Rf_1 0.39, Rf_2 0.61. *Anal.* Calcd. for $C_{14}H_{19}NO_6S$: C, 51.05; H, 5.81; N, 4.25. Found: C, 51.09; H, 5.75; N, 4.25.

b) Oxidation by $NaBO_3$: Z(OMe)-Met-OH (15.67 g) in AcOEt (100 ml) was similarly oxidized by $NaBO_3$ (9.23 g, 1.2 equiv.) in H_2O (50 ml) at room temperature overnight. On thin-layer chromatography, two spots, Rf_1 0.39 (main spot) and 0.42 (very faint spot), were detected. The product was isolated as stated above and recrystallized from MeOH and AcOEt; yield 12.99 g (79%), mp 98—101°, $[\alpha]_D^{22}$ +8.4° (c=1.9, AcOH). Rf_1 0.39. *Anal.* Found: C, 51.30; H, 6.05; N, 4.16.

The product (0.50 g) was treated with trifluoroacetic acid (2 ml) in the presence of anisole (0.5 ml) in an ice-bath for 60 min and dry ether was added. The precipitated powder was dissolved in a small amount of H_2O and the solution was neutralized with Et_3N. After evaporation of the solvent, EtOH was added to the residue to afford the powder, which was recrystallized from H_2O and EtOH; yield of H-Met(O)-OH 0.21 g (81%), mp 238° (dec.), Rf 0.29 in *n*-BuOH-AcOH-AcOEt-H_2O (1:1:1:1), $[\alpha]_D^{22}$ +35.3° (c=0.9, in 1 N HCl). (lit.[8] H-Met-(*R*,*S*)-sulphoxide, H_2O_2 oxidation product, $[\alpha]_D$ +33.6° in 1 N HCl). Ratios of the (*S*)-(*S*) and (*S*)-(*R*) isomers determined in the long column of the amino acid analyser (Hitachi KLA-5) were 1 (retention time 55 min): 1.074 (retention time 57 min). The standard sample of H-Met(O)-OH [(*S*)-(*S*)], was prepared through the corresponding picrate.[16] mp 248—251°, $[\alpha]_D^{25}$ +123.3° (c=2.0, 1 N HCl). (lit.[8] $[\alpha]_D$ +127.2° in 1 N HCl, lit.[16] $[\alpha]_D$ +131° in 1 N HCl).

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N-[(N-Nitrosobenzylamino)methyl]benzamide as a Direct Benzylating Agent

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A new application of N-[(N-nitrosobenzylamino)methyl]benzamide as a direct benzylating agent has been realized by benzylation of several protic materials. Ferric chloride functions as a catalyst in the benzylation of ethanol, acetic acid, phenol, and thiols.

Keywords——N-[(N-nitrosobenzylamino)methyl]benzamide; benzylating agent; decomposition of N-nitrosoamine; ferric chloride; phenyldiazomethane

Recently the convenient diazoalkane generation from N-[(N-nitrosoalkylamino)methyl]-amides has been reported[2] from this laboratory. In the present paper we wish to report on several new applications of N-[(N-nitrosoalkylamino)methyl]amides as a direct alkylating agent through diazoalkane generation *in situ*.

In alkali solution, N-[(N-nitrosoalkylamino)methyl]benzamides have been known to be susceptible to the decomposition into diazoalkanes.[2]

$$2C_6H_5CONHCH_2\underset{\underset{NO}{|}}{N}CH_2R \xrightarrow{^-OH} 2RCHN_2 + (C_6H_5CONH)_2CH_2 + CH_2O + H_2O$$

1) Location: *2-2-1 Oshika, Shizuoka 422, Japan.*
2) M. Sekiya, Y. Ohashi, Y. Terao, and K. Ito, *Chem. Pharm. Bull.* (Tokyo), **24**, 369 (1976).

Behaviors of these reagents toward secondary amine and carboxylic acid were first studied. N-[(N-nitrosobenzylamino)methyl]benzamide (NMB), selected as a representative, was heated in excess piperidine, whereupon N-benzylpiperidine and N-(piperidinomethyl)benzamide were obtained in 40% and 60% yields, respectively. NMB was decomposed in trifluoroacetic acid at room temperature into benzyl trifluoroacetate and N,N′-methylenebisbenzamide in 66% and 79% yields, respectively. NMB was, however, unchanged on heating in acetic acid. The above formation of N-benzylpiperidine and benzyl trifluoroacetate are suggestive of an *in situ* generation of phenyldiazomethane in the reactions. Therefore it is supposed that aliphatic amine and strong carboxylic acid affect the generation of phenyldiazomethane from NMB, presumably according to the following equations. In the latter traces of water may induce the reaction.

a) $C_6H_5CONHCH_2N(NO)CH_2C_6H_5 + HN\langle\rangle \longrightarrow C_6H_5CONHCH_2N\langle\rangle + C_6H_5CH_2N{=}N{-}OH$

$C_6H_5CH_2N{=}N{-}OH \longrightarrow C_6H_5CHN_2 + H_2O$

b) $C_6H_5CONHCH_2N(NO)CH_2C_6H_5 \xrightarrow{H^+} C_6H_5CONHCH_2\overset{+}{N}(=N{-}OH)CH_2C_6H_5 \xrightarrow{H_2O,\ -H^+}$

$C_6H_5CONHCH_2OH + C_6H_5CH_2N{=}N{-}OH$

$C_6H_5CH_2N{=}N{-}OH \longrightarrow C_6H_5CHN_2 + H_2O$

$2C_6H_5CONHCH_2OH \longrightarrow (C_6H_5CONH)_2CH_2 + CH_2O + H_2O$

It was then found that ferric chloride well functioned on an *in situ* generation of phenyldiazomethane from NMB affecting benzylation of a number of protic materials such as alcohol, phenol, carboxylic acid, and thiols. For example, benzyl ethylether was obtained in 70% yield by refluxing a tetrahydrofuran (THF) solution of equimolar amounts of NMB, ethanol, and ferric chloride. In this run, side formation of N,N′-methylenebisbenzamide was also confirmed. By the same procedure the other representative data are listed in Table I. Presumably ferric chloride in the reaction may function as a Lewis acid in the course of the reaction similar to that for acid.

Table I. Reaction of N-[(N-Nitrosobenzylamino)methyl]benzamide with Protic Materials in the Presence of Ferric Chloride

Protic material	Reaction period (hr)	Product[a]	Yield (%)
C_2H_5OH	2	$C_6H_5CH_2OC_2H_5$	67
CH_3CO_2H	3	$CH_3CO_2CH_2C_6H_5$	80
C_6H_5OH	4	$C_6H_5OCH_2C_6H_5$	40
$C_6H_5CH_2SH$	2	$(C_6H_5CH_2)_2S$	51[b]
C_6H_5SH	1	$C_6H_5SCH_2C_6H_5$	78

a) In each run N,N′-methylenebisbenzamide was additionally obtained.
b) A by-product, $C_6H_5CONHCH_2SCH_2C_6H_5$ was obtained in 12% yield.

Experimental

All melting points are uncorrected. Infrared (IR) spectra were recorded on a Hitachi EPI-G2 spectrophotometer.

Reaction of NMB with Piperidine——A mixture of 5.4 g (0.02 mol) of NMB in 20 ml of piperidine was refluxed for 4 hr. The reaction solution was concentrated under reduced pressure, and the resulting residue was distilled to give 1.4 g (40%) of 1-benzylpiperidine, bp 130—133° (20 mmHg) [lit.,[3] bp 81—82° (2 mmHg)]. The residue on distillation was solidified by washing with petr. ether and recrystallized from ethanol to give

3) M. Sekiya and Y. Terao, *Chem. Pharm. Bull.* (Tokyo), **18**, 947 (1970).

needles of N-(piperidinomethyl)benzamide, mp 128—129° (lit.,[4] mp 129—130°), which weighed 2.6 g (60%). IR spectra of both products were identical with those of the authentic specimens.

Reaction of NMB with Trifluoroacetic Acid——A solution of 5.4 g (0.02 mol) of NMB in 20 ml of trifluoroacetic acid was stirred at a room temperature for 2.5 hr. After evaporation of trifluoroacetic acid, N,N'-methylenebisbenzamide was deposited, filtered, and washed with petr. ether. Yield was 2.0 g (79%). Recrystallization from ethanol gave needles, mp 215—217° (lit.,[4] mp 218—219°). The combined filtrate was concentrated to afford an oil, which was distilled under reduced pressure to give 2.3 g (66%) of benzyl trifluoroacetate, bp 81—83° (40 mmHg) [lit.,[5] bp 178—179°]. IR spectra of both products were in agreement with those of the authentic specimens.

General Procedure for Reaction of NMB with Protic Materials in the Presence of Ferric Chloride——To a suspension of 3.2 g (0.02 mol) of powdered ferric chloride in 30 ml of THF 0.02 mol of the protic material (ethanol, acetic acid, phenol, thiophenol, and benzylmercaptan were used) was added. The mixture was refluxed for 1—4 hr. After removal of THF, 15 ml of water was added to the residue. Deposited N,N'-methylenebisbenzamide was filtered off and the filtrate was extracted with ether. The ethereal solution was dried over $MgSO_4$. After removal of ether, the residue was distilled under reduced pressure to give the product. Yields of the products are listed in Table I. Identities of the products were made by comparison of their IR spectra with those of the authentic specimens.

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Studies on the Constituents of *Hedera rhombea* Bean. I.[1] Glycosides of Hederagenin

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Four triterpenoid saponins, tentatively named saponins K_3, K_6, K_{10} and K_{12}, were isolated from the stems of *Hedera rhombea* Bean (Araliaceae). They were identified with hederagenin glycosides represented as formulae I, III, V and IX, respectively.

Keywords——*Hedera rhombea* Bean; saponin; hederagenin glycosides; hederagenin 3-O-α-L-arabinopyranoside; hederagenin 3-O-α-L-rhamnopyranosyl-(1→2)-α-L-arabinopyranoside; 3-O-α-L-arabinopyranosyl hederagenin 28-O-α-L-rhamnopyranosyl-(1→4)-β-D-glucopyranosyl-(1→6)-β-D-glucopyranosylester; 3-O-α-L-rhamnopyranosyl-(1→2)-α-L-arabinopyranosyl hederagenin 28-O-α-L-rhamnopyranosyl-(1→4)-β-D-glucopyranosyl-(1→6)-β-D-glucopyranosylester

Hedera rhombea Bean (Kizuta in Japanese) is a evergreen viny plant of the family Araliaceae, which is widely distributed in Japan, Korea and China.

On the constituents of this plant, little has been known except for fatty acids[3] and a saponin which has not been elucidated.[4]

We have now investigated on the saponin constituents in the stems of this plant.

1) The 23th Annual Meeting of the Japanese Society of Pharmacognosy, Hiroshima, Nov. 1976.
2) Location; *a*) *Sugitani, Toyama*; *b*) *3 Ho, Kanagawa-machi, Kanazawa.*
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