of *N*-alkylidenearenesulfenamides as "masked" imine derivatives of ammonia.

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(8) Products were analyzed by gas chromatography on a 6-ft 6% OV-17 on 60/80 mesh Chromosorb W (regular) column by comparison of peak areas with standard solutions of reaction products. Analysis were performed at least twice and the results averaged. With 2 equiv of MeLi at −78 °C for 4 h, **3** gave 48% **3** and 50% **4**. With 2 equiv each of MeLi and TMEDA at 25 °C, **3** gave 38% **3** and 58% **4**.
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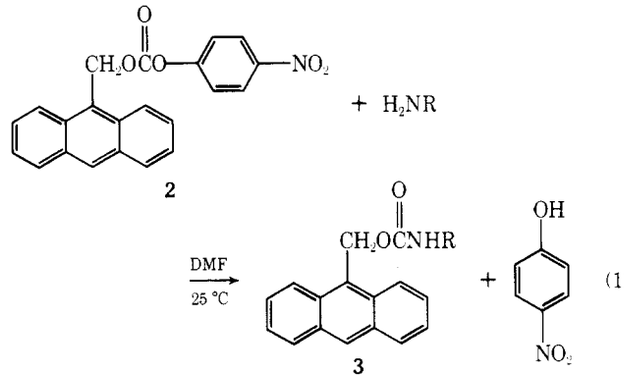
A New Method for Protecting Amines

Summary: A new method for protecting amines which hinges on the unusual chemical properties of the 9-anthrylmethyl system is described.

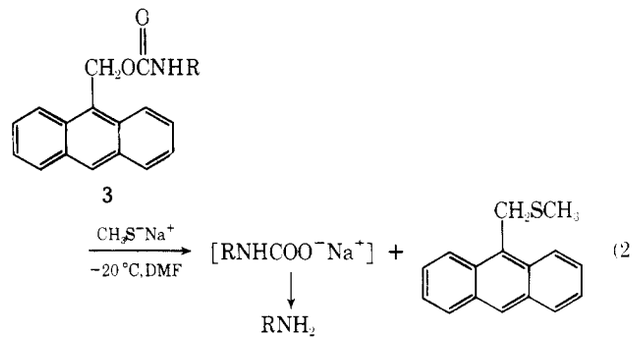
Sir: The 9-anthrylmethyl system **1** provides an excellent blocking group for carboxylic acids, phenols and thiophenols.[1] We now describe a simple procedure for protecting amines[2] which is based on their conversion to 9-anthrylmethyl carbamates **3**. Such carbamates are readily produced at room temperature by treating the amine with 9-anthrylmethyl *p*-nitrophenyl carbonate **2** (eq 1).[3]

1



(1)

Deblocking does not rely on the carbamate function but, rather, on a special property of the 9-anthrylmethyl system. What is invoked is a new type of substitution at a saturated carbon atom attached to the 9 position of the anthracene nucleus; these reactions are noteworthy for the speed with which they occur under mild conditions.[1,4] Removal of the protective group is achieved by treating the 9-anthrylmethyl carbamate with the sodium salt of methyl mercaptan (eq 2).

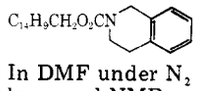


(2)

At −20 °C the reaction requires from 1 to 7 h; at 25 °C it is complete in <4 min. The results obtained with a wide variety of carbamates are summarized in Table I; the yields refer to pure, isolated amines.

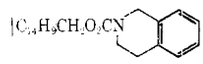
Despite the ease with which these compounds are deblocked by the sodium salt of methyl mercaptan they are resistant to the action of various bases and acids. Thus, the 9-anthrylmethyl carbamates derived from *n*-octylamine, di-*n*-octylamine, and *p*-phenetidine are unaffected by exposure for 24 h to 30 mol of anhydrous ethylamine in DMF at 25 °C. They are also unaffected by 2 equiv of lithium hydroxide (0.01 N) in aqueous dioxane after 6 h at 25 °C. These carbamates are also stable to 4 equiv of sulfuric acid (0.10 N) in aqueous dioxane for 1 h at 25 °C, and they are not affected by 10 equiv of trifluoroacetic acid (1.0 M) in dioxane after 1 h at 25 °C.

Table I. The Deblocking of 9-Anthrylmethyl Carbamates By The Sodium Salt of Methyl Mercaptan[a,b]

9-Anthrylmethyl carbamate (3)	Amine	% yield	Reaction time, hr
$C_{14}H_9CH_2O_2CNH(CH_2)_7CH_3$	*n*-Octylamine	77	7
$C_{14}H_9CH_2O_2CNH(CH_2)_2C_6H_4Cl$	2-(*p*-Chlorophenyl)ethylamine	86	*c*
$C_{14}H_9CH_2O_2CNHCH_2C_6H_4Cl$	*p*-Chlorobenzylamine	82	1
$C_{14}H_9CH_2O_2CNHCH(C_6H_5)_2$	Benzhydrylamine	97	5
$C_{14}H_9CH_2O_2CNHC_6H_4OC_2H_5$	*p*-Phenetidine	91	3
$C_{14}H_9CH_2O_2CN[(CH_2)_7CH_3]_2$	Di-*n*-octylamine	85	*c*
	Tetrahydroisoquinoline	86	2

[a] In DMF under N_2 0.3 M in carbamate and 0.6 M in CH_3SNa; at −20 °C unless otherwise stated. [b] Satisfactory elemental analyses and NMR and IR spectra were obtained for all new compounds. [c] 4 min at 25 °C.

Table II. 9-Anthrylmethyl Carbamates Deblocked by CF_3CO_2H in CH_2Cl_2[a]

9-Anthrylmethyl carbamate (3)	Amine	% yield[b]
$C_{14}H_9CH_2O_2CNHCH(C_6H_5)_2$	Benzhydrylamine	95
$C_{14}H_9CH_2O_2CNHCH(CO_2CH_3)CH_2C_6H_5$	Phenylalanine methyl ester	92
$C_{14}H_9CH_2O_2CNHCH_2C_6H_4Cl$	*p*-Chlorobenzylamine	88
	Tetrahydroisoquinoline	90

[a] 5 min at 0 °C; 0.1 M in carbamate, 1.0 M in CF_3CO_2H. [b] Pure isolated amine.

In contrast, the protective group is removed by a methylene chloride solution of trifluoroacetic acid. Thus, while the 9-anthrylmethyl carbamate derived from benzyhydrylamine is not affected by treatment for 12 h with 10 equiv of trifluoroacetic acid (1.0 M) in dioxane at 25 °C, it is completely deblocked in 5 min by 10 equiv of trifluoroacetic acid (1.0 M) in methylene chloride at 0 °C and a 95% yield of the pure amine is isolated. As can be seen from Table II this is a general phenomenon and it provides a valuable alternative deblocking procedure.

A typical example of the blocking procedure follows. To a stirred suspension of 7.46 g (20.0 mmol) of **2**[3] in 40 ml of DMF was added 2.43 ml (20.0 mmol, 2.84 g) of *p*-chlorobenzylamine. After 45 min the reaction mixture was poured into ice–water and extracted with methylene chloride. The aqueous phase was then extracted with benzene and the combined organic layers were washed with 10% hydrochloric acid, 10% sodium carbonate, and, finally, water. Drying and removing solvents yielded 7.0 g of needles, mp 167–171 °C, which on recrystallization from benzene–hexane gave 5.996 g (86% yield) of analytically pure pale yellow needles, mp 180–181 °C.

Deblocking is illustrated by the following example. A 200-ml flask containing 1.855 g (5 mmol) of 9-anthrylmethyl *p*-ethoxyphenylcarbamate and 0.701 g (10 mmol) of the sodium salt of methyl mercaptan was sealed with a rubber stopple, immersed in a bath at −20 °C, and dry N_2 was passed in for ~20 min. Then 50 ml of cooled, deoxygenated DMF was added via syringe and the resulting solution was stirred at −20 °C under N_2; the reaction was monitored by TLC [silica gel plates, hexane–ethyl acetate (2:1), short and long UV]. After 3 h the blue fluorescence of the carbamate was gone; the reaction mixture was then poured into a mixture of 100 ml of ice and 200 ml of 10% HCl and extracted with 200 ml of benzene–diethyl ether (1:1) and then with 100 ml of benzene. The resulting aqueous acid solution was rendered alkaline with 20% NaOH and extracted twice with diethyl ether and once with benzene. The organic phase was washed with water and dried ($MgSO_4$), and the solvents were removed. This gave 0.620 g (91% yield) of *p*-phenetidine which was 99+% pure by VPC and whose NMR spectrum was identical with that of an authentic sample. From the benzene–diethyl ether extract of the original acid solution 1.214 g (100% yield) of essentially pure 9-anthrylmethyl sulfide, mp 110–112 °C, was isolated.

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