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A New Convenient Synthesis of Diazoalkanes from N-[(N-Nitrosoalkylamino)methyl]benzamides

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Conformational analysis by means of nuclear magnetic resonance measurement has disclosed that N-[(N-nitrosoalkylamino)methyl]amides newly prepared are in favor of *anti* form in crystals while in state of solution form *syn-anti* equilibrium mixture. These nitrosoamines have been found smoothly to generate diazoalkanes by the influence of alkali. In the use of their benzamide analogs a new practically useful means for synthesizing a series of diazoalkanes has been established.

After development of the synthesis of N-[(alkylamino)methyl]amides reported previously[2] our intention was drawn to search for potential use of these compounds. Their N-nitroso derivatives newly prepared have now been accepted as excellent diazoalkane-generating agents of practical value. The present paper describes this diazoalkane synthesis together with conformational analysis of the starting N-nitroso compounds.

Conformational Analysis of N-[(N-Nitrosoalkylamino)methyl]amides

N-[(Alkylamino)methyl]amide hydrochlorides were easily nitrosated with aqueous sodium nitrite into the corresponding N-nitroso derivatives (see Table I). They showed all of the ultraviolet (UV) spectral characteristics of N-nitrosodialkylamines,[3] exhibiting two absorption bands in ethanol, a low intensity maximum at *ca.* 365 nm which shows fine structure and the other high intensity maximum at *ca.* 232 nm (see Table II). Their nuclear magnetic resonance (NMR) spectra in deuteriochloroform exhibited two sets of signals indicating mixtures of *syn* and *anti* isomers, similarly to those of N-nitrosodialkylamines.[4-6] Conformational analysis was made by means of NMR measurement of N-[(N-nitrosoalkylamino)methyl]benzamides possessing varying alkyls. The spectra of methyl, ethyl, isopropyl and *tert*-butyl derivatives, measured after the equilibria between the two isomers were reached (for all after 7 hr), were studied on the assumption that as the alkyl becomes bulkier it becomes more favorable for the alkyl to be *trans* to the nitroso oxygen. Being consistent with the known generalization[5,6] that α-methyl, α-methylene and β-methyl protons of N-alkyl resonate at higher magnetic field when *cis* than when *trans* to the nitroso oxygen, intensity ratio of the corres-

1) Location: *2-2-1 Oshika, Shizuoka-shi 422, Japan.*
2) Y. Watase, Y. Terao, and M. Sekiya, *Chem. Pharm. Bull.* (Tokyo), **21**, 2775 (1973).
3) R.N. Haszeldine and J. Jander, *J. Chem. Soc.*, **1954**, 691; R.N. Haszeldine and B.J.H. Mattinson, *ibid.*, **1954**, 4172.
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Table I. N-[(N-Nitrosoalkylamino)methyl]amides $R^1CONHCH_2N(NO)R^2$

R^1	R^2	Appearances (recryst. solvent)	mp (°C)	IR ν_{max}^{KBr} (cm^{-1}) NH	IR CONH	Formula	Analysis (%) Found (Calcd.) C	H	N
C_6H_5	CH_3	plates (EtOH)	120 (decomp.)	3240	1625	$C_9H_{11}O_2N_3$	56.36 (55.95)	5.83 (5.74)	21.97 (21.75)
C_6H_5	C_2H_5	plates (EtOH)	102—103	3277	1653	$C_{10}H_{13}O_2N_3$	58.03 (57.96)	6.33 (6.32)	20.09 (20.28)
C_6H_5	C_4H_9	plates (EtOH)	72— 73	3258	1645	$C_{12}H_{17}O_2N_3$	61.15 (61.25)	7.20 (7.28)	17.85 (17.86)
C_6H_5	C_8H_{17}	needles (EtOH)	64— 65	3227	1628	$C_{16}H_{25}O_2N_3$	66.32 (65.95)	8.45 (8.65)	14.84 (14.42)
C_6H_5	$CH_2C_6H_5$	plates (EtOH)	105	3264	1692	$C_{15}H_{15}O_2N_3$	67.28 (66.90)	5.66 (5.61)	15.55 (15.61)
C_6H_5	$CH_2CH_2C_6H_5$	plates (EtOH)	104	3284	1638	$C_{16}H_{17}O_2N_3$	68.24 (67.82)	6.09 (6.05)	14.79 (14.83)
C_6H_5	$CH(CH_3)_2$	needles (EtOH)	79	3222	1622	$C_{11}H_{15}O_2N_3$	59.88 (59.71)	6.96 (6.83)	18.63 (18.99)
C_6H_5	C_6H_{11}	needles (EtOH)	101	3221	1624	$C_{14}H_{19}O_2N_3$	64.48 (64.34)	7.50 (7.33)	15.62 (16.08)
C_6H_5	$C(CH_3)_3$	plates (EtOH)	116—118	3259	1641	$C_{12}H_{17}O_2N_3$	61.32 (61.25)	7.18 (7.28)	18.15 (17.86)
CH_3	CH_3	prisms (AcOEt)	56— 57	3273	1655	$C_4H_9O_2N_3$	36.41 (36.63)	6.63 (6.92)	31.74 (32.05)
CH_3	$CH_2C_6H_5$	plates (EtOH)	79— 80	3204	1652	$C_{10}H_{13}O_2N_3$	57.82 (57.96)	6.31 (6.32)	20.29 (20.28)
CH_3	$CH_2CH_2C_6H_5$	prisms (acetone)	91— 92	3279	1656	$C_{11}H_{15}O_2N_3$	59.80 (59.71)	6.72 (6.83)	19.15 (18.99)

Table II. UV Spectral Data[a] of $R^1CONHCH_2N(NO)R^2$

R^1	R^2	λ_{max} nm (log ε)	λ_{infl}[b] nm (log ε)
C_6H_5	CH_3	232.5(4.23), 353 (1.90)	356 (1.90), 372 (1.72)
C_6H_5	C_2H_5	232.5(4.27), 355 (1.90) 363.5(1.90)	373.5(1.76)
C_6H_5	C_4H_9	232.5(4.31), 356 (1.88) 363.5(1.88)	373.5(1.73)
C_6H_5	C_8H_{17}	232.5(4.29), 356 (1.86) 362 (1.86)	374 (1.71)
C_6H_5	$CH_2C_6H_5$	231 (4.32), 364 (1.85)	360 (1.85), 374 (1.73)
C_6H_5	$CH_2CH_2C_6H_5$	232 (4.26), 364 (1.87)	360.5(1.87), 379.5(1.68)
C_6H_5	$CH(CH_3)_2$	232 (4.29), 366 (1.88)	—
C_6H_5	C_6H_{11}	231 (4.18), 367 (1.76)	—
C_6H_5	$C(CH_3)_3$	229 (4.24), 368 (1.64)	—
CH_3	CH_3	230 (3.99), 353 (1.89)[c]	356 (1.89), 372.5(1.71)
CH_3	$CH_2C_6H_5$	237 (3.95), 365.5(1.86)	359 (1.84), 374 (1.75)
CH_3	$CH_2CH_2C_6H_5$	235.5(3.93), 364 (1.92)	360.5(1.89), 376 (1.74)

a) determined in EtOH solution
b) infl=inflection point,
c) 360 (2.03) in $CHCl_3$, 342 (1.87) in H_2O

ponding signals of the two sets showed reasonable change as the alkyl becomes to have more branching at the α-carbon. Generally the intensity ratio of the doublet signals at *ca.* δ 5.7 against the doublet signals at *ca.* δ 4.9 gave *anti* and *syn* equilibrium proportion in deuteriochloroform, as can be seen in Table III. Conformational analysis of the crystal form was

syn *anti*

TABLE III. NMR Spectral Data[a] of $R^1CONHCH_2N(NO)R^2$

R^1	R^2	Ratio, (%)		Chemical shifts, δ ppm[b]									
				>N-CH_2-N<		α-CH_2 (R^2)		α-CH_3 (R^2)		β-CH_3 (R^2)		CH_3CO	
		syn	*anti*	*anti*	*syn*	*syn*	*anti*	*syn*	*anti*	*syn*	*anti*	*anti*	*syn*
C_6H_5	CH_3	23	77	5.74	5.01			3.92	3.12				
C_6H_5	C_2H_5	46	54	5.73	4.96	4.29	3.68			1.47	1.09		
C_6H_5	$CH(CH_3)_2$	87	13	5.75	4.98					1.50	1.19		
C_6H_5	$C(CH_3)_3$	100	0	—	5.07					1.60	—		
C_6H_5	C_4H_9	58	42	5.67	4.90	4.20	3.59						
C_6H_5	C_8H_{17}	48	52	5.74	4.98	4.35	3.64						
C_6H_5	$CH_2C_6H_5$	52	48	5.70	4.82	5.40	4.79						
C_6H_5	$CH_2CH_2C_6H_5$	48	52	5.59	4.87	4.53	3.89						
C_6H_5	C_6H_{11}	90	10	5.77	5.00								
CH_3	CH_3	26	74	5.52	4.74			3.91	3.01			2.02	1.91
CH_3	$CH_2C_6H_5$	53	47	5.53	4.63	5.38	4.76					1.94	1.90
CH_3	$CH_2CH_2C_6H_5$	54	46	5.36	4.68	4.43	3.79					1.95	1.90

a) determined in 0.2 M $CDCl_3$ solution after 7 hr's standing,
b) relative to internal TMS

examined with the representative N-[(N-nitrosoisopropylamino)methyl]benzamide and N-[(N-nitrosomethylamino)methyl]benzamide by determining the *anti*/*syn* ratio as a function of time and extrapolating to the moment of dissolution. As results are shown in Fig. 1 the initial slopes suggest that their crystals are of *anti* conformation. Reexperiment with the materials recovered from their equilibrium solutions exhibited the same slopes. N-[(N-Nitrosoalkylamino)methyl]amide appears to tend to crystallize in *anti* conformation, since most of the materials showed higher proportion of *anti* isomer before equilibrium. The two nitrosoamines possessing bulkier alkyls, N-[(N-nitroso-*tert*-butylamino)methyl]benzamide and N-[(N-nitrosocyclohexylamino)methyl]benzamide, however, showed their NMR spectra exceeding in *syn* form even after immediate measurement. Effect of concentration in deuteriochloroform and of replacement of deuteriochloroform by benzene, methanol and trifluoroacetic acid can be seen in Table IV indicating rather small influences in isomer distribution.

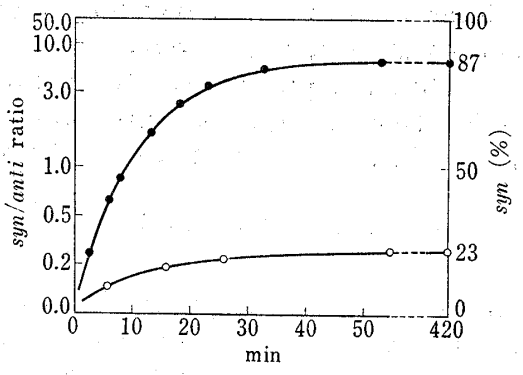

Fig. 1. *syn*/*anti* Ratio of $C_6H_5CONHCH_2$-N(NO)R in $CDCl_3$ Solution (0.2 M) as a Function of Time

—●—: R=$CH(CH_3)_2$
—○—: R=CH_3

Diazoalkane Synthesis

A convenient method for synthesis of diazoalkanes has now been provided by alkali decomposition of the N-[(N-nitrosoalkylamino)methyl]amides. They were shown to undergo moderate decomposition into diazoalkanes when warmed in alkali hydroxide medium. After examined for synthesizing phenyldiazomethane from N-[(N-nitrosobenzylamino)methyl]-benzamide selected as a representative, the best procedure was established as in the following.

Table IV. Effect of Solvent and Concentration on *syn*/*anti* Ratio of $C_6H_5CONHCH_2N(NO)R$

R	Solvent	Concentration M	Ratio,[a] (%)	
			syn	*anti*
CH_3	$CDCl_3$	2.0	20	80
CH_3	$CDCl_3$	0.2	23	77
$CH(CH_3)_2$	$CDCl_3$	2.0	75	25
$CH(CH_3)_2$	$CDCl_3$	0.2	87	13
$CH(CH_3)_2$	C_6H_6	0.2	75	25
$CH(CH_3)_2$	CH_3OH	0.2	70	30
$CH(CH_3)_2$	CF_3CO_2H[b]	0.2	66[c]	34[c]

a) determined after 7 hr's standing
b) Trifluoroacetic acid induces decomposition after standing for more than 30 min.
c) determined after 20 min's standing

N-[(N-Nitrosobenzylamino)methyl]benzamide was submitted to heating in a stirred diethyleneglycol solution of a large excess of potassium hydroxide, over which petroleum ether was layered, at a petroleum ether-refluxing temperature, while phenyldiazomethane was transferred into the petroleum ether layer as it was formed. Yield of phenyldiazomethane was determined by its conversion into benzyl *p*-nitrobenzoate. Better yield of phenyldiazomethane from N-[(N-nitrosobenzylamino)methyl]benzamide than from its acetamide analog was obtained, 60% and 52%, respectively. The same procedure was successfully extended for synthesizing other liquid diazoalkanes, 1-diazo-2-phenylethane and 1-diazooctane, from the corresponding N-[(N-nitrosoalkylamino)methyl]benzamides in 52% and 58% yield, respectively. For synthesizing gaseous diazoalkanes from the nitrosoamines possessing smaller alkyls, the procedure was conveniently carried out by the use of ether in place of petroleum ether in the above method, where distillation was allowed to give diazoalkane as a topping ethereal solution. By this procedure diazomethane, diazoethane and 1-diazobutane were obtained as their ethereal solutions from the corresponding N-[(N-nitrosoalkylamino)methyl]benzamides in 75%, 65% and 44% yield, respectively.

With a representative N-[(N-nitrosomethylamino)methyl]benzamide treatment of the residual diethyleneglycol solution gave considerable amount (88% yield) of N,N′-methylenebisbenzamide. Consequently, overall reaction equation can be written as follows.

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

In the reaction actually formaldehyde itself was not detected at all, presumably owing to its sensitivity in the strong alkaline medium.

The above representative data indicate general well-applicability of this method for synthesizing a wide range of either liquid or gaseous diazoalkanes, of course with the exception of C-dialkyl-substituted diazomethanes which have been known[7] to be unstable enough even in solution. After advent of many diazoalkane-generating agents (mostly for diazomethane) bis-(N-methyl-N-nitroso)terephthalamide[8] and N-methyl-N-nitroso-*p*-toluenesulfonamide[9] are widely favored at present. Although one of the problems has been a search for stable nitroso reagent, these two are still not entirely stable, as known to be denatured after long

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storage. The N-[(N-nitrosoalkylamino)methyl]amide reagents are stable enough to be indefinitely stored, which are of the N-nitroso type not of the known amide-, amidino- and sulfonamide-nitrogens but of secondary amine nitrogen. Furthermore, the applicability for synthesizing liquid diazoalkanes owes to insolubilities of the materials in petroleum ether and the other non-polar solvents, contrary to the prevailing above two reagents. The materials can be easily prepared by the nitrosation of N-[(alkylamino)methyl]amide hydrochlorides which are obtained in high yields by the reaction among formaldehyde, amide and primary amine hydrochloride.[2] Yields of diazoalkanes are comparable with those of any previous methods. From these view the present method, with simplicity and rapidity of the procedure, appears excellent for syntheses of not only diazomethane but also a variety of diazoalkanes.

An abundance of papers have reported the displacement reactions of the compounds of amidomethyl- and imidomethyl-linking heteroatoms with nucleophiles. A reaction pattern resembling the diazoalkane-generating reaction has appeared as the displacement at benzamidomethyl carbon of N-(dialkylaminomethyl)benzamide with nucleophiles such as sulfides,[10-12] carbanions,[13] amines[14,15] and amides,[14] usually being accompanied with the displacement at dialkylaminomethyl carbon. A mechanistic treatment[12] has referred this reaction probably to β-elimination involving an intermediate, N-methylenebenzamide. In Chart 1 is described β-elimination mechanism for the diazoalkane-generating reaction as a most probable one. Diazoalkane should be derived from the resulting diazoate as previously

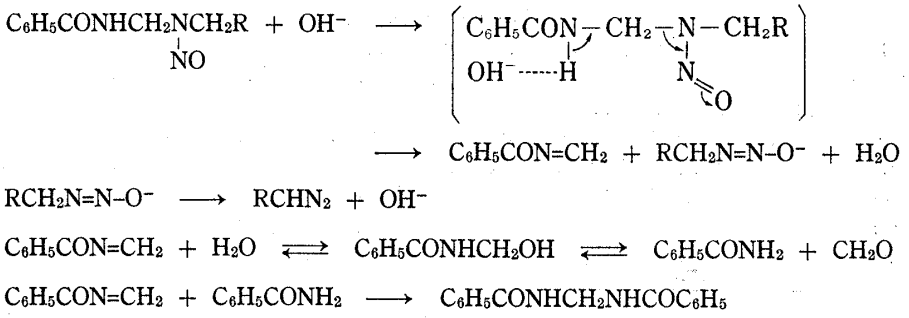

Chart 1

stated.[16] The formation of N,N′-methylenebisbenzamide is probable as a result of an interaction between N-methylenebenzamide and its hydrolyzed species, benzamide. In the course of the formation of the latter N-(hydroxymethyl)benzamide is referred to as an intermediate. This synthetically available compound brought about the production of N,N′-methylenebisbenzamide in high yield by reacting in the diazoalkane-generating medium. Mechanistically this reaction can be said to involve a reverse formation of N-methylenebenzamide which may proceed through β-elimination similar to the initial step.

Experimental

All melting points are uncorrected. UV spectra were recorded on a Hitachi EPS-3T spectrophotometer. Infrared (IR) spectra were obtained with a Hitachi EPI-G2 spectrophotometer. NMR spectra were taken with a Hitachi R-24 spectrometer using tetramethylsilane (TMS) as internal standard.

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N-[(N-Nitrosoalkylamino)methyl]amides——Into a saturated aqueous solution of 0.1 mole of N-[(alkylamino)methyl]amide hydrochloride[2] at 50—60° 5 ml of 35% HCl was added and then a solution of 8.3 g (0.12 mole) of $NaNO_2$ in 30 ml of H_2O was dropwise added with vigorous stirring. Stirring at this temperature was continued for further 30 min. After ice-cooling the resulting white precipitates in the reaction mixture were collected by filtration, washed with a small amount of H_2O and recrystallized from appropriate solvent. Only in the run with N-[(N-nitrosomethylamino)methyl]acetamide the product was liberated as oily material in the reaction solution, which was crystallized by drying its chloroform extract followed by evaporation. Yield, 75—90%. Physical and analytical data of the obtained nitrosoamines are recorded in Table I.

Diazoalkanes——Method A (for Liquid Diazoalkanes): To a solution of 5.6 g of KOH dissolved in 15 ml of diethyleneglycol 0.05 mole of finely pulverized N-[(N-nitrosoalkylamino)methyl]benzamide was added and then 80 ml of petr. ether was layered over. The mixture was stirred under refluxing of the petr. ether layer for about 30 min. Process of the reaction was indicated by color appearance characteristic of diazoalkane. After cooling the petr. ether layer was separated easily by decantation from the viscous lower layer. By addition of 20—30 ml of H_2O to the diethyleneglycol layer additional diazoalkane was liberated, which was extracted with petr. ether. The combined petr. ether solution was dried over anhydrous $MgSO_4$. Content of diazoalkane was determined by its conversion into alkyl *p*-nitrobenzoate as in the following. To a suspension of sufficient excess of *p*-nitrobenzoic acid in ether the above diazoalkane solution was dropwise added with stirring. The mixture was allowed to stand so long after disappearance of the color. Excess of *p*-nitrobenzoic acid was removed by washing with aqueous NaOH. After dried over anhydrous $MgSO_4$ evaporation gave alkyl *p*-nitrobenzoate, which weighed. By the above procedure phenyldiazomethane, 1-phenyl-2-diazoethane and 1-diazooctane were obtained from the corresponding N-[(N-nitrosoalkylamino)methyl]benzamides and their yields were estimated at 60%, 52%, and 58%, respectively, from weights of the corresponding alkyl *p*-nitrobenzoate obtained.

Benzyl *p*-nitrobenzoate, leaflets from isopropyl ether, mp 77—78°. *Anal.* Calcd. for $C_{14}H_{11}O_4N$: C, 65.36; H, 4.31; N, 5.45. Found: C, 65.56; H, 4.58; N, 5.48.

Phenethyl *p*-nitrobenzoate, leaflets from isopropyl ether, mp 58—59°. *Anal.* Calcd. for $C_{15}H_{13}O_4N$: C, 66.41; H, 4.83; N, 5.16. Found: C, 66.14; H, 4.88; N, 5.12.

Octyl *p*-nitrobenzoate, bp 130—131° (0.03 mmHg). *Anal.* Calcd. for $C_{15}H_{21}O_4N$: C, 64.49; H, 7.58; N, 5.01. Found: C, 64.12; H, 7.71; N, 4.86.

Method B (for Gaseous Diazoalkanes): In a flask fitted with a Liebig condenser, top of which is connected with a condenser set for distillation, and a dropping funnel were placed a solution of 5.6 g of KOH in 15 ml of diethyleneglycol, 0.05 mole of finely pulverized N-[(N-nitrosoalkylamino)methyl]benzamide and 50 ml of dry ether. The mixture was magnetically stirred under refluxing of the ethereal layer. Soon after the reaction mixture turned yellow distillation was started by removal of cooling water from the Liebig condenser, and the distillate was collected in a flask in which 50 ml of ice-cooled dry ether was placed beforehand. During the distillation dry ether was dropwise added from the dropping funnel to maintain the initial volume of ether. The distillation was ended after the distillate became colorless. Content of diazoalkane in the distilled ethereal solution was determined by its conversion into alkyl *p*-nitrobenzoate similarly to the method A, which was processed by addition of excess *p*-nitrobenzoic acid into the solution. By the above procedure yields of diazomethane, diazoethane and 1-diazobutane obtained from the corresponding N-[(N-nitrosoalkylamino)methyl]benzamides were estimated at 75%, 65%, and 44%, respectively.

Methyl *p*-nitrobenzoate, leaflets from isopropyl ether, mp 91—92°. *Anal.* Calcd. for $C_8H_7O_4N$: C, 53.04; H, 3.90; N, 7.73. Found: C, 53.10; H, 4.01; N, 7.72.

Ethyl *p*-nitrobenzoate, leaflets from isopropyl ether, mp 54°. *Anal.* Calcd. for $C_9H_9O_4N$: C, 55.38; H, 4.65; N, 7.18. Found: C, 55.42; H, 4.70; N, 7.11.

Butyl *p*-nitrobenzoate, leaflets from isopropyl ether, mp 33°. *Anal.* Calcd. for $C_{11}H_{13}O_4N$: C, 59.18; H, 5.87; N, 6.28. Found: C, 59.27; H, 5.84; N, 6.22.

In the selected run with N-[(N-nitrosomethylamino)methyl]benzamide, from the residual diethyleneglycol solution N,N′-methylenebisbenzamide was obtained in 88% yield by the same treatment as described in the following experiment.

N,N′-Methylenebisbenzamide——To a solution of 5.6 g of KOH in 15 ml of diethyleneglycol 7.1 g of N-(hydroxymethyl)benzamide was added. The mixture was stirred at 40—50° for 1 hr. A part of N,N′-methylenebisbenzamide was deposited by addition of H_2O and neutralization with aqueous HCl. Most of the product was obtained by concentration of the filtrate followed by washing of the resulting residue with H_2O. Total yield, 5.8 g (90%). Needles from EtOH, mp 218° (lit.[17] mp 218—219°). *Anal.* Calcd. for $C_{15}H_{14}O_2N_2$: C, 70.85; H, 5.55; N, 11.02. Found: C, 71.01; H, 5.61; N, 11.23.

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