Synthesis of Mesoionic Triazolopyridine. II. *N*-Acylation of 1,2,4-Triazolo[4,3-*a*]pyridin-3(2*H*)-one

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(Received December 25, 1982)

N-Acyl and *N*-alkoxycarbonyl mesoionic triazolopyridines were synthesized by selective *N*-acylation of 1,2,4-triazolo[4,3-*a*]pyridin-3(2*H*)-one. Some properties of these new-type azolides were also investigated.

In a previous work[1] in this series, we reported a novel approach for the synthesis of mesoionic triazolopyridines (**2**) by the selective alkylation of 1,2,4-triazolo[4,3-*a*]-pyridin-3(2*H*)-one (**1**). The interesting properties of *N*-alkyl mesoionic triazolopyridines (**2**) have called our attention to mesoionic *N*-acyl derivatives (**3**). These compounds (**3**) are characterized by combination of *N*-acyl azole(azolide) with mesoionic ring. Hence, a term "mesoionic azolide" will be used for these compounds. Only one example of this class of compounds has so far been reported.[2]

N-Acyl azoles, such as imidazolides (**4**) or triazolides (**5**) have been known as active amides, and widely used as acylating reagents.[3-8] The remarkable reactivity of these azolides has been attributed[7] to their resonance structures. Hence, it is thought that the reactivity of the acyl group of **3** reflects the particular resonance structure of the mesoionic ring. Possible use of the compounds (**3**) as acylating reagents would also be expected. Therefore, we have studied *N*-acylation of **1**. In this paper, we wish to report the selective *N*-acylation of **1** and some properties of the *N*-acyl mesoionic triazolopyridines.

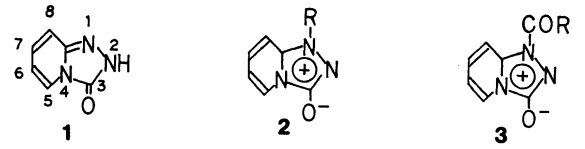


Fig. 1.

Results and Discussion

The followings are typical known preparative methods of *N*-acyl azoles(azolides): 1) direct acylation of parent azoles with acid halides,[5,9,10] 2) acylation of *N*-(trimethylsilyl)azoles with acid halides,[11] 3) reaction of carbonyl(diazolide)s with carboxylic acids.[5,12] We attempted several methods for the preparation of the mesoionic azolides (Fig. 2).

Almost all attempts to obtained the *N*-acyl mesoionic triazolopyridinones (**3**) by the reaction of **1** with acid chloride failed. Thus, heating of **1** with acid chloride in boiling chloroform resulted in the exclusive formation of

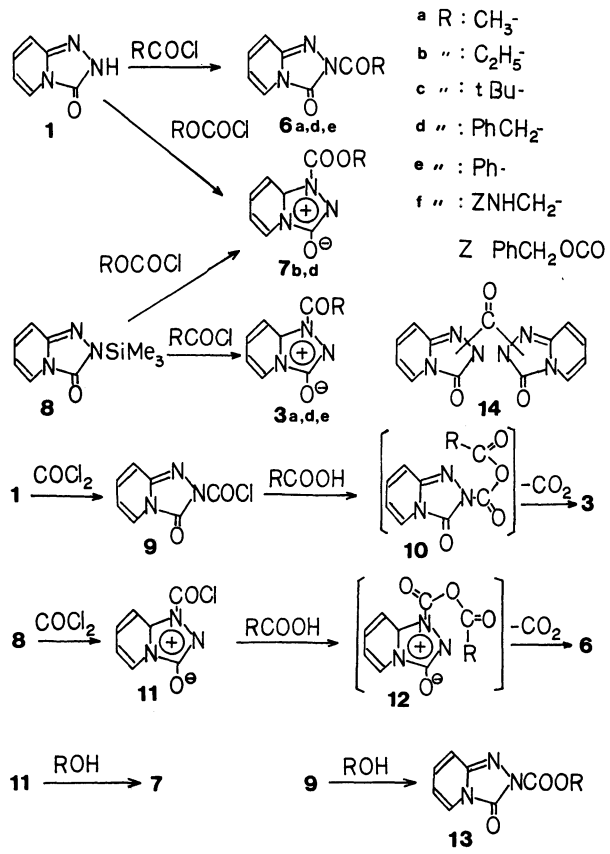


Fig. 2.

nonmesoionic compounds, which were assigned to N^2-acyltriazolopyridinones (**6**) based on their physical data. Details on the structural assignment are described in the following section. On the other hand, reaction of **1** with alkokycarbonyl chlorides gave mesoionic compounds (**7**) in moderate yields. For example, heating **1** with benzyl chloroformate gave a pale yellowish crystalline product which showed strong fluorescence when it was dissolved in an aprotic solvent. By comparing its IR, UV, and NMR spectra with those of *N*-alkyl mesoionic triazolopyridinones (**2**), this compound was found to have a mesoionic structure (**7d**) as shown in Table 1. *N*-acyl mesoionic triazolopyridinones (**3**) were obtained by using 2-(trimethylsilyl)triazolopyridine (**8**)[1] instead of **1**. Reaction of **8** with acid chlorides proceeded smoothly to give the desired mesoionic compounds (**3**) even at low temperature. When the reaction is carried out in a nonpolar solvent, such as benzene, the product is easily isolated by filtration, because it precipitates during reaction in most cases. Reaction of

Table 1. Comparison of physical data of mesoionic azolide with those of N^2-acyl and N-alkyl analogs

Compound	UV(H_2O) λ/mm	UV(THF) λ/mm	IR $\tilde{\nu}$/cm^{-1} (ring C=O)	NMR (δ) 5H	6H	CH_2 (benzyl)
3d	338	385 (ε 7550)	1700	8.14	7.25	4.42
7d	—	377 (ε 6100)	1705	8.55	7.55	5.48
2d	330	384 (ε 7550)	1660	8.19	7.02	5.41
6d	—	350 (ε 4000)	1740	7.75	6.50	4.45
13d	337	347 (ε 3600)	1730	7.88	6.64	5.47
15	338	350 (ε 4000)	1720	7.89	6.63	5.15

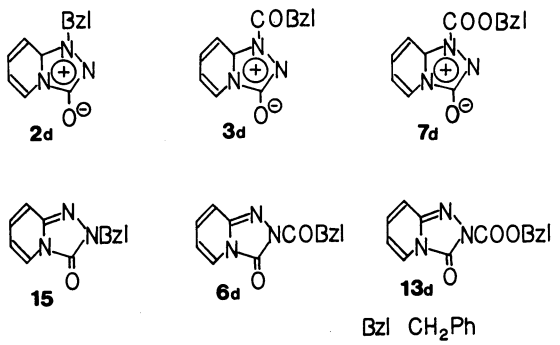
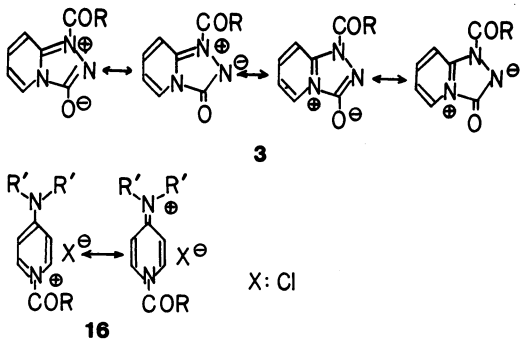


Fig. 3.



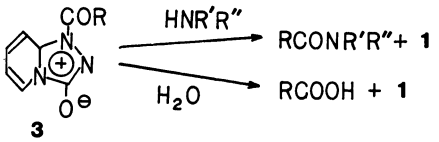


Fig. 4.

8 with alkoxycarbonyl chlorides gave the urethane-type mesoionic triazolopyridines (**7**) in the same manner.

When phosgene was used as the acylating reagent for the reaction of **1** or **8**, the N-chloroformyl derivative, **9** or **11** respectively, was obtained instead of the expected[4] carbonyldi(triazolopyridine) (**14**).

Structure of **9** and **11** were assigned on the basis of their UV spectra. It became clear that these compounds were useful reagents for the preparation of N-acyltriazolopyridines, similar to the carbonyldi(azole) for the preparation of N-acyl azoles[5,12] Thus, reaction of **9** with a variety of carboxylic acids proceeded in the presence of one equivalent-molar bases to give the mesoionic azolides (**3**) accompanying evolution of carbon dioxide. Since **3** was the sole product in this reaction, it was supposed that intramolecular transacylation of the intermediate mixed anhydride (**10**) occurred exclusively on the N^1-atom of the triazolopyridine ring. Similar transacylation was assumed in the reaction of **11** with a carboxylic acid, in this case **6** was the sole product. Reactions of these reagents, **9** and **11**, with alcohols in the presence of pyridine gave urethane-type mesoionic and nonmesoionic triazolopyridines, **7** and **13**, respectively. Thus, it became possible to obtain these mesoionic azolides (**3** and **7**) from appropriate carboxylic acids or alcohols by using these reagents (**9** or **11**). Both reagents are stable crystalline masses and may be stored in a desiccator at room temperature for a few months, but preferably in a refrigerator for longer storage.

Some Properties of the Mesoionic Azolides (3 and 7). A comparison of physical data of the mesoionic azolides (**3d** and **7d**) with those of N-alkyl and N^2-acyl analogs (Fig. 3) is shown in Table 1. It can be seen that the spectra of the N-acyl mesoionic triazolopyridines (**3d** and **7d**) are closely related to those of N-benzyl mesoionic triazolopyridine (**2d**). In an aprotic solvent, mesoionic triazolopyridines (**2**, **3**, and **7**) showed characteristic UV absorption in the region from 360 to 400 nm with intensity (ε 5500—10000) and large hypsochromic shifts (35—40 nm) of the maxima were observed when the solvents were changed to a protic solvent. In the case of nonmesoionic triazolopyridines (**6**, **13**, and **15**), these maxima were found in the region from 350 to 360 nm in an aprotic solvent with relatively low intensity (ε 3500—4500), and small hypsochromic shifts (*ca.* 10 nm) were observed. In the IR spectra, absorption bands for ring carbonyl of these mesoionic compounds (**3**, **7**, and **2**) were found in a lower frequency region than those of the corresponding nonmesoionic N^2-analogs (**6**, **13**, and **15**). In the NMR spectra, the chemical shifts of the pyridine-ring protons of the mesoionic compounds (**3**, **7**, and **2**) were always found at a lower field than those of the nonmesoionic analogs (**6**, **13**, and **15**). Thus, UV absorption and chemical shift of the pyridine-ring protons are effective in discriminating mesoionic compounds from their nonmesoionic analogs.

The mesoionic azolides (**3**) were found to have a tendency to transform to the thermodynamically more stable N^2-acyl analogs (**6**) under the conditions described below.

On heating in boiling 1,2-dichloroethane, slow conversion of **3d** to **6d** was found. In a previous paper,[1]

it was found that benzyl bromide acted as an effective catalyst for the N^1—N^2 benzyl migration on the triazolopyridine ring. Conversion of **3d** to **6d** was accelerated by addition of phenylacetyl chloride. The exclusive formation of **6** in the reaction of **1** with acyl chloride may be explained by the finding described above. Tertiary amine was found to be a more efficient catalyst for the conversion. When triethylamine was used as a catalyst, conversion of **3d** to **6d** took place even at room temperature, and completed within 3 h. The resonance structure of the mesoionic ring is illustrated in Fig. 4, which is very close to that of 1-acyl-4-dialkylaminopyridinium chloride (**16**),[13,14] a very reactive acylating reagent (Fig. 4). This similarity indicates that these acyl azolides (**3** or **7**) should act as powerful acylating agents. In fact, a reaction of **3d** with aniline in dichloromethane at room temperature completed within 2 h, yielding phenylacetanilide in nearly quantitative yield.

Relative reactivity of the mesoionic azolide (**3**) was determined on the reaction of **3a** with diethylamine or water, according to the method of Staab.[3] The mesoionic azolide (**3a**) was found to be 4 times more reactive than *N*-acetylimidazole[3] toward diethylamine in THF. On the other hand, hydrolytic decomposition of **3a** was found to proceed fairly slowly in spite of the high reactivity to an amine. The half life of the mesoionic azolide (**3a**) in water was found to be 380 min as determined by the change of the UV absorption at 25 °C. In the literature, the half lives of *N*-acetylimidazole,[3] *N*-acetyltriazole,[3] and 1-acetyl-4-dimethylaminopyridinium chloride were reported as 33—45, 6.6, and 3.9 min respectively under the same conditions. From these facts it appears that *N*-acyl mesoionic triazolopyridines (**3**) should be quite stable against water but very reactive toward amines. Although the relationship between the mesoionic structure and the selective reactivity of the mesoionic azolide against different nucleophiles is still uncertain, the stability toward hydrolytic decomposition makes the reagent (**3**) easy to handle. These findings together with their easy preparation suggest the usefulness of these mesoionic azolides (**3** and **7**) as acylating reagent. Details of their applications as acylating reagents will be reported in a subsequent paper.

Experimental

Melting points were determined on a Yazawa hot-stage apparatus and are uncorrected. IR, UV, and NMR spectra were recorded on JASCO A-102, Hitachi 200-20 and Varian EM 360L spectrometers, respectively. Triazolopyridine (**1**) was prepared by the method of Potts and Burton.[16]

1-Ethoxycarbonyl-1,2,4-triazolo[4,3-a]pyridinium-3-olate (7b). *a)*: A mixture of 5.4 g (40 mmol) of 1,2,4-triazolo[4,3-*a*]-pyridin-3(2*H*)-one (**1**) and ethyl chloroformate (100 ml) was heated under reflux for 3 h, cooled, and evaporated *in vacuo*. The residue was crystallized from methanol to give yellow fine needles, mp 144—145 °C. Yield 5.87 g (71%). UV (THF) λ_{max}: 378 nm (ε 5500). IR (Nujol): 1735, 1720 cm^{-1} (C=O). NMR ($CDCl_3$–DMSO-d_6); δ=8.57 (m, 1, H-5), 8.40 (m, 1, H-8), 8.16 (m, 1, H-7), 7.54 (m, 1, H-6), 4.51 (q, J=7 Hz, 2, $COOC\underline{H}_2$), 1.47 (t, J=7 Hz, 3, $COOCH_2C\underline{H}_3$). Found: C, 51.96; H, 4.23; N, 20.16%. Calcd for $C_9H_9N_3O_3$: C, 52.17; H, 4.23; N, 20.27%.

b): To a solution of 2.07 g (10 mmol) of 2-trimethylsilyl-1,2,4-triazolo[4,3-*a*]pyridin-3(2*H*)-one (**8**)[1] in dry benzene(20 ml) was added ethyl chloroformate (1.19 g, 11 mmol) with stirring. After the mixture had been stirred for 1 h, the crystalline precipitate was collected by filtration, washed with dry benzene and recrystallized from methanol to give pure **7b** (1.81 g, 87%). This product was identical with the sample prepared by route *a)*.

1-Benzyloxycarbonyl-1,2,4-triazolo[4,3-a]pyridinium-3-olate (7d). *a)*: A mixture of **1** (3.95 g, 2.93 mmol) and benzyl chloroformate (50 ml) was stirred at 90 °c for 1 h, and evaporated *in vacuo*. The residue was crystallized from ethanol to give **7d** as fine needles, mp 140°C. Yield 4.10 g (52%). UV (THF) λ_{max}: 224 (ε 4800), 254 (4300), 314 (3300), 377 nm (6100). IR (Nujol): 1745, 1710 cm^{-1} (C=O). NMR ($CDCl_3$–DMSO-d_6); δ=8.55 (m, 1, H-5), 8.4—8.0 (m, 2, H-7 and H-8), 7.42 (m, 1, H-6), 7.41 (s, 5, $C_6\underline{H}_5$), 5.48 (s, 2, $PhC\underline{H}_2$). Found: C, 62.48; H, 4.09; N, 15.81%. Calcd for $C_{14}H_{11}N_3O_3$: C, 62.45; H, 4.12; N, 15.61%.

b): To a solution of **8** (2.07 g, 10 mmol) in dry benzene (20 ml) was added benzyl chloroformate (1.82 g, 10.7 mmol) with stirring. After the mixture had been stirred for 1 h at room temperature, the crystalline precipitate was collected, recrystallized from ethanol to give **7d** (2.48 g, 92%). This product was identical with the sample prepared by route *a)*.

1-Acetyl-1,2,4-triazolo[4,3-a]pyridinium-3-olate (3a). To a solution of **8** (2.07 g, 10.0 mmol) in dry THF (20 ml) was added 0.80 g (10.2 mmol) of acetyl chloride with stirring. The reaction was slightly exothermic, and yellow crystals precipitated off immediately from the solution. After the mixture had been stirred for 1 h at room temperature, the product was collected by filtration, washed with dry THF and dried *in vacuo*: 1.29 g (73%) of **3a** was obtained, mp 150—153°C. UV (THF) λ_{max}: 374 nm (ε 6220). IR (Nujol): 1720 cm^{-1} (C=O). Found: C, 53.97; H, 4.00; N, 23.76%. Calcd for $C_8H_7N_3O_2$: C, 54.24; H. 3.98; N, 23.72%.

Reactions of 1 with Acid Chlorides. *a) With Acetyl Chloride*: A mixture of **1** (1.35 g, 10 mmol) and acetyl chloride (1.57 g, 20 mmol) in chloroform (15 ml) was boiled under reflux for 4 h, then, cooled to room temperature. A small amount of solid was filtered off, and the filtrate was evaporated *in vacuo* to dryness. The residue was crystallized from chloroform–hexane to give 1.63 g (92%) of 2-acetyl-1,2,4-triazolo[4,3-*a*]pyridin-3-(2*H*)-one (**6a**), mp 176 °C. UV (THF) λ_{max}: 351 nm (ε 3750). IR (Nujol): 1720 cm^{-1} (C=O). NMR ($CDCl_3$); δ=7.79 (m, 1, H-5), 7.4—7.1 (m, 2, H-7 and H-8), 6.55 (m, 1, H-6), 2.72 (s, 3, $C\underline{H}_3CO$). Found: C, 54.34; H. 3.86; N, 23.83%. Calcd for $C_8H_7N_3O_2$: C, 54.24; H, 3.98; N, 23.72%.

b) With Phenylacetyl Chloride: A mixture of **1** (1.35 g, 10 mmol) and phenylacetyl chloride (1.57 g, 20 mmol) in chloroform (15 ml) was boiled under refiux, and the reaction mixture was worked up in the manner described above expt; 2.43 g (96%) of 2-phenylacetyl-1,2,4-triazolo[4,3-*a*]pyridin-3(2*H*)-one (**6d**) was obtained, mp 142—143 °C. UV (THF) λ_{max}: 257 (ε 4300), 266 (4100), 350 nm (4000). IR (Nujol): 1740 cm^{-1} (C=O). NMR ($CDCl_3$); δ=7.75 (m, 1, H-5), 7.40 (s, 5, $C_6\underline{H}_5$), 7.5—7.0 (m, 2, H-7 and H-8), 6.50 (m, 1, H-6), 4.45 (s, 2, $PhCH_2$). Found: C, 66.56; H, 4.22; N, 16.71%. Calcd for $C_{14}H_{11}N_3O_2$: C, 66.39; H, 4.38; N, 16.59%.

c) With Benzoyl Chloride: A mixture of **1** (1.35 g, 10 mmol) and benzoyl chloride (2.81 g, 20 mmol) in chloroform (15 ml) was boiled under reflux for 96 h and the reaction mixture was worked up in the manner described above to give 1.78 g (74%) of 2-benzoyl-1,2,4-triazolo[4,3-*a*]pyridin-3(2*H*)-

one (**6e**), mp 145 °C. UV (THF) λ_{max}: 358 nm (ε 4300). IR (Nujol): 1730, 1695 cm^{-1}. NMR (DMSO-d_6): δ=8.03 (m, 1, H-5), 8.0—7.0 (m, 7, H-7, H-8 and $C_6\underline{H}_5$), 6.66 (m, 1, H-6). Found: C, 65.28; H, 3.59; N, 17.70%. Calcd for $C_{13}H_9N_3O_2$: C, 65.27; H, 3.79; N, 17.57%.

*2-Chloroformyl-1,2,4-triazolo[4,3-a]pyridin-3(2H)-one (**9**).* To a suspension of **1** (27 g, 200 mmol) in dry THF (600 ml) was introduced phosgene (40 g) with stirring. The resulting mixture was boiled under reflux for 2 h to afford a clear soln and then cooled to room temperature. The resulting crystalline product was collected by filtration, washed with a small amount of dry THF, and dried *in vacuo* to give **9**. The filtrate was combined with the washing, concentrared *in vacuo*, giving a second crop of **9**. Mp 230 °C. Yield 36.78 g (93%). UV (CH_2Cl_2) λ_{max}: 262, 272, 283, 356 nm. Found: C, 42.30; H, 2.33; N, 21.26; Cl, 17.99%. Calcd for $C_7H_4N_3O_2Cl$: C, 42.55; H, 2.04; N, 21.27; Cl, 17.95%.

*1-Chloroformyl-1,2,4-triazolo[4,3-a]pyridinium-3-olate (**11**).* To a solution of **8** (20.7 g, 100 mmol) in dry benzene was slowly added a solution of phosgene (9.90 g, 100 mmol) in dry THF (50 ml) at a temperature between 4 °C and 10 °C with stirring. After the mixture had been stirred at room temperature for 1 h, the crystalline precipitate was collected by filtration, washed with dry benzene, and dried *in vacuo* to give **11**, mp 320 °C (decomp). UV (CH_2Cl_2) λ_{max}: 247, 375 nm. Found: C, 42.56; H, 2.14; N, 21.54; Cl, 17.72%. Calcd for $C_7H_4N_3O_2Cl$: C, 42.55; H, 2.04; N, 21.27; Cl, 17.95%.

*Reaction of **9** with Carboxylic Acids.* *a) With Acetic Acid*: To a solution of acetic acid (0.48 g, 10 mmol) in dichloromethane (40 ml) was added triethylamine (1.40 ml, 10 mmol). The mixture was cooled to 4 °C and 1.98 g (10 mmol) of **9** was added. With evolution of gas, the solution became yellow-green. After 1 h-stirring at 4 °C, the solution was washed twice with cold water, dried over anhydrous sodium sulfate, and concentrated *in vacuo* to *ca.* 10 ml. Ether was added to give a crystalline product of 1-acetyl-1,2,4-triazolo[4,3-*a*]-pyridinium-3-olate (**3a**), mp 167 °C. Yield 1.10 g (62%). The physical properties of this product agreed with those of the sample obtained in the above expt.

b) With Phenylacetic Acid: By treating phenylacetic acid (1.36 g, 10 mmol) with **9** (1.98 g, 10 mmol) as in the previous experiment, 2.26 g (89%) of 1-phenylacetyl-1,2,4-triazolo[4,3-*a*]pyridinium-3-olate (**3d**) was obtained, mp 155—157 °C. UV (THF) λ_{max}: 232 (ε 8150), 258 (3100), 384 nm (7550). IR (Nujol): 1720, 1700 cm^{-1} (C=O). NMR ($CDCl_3$); δ=8.16 (m, 1, H-5), 8.0—7.3 (m, 7, H-7, H-8, and $C_6\underline{H}_5$), 7.25 (m, 1, H-6), 4.42 (s, 2, $PhCH_2$). Found: C, 66.50; H, 4.28; N, 16.65%. Calcd for $C_{14}H_{11}N_3O_2$: C, 66.39; H, 4.38; N, 16.59%.

c) With Benzoic Acid: By treating benzoic acid (1.22 g, 10 mmol) with **9** (1.98 g, 10 mmol) in the manner described above, 1-benzoyl-1,2,4-triazolo[4,3-*a*]pyridinium-3-olate (**3e**) was obtained, mp 134—136 °C. Yield 2.06 g (86%). UV (THF) λ_{max}: 398 nm (ε 9950). IR (Nujol): 1730, 1695 cm^{-1} (C=O). NMR ($CDCl_3$); δ=8.8—7.3 (m, triazolopyridine ring and benzene ring protons). Found: C, 65.22; H, 3.63; N, 17.74%. Calcd for $C_{13}H_9N_3O_2$: C, 65.27; H, 3.79; N, 17.57%.

d) With N-(Benzyloxycarbonyl)glycine: By treating *N*-*Z*-glycine (2.09 g, 10 mmol) with **9** (1.98 g, 10 mmol) in the manner described above, 1-[*N*-(benzyloxycarbonyl)glycyl]-1,2,4-triazolo[4,3-*a*]pyridinium-3-olate (**3f**) was obtained, mp 173—176 °C. Yield 2.87 g (88%). UV (THF) λ_{max}: 375 nm. IR (Nujol): 1720, 1695 cm^{-1} (C=O). Found: C, 58.69; H, 4.23; N, 17.34%. Calcd for $C_{16}H_{14}N_4O_4$: C, 58.89; H, 4.32; N, 17.17%.

*Reaction of **11** with Phenylacetic Acid.* To a solution of phenylacetic acid (0.68 g, 5 mmol) in dichloromethane (20 ml) was added triethylamine (0.70 ml, 5 mmol), and the mixture was cooled to 4 °C, then, **11** (0.985 g, 5 mmol) was added. After stirring at room temperature for 1 h, the reaction mixture was washed twice with cold water, dried over anhydrous sodium sulfate, and evaporated *in vacuo* to dryness. The residue was crystallized from chloroform–hexane to give 1.18 g (93%) of **6d**. The physical properties of this product agreed with those of the sample obtained in the above expt.

*Reaction of **11** with Alcohols.* *a) With Benzyl Alcohol*: A suspension of **11** (1.98 g, 10 mmol) in ethanol-free chloroform (50 ml) prepared by passing through an alumina column before use was cooled to 4 °C, and 1.05 ml of pyridine was added. After the mixture had been stirred at 4 °C for 1 h, benzyl alcohol (1.19 g, 11 mmol) was added. The reaction mixture became a clear solution, and soon after yellow crystals separated out from the solution. After the mixture had been stirred at room temperature for 30 min, the product was collected by filtration, washed with chloroform, and dried *in vacuo* to give **7d**. The filtrate and washings were combined, washed twice with water, dried over anhydrous sodium sulfate, and concentrated *in vacuo*, giving a second crop of **7d**. The total yield of **7d** was 2.50 g (94%). The physical properties of this product were identical to those of the sample in the above expt.

b) With t-Butyl Alcohol: A suspension of **11** (1.98 g, 10 mmol) in ethanol-free chloroform was cooled to 4 °C, dry pyridine (1.05 ml) was added, and the mixture was stirred at 4 °C for 40 min then, anhydrous *t*-butyl alcohol (2 ml) was added. On stirring at room temperature, the reaction mixture became a clear solution within 20 min. After a further 1 h-stirring, the solution was washed twice with cold water, dried over anhydrous sodium sulfate, and evaporated *in vacuo*. The residue was crystallized from chloroform–ether to give 2.04 g (69%) of 1-(*t*-butoxycarbonyl)-1,2,4-triazolo-[4,3-*a*]pyridinium-3-olate (**7c**) as a chloroform adduct, mp 119—121 °C. UV (THF) λ_{max} 374 nm. IR (Nujol): 1757, 1722 cm^{-1} (C=O). Found: C, 46.95; H, 4.62; N, 14.47%. Calcd for $C_{11}H_{13}N_3O_3 \cdot 1/2CHCl_3$: C, 46.82; H, 4.61; N, 14.25 %.

*2-Benzyloxycarbonyl-1,2,4-triazolo[4,3-a]pyridin-3(2H)-one (**13d**).* To a suspension of **9** (1.0 g) in dichloromethane were added pyridine (0.40 g) and benzyl alcohol (0.65 g), and the mixture was stirred for 1 h at room temperature. The resulting solution was washed twice with water, dried over anhydrous sodium sulfate, and evastallized *in vacuo* to dryness. The residue was crystallized from ether to give **13d** (1.257 g, 93%), mp 138 °C. UV (THF)λ_{max}: 254 (ε 3500), 264 (3500), 276 (2200), 347 nm (3600). IR (Nujol): 1730 cm^{-1} (C=O). NMR (DMSO-d_6); δ=7.88 (m, 1, H-5), 7.7—7.0 (m, 2, H-7 and H-8), 7.51 (s, 5, C_6H_5), 6.64 (m, 1, H-6), 5.47 (s, 2, $PhC\underline{H}_2$). Found: C, 62.24; H, 4.00; N, 15.60%. Calcd for $C_{14}H_{11}N_3O_3$: C, 62.45; H, 4.12; N, 15.61%.

*Conversion of **3d** to **6d**.* *a) Thermal Conversion*: A solution of **3d** (100 mg) in 5 ml of 1,2-dichloroethane was heated under reflux for 20 h, then, the solvent was removed by evaporation *in vacuo*. The NMR spectrum of the residue in $CDCl_3$ showed that it consisted of **3d** and **6d** (43 : 57).

b) Conversion Catalyzed by Acid Chloride: A mixture of **3d** (253 mg, 1 mmol) and phenylacetyl chloride (155 mg, 1 mmol) in 1,2-dichloroethane (2.5 ml) was stirred at 80 °C for 45 min; TLC on silica gel in 40% ethyl acetate in benzene showed disappearance of the starting material (**3d**) within 40 min. The reaction mixture was evaporated *in vacuo*, and the residue was crystallized from chloroform–hexane to give 232 mg of **6d**.

c) Conversion Catalyzed by Triethylamine: To a solution of

3d (100 mg) in 1,2-dichloroethane (5 ml) was added triethylamine (0.04 ml), and the mixture was stirred at room temperature. TLC on silica gel showed that **3d** was almost completely converted to **6d** within 3 h.

Reaction of Mesoionic Azolide (3d) with Aniline. A mixture of **3d** (1.27 g, 5 mmol) and aniline (0.49 g, 5.25 mmol) in dichloromethane (10 ml) was stirred at room temperature for 2 h, filtered, and the filtrate was washed successively with 0.5 M citric acid, water, 4% sodium hydrogencarbonate, and water. The dichloromethane solution was dried over anhydrous sodium sulfate, and evaporated *in vacuo* to give crystalline phenylacetanilide (1.02 g, 97%), mp 117—118 °C. The physical properties of this product agreed with those of authentic phenylacetanilide.

Measurement of the Reactivities of 3a. The rates of aminolysis and hydrolysis were measured at 25 °C according to the direction of Staab.[3] The rate of the aminolysis of **3a** (1.830×10^{-4} mmol/ml) in THF containing 5% diethylamine was measured by observing the decrease in its UV absorption maximum at 389 nm. The rate of the hydrolysis of **3a** in water (2.25×10^{-4} mmol/ml) was also measured by means of the change of the maximum at 340 nm. Pseudo-first order rate constants of the amonolysis in 5% diethylamine–THF was 3.84×10^{-2} and that of hydrolytic decomposition was 1.8×10^{-3}.

The authors wish to thank Dr. Genshun Sunagawa, Dr. Keisuke Murayama, and Dr. Hideo Nakao for their continuing interest and encouragement and Dr. Masakatsu Kaneko for his helpful comments.

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