In conclusion, although there is strong evidence for the existence of a tetrahedral intermediate as an obligatory species along the reaction path for hydrolysis of trifluoroacetanilide,[19-26] there is no evidence concerning the concentration of this species except that it is less than 0.5% of the total at all times.

J. Peter Guthrie

Department of Chemistry, University of Western Ontario
London, Ontario, Canada. N6A 3K7

A New Method for Protecting Carboxylic Acids, Phenols, Thiophenols, and Mercaptans

Sir:

We describe a new blocking group for carboxylic acids, phenols, thiophenols, and mercaptans which is readily attached to these functions, which remains in place under a variety of circumstances, and which is rapidly detached under mild, highly specific conditions. This protective device derives from the unusual chemical properties of the 9-anthrylmethyl system, a system which has recently been found to undergo a new type of substitution at the saturated carbon atom.[1]

Carboxylic acids are protected as esters (I).[2,3] The general procedure for deblocking these esters involves treatment for 1 hr at −20° with the sodium salt of methyl mercaptan in DMF (eq 1); the yields given in
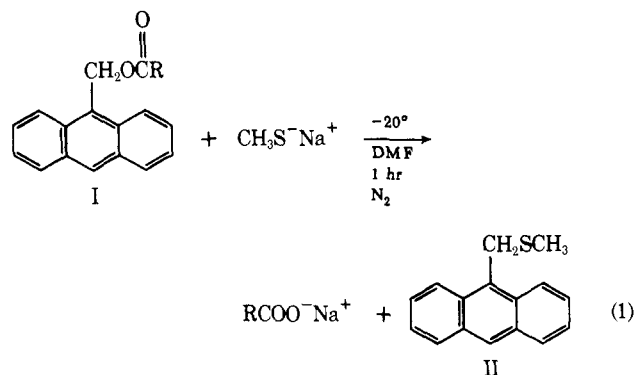
(1)

Table I refer to pure, isolated acids.[4] In hexamethylphosphoramide (HMPA) the reaction of eq 1 is extraordinarily fast; at 25° 9-anthrylmethyl mesitoate is completely deblocked in less than 30 sec and a 93% yield of pure mesitoic acid is obtained.

The study of 9-anthrylmethyl mesitoate provides an insight into the intrinsic properties of 9-anthrylmethyl esters for, here, the usual acid and base catalyzed acyl-oxygen cleavage processes do not occur easily. Thus, the mesitoate ester is recovered quantitatively after a 24-hr treatment with 24 mol of anhydrous ethylamine

Table I. 9-Anthrylmethyl Esters Deblocked at −20°[a]

Ester (I)	Acid	% yield
p-Toluate	p-Toluic	95
Mesitoate	Mesitoic	99
p-Methoxyphenylacetate	p-Methoxyphenylacetic	93
n-Heptanoate	n-Heptanoic	89
m-Nitrobenzoate	m-Nitrobenzoic	86
trans-Cinnamate	trans-Cinnamic[b]	94

[a] In DMF; 0.1 M in ester, 0.2 M in CH$_3$SNa; 1 hr, under N$_2$. [b] 0.1 M in ester and in CH$_3$SNa, 6 hr reaction time.

in DMF at 25°. In aqueous dioxane the mesitoate is completely unaffected by 2 mol of lithium hydroxide (0.07 M) after 8 hr at 25°.

The behavior of 9-anthrylmethyl mesitoate toward acids is noteworthy. An aqueous dioxane solution containing 4 equiv of 0.14 N sulfuric acid is without effect after 3 hr at 25°; nor is there any reaction on exposure to 10 equiv of trifluoroacetic acid in dioxane for 1 hr at 25°. However, when the mesitoate ester is treated with a methylene chloride solution containing 10 equiv of trifluoroacetic acid, it is completely deblocked after 10 min at 0° and a 97% yield of pure mesitoic acid is isolated. Thus the ester is stable to acids in oxygenated solvents such as dioxane or aqueous dioxane but is rapidly and cleanly cleaved by trifluoroacetic acid in an oxygen free solvent — presumably as an alkyl-oxygen cleavage process involving the 9-anthrylmethyl carbonium ion. This selective sensitivity to acid provides a valuable alternative deblocking procedure.

Some of the other esters of Table I are also of interest. The fact that the m-nitrobenzoate gives an excellent yield of m-nitrobenzoic acid shows that reduction of a nitro group does not compete with the reaction of eq 1. The cinnamate is an example of an ester capable of undergoing the Michael condensation; it turns out that this complication can be avoided merely by using 1 equiv of the mercaptide salt (Table I).[5]

Phenols, thiophenols, and mercaptans are protected as the 9-anthrylmethyl ethers or thioethers—readily prepared by the reaction of their sodium salts with 9-chloromethylanthracene at room temperature in DMF. Two phenolic ethers were studied: III and IV. At
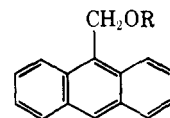
III, R = p-tert-butylphenyl
IV, R = p-benzylphenyl

25° they are completely deblocked by treatment with a DMF solution of the sodium salt of methyl mercaptan for 20 min; ether III gives an 86% yield of pure p-tert-butylphenol while from ether IV a 99% yield of pure p-benzylphenol is isolated.

The cleavage of thioethers V and VI by the sodium salt of methyl mercaptan is also a rapid process; in DMF deblocking is complete after 2 hr at 0°. From thioether V a 92% yield of p-bromothiophenol is obtained while thioether VI gives p-thiocresol in 85% yield. Thioethers derived from mercaptans are, not

(1) C. W. Jaeger and N. Kornblum, *J. Amer. Chem. Soc.,* **94,** 2545 (1972).

(2) Readily obtained from the acid, 9-chloromethylanthracene and triethylamine in acetonitrile solution; *cf.* F. H. C. Stewart, *Aust. J. Chem.,* **18,** 1701(1965). Esterification with 9-hydroxymethylanthracene should be equally effective.

(3) Satisfactory elemental analyses and nmr and ir spectra were obtained for all new compounds.

(4) Thioether II is not completely stable to CH$_3$SNa; this matter will be discussed in the full paper.

(5) The *trans*-crotonate is also completely deblocked under these conditions but quantitative isolation of crotonic acid is relatively difficult, and the matter was not pursued.
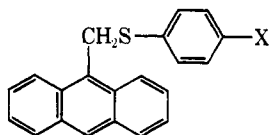
V, X = Br
VI, X = CH₃

surprisingly, cleaved less rapidly than V or VI. In DMF, using 10 equiv of the sodium salt of methyl mercaptan, cleavage of VII and VIII is about 90%
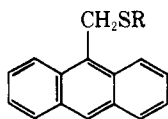
VII, R = 1-hexyl
VIII, R = benzyl

complete after 5 hr at 25°. When, however, HMPA is employed as the reaction medium, deblocking is complete in less than 2 hr at 25° and n-hexyl mercaptan and benzyl mercaptan are isolated in 68 and 74% yields.

A dioxane solution containing 10 equiv of trifluoroacetic acid is without effect on ether IV, even after 1 hr at 25°; but after 10 min at 0° the ether is completely cleaved by trifluoroacetic acid in methylene chloride. On the other hand, thioether VI is recovered quantitatively after being treated with trifluoroacetic acid in methylene chloride for 10 min at 0°.[6]

The possibility of utilizing the 9-anthrylmethyl system for protecting amines and alcohols is being studied. Also under investigation are a number of interesting questions relating to other nucleophiles and to the matter of mechanism.

(6) Both IV and VI are unaffected by ethylamine in DMF, even after 24 hr at room temperature. The thioether (VI) was also recovered quantitatively after being treated with lithium hydroxide in aqueous dioxane for 8 hr at 25°.

Nathan Kornblum,* **Allen Scott**
Purdue University, Department of Chemistry
West Lafayette, Indiana 47907

X-Ray Photoelectron Spectroscopic Studies of Silver(III) Octaethylporphyrin

Sir:

The redox properties of metalloporphyrins[1–3] are of recent interest because of their potential relevance as models in biological redox systems. Two points are of special interest. One is the question of whether or not an electron can be removed (or added) directly to the central metal ion or whether the electronic levels of the porphyrin ring are involved. The second is to what extent changing oxidation states of the metal ions

(1) J. Manassen and A. Wolberg, *J. Amer. Chem. Soc.*, **92**, 2982 (1970).
(2) J. Fajer, D. C. Borg, A. Forman, D. Dolphin, and R. H. Felton, *J. Amer. Chem. Soc.*, **92**, 3451 (1970).
(3) J. Fuhrhop, K. M. Kadish, and D. G. Davis, *J. Amer. Chem. Soc.*, **95**, 5140 (1973), and references therein.

affects the porphyrin ring charge and therefore its reactivity. The latter question has been considered theoretically.[4] The technique of X-ray photoelectron spectroscopy (XPS or ESCA) has been suggested to be an appropriate tool for probing the charge distribution of these systems[5] since in the absence of complicating factors like atomic relaxation and gross structural differences, chemical shifts of core electron binding energies directly reflect the nuclear charge felt by these electrons. In this study we wish to present the ESCA spectra of several silver porphyrins. These results establish unequivocal evidence for the existence of a stable Ag(III) complex and illustrate the power of using the binding energies of the metal, N 1s, and C 1s electrons in understanding the electron distribution in these systems.

All compounds were prepared by previously reported synthetic methods.[3] Samples were prepared for spectral analysis by smearing several micrograms of material onto a gold plate and burnishing it into a very thin film with a sapphire ball. Samples burnished to a very thin film did not show any signs of charging as evidenced by (a) a high reproducibility of results (±0.1 eV) from one sample preparation to the next and by (b) a lack of movement of the peaks during exposure to low-energy electrons flooding the sample. Unlike the previous ESCA study on porphyrins,[5] we found the compounds to be very easy to handle and the measured binding energies to be very reproducible.

To interpret chemical shifts of the silver porphyrins in terms of their charge distribution, we have studied a series of molecules with similar structure. A compilation of these results is given in Table I. The binding

Table I. Binding Energies^a (eV) of Silver Porphyrins and Related Compounds

	Ag 3d₃/₂	Ag 3d₅/₂	C₁ₛ	N₁ₛ
Ag(0)	374.0	367.9		
H₂OEP			284.5	399.4
				397.3
H₂TPP			284.0	399.1
				397.0
Ag^{II}OEP	374.3	368.3	284.3	397.6
Ag^{II}TPP	373.7	367.6	284.3	398.3
Ag^{III}OEP(ClO₄)	377.1	371.0	284.2	398.7

^{a} All spectra were recorded on a Hewlett-Packard 5950A ESCA spectrometer. Binding energies were all reproducible to ±0.1 eV.

energy for the 3d₃/₂,₅/₂ electrons of evaporated silver are shown as 374.0 and 367.9 eV, respectively, vs. the gold 4f₇/₂ electrons at 84.0 eV and are presented as a reference value. The binding energy values for the C 1s and N 1s electrons of octaethylporphyrin (OEP) and tetraphenylporphyrin (TPP) free bases are also shown in order to characterize the system in the absence of metal ion. The N 1s spectrum exhibits a doublet due to the selective protonation of two of the central nitrogens. This result is in agreement with a previous study[5] and settles a long standing controversy over the configuration of the attached protons. The C 1s

(4) (a) M. Zerner, M. Gouterman, and H. Kobayashi, *Theor. Chim. Acta*, **6**, 363 (1966); (b) M. Zerner and M. Gouterman, *ibid.*, **4**, 44 (1965); **8**, 26 (1967); (c) A. M. Schaffer and M. Gouterman, *ibid.*, **18**, 1 (1970).
(5) M. V. Zeller and R. G. Hayes, *J. Amer. Chem. Soc.*, **95**, 3855 (1973).