apart from the base-sensitivity of the derivatives of *(1d)*, the lability of urethanes derived from *(1a)* and *(1b)* in alkali hydroxide solution, and the ease of reductive cleavage of the C—X bonds, the protecting groups mentioned are inert towards the deblocking reagents commonly used in peptide chemistry.

We have now found that β-halogenated alkyl esters and urethanes can be cleaved by cobalt(I)-phthalocyanine *(3)*[3] with Li^+ or Na^+ as counterion in methanol, acetonitrile, or acetone at 0 to 20°C. Preliminary experiments had shown that *(3)* is superior to cobaloxime(I)[4] for various reasons.

Cleavage generally proceeds in 60 to 98% yield at a rate that is determined primarily by the constitution of the β-haloalkyl group (see Tables 1 and 2). The reaction is usually three- to ten times slower when performed in acetonitrile and acetone.

Table 1. Reaction times for complete removal of N terminal 2-haloalkoxycarbonyl protecting groups from the urethanes *(9)* with *(3)* in 0.1 M solution at 20°C and the yields of isolated amine component obtained.

N terminal protecting group	Reaction time in methanol	acetone	Yield of amine component [%]
$Cl—CH_2—CH_2—O_2C—$	40 h	—	83 [a]
$Br—CH_2—CH_2—O_2C—$	30—90 min	20 h	70—89 [b]
$H_3C—CBr_2—CH_2—O_2C—$	< 1 min	3 min	77 [c]
$Cl_3C—CH_2—O_2C—$	< 1 min	5 min	91 [c]

[a] Aniline.
[b] Aniline (70—86), amino ester (76—89), dipeptide ester (82), tripeptide ester (80).
[c] Amino ester.

Table 2. Reaction times for complete removal of C terminal 2-haloalkyl protecting groups from the esters *(2)* with *(3)* in 0.1 M solution at 20°C and the yields of isolated acid component obtained.

C terminal protecting group	Reaction time in methanol	aceto-nitrile	acetone	Yield of acid component [%]
$Cl—CH_2—CH_2—$	50 h	—	—	66 [a]
$Br—CH_2—CH_2—$	30—50 min	—	4 h	57—85 [b]
$H_3C—CBr_2—CH_2—$	—	< 1 min	—	95 [a]
$Cl_3C—CH_2—$	< 1 min	—	1 min	98 [a]
$Cl_3C—(CH_3)_2C—$	—	< 1 min	—	92 [a]

[a] Benzoic acid.
[b] Benzoic acid (77), *N*-acyl amino acid (57), *N*-acyl dipeptide (85), *N*-acyl tripeptide.

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(1a), 107-07-3; *(1b)*, 540-51-2; *(1c)*, 59992-05-1; *(1d)*, 115-20-8; *(1e)*, 57-15-8; *(2a)*, 939-55-9; *(2b)*, 939-54-8; *(2c)*, 59992-06-2; *(2d)*, 37934-99-9; *(2e)*, 59992-07-3; *(3)*, 18974-06-6; *(8a)*, 627-11-2; *(8b)*, 4801-27-8; *(8c)*, 59992-08-4; *(8d)*, 17341-93-4; *(9a)*, 3747-48-6; *(9b)*, 32353-12-1; $C_6H_5NH_2$, 62-53-3; $C_6H_5CO_2H$, 65-85-0

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[2] *J. Grimshaw*, J. Chem. Soc. *1965*, 7136; *H. Büchi*, Dissertation, ETH Zürich (1965); *M. Brugger*, Dissertation, ETH Zürich (1965); *R. B. Woodward*, *K. Heusler*, *S. Gosteli*, *D. Naegeli*, *W. Oppolzer*, *R. Ramage*, *S. Ranganathan*, and *H. Vorbrüggen*, J. Am. Chem. Soc. *88*, 852 (1966).
[3] *R. Taube*, J. Pure Appl. Chem. *38*, 427 (1974); *H. Eckert* and *I. Ugi*, Angew. Chem. *87*, 847 (1975); Angew. Chem. Int. Ed. Engl. *14*, 825 (1975).
[4] *H. Eckert*, *G. N. Schrauzer*, and *I. Ugi*, Tetrahedron *31*, 1399 (1975); see also parts 2 and 3 [1].