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N,Ń-술피닐 비스 1,2,4-트리아졸을 이용한 에스테르와 β-락탐의 합성

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〈要 約〉

N,Ń-술피닐 비스-1,2,4-트리아졸은 THF용매에서 $SOCl_2$, 아민 및 1,2,4-트리아졸로부터 쉽게 만들어진다. 이 화합물은 카르복시산의 직접 에스테르화 축합제로, 또한 β-아미노산으로부터 β-락탐을 만드는 탈수제로 이용될 수 있었다. 이 방법을 몇가지 카르복시산과 β-아미노산에 적용시켜 보았다.

이 합성시약의 이점은 첫째 반응 후 형성되는 1,2,4-트리아졸이 중성이기 때문에 대부분의 반응이 거의 중성에서 이루어질 수 있다는 점과 둘째로 1,2,4-트리아졸이 물에 잘 녹기 때문에 일반적인 물에 의한 처리로 생성물을 정제할 수 있어서 유기합성에 흔히 사용되는 크로마토그라피에 의한 분리가 요구되지 않는다는 점이다.

Synthesis of Esters and β-Lactams Using N,Ń-Sulfinyl bis-1,2,4-triazole

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〈Abstract〉

N,Ń-Sulfinyl bis-1,2,4-triazole was conveniently prepared by the reaction of thionyl chloride with 1,2,4-triazole. The reagent was efficient for the direct esterification of carboxylic acids and could be used as dehydrating reagent for the preparation of β-lactams from several β-amino acids.

Several noteworthy featrures of this reagent are apparent as compared with previously known reagents. First, since the 1,2,4-triazole formed as only byproduct is a neutral compound, the reactions occur normally under neutral conditions. Second, the present methods are much simpler and less laborious than the conventional methods because obtained byproduct, 1,2,4-triazole can be easily removed by the usual aqueous workup and does not require chromatographic separation in most cases.

Introduction

As synthetic organic chemists attempt synthesis of increasingly complex molecules, the need for efficient, mild and selective functional group transformation and elaboration become even more apparent. The use of the dehydrating agent for such conversion is not a new idea and began with earyl history of chemistry. Nowadays, a variety of

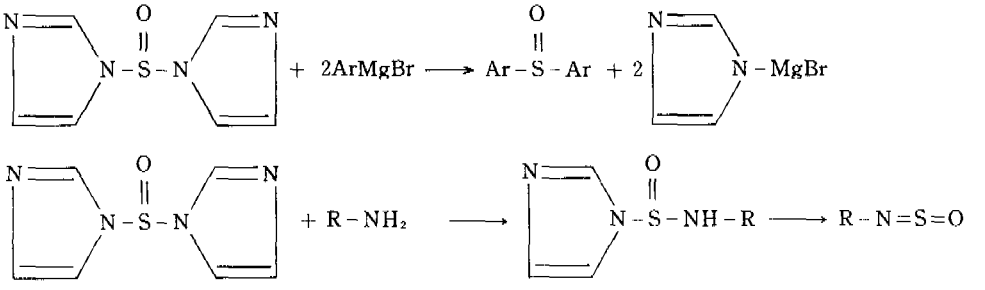
dehydrating agents including inorganic and organic compounds have been developed and widely studied as reagents for organic synthesis.[1]

The widespread use of dehydrating agents on organic synthesis and manipulation of complex organic molecules led to numerous agents available and some of them are very useful for selective conversion of bifunctional compounds. The reagent, developed formerly for the dehydration reaction of organic compound may be also applicable for other reactions like dehydrosulfurization of organosulfur compounds.

Although many reliable methods for dehydration reaction have been reported in the literature-,[2] a great need still exists for a versatile and simple process, whereby complex molecules may be synthesized under very mild conditions.

Phosgene, phosphorus (oxy)chlorides, and thionly chloride are oldest and most widely used reagents for the purpose till now. But their severe toxicity, inconvenience for handling and generation of hydrogen chloride gas prompted many synthetic chemists to develop their derivatives or completely new agents.

Concerning thionyl chloride derived condensing agents, N,Ñ - sulfinyl diimidazole[3] has been known for a long time and it is useful for the synthesis of diaryl sulfoxide and N - sulfonamine.

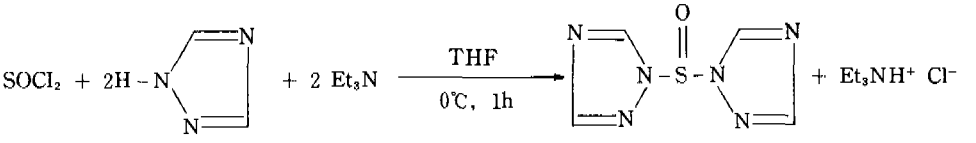


Since several noteworthy features with 1,1́-sulfinyl bis-1,2,4-triazole could be expected, the author has studied the synthetic utility of 1,1́-sulfinyl bis-1,2,4-triazole. It includes the followings. (i) 1,1́-thiocabonyl 1,2,4-triazole is more reactive than 1,1́-thiocabonyl diimidazole.[4] Thus, it is expected that 1,1́-sulfinyl bis-1,2,4-triazole may be more reactive than N,Ñ-sulfinyl diimidazole. (ii)N,Ñ-sufinyl diimidazole produces basic imidazole (pKa 6.95) as a product, Which might cause some problems in the synthesis of base sensitive compounds. However, 1,2,4-triazole(pKa 2.55) is much less basic than imidazole and could avoid such problems.[5] (iii) comparison of the reactivity with other similar reagents would be useful to determine the utility of thiocarbonyl derived condensing agents. (iv) furthermore, thionyl chloride derived condensing agents have not extensively studied.

Results and Discussion

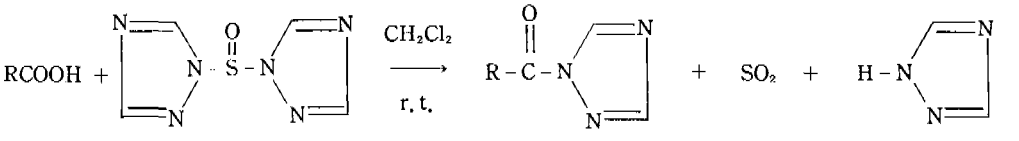
1. Preparation of 1,1́-Sulfinyl bis-1,2,4-triazole

1,1́-Sulfinyl bis-1,2,4-triazole was easily prepared by the reaction of thionyl chloride with 2 equiv of 1,2,4-triazole and triethylamine in tetrahydrofuran at 0℃. Since 1,1́-sulfinyl bis-1,2,4-triazole was hydrolyzed during aqueous workup or silica gel column chromatographic purification, it was used as a crude form after removal of triethylamine hydrochloride and subsequent solvent removal. 1,1́-Sulfinyl bis-1,2,4-triazole was obtained in 85-95% yield as a yellow solid and could be stored in a fefrigerator for a week without any decomposition.



2. Preparation of 1-Acyl 1,2,4-triazole

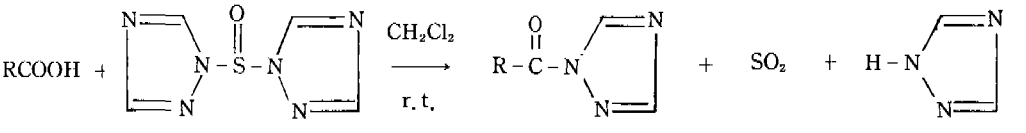
Synthetic usefulness of acylimidazole has been demonstrated in the synthesis of ketones, esters, and thioesters and its partial reduction to aldehydes.[6] Thus, it is expected that 1-acyl 1,2,4-triazole could show similar behaviors, as compared with acyl imidazole. Most unhindered aliphatic carboxylic acids, upon treatment with equimolar amount of the reagent, yielded the corresponding 1-acyl 1,2,4-triazole smoothly and rapidly in high yields at room temperature without the formation of anhydride (eq.1). The resulting 1,2,4-triazole was easily removed by filtration with a short silica gel column.



(eq. 1)

In the case of sterically hindered acids, such as pivalic acid, 1-pivaloyl 1,2,4-triazole was unstable and underwent decomposition to some extent during the filtration. Furthermore, the reaction with benzoic acid occurred very slowly and a small amount of benzoic anhydride was formed. Pure benzoyl 1,2,4-triazole was separated from the anhydride and thus the yield of triazolide was somewhat reduced during separation by the column chromatography. Some experimental results are summarized in Table 1.

Table 1. Preparation of 1-Acyl 1,2,4-triazolide.



R	Time, h	Yield, %[a]
$CH_3(CH_2)_6$	0.5	97
$PhCH_2CH_2CH_2$	0.5	97
Cyclohexyl	0.5	96
$PhCH_2$	1	80
$(CH_3)_3C$	0.5	59
Ph	24	75

a : The isolated yield of the corresponding 1,2,4-triazolide.

3. Alcoholysis of 1-Acyl 1,2,4-triazolides into Esters.

The conversion of 1-acyl 1,2,4-triazolides into esters has been investigated. The experimental results are tabulated in Table 2.

When 1-phenylacetyl triazolide was carried out with benzyl alcohol in absence of base, the reaction did not occur. However, in the presence of an equimolar amount of DMAP,[7] alcoholysis of primary aliphatic 1-acyl 1,2,4-triazolide into the corresponding esters proceeded cleanly at room temperature in methylene chloride. The reaction was complete within 3 h, indicating that 1-acyl 1,2,4-triazole is more reactive than 1-acyl imidazole. The use of triethylamine was less effective in terms of yield and reaction time, although the ester was obtained in a good yield. In case of the reaction of 1-benzoyl 1,2,4-triazolide, alcoholysis proceeded slowly. Furthermore, alcoholysis of 1-acyl triazole with tertiary butanol did not occur under the present condition.

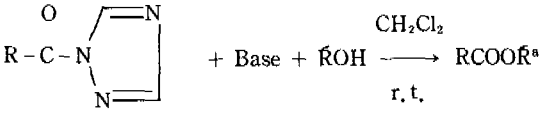


Table 2. Conversion of 1-Acyl 1,2,4-triazolides into Esters.

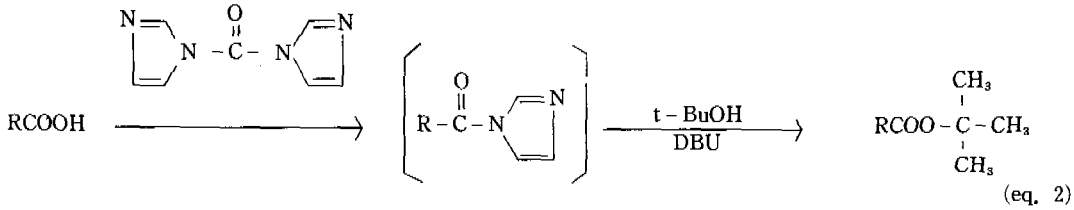
R	R̂OH	Base	Time, h	Yield, (%)
$PhCH_2$	$PhCH_2OH$	none	3	0
$PhCH_2CH_2CH_2$	$PhCH_2OH$	Et_3N	3	77
$PhCH_2CH_2CH_2$	$PhCH_2OH$	DMAP[b]	3	78
$PhCH_2CH_2CH_2$	$PhCH_2OH$	DMAP	2	95
$CH_3(CH_2)_7$	$PhCH_2OH$	DMAP	3	98
$PhCH_2$	$PhCH_2OH$	DMAP	1	96
Ph	$PhCH_2OH$	DMAP	2	48
$PhCH_2CH_2CH_2$	$(Ph)_2CH_2OH$	DMAP	3	85
$PhCH_2CH_2CH_2$	$CH_3CH_2(CH_3)_2COH$	DMAP	24	0

a ; 1.2 equiv of base were used.

b ; 0.1 equiv of DMAP was used.

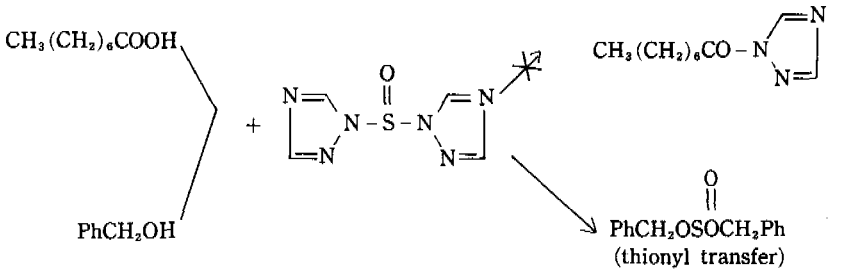
4. Direct Esterification of Carboxylic Acids using 1,1̂-sulfinyl bis-1,2,4-triazole.

It was reported that carbonyl diimidazole (CDI) could useful for the preparation of esters in the presence of small amount of sodium alkoxide or an equimolar amount of N-bromosuccinimide (NBS).[8] But this method is not applicable to alkanoic acids having one or two H-atoms at C-2 because of the competitive formation of 3-oxoalkanoic esters. Recently, S. Ohta et al[9] reported an improved procedure by using an equimolar amounts of DBU(1,8-diazabicyclo (5,4,0) 7-undecene) instead of alkoxide or NBS(eq. 2).



(eq. 2)

As shown in eq. 2, it is believed that the esterification may be proceeded via 1 - acyl imidazolide. Because alkanoyl 1,2,4 - triazolides are easily formed by using 1,1̂ - sulfinyl bis - 1,2,4 - triazole, we expected that our reagent might be useful for the esterification and decided to investigate the usefulness of our reagent for the esterification. At first, the author tried to investigate the possibility of direct esterification using only equimolar amounts of 1,1̂ - sulfinyl bis - 1,2,4 - triazole, a carboxylic acid, and an alcohol. When the reagent was added to a solution of caprylic acid and benzyl alcohol in methylene chloride at room temperature, benzyl caprylate was not isolated but dibenzyl sulfite was obtained due to the transfer of thionyl group(eq. 3)

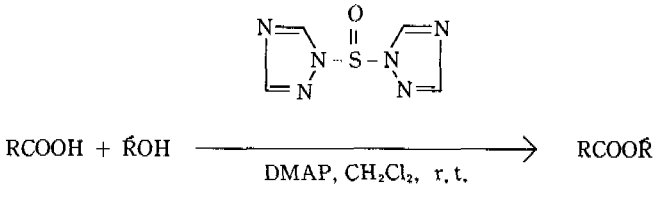


(eq. 3)

In order to suppress thionyl transfer reaction, some organic bases were added to the reaction mixture. As shown in Table 3, the esterification occurred in the presence of equimolar amounts of triethylamine, but yielding the desired esters in moderate yield(entry 2).

Thus, the author turned his attention to 4 - dimethyl aminopyridine (DMAP)[7]which is a highly active acylation catalyst. When phenylacetic acid was treated with an equimolar mixture of 2 - butanol and triethylamine in the presence of 0.1 equiv of DMAP in dichloromethane at room temperature for 24 h, the corresponding ester was obtained in only 52% yield.

Therefore, the author decided to carry out the esterification using equimolar amounts of DMAP(eq. 4). Treatment of equimolar amounts of phenyl acetic acid and 1,1̂ - sulfinyl bis - 1,2,4 - triazole with 1 equiv of DMAP and 1 equiv of benzyl alcohol in methylene chloride at room temperature for 1 h gave the benzyl phenylacetate in 85% yield after simple filtration through a short silica gel column(entry 5).



(eq. 4)

On the basis of the above results, esterification of several carboxylic acids and alcohols was carried out with equimolar amounts of DMAP and the reagent. Simple aliphatic acids like caprylic acid worked well with unhindered alcohols in high yields. However, in case of aromatic acid like benzoic acid, the reaction did not complete even after 24 h(entry 7). Furthermore, the use of acetonitrile as solvent did not improve the reaction.

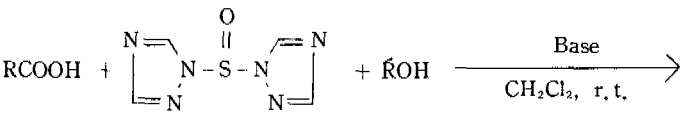


Table 3. Direct Esterification Using 1,1̂ - Sulfinyl bis - 1,2,4 - triazolide.

Entry	R	R̂	Base	Eq. of Base	Time, h	Product	Yield, %
1	$CH_3(CH_2)_7$	$PhCH_2$	none	—	5	$(PhCh_2O)_2SO$	98
2	Ph	n - Bu	Et_3N	1.0	20	PhCOO - n - Bu	62
3	$PhCH_2$	s - Bu	Et_3N	1.0	24	$PhCH_2COO$ - s - Bu	52
			DMAP	0.1			
4	$PhCH_2$	$PhCH_2$	Et_3N	1.0	20	$PhCH_2COOCH_2Ph$	55
			DMAP	0.1			
5	$PhCH_2$	$PhCH_2$	DMAP	1.0	1	$PhCH_2COOCH_2Ph$	85
6	$CH_3(CH_2)_8$	$PhCH_2$	DMAP	1.0	3	$CH_3(CH_2)_8COOCH_2Ph$	76
7	Ph	$PhCH_2$	DMAP	1.0	24	$PhCOOCH_2Ph$	76
8	Ph	$PhCH_2$	DMAP	1.0	5	$PhCOOCH_2Ph$	65[a]

a ; The reaction was carried out in acetonitrile at 60℃.

5. β - Lactam Formation from β - Amino Acids

β - Lactams are known to be key components of many biologically active compounds such as penicillin and cephalosphorin antibiotics.[10] Although a great deal of synthetic work has been already carried out in the formation of β - lactam ring, one of the most important methods is the dehydration of β - amino acids. However, known methods have some limited use because of dependency upon the structural features of a substrate, requirement of basic or acidic conditions, and a large excess of reagents or limitation of functional groups located at other parts of the molecule.

The cyclization through the use of reagents such as AcCl, PCl_3, and $SOCl_2$ has been accomplished in a limited number of case.[11] The base catalyzed cyclization of a β - amino acid ester using a Grignard reagents[12] as the base is often used, if the substituents are inert to the reagent and was improved recently by silylation of the amino group.

The cyclization of a β - amino acid ester was achieved with organoaluminum compounds[13] in a special case. The DCC method[14] is most commonly applied to β - lactam formation from β - amino acid, but the yields markedly depend upon the structural features and solvents employed. Recently, Mukaiyama reagents, $ph_3P(PyS)_2$[15] or 2 - chloro 1 - methyl pyridium iodide[16] have been reported to give the β - lactams in very high yields. However, these methods are needed rather high reaction temperature and tedious purification of the product.

In spite of many dehydrating agents for β - lactam synthesis, no report has been appeared for applications of thionyl chloride based reagents. This fact prompted us to examine the utility of thionyl compounds for such conversion. Recently it was found by S. Kim and et al that di - 2 - pyridyl sulfite is successfully applied to the β - lactam formation.[17] Therefore, extending the previous work, the author has investigated the possibility of intramoleular condensation of β - amino acids into

β-lactams with 1,1′-sulfinyl bis-1,2,4-triazole.

In order to find out optimum conditions, the author carried out several reactions by using a mixture of 3-(benzylamino) butyric acid and 1.2 equiv of 1,1′-sulfinyl bis-1,2,4-triazole as a model study and the results are summarized in Table 4.

The reaction occurred at room temperature in methylene chloride and N-benzyl-4-methyl-2-azetidinone was normally obtained in moderate yields. It is noteworthy that the presence of triethylamine and high dilution did not effect the yield of the β-lactam. However, high dilution and the precence of triethylane gave better results in acetonitrile. Tetrahydrofuran was also effective to some extent but it was slightly less satisfactory than acetonitrile. Based on a model study, the remaining reactions were carried out in the precence of 1 equiv of triethylamine in acetonitrile at 80℃. Some experimental results are summarized in Table 5.

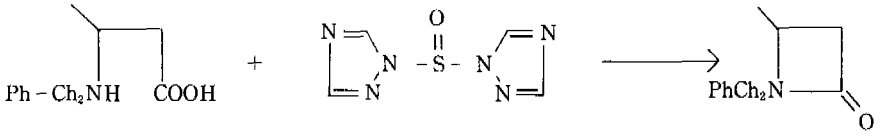


Table 4. Effect of Base, Solvent, Temperature, and Concentration on the Formation of β-Lactam from 3-Benzoylaminobutyric acid.

Solvent	Conc. M	Base	Temp. ℃	Time, h	Yield, %
CH_2Cl_2	0.1	none	r.t.	2	41
CH_2Cl_2	0.01	none	r.t.	12	40
CH_2Cl_2	0.01	Et_3N	r.t.	12	36
CH_2Cl_2	0.01	Et_3N[a]	r.t.	12	37
CH_3CN	0.01	none	80	2	48
CH_3CN	0.01	Et_3N	80	2	59
CH_3CN	0.1	none	80	2	18
THF	0.01	Et_3N	68	10	53

a ; 2 equiv of triethylamine were used.

In general, N-substituted β-amino acids were cyclized to the corresponding β-lactams in moderate yields. Furthermore, this method did not work with 2, 3-unsubstituted β-amino acids and N-substituted β-amino acids.

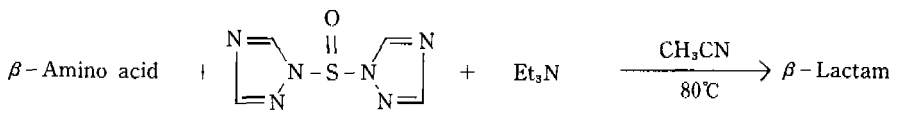
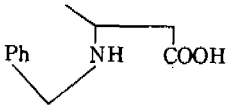
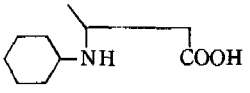
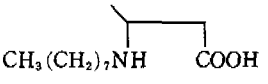
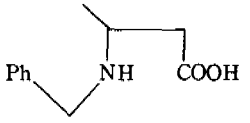
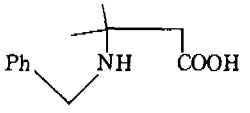
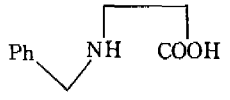
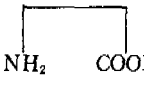


Table 5. β-Lactam Formation from β-Amino Aicds Using 1,1'-Sulfinyl bis-1,2,4-triazole.

β-Amino Acid	Time, h	Isolated Yield, %
	2	59
	2	52(42)[b]
	2	48
	2	58
	2	72
	2	5
	6	0

a ; Solutions were maintained at 0.01 M.

b ; The number in parenthesis indicates the yield when the reaction was carried out in absence of base.

CONCLUSION

1,1'-Sulfinyl bis-1,2,4-triazole was conveniently prepared by the reaction of thionyl chloride with 1,2,4-triazole. The reagent was efficient for the direct esterification of carboxylic acids and could be used as a dehydrating reagent for the preparation of β-lactams from β-amino acids. This method was applied to various different N-unsubstituted β-amino acid and 2,3-unsubstituted β-amino acids.

Several noteworthy features of the reagents are apparent as compared with previously known reagents. First, since 1,2,4-triazole(pKa 2.55), the only other product formed, is a neutral compound, the reactions occur normally under essentially neutral conditions. Second, the present methods are much simpler and less laborious than the conventional methods because water-soluble 1,2,4-triazole, can be completely removed by the usual aqueous workup and does not normally require chromatographic separation in most cases. Therefore, the author believed that the reagents should find many useful applications in organic synthesis.

Experimental

Instruments and Materials

^{1}H NMR spectra were recorded with Varian T-

60A or FT-80A spectrometers, and chemical shifts are expressed as δ-units relative to TMS. Infrared spectra were measured on a Perkin-Elmer 267 spectrometer and frequences are given in reciprocal centimeters. Mass spectra were obtained on a Hewlett Packard 5985A GC/MS system using electron impact (ET) method. Melting points were determined on an Electrothermal Melting point apparatus and uncorrected. Reported boiling points are those observed during distillation with a Kugelrohr apparatus and are uncorrected. Analytical thin layer chromatography (TLC) was performed on precoated glass plates (0.25mm) coated with silica gel 60F-254 (E. Merck). Merck silical gel 60(0.040-0.063mm and 0.063-0.200mm) were used for column chromatography.

Most of the reagents in this study were commercial products and when necessary, further purified by distillation or recystallization. Some compounds were prepared by known procedures and spectral and physical data of the products were in accord with reported data.

Methylene chloride were distilled over lithium aluminum hydride under nitrogen. Tetrahydrofuran was distilled under nitrogen from sodium-benzophenone kettle. Acetonitrile were distillld from phosphorous pentoxide. Toluene was refluxed over sodium for 12 h under nitrogen and distilled prior to use. Triethylamine and pyridine were purified by distillation from KOH.

1. Preparation of 1,1̄-Sulfinyl bis-1,2,4-triazole(SBT)

To a stirred solution of 1,2,4- (3.96g, 57.4mmol) and triethylamine (8.10ml, 58.8mmol) in dry tetrahydrofuran (80ml) at 0℃ under nitrogen was slowly added thionyl chloride (2.10ml, 28.0mmol). After the reaction mixture was stirred at 0℃ for 1h, triethylamine hydrochloride was removed by filtration and solvent removal under reduced pressure afforded 1,1̄-sulfinyl bis-1,2,4-triazole sulfite (4.33g, 82%) as a yellow solid(mp 98-101℃).

The 1H NMR spectrum ($CDCl_3$) of the reagent exhibit two singlets at 8.20 and 9.10 ppm and infrared spectrum(KBr) exhibited the absorption bands at 2850cm^{-1}. Mass spectrum did not show the molecular peak of the reagent ($C_4H_4ON_6S$), but almost coincided with that of 1,2,4-triazole. This may be due to the unstablitity of the reagent at high temperature.

2. Preparation of 1-phenylacetyl-1,2,4-triazolide

To a stirred solution of 1-phenyl acetic acid (171.5mg, 1.26mmol) in methylene chloride (4ml) was added 1,1̄-sulfinyl bis-1,2,4-triazole (250mg, 1.37mmol). After being stirred at room temperature for 1 h, the reaction mixture was concentrated to 1ml and filtered through a short column of silica gel using methylene chloride as an eluent to afford 1-phenyl-acetyl 1,2,4-triazolide as a white solid (145mg, 75%);mp 79-80℃;1H NMR ($CDCl_3$) 4.05(s, 2H), 7.15(s, 5H), 7.35(s, 1H) 8.08(s, 1H) ; IR(KBr) 1710cm^{-1} (C=O);Mass, m/e+(rel intensity) 187 (M+, 2.0), 119($PhCH_2CO$+, 9.4), 118(100.0), 91($PhCH_2$+, 71.7), 77(C_6H_5+, 1.2).

Physical and Spectral Data of 1-Acyl 1,2,4-triazolides.

1-Octanoyl 1,2,4-triazole ; mp 56-58℃ : 1H NMR ($CDCl_3$) 0.90-1.15(m, 3H), 1.20-2.30(m, 10H), 3.20(br t, 3H), 0.85(s, 1H), 9.02(s, 1H) : IR(KBr) 1718(C=O).

1-(4-phenyl)-butanoyl 1,2,4-triazole ; mp 62-63℃ : 1H NMR ($CDCl_3$) 2.00-2.48(m, 2H), 2.55-2.90(m, 2H), 3.12(t, 2H, J=8Hz), 7.19(s, 5H), 8.00(s, 1H), 8.95(s, 1H) : IR 1720(C=O).

1-Cyclohexyl carbonyl 1,2,4-triazole ; bp 110-113℃(2.5mmHg) : 1H NMR ($CDCl_3$) 1.20-2.30(br m, 10H), 3.22-3.70(br, m, 1H), 8.16(s, 1H), 8.98(s, 1H) : IR(film) 1718(C=O).

1-Benzoyl 1,2,4-triazole ; 1H NMR 7.38-7.75(m, 3H), 8.00-8.36(m, 3H), 9.18(s, 1H) : IR(KBr) 1710(C=O).

1-Privaloyl-1,2,4-triazolide ; 1H NMR 1.56(s, 9H), 8.02(s, 1H), 8.98(s, 1H) : IR(film) 1716(C=O).

3. Preparation of Benzyl Phenylacetate

Using 1,1'-Sulfinyl bis-1,2,4-triazole

To a stirred solution of phenylacetic acid (136mg, 1.0mmol) and 1,1'-sulfinyl bis-1,2,4-triazole (192mg, 1.0mmol) in methylene chloride (3ml) was added DMAP (128mg, 1.0mmol) and benzyl alcohol (110mg, 1.0mmol). The resulting solution was stirred at room temperature for 1 h, diluted with methylene chloride (30ml), and washed with 0.5M HCl (20ml), saturated $NaHCO_3$ (20ml), and saturated NaCl (20ml). The aqueous layers were extracted with methylene chloride (30ml). The combined extracts were dried over anhydrous $MgSO_4$, filtered, and evaporated to dryness. The residue was distilled to afford benzyl phenylacetate (178mg, 85%).

4. Preparation of Ester from 1-Acyl 1,2,4-triazolide

To a stirred solution of 1-(phenylacetyl) 1,2,4-triazolide (187mg, 1.0mmol) and DMAP (123mg, 1.0mmol) was in methylene chloride (3ml) was added benzyl alcohol (104μl, 1.0mmol). After being stirred at room temperature for 1 h, the reaction mixture was diluted with methylene chloride (30ml), washed with 5% aqueous HCl (30ml), 5% aqueous NaHCO (30ml), and saturated brine (30ml). The organic layer was dried over anhydrous $MgSO_4$, and evaporated to dryness under reduced pressure. The desired ester, benzyl phenylacetate (238mg, 96%) was the only compound.

Physical and Spectral Data of Products

Benzyl phenylacetate ; bp 133-135℃ (1.3 mmHg) : 1H NMR ($CDCl_3$) 3.56(S, 2H) 5.05(S, 2H), 7.23(S, 10H) : IR(film) 1735cm^{-1} (C=O).

Benzyl caprylate;1H NMR ($CDCl_3$) 0.92(br t, 3H, CH), 1.06-1.86(m, 12H, 5CH), 2.23(t, 3 H, J=6Hz, CH CO), 4.93(s, 2H, CH_2O), 7.15(s, 5H, ph) : IR(film) 1740cm^{-1}(C=O).

n-Butyl benzoate;bp 85-88℃(2.0mmHg)):1H NMR ($CDCl_3$) 0.7-2.0(br m, 7H, $CH_3(CH_2)_3$), 3.05(br t, J=7Hz, 2H, OCH), 7.2-7.6 and 7.8-8.2(m, 5H ph) : IR(film) 1915cm^{-1}.

s-Butyl phenylacetate; 1H NMR ($CDCl_3$) 0.96(t, J=5Hz, 3H, CH), 1.33(d, J=8Hz, 3H CH_2CH), 1.45-2.00(M, 2H, CH_2), 3.51(M, 1 H, OCH), 3.79(s, 2H CH CO), 7.30(s, 5H, ph) : IR(film) 1705cm^{-1}(C=O).

Benzyl benzoate;mp 120℃:1H NMR 5.3(s, 2H, CH), 7.2-7.5 and 7.9-8.1(M, 10H, ph):IR(film) 1719cm^{-1}(C=O).

Benzyl (4-Phenyle) butanoate;1H NMR 1.91-2.90(M, 6H, $CH_2CH_2CH_2$), 5.19(s, 2H, OCH_2), 7.20(s, 5H, ph), 7.38(s, 5H, ph) : IR(film) 1735 cm^{-1}(C=O).

Diphenylmethyl (4-Phenyl) butanoate;1H NMR 1.80-2.72(m, 7H, $CH_2CH_2CH_2$, OCH), 7.10(s, 5 H, ph), 7.28(s, 10H, ph) : IR(film) 1740cm^{-1} (C=O).

Spectral Data of β-Lactams

1-Benzyl-4-methyl-2-azetidionone;IR(film) 1760 (C=O) cm^{-1} : 1H NMR ($CDCl_3$) 1.25(d, 3H, J=6Hz), 2.53(dd, 1H, J=14.0Hz and 3.0Hz), 3.12(dd, 1H, J=14.0 and 5.0Hz), 3.33-3.80(dd, 1H), 4.12(d, 1H, J=15Hz), 4.65(d, 1 H, J=15Hz), 7.34(s, 5H).

1-Cyclohexyl-4-methyl-2 azetidinone ; IR (film) 1755 (C=O)cm^{-1} : 1H NMR ($CDCl_3$) 1.42(d, 3H, J=6Hz), 2.46(dd, 1H, J=14.0 and 3.0Hz), 3.07(dd, 1H, J=14.0 and 5.0Hz), 1.9-2.20(M, 10H), 3.17-4.07(m, 2H).

1-n-Octyl-4-methyl-2-azetidinone ; IR (film) 1760 (C=O)cm^{-1} : 1H NMR ($CDCl_3$) 0.93(br t, 3H), 1.30(m, 12H), 1.35(d, 3H, J=6 Hz), 2.48(dd, 1H, J=14.0 and 3.0Hz), 2.73-3.40(m, 2H), 3.08(dd, 1H, J=14.0 and 5.0 Hz), 3.40-3.93(m, 1H).

1-Benyl-3-methyl-2-azetidinone ; IR(film) 1750 (C=O)cm^{-1} : 1H NMR ($CDCl_3$) 1.21(s, 6 H), 2.73(s, 2H), 4.30(s, 2H), 7.30(s, 5H).

1-Benzyl-2-azetidinone ; IR(film) 1760 (C=O)cm^{-1} : 1H NMR ($CDCl_3$) 3.07(t, 2H, J=3 Hz), 3.15(t, 2H, J=3Hz), 4.38(s, 2H), 7.29(s, 5H).

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