3,6-Bis(4-methoxyphenyl)-1,2,4,5-tetrazine (2j). mp 221-223 ℃) lit[19] mp 151 ℃): ^{1}H NMR ($CDCl_3$) δ 8.64-8.41 (m, 4H), 7.15-7.05 (m, 4H), 3.93 (s, 6H); Mass m/z 294 (M^+, 3), 268 (20), 134 (30), 133 (100); Anal. Calcd for $C_{16}H_{14}N_4O_2$: C, 65.31; H, 4.76; N, 19.05. Found: C, 65.62; H, 4.97; N, 19.03.

3,6-Bis(2'-pyridyl)-1,2,4,5-tetrazine (2k). mp 222 ℃ (lit[22]., mp 224 ℃); NMR ($CDCl_3$-DMSO-d_6) δ 8.80-7.45 (m, 8H); Mass m/z 236 (M^+, 10), 105 (12), 104 (100), 77 (18). Anal. Calcd for $C_{12}H_8N_6$: C, 61.02, H, 3.39; N, 35.59. Found: C, 61.05; H, 3.38; N, 35.57.

3,6-Bis(4'-pyridyl)-1,2,4,5-tetrazine (2l). mp 254 ℃ (lit[22]., mp 256 ℃): ^{1}H NMR ($CDCl_3$-DMSO-d_6) δ 9.00-8.93 (m, 4H), 8.55-8.47 (m, 4H); Mass m/z 236 (M^+, 12), 105 (15), 104 (100), 77 (18); Anal. Calcd for $C_{12}H_8N_6$: C, 61.02; H, 3.39; N, 35.59. Found: C, 61.07; H, 3.41; N, 35.52.

3,6-Dibenzyl-1,2,4,5-tetrazine (2m). mp 74 ℃ (lit[23], mp 74 ℃): ^{1}H NMR ($CDCl_3$) δ 7.30-7.20 (broad singlet, 10H), 4.56 (s, 4H); Mass m/z 262 (M^+, 1), 117 (100), 90 (54); Anal. Calcd for $C_{16}H_{14}N_4$: C, 73.28; H, 5.34; N, 21.37. Found: C, 73.32; H, 5.65; N, 21.33.

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Alcoholysis of Primary Amides to Esters by Sodium Nitrite or *t*-Butyl Nitrite/Chlorotrimethylsilane Pairs

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Amides are very stable and one of the least reactive acid derivatives. Although unsubstituted carboxamides are readily prepared from the corresponding more reactive acid halides and esters, the reverse transformation is often difficult.[1] The existing methods for the hydrolysis of amides usually call for a treatment with a strong acid or base under reaction conditions generally incompatible with sensitive substrates.[1] Alcoholysis of carboxamide to esters are even more difficult. Strong acids or bases in alcohol solvents are required for the alcoholysis.[1,2]

A number of nitrosating agents were reported to be effective for the hydrolysis of amides. Nitrogen tetroxide,[3] butyl

Table 1. Alcoholysis of Primary Amides to Esters Using Chlorotrimethylsilane and Sodium Nitrite or *t*-Butyl Nitrite in Alcohol Solvent[a]

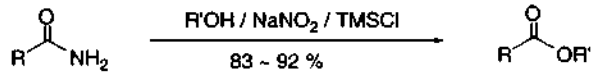
Entry	Amide	Alcohol	Nitrite	Reaction Time (hr)	Esters % Yield[b]
1	*p*-nitrobenzamide	CH_3OH	$NaNO_2$	10	98 (94)
2		CH_3OH	*t*-BuONO	8	99 (92)
3		CH_3CH_2OH	$NaNO_2$	12	100 (94)
4	*p*-methoxybenzamide	CH_3OH	$NaNO_2$	12	97 (90)
5		CH_3OH	*t*-BuONO	8	98 (91)
6		CH_3CH_2OH	$NaNO_2$	11	95 (87)
7	pivalamide	CH_3OH	NH_4NO_2	10	95 (94)
8		CH_3CH_2OH	$NaNO_2$	10	97
9	hexanamide	CH_3OH	NH_4NO_2	7	98 (92)
10		CH_3CH_2OH	$NaNO_2$	10	99 (94)
11		CH_3CH_2OH	*t*-BuONO	12	99
12	cyanoacetamide	CH_3OH	$NaNO_2$	10	88 (83)
13	acetamide	CH_3CH_2OH	$NaNO_2$	10	99
14		$CH_3(CH_2)_3OH$[c]	$NaNO_2$	10	96 (90)
15		$C_6H_5CH_2OH$[c]	$NaNO_2$	10	96 (89)
16		$C_6H_{12}OH$[c]	$NaNO_2$	12	92 (89)
17	*N*-methyl-*o*-toluamide	CH_3OH	$NaNO_2$	25	NR[d]
18		CH_3OH	*t*-BuONO	23	NR[d]
19	*N*-benzylbenzamide	CH_3OH	$NaNO_2$	23	NR[d]
20	*p*-toluenesulfonamide	CH_3OH	$NaNO_2$	28	NR[d]

[a] Molar ratios of amide : $NaNO_2$ (or NH_4NO_2) : TMSCl = 1 : 2 : 4, and amide : *t*-BuONO : TMSCl = 1 : 1.5 : 2.0 were used. Reaction mixture was refluxed for the period shown. [b] GC yield. Isolated yields in the parenthesis. Not optimized. [c] 30-50% molar excess of alcohol (butanol, benzyl alcohol, and cyclohexanol) was employed using acetonitrile as a solvent. [d] The starting material was recovered unreacted.

nitrite-hydrogen chloride,[4] nitrosonium tetrafluoroborate,[5] and nitrosylsulfuric acid[6] are such nitrosonium donors. These reagents have disadvantages in handling and availability. We now report that sodium nitrite-chlorotrimethylsilane in alcohol solvent are remarkably effective for the alcoholysis of primary amides.

In holoalkane solvents, sodium nitrite or alkyl nitrites react with chlorotrimethylsilane and generates nitrosyl chloride.[7] The reagent pairs serve as excellent nitrosonium donors in the regeneration of carbonyl compounds from oximes,[7] hydrazones, and 1,3-dithianes. They were found to be also effective for the transformation of anilines to aryl halides[8] *via* diazonium formation.

When *p*-Nitrobenzamide was added to the stirring mixture of sodium nitrite and chlorotrimethylsilane in methanol and brought to reflux, the amide was converted to the corresponding ester in almost quantitative yield. Addition of a catalytic amount of benzyltriethylammonium accelerates the reaction and shortens the reaction time.



Methanolysis of other aromatic as well as aliphatic primary amides with sodium nitrite and chlorotrimethylsilane in methanol produced the corresponding methyl esters in high yields (entry 1, 4, 9, 12, 17). Various esters similarly obtained are listed in Table 1. Even the sterically very hindered trimethylacetamide (pivalamide) produced the corresponding esters in an excellent yield.

Ammonium nitrite can be used instead of sodium nitrite, and ammonium nitrite-chlorotrimethylsilane pair were equally effective for the methanolysis of amides (entry 7, 9). Using ethanol as a solvent, the corresponding ethyl esters were obtained from primary amides following the similar procedure (entry 3, 6, 8, 10, 12). Alkoxy, nitro, halogen, cyano, and carbonyl substituents on the phenyl ring or on the alkyl chain did not cause any problems under the reaction conditions.

t-Butyl nitrite-chlorotrimethylsilane pair in methanol were also found to be effective for the methanolysis of amides (entry 2, 5, 11). A quaternary ammonium salt was not needed and only one equivalent of chlorotrimethylsilane was enough per equivalent of alkyl nitrile. Formation of *t*-butyl ester was not observed at all when *t*-butyl nitrite was used as a nitrosonium ion source.

When the reaction was carried out in the presence of an alcohol other than methanol and ethanol, the corresponding esters could be obtained. In a better and more convenient proceaure a slight excess of an alcohol was employed using acetonitrile as a solvent. For example, when a mixture of acetamide and butanol was allowed to react with chlorotrimethylsilane-sodium nitrite in acetonitrile, butyl acetate was obtained in 96% yield (entry 14). Similarly, benzyl and cyclohexyl acetate were produced from acetamide using benzyl alcohol and cyclohexanol, respectively (entry 15, 16).[9]

In the methanolysis of the amides by *t*-butyl nitrite and chlorotrimethylsilane, nitrosyl chloride seems to be formed and serve as a nitrosonium ion donor. This formation of nitrosyl chloride from the reaction of alkyl nitrites with chlorotrimethylsilane was reported earlier.[10] When sodium nitrite and chlorotrimethylsilane were mixed in the presence of an alcohol, the corresponding alkyl nitrite was produced in high yield with the evolution of hydrogen chloride.[11] A part of the alkyl nitrite undergo a further reaction with chlorotrimethylsilane resulting in the formation of nitrosyl chloride along with alkoxytrimethylsilane.

Although the nitrogen atom of an amide is a poor electron pair donor, the amide is *N*-nitrosated by nitrosyl chloride generated from the reaction of chlorotrimethylsilane with either sodium nitrite or *t*-butyl nitrite. The *N*-nitrosamide rearranges and subsequently loses water to produce an acyldiazonium ion, which can be readily alcoholized to an ester. An acyldiazonium ion was the postulated intermediate in the hydrolysis of amides using nitrosating agents.[3~6]

N-Alkylamides failed to produce the corresponding esters in the reaction with chlorotrimethylsilane-sodium nitrite pair in methanol (entry 17-19). *p*-Toluenesulfonamide was not

converted to the sulfonate ester, either (entry 20). Despite of this limitation, the present method would be advantageous over the existing ones, because of the mild reaction conditions and high yields.

Experimental

Alcoholysis of amides by sodium nitrite-chlorotrimethylsilane. To a stirred solution of an amide (10 mmol), sodium nitrite (1.4 g, 20 mmol) and benzyltriethylammonium chloride (0.22 g, 1 mmol) in 20 mL of methanol was added chlorotrimethylsilane (4.3 g, 40 mmol). After 7-12 hours of reflux, the crude reaction mixture was analyzed by TLC or GC. The reaction mixture was treated with water (50 mL) and the product was extracted with ether (20 mL) twice. The combined ether extract was dried over anhydrous magnesium sulfate. The filtrate was concentrated on a rotatory-evaporator. The residue was purified either by silica gel column chromatography or by distillation through a short path.

Alcoholysis of amides by *t*-butyl nitrite-chlorotrimethylsilane. To a stirred solution of *t*-butyl nitrite (1.1 g, 15 mmol), an amide (10 mmol) in 20 mL of methanol was added chlorotrimethylsilane (2.2 g, 20 mmol). After refluxing the mixture for 14 hours, the product was isolated and purified following the procedure described above.

Acetylation of alcohols by acetamide in acetonitrile. In a 50 mL flask were placed sodium nitrite (20 mmol), acetamide (10 mmol), and an alcohol (30% excess) and acetonitrile (20 mL). Chlorotrimethylsilane (20 mL) was added to the mixture. After 10-12 hours of reflux, the crude reaction mixture was filtered and concentrated. The residue was treated with water, and extracted with ether. The product was isolated and purified following the procedure described above.

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Ab initio and Spectroscopic Studies of Bis(4,4-dimethyl-2,5-cyclohexadiene-1-ylidene)

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The electronic structure of the cross conjugated polyenes has drawn a great deal of attention due to their central double bond distortion in the electronically excited and low-lying ionized doublet states.[1,2] Evidence of this structural behavior is supported by the spectroscopic observation that the spectral shape of bis(4,4-dimethyl-2,5-cyclohexadiene-1-ylidene) (I) in the fundamental state corresponds to that of biphenyl (II) in the first electronically excited state and vice versa.[3] This spectroscopic behavior is explained by the specific difference of their π-electron distribution.[3]

The molecular structure of I has been studied in the gas phase[4] and crystal[5] by the gas electron and X-ray diffraction methods, respectively. In the gas phase, molecule I was found to have a dihedral angle of 9.7° in nonplanar carbocyclic rings that is described by C_6-C_1-C_2=C_3.[4] In the crystal, however, the molecule was found to deviate from planarity to different extent such that the torsional angles about single bonds and double bonds vary by only 5.1° and 1.2°, respectively.[5] It is noted for comparison that the torsional angle of the bond between the two phenyl rings in II is about 42° in the gas phase. In the solid state, however, the biphenyl molecule is planar.[6~10] This can be taken as an indication that crystal packing forces are sufficiently large to favorably compensate the steric strain. All six-membered rings are slightly in boat conformations due to the interactions between the ortho hydrogen atoms across the central double bond.[5]

Here we report fluorescence excitation spectroscopic studies of I cooled in pulsed supersonic expansions of He in the ranges 307-345 nm and *ab initio* studies of the electronic