tracted with hot benzene. The benzene extract was evaporated *in vacuo* to leave crystals. Recrystallization from petroleum ether (bp 60–75°) gave 0.34 g (52%) of 2,5-diphenyl-*s*-triazolo[3,4-*b*]-1,3,4-oxadiazole (**5a**) as colorless prisms: mp 179–180° dec; ir (KBr) 1600, 1550, 1460, 1380, 1150, 1050, 960, 768, 730, 700, 680, cm^{-1}; mass spectrum *m/e* 262 (M^+), 245, 234 ($M^+ - N_2$), 206 ($234^+ - N_2$ or CO), 192 ($234^+ - NCO$), 145 ($234^+ - PhC$), 117 ($PhCN_2^+$), 105 ($PhCO^+$), 103 ($PhCN^+$), 77 (Ph^+).

Anal. Calcd for $C_{15}H_{10}N_4O$: C, 68.69; H, 3.84; N, 21.37. Found: C, 68.84; H, 3.56; N, 21.59.

The glyme filtrate was concentrated *in vacuo* below 50° to leave resinous materials, which were chromatographed on silica gel to give trace amounts of 4 and 95 mg (13%) of 2,5-diphenyl-1,3,4-oxadiazolo[2,3-*e*]-1,2,4,6-pentazepine (**6**). The formation of benzonitrile was confirmed by gas chromatography of the glyme filtrate.

6 had mp 124–125° dec [from petroleum ether (bp 60–70°)] and was obtained as colorless plates: ir (KBr) 1600, 1550, 1500, 1460, 1350, 1300, 1170, 1080, 980, 790, 755, 730, 700 cm^{-1}; mass spectrum *m/e* 262 ($M^+ - N_2$ or CO), 145, 117, 105, 103, 77.

Anal. Calcd for $C_{15}H_{10}N_6O$: C, 62.06; H, 3.47; N, 28.95. Found: C, 62.18; H, 3.26; N, 28.71.

Hydrolysis of 5a. A solution of 0.5 g of **5a** in 30 ml of ethanol was refluxed with 20 ml of 1 *N* hydrochloric acid for 9 hr, and then the mixture was neutralized with aqueous sodium carbonate. The precipitate was filtered and recrystallized from acetone to give 0.35 g (66%) of 4-benzoylamino-3-phenyl-Δ^2-1,2,4-triazolin-5-one (**7a**) as colorless prisms: mp 259.5–260° dec; ir (KBr) 3300–3000 (NH), 1745, 1670 cm^{-1} (C=O); nmr (DMSO-d_6) δ 7.4–8.05 (m, 10, aromatic protons), 11.64, 12.22 (each s, 1, NH); mass spectrum *m/e* 280 (M^+), 161 ($M^+ - PhNCO$), 119, 118 ($161^+ - HNCO$), 105 ($PhCO^+$, base peak); uv max (EtOH) 267 nm (log ϵ 4.0).[21]

Anal. Calcd for $C_{15}H_{12}N_4O_2$: C, 64.27; H, 4.32; N, 19.99. Found: C, 64.02; H, 4.14; N, 19.79.

Preparation of 5a. After a solution of 1.0 g of 1,5-dibenzoylcarbohydrazide (**8**)[22] in 10 ml of phosphorus oxychloride was heated at 80–90° for 2 hr, the reaction mixture was poured into ice–water. The precipitate was filtered and recrystallized from benzene to afford 0.29 g (29%) of 4-benzoylamino-5-chloro-3-phenyl-1,2,4-triazole (**9**) as colorless needles: mp 152.5–153° dec; ir (KBr) 3400 (broad, NH), 1640 cm^{-1} (C=O); mass spectrum *m/e* 300, 298 (M^+).

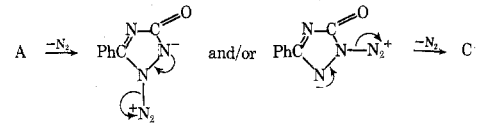
Anal. Calcd for $C_{15}H_{11}N_4OCl$: C, 60.31; H, 3.71; N, 18.75. Found: C, 60.54; H, 3.64; N, 18.63.

A solution of 0.17 g of **9** in 20 ml of acetone–water mixture (10:1 v/v) was stirred with 1.0 g of sodium carbonate at room temperature for 4 hr. The reaction mixture was neutralized with dilute hydrochloric acid to precipitate a solid, which on recrystallization from petroleum ether (bp 60–75°) gave 0.11 g (74%) of colorless prisms, mp 179–180° dec. This compound was identical with the product **5**.

Registry No.—**1**, 4547-71-1; **2**, 33655-23-1; **4**, 18039-42-4; **5a**, 32550-72-4; **6a**, 51003-52-2; **7**, 3658-32-0; **8**, 51003-53-3; thiobenzoyl isocyanate, 3553-61-5.

References and Notes

(1) Government Industrial Research Institute, Osaka, Ikeda, Osaka 563, Japan.
(2) R. Neidlein and W. Haussmann, *Tetrahedron Lett.*, 2423 (1965); *Chem. Ber.*, **99**, 239 (1966).
(3) S. Yanagida, H. Hayama, M. Yokoe, and S. Komori, *J. Org. Chem.*, **34**, 4125 (1969).
(4) E. Degener, H. G. Schmelzer, and H. Holtschmidt, *Angew. Chem.*, **78**, 981 (1966).
(5) S. Yanagida, M. Yokoe, M. Ohoka, and S. Komori, *Bull. Chem. Soc. Jap.*, **44**, 2182 (1971).
(6) O. Tsuge, M. Tashiro, R. Mizuguchi, and S. Kanemasa, *Chem. Pharm. Bull.*, **14**, 1055 (1966).
(7) O. Tsuge and K. Sakai, *Bull. Chem. Soc. Jap.*, **45**, 1534 (1972).
(8) O. Tsuge and S. Kanemasa, *Bull. Chem. Soc. Jap.*, **45**, 3591 (1972).
(9) O. Tsuge and S. Kanemasa, *Tetrahedron*, **28**, 4737 (1972).
(10) R. Stolle and W. Kind, *J. Prakt. Chem.*, **70**, 423 (1904).
(11) M. Kanaoka, *Yakugaku Zasshi*, **76**, 1133 (1956).
(12) S. Yoshida and M. Asai, *Yakugaku Zasshi*, **74**, 951 (1954).
(13) The following possible route to C can be excluded because of the formation of **6**.



(14) B. T. Gillis and J. G. Dain, *J. Org. Chem.*, **36**, 518 (1971).
(15) From the reaction of **1** with active methylene compounds, it has been found that the carbamoyl chlorine atom is more reactive than the imidoyl chlorine atom: O. Tsuge, M. Tashiro, and S. Hagio, *J. Org. Chem.*, **39**, 1228 (1974).
(16) All melting points are uncorrected. The mass spectra were obtained on a Hitachi RMS-4 mass spectrometer with a direct inlet and an ionization energy of 70 eV. The nmr spectrum was determined at 60 MHz with a Hitachi R-20 nmr spectrometer with TMS as an internal reference.
(17) J. Goerdeler and H. Schenk, *Angew. Chem.*, **75**, 675 (1963).
(18) J. Goerdeler and H. Schenk, *Chem. Ber.*, **98**, 2954 (1965).
(19) L. Wheeler, *J. Amer. Chem. Soc.*, **23**, 323 (1901).
(20) R. Huisgen and J. Sauer, *Justus Liebigs Ann. Chem.*, **654**, 146 (1962).
(21) The uv spectrum of 3-phenyl-Δ^2-1,2,4-triazolin-5-one: uv max (EtOH) 265 nm (log ϵ 4.05) [O. Tsuge, S. Kanemasa, and M. Tashiro, *Tetrahedron*, **24**, 5205 (1968)].
(22) R. Stollé and K. Krauch, *Ber.*, **47**, 724 (1914).

Studies on *N*-(α-Chlorobenzylidene)carbamoyl Chloride. II.[1] Reaction of *N*-(α-Chlorobenzylidene)carbamoyl Chloride with Active Methylene Compounds

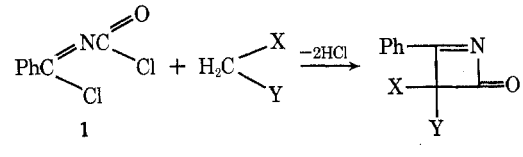
Otohiko Tsuge,* Masashi Tashiro, and Shigeru Hagio

Research Institute of Industrial Science, Kyushu University, Hakozaki, Higashi-ku, Fukuoka 812, Japan

Received August 14, 1973

The reaction of *N*-(α-chlorobenzylidene)carbamoyl chloride (**1**) with active methylene compounds has been investigated. In general, the imidoyl chlorine atom in **1** reacts faster with active methylene compounds in the presence of NEt_3. An azetinone intermediate (**7**) is proposed as an initial product in the reaction with ethyl cyanoacetate (**2**) in the presence of 2 equiv of NEt_3. The reactions of **1** with acenaphthenone (**13**) and dimedone (**18**) give oxazin-2-one (**14a**) and oxazin-4-one derivatives (**19**), respectively. On the other hand, **1** reacts with **13** in the presence of metallic sodium to yield a pyridine derivative (**17**).

In the preceding paper,[1] we have reported a convenient synthesis of *N*-(α-chlorobenzylidene)carbamoyl chloride (**1**), which is useful as a precursor for the synthesis of heterocycles.[1-3] It could be expected that **1** might react with active methylene compounds to form azetinones, and fur-



1

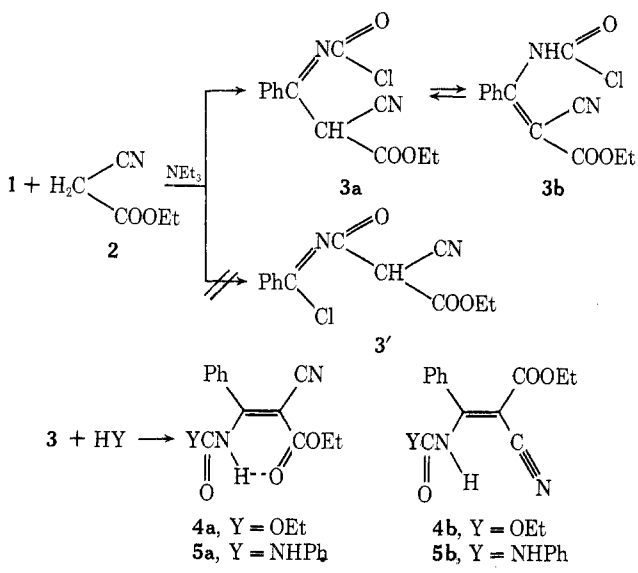
thermore, we were interested in studying which chlorine in 1 is more reactive. These considerations prompted us to investigate the reaction of 1 with active methylene compounds.

Results and Discussion

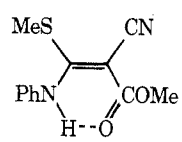
Reaction with Ethyl Cyanoacetate (2). In order to determine which chlorine in 1 reacts faster with 2, the reaction of 1 with 1 equiv of 2 in the presence of equimolar triethylamine (NEt_3) was carried out in ether at room temperature; an unstable, oily product 3 whose ir spectrum showed bands at 3280 (NH), 2200 (C≡N), 1745, and 1710 cm^{-1} (C=O) was obtained and it could not be purified. Treatment of 3 with ethanol or aniline afforded ethyl α-cyano-β-(*N*-ethoxycarbonylamino)acrylate (4) or -β-phenyl-β-(3-phenylureido)acrylate (5).

In view of the formation of 4 and 5 from 3, it is evident that the imidoyl chlorine is more reactive than the carbamoyl chlorine under the conditions, and the initial oily product is 3, which would predominantly exist in the form 3b on the basis of its ir spectrum, but not 3′ (Scheme I).

Scheme I

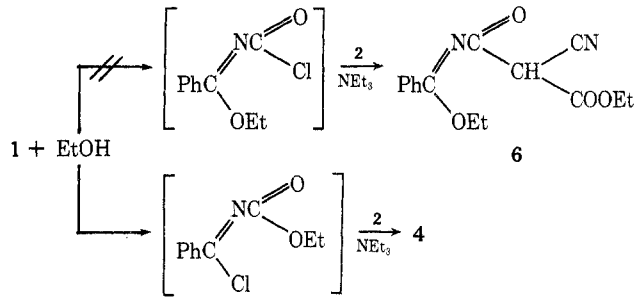


Shvo and Belsky[4] have investigated the thermal isomerization of conjugated ketene mercaptoaminals involving rotation about a C=C double bond. They clarified that methyl β-anilino-β-methylmercapto-α-cyanoacrylate exists in the following configuration on the basis of its nmr



and ir spectroscopic studies. The ir spectrum (CCl_4) of 4 exhibited the hydrogen-bonded NH and C=O absorption bands at 3240 and 1690 cm^{-1}, besides the nonbonded C=O absorption band at 1775 cm^{-1} (these absorption bands were independent of concentration). Furthermore, the nmr spectrum of 4 showed one signal ascribable to NH even at −60°.[5] These results can be reconciled only with the configuration 4a depicted in Scheme I, since the linear nitrile group in 4b is not in the appropriate geometrical disposition for internal hydrogen bonding. Similarly, it was deduced that 5 exists in the same configuration 5a as 4 does.

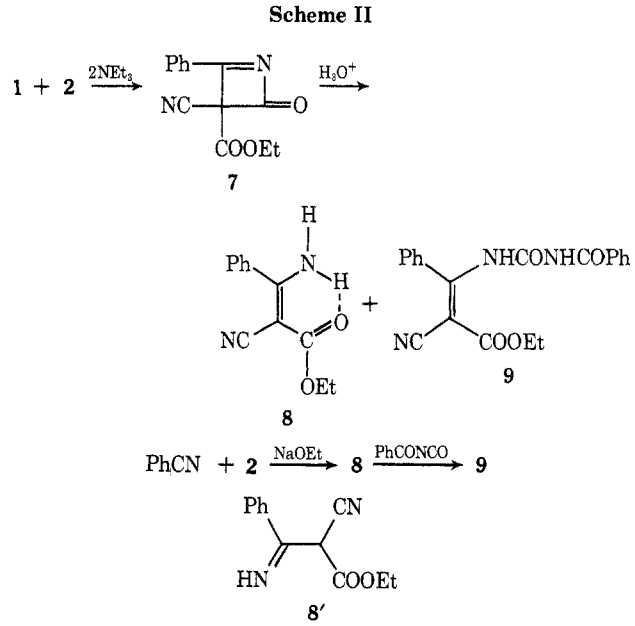
It was thus reasoned that, if the imidoyl chlorine in 1 is more reactive, the reaction of 1 with ethanol would yield the imidate, which should condense with 2 to give the isomeric compound 6. Thus, 1 was initially treated with 1 equiv of ethanol, followed by a mixture of 2 and NEt_3. However, contrary to expectation, it was found that 4 was isolated rather than 6. This suggests that the carbamoyl



chlorine in 1 reacts faster with ethanol in the absence of NEt_3. On the basis of these observations, the NEt_3 might initially react with the carbamoyl chlorine to form a kind of salt which would be less reactive than the imidoyl chlorine, if the NEt_3 is present from the start in the reaction system.

If 2 equiv of NEt_3 is used as a dehydrochlorinating agent, it would be expected that azetinone 7 would be formed from the reaction of 1 with 2. When 2 equiv of NEt_3 was added to a mixture of equimolar amounts of 1 and 2, an unstable, oily product was obtained, together with triethylammonium chloride in an almost quantitative yield.

Scheme II

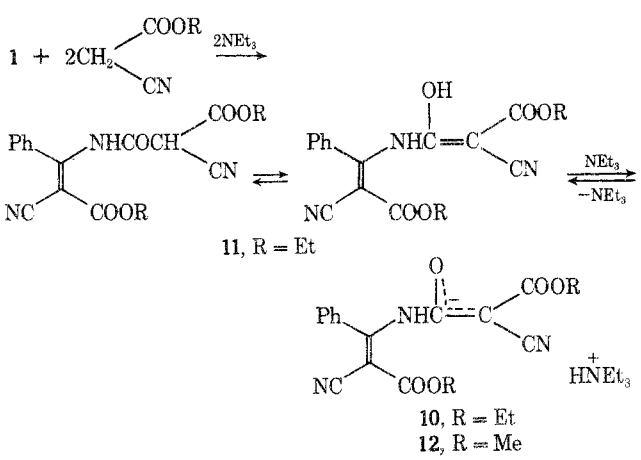


The oily product was deduced as the expected azetinone 7 on the basis of the following evidence. Its ir spectrum showed C=O absorption bands at 1800 and 1745 cm^{-1}. Chromatography of the oily product on alumina afforded ethyl α-cyano-β-amino-β-phenylacrylate (8) and α-cyano-β-phenyl-β-(3-benzoylureido)acrylate (9). The compounds 8 and 9 were also formed by hydrolysis of the oily product with hydrochloric acid in ethanol.[6] The formation of 8 from 7 can be easily understood in terms of the hydrolytic cleavage of the azetinone ring with the subsequent decarboxylation, but the pathway for the formation of 9 is not clear, since 1 did not react with 8 even in the presence of NEt_3.

The structures of 8 and 9 were confirmed on the basis of their spectral data and of comparison with authentic samples prepared from the reaction of benzonitrile with 2[7] and of the reaction of 8 with benzoyl isocyanate, respectively. Although Atkinson, *et al.*,[7] reported that the product from the reaction of benzonitrile with 2 was ethyl α-cyano-β-imino-β-phenylpropionate (8′), its ir and nmr spectra supported strongly that the product is the enamine as depicted in Scheme II. The ir spectrum in CCl_4 showed absorption bands ascribable to nonbonded NH (3520), bonded NH (3260), and C=O (1680 cm^{-1}) (These bands were independent of concentration), and the nmr spectrum exhibited signals due to single ethyl and two NH groups even at −60°.

On the other hand, when a mixture of equimolar amounts of 1 and 2 was added to a solution of 2 equiv of NEt_3 in ether, a product 10 was obtained as yellow needles. The molecular formula of 10 agreed with that of the compound derived from NEt_3 and 1:2 condensation product of 1 and 2. In fact, the reaction of 1 with 2 equiv of 2 in the presence of 3 equiv of NEt_3 afforded 10 in a good yield. Treatment of 10 with hydrochloric acid gave 1:2 condensation product 11 as colorless needles, which was converted into 10 on treatment with NEt_3. Structures of 10 and 11 as shown in Scheme III were confirmed on the basis of their spectral data. The absence of methine proton and the appearance of NH and OH in the nmr spectrum of 11 in deuteriochloroform ($CDCl_3$) suggests that 11 exists exclusively in the enol form in the solvent.

Scheme III

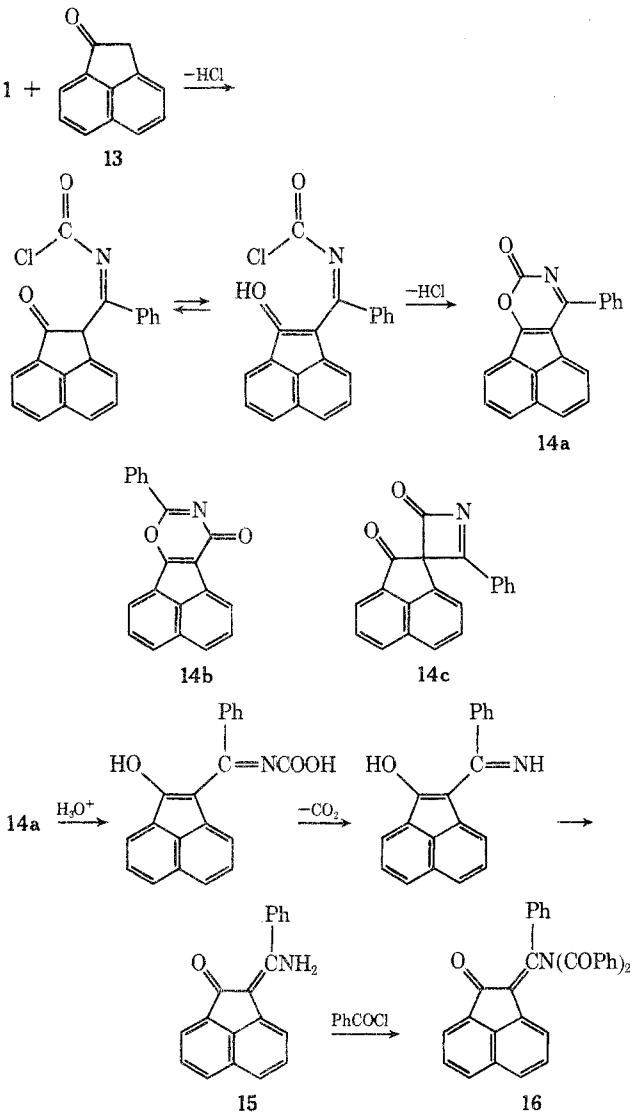


Similarly, 1 reacted with methyl cyanoacetate and NEt_3 under the same conditions to form salt 12 of the type 10.

Reaction with Acenaphthenone (13). In the reaction of 1 with 13, the formation of oxazinones 14a and 14b would be expected, besides azetinone derivative 14c. When 1 was treated with 1 equiv of 13 in the presence of 2 equiv of NEt_3, a product 14 was formed whose molecular formula agreed with that of the compound derived from a 1:1 adduct of 1 and 13 by the elimination of 2 mol of hydrogen chloride. Since the ir spectrum of 14 showed the single carbonyl absorption band at 1735 cm^{-1}, azetinone 14c could be excluded from possible structures for 14.

Although the spectral data of 14 did not permit a clear assignment as to whether 14a or 14b would be more reasonable for 14, the formation of 2-(1′-aminobenzylidene)-acenaphthenone (15), which was converted into the dibenzoyl derivative 16 by acidic hydrolysis, indicated that 14 is 10-phenylacenaphtho[1,2-*e*]-2*H*-1,3-oxazin-8-one (14a), but not the 8-phenyl derivative 14b. The formation of 15 from 14a can be easily rationalized by an initial hydrolytic cleavage of the C–O bond of the oxazinone ring, followed by decarboxylation as shown in Scheme IV.

Scheme IV



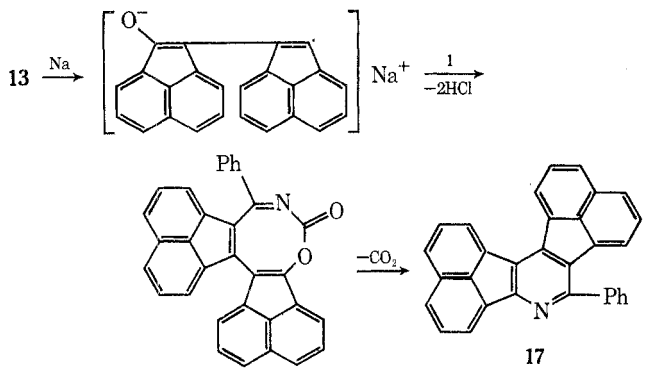
It is known that 13 is exclusively in the keto form.[8] Consequently, the formation of 14a can be also understood by an initial reaction of the imidoyl chlorine atom in 1 with the active methylene group in 13, and then subsequent ring closure to the oxazinone *via* the enol tautomer (Scheme IV).

On the other hand, the reaction of 1 with 13 in the presence of metallic sodium afforded 2-phenyldiacenaphtho[1,2-*b*:1′,2′-*d*]pyridine (17), besides tarry materials. The structure of 17 was established by its spectral data as well as by comparison with an authentic sample.[9]

When metallic sodium was added to a solution of 13 in ether, the colorless solution changed to a violet color. It has been reported that benzophenone gives a violet metal ketyl intermediate with sodium amalgam.[10] Although the exact pathway of formation of 17 is not clear, it may be viewed as proceeding *via* metal ketyl intermediate as shown in Scheme V.

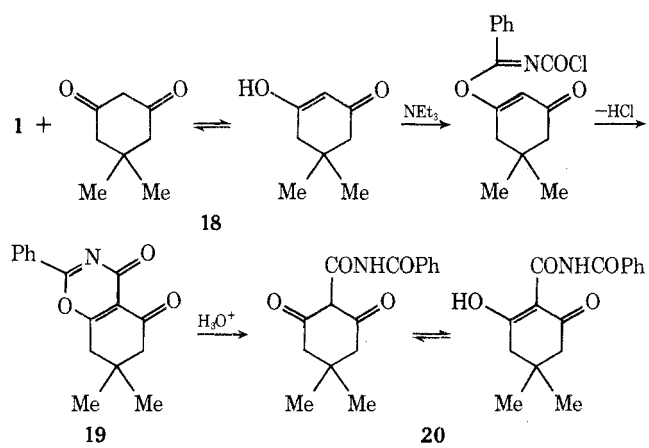
Reaction with 5,5-Dimethylcyclohexane-1,3-dione (18). It is well known that dimedone (18) exists predominantly in the enol form.[11] Therefore, it was expected that, in the presence of NEt_3, the imidoyl chlorine of 1 would initially react with the enolic hydroxyl group of 18, leading to the formation of 4*H*-1,3-oxazinone derivative 19. In fact, the reaction of 1 with 18 in the presence of NEt_3

Scheme V



gave the expected 4*H*-1,3-oxazinone derivative **19**. The structure of **19** was confirmed by its spectral data as well as by the result of hydrolysis. Hydrolysis of **19** with hydrochloric acid afforded 2-benzoylcarbamoyl-5,5-dimethylcyclohexane-1,3-dione (**20**) in a good yield. It was clarified by the nmr spectrum that **20** exists in the enol form as **18** does (Scheme VI).

Scheme VI



Experimental Section[12]

Reaction with Ethyl Cyanoacetate (2). In the Presence of Equimolar NEt_3. A. A solution of NEt_3 (0.5 g, 4.95 mmol) in diethyl ether (15 ml) was added, drop by drop, to a solution of carbamoyl chloride **1**[1] (1.0 g, 4.95 mmol) and **2** (0.56 g, 4.95 mmol) in diethyl ether (15 ml). The reaction mixture was stirred at room temperature for 1 hr and then filtered to give 0.67 g (98.5%) of triethylamine hydrochloride. To the filtrate was added ethanol (0.25 g, 5.4 mmol) and the resulting mixture was stirred at room temperature for 2 hr to yield crystals. Filtration and recrystallization from ethanol gave 0.63 g (44%) of ethyl α-cyano-β-(*N*-ethoxycarbonylamino)acrylate (**4**) as colorless needles: mp 151.5–153.5°; ir (KBr) 3200 (NH), 2235 (C≡N), 1780, 1760 (sh), 1680 cm^{-1} (C=O); nmr ($CDCl_3$) δ 1.20, 1.39 (each t, 3, CH_2CH_3, J = 7 Hz), 4.10, 4.35 (each q, 2, CH_2Me, J = 7 Hz), 7.5 (m, 5, aromatic protons), 11.31 (broad, 1, NH, exchanged with D_2O); mass spectrum m/e (rel intensity) 288 (M^+, 30), 242 (M^+ − EtOH, 58), 216 (242^+ − OEt, 100), 197 (242^+ − CO, 40), 171 (197^+ − CO, 58), 116 (38), 104 (60), 77 (38).

Anal. Calcd for $C_{15}H_{16}N_2O_4$: C, 62.49; H, 5.59; N, 9.72. Found: C, 62.43; H, 5.46; N, 9.85.

B. Similarly, treatment of the filtrate obtained from the same reaction as in A with aniline (0.5 g, 5.3 mmol) in place of ethanol at room temperature for 30 min gave 0.43 g (26%) of ethyl α-cyano-β-phenyl-β-(3-phenylureido)acrylate (**5**) as colorless needles: mp 173–173.5°; ir (KBr) 3260, 3160 (NH), 2235 (C≡N), 1720 (sh), 1700, 1680 cm^{-1} (sh) (C=O); nmr ($CDCl_3$) δ 1.40 (t, 3, CH_2CH_3, J = 7 Hz), 4.45 (q, 2, CH_2Me, J = 7 Hz), 7.45–8.0 (m, 10, aromatic protons), 8.73, 13.3 (each broad, 1, NH, exchanged with D_2O).

Anal. Calcd for $C_{19}H_{17}N_3O_3$: C, 68.05; H, 5.11; N, 12.53. Found: C, 67.93; H, 4.98; N, 12.34.

C. Initially, **1** (1.0 g, 4.95 mmol) was treated with ethanol (0.25 g, 5.4 mmol) in diethyl ether (15 ml) at room temperature for 10 hr. A solution of **2** (0.56 g, 4.95 mmol) and NEt_3 (0.5 g, 4.95 mmol) in diethyl ether (15 ml) was added, drop by drop, to the above mixture and the resulting mixture was then stirred at room temperature for 2 hr to precipitate crystals. Crystals were collected by filtration and washed with water. Recrystallization of insoluble crystals from ethanol afforded 0.52 g (36%) of **4**.

In the Presence of 2 Equiv of NEt_3. A. A solution of **2** (1.33 g, 11.8 mmol) and NEt_3 (2.4 g, 23.7 mmol) in diethyl ether (20 ml) was added, drop by drop, to a solution of **1** (2.4 g, 11.8 mmol) in diethyl ether (10 ml), and the reaction mixture was then stirred at room temperature for 4 hr. Filtration gave 3.0 g of triethylamine hydrochloride. The filtrate was concentrated *in vacuo* to leave a brown, oily product **7**, which was chromatographed on alumina.

Crystals were obtained from the elution with benzene–chloroform (1:1 v/v) and recrystallized from diethyl ether to afford 0.84 g (33%) of ethyl α-cyano-β-amino-β-phenylacrylate (**8**) as colorless needles: mp 125–125.5°; ir (KBr) 3320, 3180 (NH), 2210 (C≡N), 1665 cm^{-1} (C=O); nmr ($CDCl_3$) δ 1.34 (t, 3, CH_2CH_3, J = 7 Hz), 4.28 (q, 2, CH_2Me, J = 7 Hz), 7.4–7.75 (m, 5, aromatic protons), 5.85, 9.45 (each broad, 1, NH, exchanged with D_2O); mass spectrum m/e (rel intensity) 216 (M^+, 79), 187 (M^+ − Et, 65), 171 (M^+ − OEt, 83), 143 (171^+ − CO and/or 187^+ − CO_2, 65), 127 (143^+ − NH_2, 71), 117 (143^+ − CN, 74), 104 (100), 89 (76), 77 (65).

Anal. Calcd for $C_{12}H_{12}N_2O_2$: C, 66.65; H, 5.59; N, 12.96. Found: C, 66.72; H, 5.66; N, 12.96.

The compound **8** was identical with an authentic sample prepared from the reaction of **2** with benzonitrile in the presence of sodium ethoxide.[7]

On the other hand, crystals were obtained from the elution with methanol and recrystallized from ethanol to give 0.28 g (6.5%) of ethyl α-cyano-β-phenyl-β-(3-benzoylureido)acrylate (**9**) as colorless needles, which was identical with an authentic sample prepared from **8** and benzoyl isocyanate: mp 172.5–173.5° dec; ir (KBr) 3220, 3150 (NH), 2220 (C≡N), 1740 (sh), 1710, 1700, 1690 (sh), 1670 cm^{-1} (C=O); nmr ($CDCl_3$) δ 1.40 (t, 3, CH_2CH_3, J = 7 Hz), 4.45 (q, 2, CH_2Me, J = 7 Hz), 7.4–8.0 (m, 10, aromatic protons), 8.73, 13.38 (each broad s, 1, NH, exchanged with D_2O); mass spectrum m/e (rel intensity) 363 (M^+, 54), 318 (M^+ − OEt, 25), 290 (318^+ − CO, 13), 247 (290^+ − HNCO, 57), 242 (M^+ − $PhCONH_2$, 43), 216 (242^+ − CN, 80), 197 (242^+ − OEt, 81), 188 (216^+ − CO_2, 89), 171 (197^+ − CO, 92), 144 (188^+ − MeCHO, 51), 116 (144^+ − CO, 57), 105 ($PhCO^+$, 100), 89 (40), 77 (60).

Anal. Calcd for $C_{20}H_{17}N_3O_4$: C, 66.11; H, 4.72; N, 11.57. Found: C, 66.34; H, 4.65; N, 11.49.

B. A solution of **7** (obtained from the reaction under the same conditions) in ethanol (10 ml) was stirred with concentrated hydrochloric acid (5 ml) at room temperature for 12 hr, during which time crystals precipitated. Filtration and recrystallization from ethanol afforded 0.36 g (8.3%) of **9**. The filtrate was neutralized with aqueous sodium hydroxide and then extracted with diethyl ether. The ether extract was evaporated to leave crystals, which on crystallization from diethyl ether gave 0.89 g (35%) of **8**.

In the Presence of 3 Equiv of NEt_3. A solution of **1** (0.5 g, 2.47 mmol) and **2** (0.6 g, 5.3 mmol) in diethyl ether (30 ml) was added, drop by drop, to a solution of NEt_3 (0.75 g, 7.4 mmol) in diethyl ether (20 ml), and the reaction mixture was then stirred at room temperature for 5 hr, during which time crystals appeared. Crystals were collected by filtration and washed with water to leave yellow crystals. Recrystallization from ethanol–diethyl ether afforded 0.76 g (67%) of salt **10** as yellow needles: mp 127.5–128.5° dec; ir (KBr) 3200 (NH), 3000–2800 (NH^+), 2250, 2225 (C≡N), 1740 (sh), 1720 (sh), 1700, 1670, 1635 cm^{-1} (C=O); nmr ($CDCl_3$)[13] δ 1.01 (t, 9, NCH_2CH_3), 1.28, 1.32 (each t, 3, OCH_2CH_3), 2.5–3.0 (m, 6, NCH_2Me), 4.25, 4.36 (each q, 2, OCH_2Me), 7.41 (s, 5, aromatic protons), 9.60, 13.15 (each broad, 1, NH).

Anal. Calcd for $C_{24}H_{32}N_4O_5$: C, 63.14; H, 7.07; N, 12.21. Found: C, 62.91; H, 6.87; N, 12.25.

Treatment of Salt 10 with Hydrochloric Acid. A suspension of **10** (70 mg) in 1 *N* hydrochloric acid (20 ml) was stirred at room temperature for 1 hr, and crystals were filtered and washed with water. Recrystallization from diethyl ether gave 40 mg (73%) of the enol **11** as colorless needles, which on treatment with NEt_3 was converted into **10**: mp 92–93° dec; ir (KBr) 3080 (NH), 2210, 2190 (C≡N), 1730 (sh), 1710 (sh), 1690 (sh), 1640, 1630 cm^{-1} (C=O); nmr ($CDCl_3$) δ 1.35, 1.39 (each t, 3, CH_2CH_3), 4.31, 4.45

(each q, 2, CH_2Me), 7.52 (s, 5, aromatic protons), 10.0, 12.45 (each 1, OH or NH, exchanged with D_2O).

Anal. Calcd for $C_{18}H_{17}N_3O_5$: C, 60,84; H, 4.82; N, 11.83. Found: C, 61.07; H, 4.92; N, 11.76.

Reaction with Methyl Cyanoacetate. The reaction of **1** (0.5 g, 2.47 mmol) with methyl cyanoacetate (0.6 g, 6 mmol) in the presence of NEt_3 (0.75 g, 7.4 mmol) in diethyl ether at room temperature for 5 hr afforded 0.7 g (66%) of salt **12** as yellow needles: mp 157–159° dec; ir (KBr) 3180 (NH), 3000–2800 (NH^+), 2190, 2180 (C≡N), 1700, 1650, 1620 cm^{-1} (C=O); nmr ($CDCl_3$)[13] δ 1.02 (t, 9, NCH_2CH_3), 2.5–3.05 (m, 6, NCH_2Me), 3.80, 3.91 (each s, 3, OCH_3), 7.43 (s, 5, aromatic protons), 9.60, 13.18 (each broad, 1, NH).

Anal. Calcd for $C_{22}H_{28}N_4O_5$: C, 61.66; H, 6.59; N, 13.08. Found: C, 61.49; H, 6.69; N, 12.78.

Reaction with Acenaphthenone (13) in the Presence of NEt_3. A solution of **1** (0.5 g, 2.47 mmol) and **13** (0.4 g, 2.4 mmol) in diethyl ether (30 ml) was stirred with NEt_3 (0.5 g, 4.95 mmol) at room temperature for 2 hr, during which time crystals precipitated. Crystals were collected by filtration and washed with water to leave yellow crystals Recrystallization from benzene–petroleum ether (bp 45–65°) gave 0.2 g (27%) of 10-phenylacenaphtho[1,2-*e*]-2*H*-1,3-oxazin-8-one (**14a**) as yellow needles: mp 180–180.5° dec; ir (KBr) 1735 (C=O), 1710 cm^{-1} (C=N); nmr ($CDCl_3$) δ 7.25–8.4 (m, aromatic protons); mass spectrum *m/e* (rel intensity) 297 (M^+, 87), 296 (100), 269 ($M^+ - CO$, 7), 255 ($M^+ - NCO$, 7), 240 ($269^+ - CO - H$, 17), 226 ($269^+ - HNCO$, 17), 138 ($241^+ - PhCN$, 25).

Anal. Calcd for $C_{20}H_{11}NO_2$: C, 80.79; H, 3.73; N, 4.71. Found: C, 80.97; H, 3.99; N, 4.58.

Hydrolysis of 14a. After a suspension of **14a** (0.2 g) in 15% hydrochloric acid (20 ml) was stirred at room temperature for 4 hr, filtration gave crystals, which were washed with water and chromatographed on alumina. From the elution with chloroform yellow crystals were obtained. Recrystallization from benzene–petroleum ether (bp 50–65°) afforded 0.18 g (98.7%) of 2-(1′-aminobenzylidene)acenaphthenone (**15**) as yellow needles: mp 143–144° dec; ir (KBr) 3440, 3260 (NH), 1635 cm^{-1} (C=O); nmr ($CDCl_3$) δ 5.0, 9.9 (each broad, 1, NH, exchanged with D_2O), 7.0–8.15 (m, 11, aromatic protons); mass spectrum *m/e* (rel intensity) 271 (M^+, 82), 270 (100), 254 ($270^+ - NH_2$, 30), 243 ($271^+ - CO$, 15) 226 ($154^+ - CO$, 12), 136 (20), 120 (20).

Anal. Calcd for $C_{19}H_{13}NO$: C, 84.11; H, 4.83; N, 5.16. Found: C, 83.91; H, 5.10; N, 5.25.

Benzoylation of 15. After a solution of **15** (0.2 g, 0.74 mmol) in pyridine (2 ml) was heated with benzoyl chloride (0.28 g, 2 mmol) at 80° for 15 min, the reaction mixture was poured into water, giving yellow crystals. Recrystallization from benzene–petroleum ether (bp 45–60°) afforded 0.19 g (53.7%) of dibenzoyl compound **16** as yellow needles: mp 188° dec; ir (KBr) 1710, 1670 cm^{-1} (C=O); mass spectrum *m/e* 479 (M^+).

Anal. Calcd for $C_{33}H_{21}NO_3$: C, 82.56; H, 4.41; N, 2.92. Found: C, 82.39; H, 4.31; N, 3.04.

Reaction with 13 in the Presence of Metallic Sodium. When metallic sodium (0.46 g, 0.02 g-atom) was added to a solution of **13** (1.4 g, 8.3 mmol) in diethyl ether (30 ml), the colorless solution changed to a violet color. The violet solution was stirred with **1** (1.0 g, 4.95 mmol) at room temperature for 10 hr to yield a brown solid, which was extracted with hot benzene. The extract was concentrated *in vacuo*, and a residue was chromatographed on alumina using benzene as an eluent to give yellow crystals. Recrystallization from benzene afforded 0.2 g (20%) of 2-phenyldiacenaphtho[1,2-*b*:1′,2′-*d*]pyridine (**17**), mp 287°, as yellow needles, which was identical with an authentic sample obtained from the pyrolysis of acenaphthenone *N*-benzoylhydrazone[9] [*Anal.* Calcd for $C_{31}H_{17}N$: C, 92.31; H, 4.22; N, 3.47. Found: C, 92.24; H, 3.97; N, 3.25. Mass spectrum *m/e* 403 (M^+)].

Reaction with 5,5-Dimethylcyclohexane-1,3-dione (18). A solution of **1** (0.5 g, 2.47 mmol) and **18** (0.35 g, 2.5 mmol) in diethyl ether (30 ml) was stirred with NEt_3 (0.5 g, 4.95 mmol) at room temperature for 2 hr, during which time crystals appeared. Crystals were collected by filtration and washed with water. Recrystallization from benzene–petroleum ether (bp 45–65°) afforded 0.2 g (30%) of 4*H*-1,3-oxazinone derivative **19** as yellow needles: mp 184–184.5°; ir (KBr) 1715, 1660, 1640 cm^{-1} (C=O, C=N); nmr ($CDCl_3$) δ 1.20 (s, 6, CH_3), 2.50, 2.85 (each s, 2, CH_2), 7.5–7.7 (m, 3, aromatic protons), 8.15–8.35 (m, 2, aromatic protons); mass spectrum *m/e* (rel intensity) 269 (M^+, 100), 254 ($M^+ - Me$, 10), 166 ($M^+ - PhCN$, 20), 165 (50), 151 ($254^+ - PhCN$, 65), 138 ($166^+ - CO$, 74), 104 (40), 103 (70).

Anal. Calcd for $C_{16}H_{15}NO_3$: C, 71.36; H, 5.61; N, 5.20. Found: C, 71.62; H, 5.89; N, 5.29.

Hydrolysis of 19. After a suspension of **19** (0.2 g) in 15% hydrochloric acid (20 ml) was stirred at room temperature for 2 hr, crystals were collected by filtration and washed with water. Recrystallization from diethyl ether afforded 0.18 g (84.5%) of 2-benzoylcarbamoyl-5,5-diemethylcyclohexane-1,3-dione (**20**) as yellow prisms: mp 149–150.5° dec; ir (KBr) 3175 (NH), 1720, 1650, 1625 cm^{-1} (C=O); nmr ($CDCl_3$) δ 1.13 (s, 6, CH_3), 2.47, 2.62 (each s, 2, CH_2), 7.5–7.72 (m, 3, aromatic protons) 8.0–8.2 (m, 2 aromatic protons), 13.2 16.92 (each broad, 1, NH or OH, exchanged with D_2O); mass spectrum *m/e* (rel intensity) 287 (M^+, 95), 272 ($M^+ - Me$, 10), 259 ($M^+ - CO$, 15) 231 ($259^+ - CO$, 38), 203 ($231^+ - CO$, 26), 167 ($272^+ - PhCO$, 26), 105 (100).

Anal. Calcd for $C_{16}H_{17}NO_4$: C, 66.88; H, 5.96; N, 4.88. Found: C, 67.17; H, 5.84; N, 4.97.

Registry No.—**1**, 4547-71-1; **2**, 105-56-6; **4**, 51003-09-9; **5**, 51003-10-2; **7**, 51002-93-8; **8**, 39491-78-6; **9**, 51003-08-8; **10a**, 51003-04-4; **10b**, 51003-06-6; **11**, 51003-07-7; **12**, 2235-15-6; **13a**, 51003-25-9; **14**, 51003-26-0; **15**, 51003-27-1; **16**, 51003-28-2; **17**, 23952-27-4; **18**, 126-81-8; **19**, 51003-29-3; **20**, 51003-30-6.

References and Notes

(1) Part I: O. Tsuge, M. Yoshida, and S. Kanemasa, *J. Org. Chem.*, **39**, 1226 (1974).
(2) E. Degener, H. G. Schmelzer, and H. Hotschmidt, *Angew. Chem.*, **78**, 981 (1966).
(3) S. Yanagida, M. Yokoe, M. Ohoka, and S. Komori, *Bull. Chem. Soc. Jap.*, **44**, 2182 (1971).
(4) Y. Shvo and I. Belsky, *Tetrahedron*, **25**, 4649 (1969).
(5) In the nmr spectra in $CDCl_3$ at −20, −50, and −60°, the NH signal appeared as a singlet at δ 11.40, 11.45, and 11.47, respectively.
(6) Hydrolysis of **3** under the same conditions gave **4** as a sole product.
(7) E. F. J. Atkinson, H. Ingham, and J. F. Thorpe, *J. Chem. Soc., London, Trans.*, **91**, 579 (1907).
(8) O. Tsuge, M. Tashiro, and I. Shinkai, *Bull. Chem. Soc. Jap.*, **42**, 181 (1969).
(9) O. Tsuge, K. Hokama, and M. Koga, *Yakugaku Zasshi*, **89**, 789 (1969).
(10) J. F. Garst, D. Walmsley, and W. R. Richards, *J. Org. Chem.*, **27**, 2924 (1962).
(11) C. L. Angell and R. L. Werner, *Aust. J. Chem.*, **6**, 294 (1953).
(12) All melting points are uncorrected. The nmr spectra were determined at 60 MHz with a Hitachi R-20 nmr spectrometer with TMS as an internal reference. The mass spectra were obtained on a Hitachi RMS-4 mass spectrometer with a direct inlet and an ionization energy of 70 eV.
(13) It has been found that the difference of chemical shift between methyl and methylene protons in the nmr spectrum of NEt_3 in $CDCl_3$ was 1.50 ppm, while that between methyl and methylene protons in triethylamine hydrochloride was 1.75 ppm. The difference of chemical shift between methyl and methylene protons in the NEt_3 group in **10** and **12** was found to be 1.75 ppm.