# Studies of Acyl and Thioacyl Isocyanates. XIII.[1] The Reactions of Benzoyl and Thiobenzoyl Isocyanates with Hydrazobenzenes and Further Investigation of the Reaction of Thiobenzoyl Isocyanate with Phenylhydrazine

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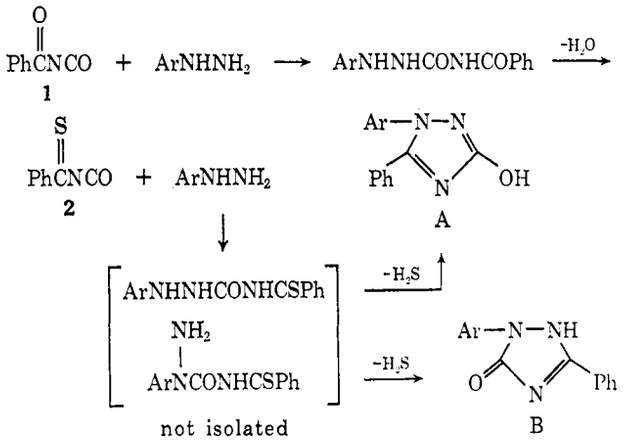
Benzoyl isocyanate (1) reacts exclusively with the more basic nitrogen atom in hydrazobenzenes (3) to give the corresponding 1,2-diaryl-4-benzoylsemicarbazides (4), which on treatment with hydrochloric acid underwent ring closure to the triazolinones (5) by the loss of water. On the other hand, thiobenzoyl isocyanate (2) attacks both nitrogen atoms to afford a mixture of semicarbazides (6 and 7), which on heating was easily converted into two isomeric triazolinones (5 and 8) with the elimination of hydrogen sulfide. On the basis of the relative amounts of 5 and 8, it is clear that 2 reacts preferentially with the more basic nitrogen atom in 3. In this context, the reaction of 2 with phenylhydrazine (16) has been reinvestigated, and the pathway for the formation of 1,3-diphenyl-$\Delta^3$-1,2,4-triazolin-5-one (19) has been elucidated.

In a previous paper,[2] we reported that benzoyl isocyanate (1) reacted with arylhydrazine to yield the corresponding 1-aryl-4-benzoylsemicarbazide, which on treatment with hydrochloric acid underwent ring closure to 1-aryl-3-hydroxy-5-phenyl-1,2,4-triazole (A), while in the same reaction of thiobenzoyl isocyanate (2) 1-aryl-3-phenyl-$\Delta^3$-1,2,4-triazolin-5-one (B) or A, or both, were obtained. The relative amounts of triazole A and triazolinone B depended on the nature



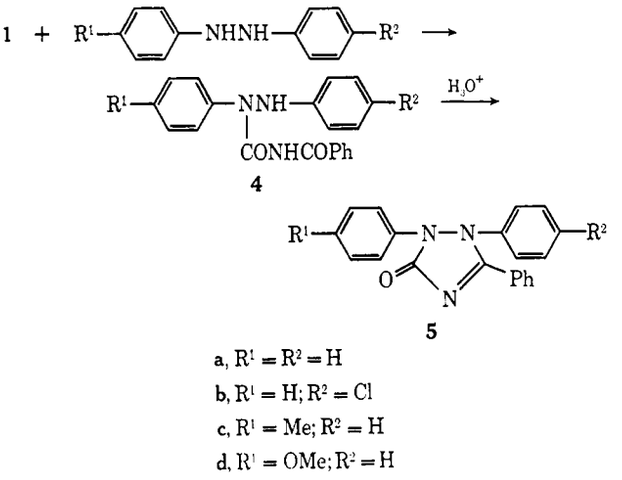

of the substituent of arylhydrazine. These facts seem to indicate that 1 reacts invariably with the $\beta$-nitrogen atom, and 2 attacks competitively the $\alpha$- and $\beta$-nitrogen atoms in arylhydrazine.

In order to obtain information on the difference between the reactivity of 1 and 2 toward arylhydrazine, the reactions of 1 and 2 with hydrazobenzenes (3) were studied. In this context, the reaction of 2 with phenylhydrazine was also reinvestigated.

## Results and Discussion

**Reaction with Hydrazobenzenes.**—The reaction of isocyanate 1 with hydrazobenzene (3a) in benzene at room temperature afforded 1,2-diphenyl-4-benzoylsemicarbazide (4a) in an excellent yield. In the reaction of 1 with asymmetrical hydrazobenzenes, 1 would be expected to attack competitively the both nitrogen atoms in the hydrazobenzenes. However, 1 reacted with *p*-chloro- (3b), *p*-methyl- (3c), and *p*-methoxyhydrazobenzene (3d) to give only 1-*p*-chlorophenyl-2-phenyl- (4b), 1-phenyl-2-*p*-tolyl- (4c), and 1-phenyl-2-*p*-anisyl-4-benzoylsemicarbazide (4d) in good yields, respectively (Scheme I): this indicates that 1 attacks exclusively the more basic nitrogen atom in 3.

SCHEME I

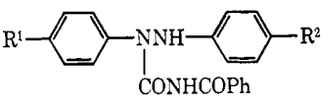



a, $R^1 = R^2 = H$
b, $R^1 = H; R^2 = Cl$
c, $R^1 = Me; R^2 = H$
d, $R^1 = OMe; R^2 = H$

The structures of semicarbazides 4 (Table I) were confirmed by the spectral data as well as by chemical conversions.

TABLE I

1,2-DIARYL-4-BENZOYLSEMICARBAZIDES[a]




| Compd[b] | $R^1$ | $R^2$ | Yield, % | Mp, °C[c] | Ir, cm$^{-1}$ $\nu_{NH}$ | Ir, cm$^{-1}$ $\nu_{C=O}$ |
|---|---|---|---|---|---|---|
| 4a | H | H | 95 | 209 | 3320, 3250 | 1740, 1720 |
| 4b | H | Cl | 99 | 187 | 3320, 3260 | 1740, 1730 |
| 4c | Me | H | 94 | 201.5–202 | 3320, 3250 | 1740, 1730 |
| 4d | OMe | H | 94 | 178–179.5 | 3320, 3240 | 1740, 1720 |

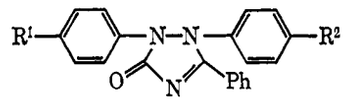
[a] Satisfactory analyses (±0.4% for C, H, and N) were reported for all new compounds listed in the table. [b] All the compounds are colorless prisms. [c] All the compounds melted with decomposition.

(1) Part XII of this series: O. Tsuge, K. Sakai, and M. Tashiro, *Tetrahedron*, in press.

(2) O. Tsuge, S. Kanemasa, and M. Tashiro, *Tetrahedron*, **24**, 5205 (1968).

TABLE II

1,2,3-TRIARYL-$\Delta^3$-1,2,4-TRIAZOLIN-5-ONES[a]



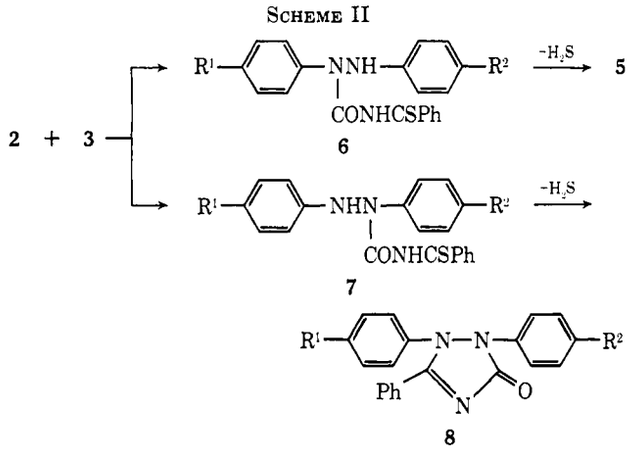
| Compd[b] | R[1] | R[2] | Reaction conditions: Acid | Temp, °C | Time, hr | Yield, % | Mp, °C | Ir (C=O), cm$^{-1}$ | Mol wt, *m/e* |
|---|---|---|---|---|---|---|---|---|---|
| **5a** | H | H | 15% HCl | 90–95 | 3 | 93 | 233–234 | 1690 | 313 |
| **5b** | H | Cl | 15% HCl | 90–95 | 1 | 84 | 249–250 | 1710 | 347, 349[c] |
| **5c** | Me | H | 10% HCl | 95–100 | 1 | 97 | 222–223 | 1690, 1680 | 327[c] |
| **5d** | OMe | H | 10% HCl | 95–100 | 10 min | 74 | 217.5 | 1705 | 343 |

[a] Satisfactory analyses (±0.4% for C, H, and N) were reported for all new compounds listed in the table. [b] All the compounds are colorless prisms. [c] Compound **5b** showed fragment ions at *m/e* 244, 246 ($M^+$ − PhCN) (rel intensity 3:1), 216, 218 ($[ClC_6H_4N{=}NPh]\cdot^+$) (3:1), 214, 216 ($ClC_6H_4\overset{+}{N}{\equiv}CPh$) (3:1), and **5c** exhibited fragment ions at *m/e* 224 ($M^+$ − PhCN), 196 ($[MeC_6H_4N{=}NPh]\cdot^+$) and 180 ($Ph\overset{+}{N}{\equiv}CPh$) in the respective mass spectrum.

Treatment of **4** with hydrochloric acid yields 1-($R^1$ substituted phenyl)-2-($R^2$ substituted phenyl)-3-phenyl-$\Delta^3$-1,2,4-triazolin-5-ones (**5a–5d**) in good yields (Table II).

In the reaction with **3a** in xylene at room temperature, isocyanate **2** gave 1,2-diphenyl-4-thiobenzoylsemicarbazide (**6a**), which on warming in ethanol or benzene was easily converted into the triazolinone **5a** with the elimination of hydrogen sulfide. However, semicarbazides formed by the reaction of **2** with asymmetrical hydrazobenzenes were rather unstable and converted into the corresponding triazolinones during purification. The reaction of **2** with **3b** or **3c** in xylene at 95° afforded two isomeric triazolinones **5b** and 1-*p*-chlorophenyl-2,3-diphenyl-$\Delta^3$-1,2,4-triazolin-5-one (**8b**), or **5c** and 2-*p*-tolyl-1,3-diphenyl derivative (**8c**), respectively. In the reaction with **3d**, however, **2** gave only the triazolinone **5d**. It is evident that triazolinones **5** and **8** are formed *via* semicarbazides **6** and **7** with the elimination of hydrogen sulfide, respectively (Scheme II). Thus, the stronger

SCHEME II



a, $R^1 = R^2 = H$

b, $R^1 = H$; $R^2 = Cl$

c, $R^1 = Me$; $R^2 = H$

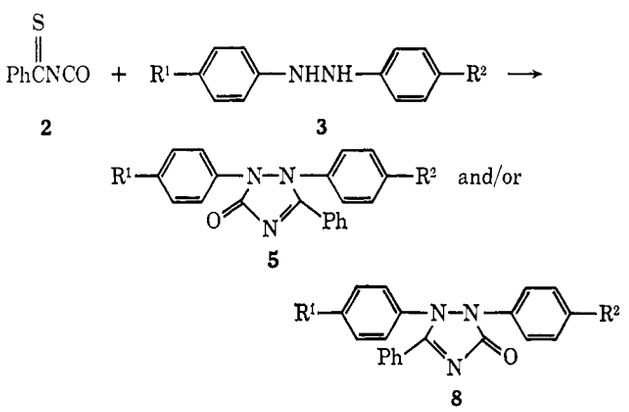
d, $R^1 = OMe$; $R^2 = H$

the electron-donating property of substituent ($R^1$) in **3**, the more easily the nitrogen atom having the $R^1$–$C_6H_4$ group is attacked.

The structures of isomeric triazolinones **5** and **8** were confirmed by the spectral data shown in Tables II and III as well as by the identification with authentic samples. The ir spectra of **5** were quite similar to those of **8**, and the mass spectra supported the proposed structures for **5** and **8**, respectively.

TABLE III

REACTION OF **2** WITH **3**

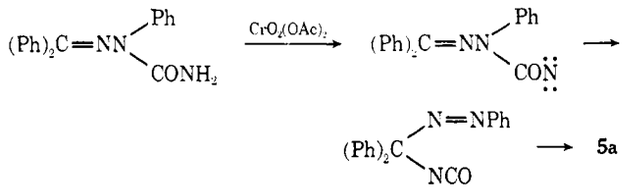


| | R[1] | R[2] | Yield, % **5** | Yield, % **8** | Compd[a] | Mp, °C | Ir (C=O), cm$^{-1}$ | Mol wt, *m/e* |
|---|---|---|---|---|---|---|---|---|
| **a** | H | H | 92[b] | | | | | |
| **b** | H | Cl | 52.5 | 22.5 | **8b** | 201–202 | 1700 | 347, 349[c] |
| **c** | Me | H | 59 | 25 | **8c** | 235.5–236 | 1705 | 327[c] |
| **d** | OMe | H | 90 | 0 | | | | |

[a] Satisfactory analyses (±0.4% for C, H, and N) were reported for all new compounds listed in the table. Compounds **8b** and **8c** are colorless prisms. [b] From 1,2-diphenyl-4-thiobenzoylsemicarbazide (**6a**). [c] Compound **8b** showed fragment ions at *m/e* 244, 246 ($M^+$ − PhCN) (rel intensity 3:1), 216, 218 ($[ClC_6H_4N{=}NPh]\cdot^+$) (3:1) and 180 ($PhC{\equiv}\overset{+}{N}Ph$), and **8c** exhibited fragment ions at *m/e* 224 ($M^+$ − PhCN), 196 ($[MeC_6H_4N{=}NPh]\cdot^+$), and 194 ($MeC_6H_4\overset{+}{N}{\equiv}CPh$) in the respective spectrum.

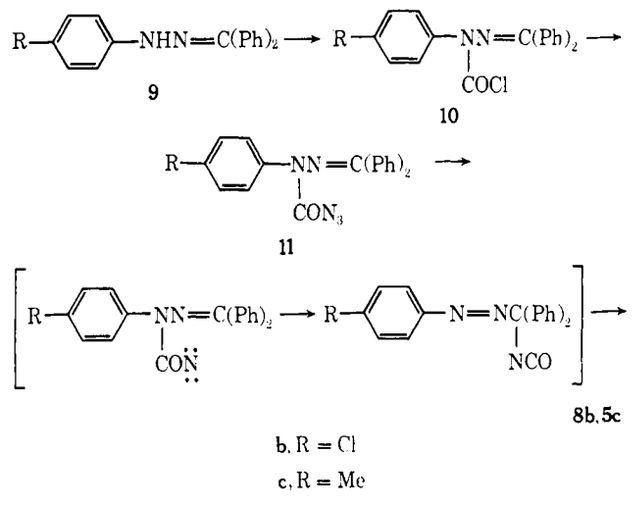
Recently, Schildknecht and Hatzmann[3] found that heating of 1-phenylazo-1,1-diphenylmethyl isocyanate, which was obtained by the oxidation of benzophenone 2-phenylsemicarbazone with chromyl acetate, afforded triazolinone **5a** (reported mp 236–238°) in a good yield. They proposed the following pathway *via* an acylnitrene intermediate.

(3) H. Schildknecht and G. Hatzmann, *Angew. Chem.*, **80**, 287 (1968); *ibid.*, **81**, 469 (1969).



We had success with our attempt to prepare triazolinones **5** and **8** from benzophenone *N*-aryl-*N*-azidocarbonylhydrazones as precursors of acylnitrene intermediates. Benzophenone *N*-*p*-chlorophenyl-*N*-chlorocarbonylhydrazone (**10b**), obtained from benzophenone *N*-*p*-chlorophenylhydrazone (**9b**) and phosgene, reacted with tetramethylguanidium azide to yield benzophenone *N*-*p*-chlorophenyl-*N*-azidocarbonylhydrazone (**11b**).[4] Thermal decomposition of acylazide **11b** in xylene at 135° for 2 hr afforded the expected triazolinone, which was identical with **8b** obtained from **2** and **3b** (Scheme III).

SCHEME III

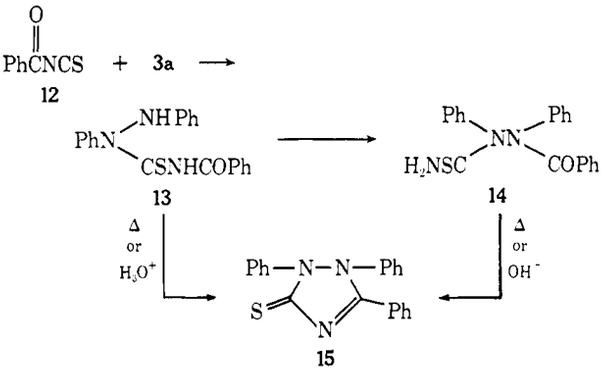


Similarly, benzophenone *N*-*p*-tolyl-*N*-azidocarbonylhydrazone (**11c**) prepared from the corresponding carbamoyl chloride (**10c**) gave triazolinone **5c**. The structures of carbamoyl chlorides **10** and acyl azides **11** were confirmed on the basis of spectral data and microanalyses. The pathway for the formation of triazolinone **5** or **8** from acyl azide **11** can be viewed as *via* acylnitrene and isocyanate intermediates as shown in Scheme III.

Thus, the reaction of **1** or **2** with **3** is a very convenient preparative method for 1,2,3-triaryl-$\Delta^3$-1,2,4-triazolin-5-ones.

We investigated the reaction of benzoyl isothiocyanate (**12**) with hydrazobenzenes (**3**) for comparison of that of acyl isocyanate **1** or **2**. Isothiocyanate **12** easily reacted with **3a** at room temperature to yield a 1:1 adduct **13** as yellow crystals, which on heating in ethanol or benzene transformed into an isomeric 1:1 adduct **14** as colorless prisms. The ir spectrum of **13** exhibited absorption bands due to $\nu_{NH}$ and $\nu_{C=O}$ at 3280 and 1700 $cm^{-1}$, while **14** showed characteristic bands ascribable to $\nu_{NH}$ and $\nu_{C=O}$ at 3400, 3240, 3140, and 1680 $cm^{-1}$ in its spectrum, respectively. The nmr spectrum of **14** showed a broad signal (2 H) ascribable to $NH_2$. On the basis of the above observations and of the inspection of the mass spectra, the structures of **13** and **14** were deduced as 1,2-diphenyl-4-benzoylthiosemicarbazide and 1,2-diphenyl-1-benzoylthiosemicarbazide, respectively (Scheme IV).

SCHEME IV



On heating at 160° or treatment with hydrochloric acid, **13** was converted into 1,2,3-triphenyl-$\Delta^3$-1,2,4-triazoline-5-thione (**15**), which was also obtained from **14** by heating at 220° or action with aqueous sodium hydroxide solution. The structure of **15** was deduced on the basis of its spectral data and microanalysis.

However, a mixture of triazolinethiones of type **15** was obtained in the reaction of **12** with asymmetrical hydrazobenzenes; isolation of pure triazolinethiones was unsuccessful in all cases.

**Reaction of Thiobenzoyl Isocyanate (2) with Phenylhydrazine.**—Previously,[2] we reported that the reaction of **2** with phenylhydrazine (**16**) gave 1,3-diphenyl-$\Delta^3$-1,2,4-triazolin-5-one (**19**), and suggested that **2** would react with the less basic $\alpha$-nitrogen atom in **16** to form 2-phenyl-4-thiobenzoylsemicarbazide (**18**) which underwent very rapid ring closure.

To resolve this contradiction, the reaction of **2** with **16** was reinvestigated. Compound **2** reacted with **16** at a low temperature (−5°) to yield an unstable yellow product **17**. When treated with hydrochloric acid or heated at 140–160°, **17** transformed into 3-hydroxy-1,5-diphenyl-1,2,4-triazole (**20**), which was identical with an authentic sample prepared from 1-phenyl-4-benzoylsemicarbazide,[5] with the elimination of hydrogen sulfide. This fact indicates that **17** is 1-phenyl-4-thiobenzoylsemicarbazide formed by the reaction of **2** with the more basic $\beta$-nitrogen atom in **16**.

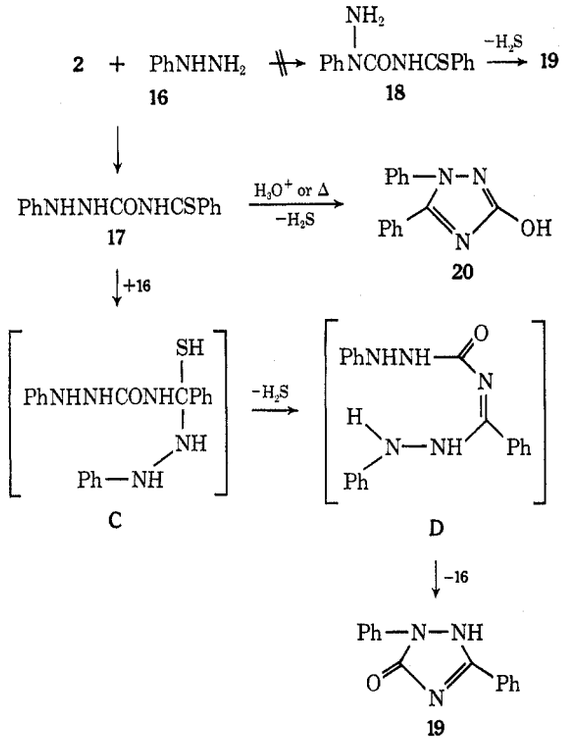
Many experiments were done in order to obtain information on the pathway for the formation of triazolinone **19** from semicarbazide **17**. We found that, when a benzene solution of semicarbazide **17** was refluxed in the presence of small amounts of **16**, the product was not the 3-hydroxy-1,2,4-triazole **20**, but $\Delta^3$-1,2,4-triazolin-5-one **19**. On the basis of the above fact, it is evident that the presence of **16** is indispensable for the formation of triazolinone **19** from semicarbazide **17**. The pathway for the formation of **19** can be viewed as shown in Scheme V.

That is, **16** would react with the carbon atom of thiobenzoyl group of semicarbazide **17** to form an intermediate C, followed by the elimination of hydrogen

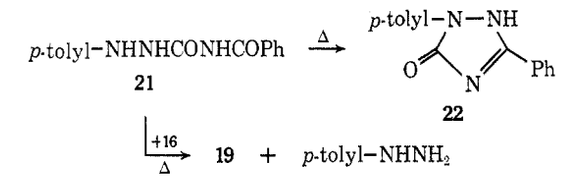
(4) The reaction of carbamoyl chloride **10b** with sodium azide did not give the expected acyl azide **11b**.

(5) O. Tsuge, T. Ito, and S. Kanemasa, *Nippon Kagaku Zasshi*, **89**, 69 (1968).

SCHEME V



sulfide to yield D. The loss of **16** from D would give the triazolinone **19**. This pathway is also supported by the following fact. Although heating of 1-*p*-tolyl-4-benzoylsemicarbazide (**21**)[5] at 215–220° gave 1-*p*-tolyl-3-phenyl-$\Delta^3$-1,2,4-triazolin-5-one (**22**) in a good yield, the treatment of **21** with an equimolar amount of **16** under the same conditions afforded the triazolinone **19**.



Previously,[5] we reported that the thermal ring closure of **21** and *p*-chloro derivative gave the corresponding 3-hydroxy-1,2,4-triazole as a main product, respectively. These semicarbazides used previously might be contaminated with arylhydrazine hydrochloride, because the thermal ring closure of the semicarbazides in the presence of trace of arylhydrazine hydrochloride afforded the 3-hydroxy-1,2,4-triazole. We now find that heating of pure semicarbazide gave the triazolinone in a good yield: **21** (255°, 5 min) and *p*-chloro derivative (235°, 3 min) afforded the corresponding triazolinone in 94 and 86% yields, respectively.

## Experimental Section[6]

**Materials.**—Benzoyl isocyanate (**1**) was prepared by the reported method.[7] To prepare thiobenzoyl isocyanate (**2**) a solution of 1.0 g of 2-phenylthiazoline-4,5-dione in 10 ml of xylene was heated at 120°, giving a reddish-violet solution of **2** which was used *in situ*.[8] This solution is referred to as the standard solution of **2**. Benzoyl isothiocyanate (**12**), bp 133–137° (18 mm) [lit.[9] bp 119° (10 mm)], was obtained from benzoyl chloride and lead thiocyanate in boiling benzene.

Hydrazobenzenes (**3**) were prepared by the reported methods, respectively: hydrazobenzene (**3a**), mp 124–125° (lit.[10] mp 126°); *p*-chloro- (**3b**), mp 91–92° (lit.[11] mp 89–90°); *p*-methyl- (**3c**), mp 88° (lit.[12] mp 86–87°); *p*-methoxyhydrazobenzene (**3d**), mp 75° (lit.[13] mp 74–75°).

**Reaction of 1 with 3a.**—A solution of **3a** (2.8 g) in dry benzene (50 ml) was added dropwise to a solution of **1** (2.25 g) in dry benzene (10 ml) at room temperature; crystals precipitated immediately. Recrystallization from ethanol afforded 1,2-diphenyl-4-benzoylsemicarbazide (**4a**).

Similarly, reactions of **1** with **3b**, **3c**, and **3d** gave the corresponding semicarbazides **4b**, **4c**, and **4d**, respectively. The yields and physical properties of **4** are given in Table I.

**Ring Closure of Semicarbazides 4.**—A solution of semicarbazide **4a** (0.5 g) in 15% hydrochloric acid (30 ml) was heated at 90–95° for 3 hr. After cooling, the reaction mixture was neutralized with aqueous ammonium hydroxide to give 0.44 g (93%) of colorless crystals. Recrystallization from ethanol afforded 1,2,3-triphenyl-$\Delta^3$-1,2,4-triazolin-5-one (**5a**), mp 233–234°, as colorless prisms.

Similarly, semicarbazides **4b–4d** underwent ring closure to the corresponding triazolinones **5b–5d**. Reaction conditions, yields, and physical properties of **5** are summarized in Table II.

**Reaction of 2 with 3. A. With 3a.**—To a standard solution of **2** was added 0.97 g of **3a**, and the reaction mixture was then stirred at room temperature for 30 min. Filtration gave 1.6 g (87%) of 1,2-diphenyl-4-thiobenzoylsemicarbazide (**6a**), mp 138° dec, as reddish-orange crystals, which were washed with benzene. The microanalysis of **6a** was submitted without further purification, because **6a** was rather unstable, ir (KBr) 3280 (NH), 1700 $cm^{-1}$ (C=O).

*Anal.* Calcd for $C_{20}H_{17}N_3OS$: C, 69.15; H, 4.93; N, 12.10. Found: C, 69.08; H, 4.81; N, 11.48.

**B. With 3b.**—To a standard solution of **2** was added 1.15 g of **3b** at room temperature, and the reaction mixture was heated at 95° for 2 hr, during which time hydrogen sulfide evolved. After cooling, filtration gave 0.95 g (52.5%) of triazolinone **5b**, which was identical with the product obtained from semicarbazide **4b**.

The filtrate was concentrated to leave colorless crystals, which on recrystallization from ethanol gave 0.4 g (22.5%) of 1-*p*-chlorophenyl-2,3-diphenyl-$\Delta^3$-1,2,4-triazolin-5-one (**8b**), mp 201–202°, as colorless prisms.

Similarly, the reaction of **2** with **3c** and **3d** gave the corresponding triazolinones **5** and/or **8**. The results and physical properties of **8** are given in Table III.

**Benzophenone *N*-*p*-Chlorophenyl-*N*-chlorocarbonylhydrazone (10b).**—To a solution of 15 g of benzophenone *N*-*p*-chlorophenylhydrazone (**9b**) in a mixture of pyridine (8 ml) and benzene (150 ml) was added dropwise 30% phosgene–toluene solution (30 ml) at 0°. The reaction mixture was refluxed for 1.5 hr, and then it was poured into ice–water, which was extracted with benzene. The benzene extract was dried ($CaCl_2$), and evaporated *in vacuo* to leave 14 g (78%) of solid. Recrystallization from petroleum ether (bp 60–80°) gave **10b**, mp 103–104°, as colorless prisms, ir (KBr) 1740 $cm^{-1}$ (C=O).

*Anal.* Calcd for $C_{20}H_{14}N_2OCl_2$: C, 65.05; H, 3.82; N, 7.59. Found: C, 65.09; H, 3.74; N, 7.64.

Similarly, the reaction of *N*-*p*-tolylhydrazone **9c** (15 g) with phosgene (32 ml of 30% phosgene–toluene solution) in a mixture of pyridine (8 ml) and benzene (150 ml) gave 16.8 g of the corresponding chlorocarbonylhydrazone (**10c**) as liquid, which was used without further purification, ir (neat) 1735 $cm^{-1}$ (C=O).

**Benzophenone *N*-*p*-Chlorophenyl-*N*-azidocarbonylhydrazone (11b),**—To a solution of tetramethylguanidium azide[14] (1.58 g) in dry chloroform (20 ml), a solution of carbamoyl chloride **10b** (3.69 g) in dry chloroform (20 ml) was added, drop by drop, be-

(6) All melting points are uncorrected. The ir spectra were measured as KBr disks, and 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.

(7) A. J. Speziale and L. R. Smith, *J. Org. Chem.*, **27**, 4361 (1962); *ibid.*, **28**, 1805 (1963).

(8) J. Goerdeler and H. Schenk, *Chem. Ber.*, **98**, 2954 (1965).

(9) P. A. S. Smith and R. O. Kan, *J. Org. Chem.*, **29**, 2261 (1964).

(10) P. Jacobson and A. Hugershoff, *Chem. Ber.*, **36**, 3841 (1904).

(11) K. Heumann and E. Mentha, *ibid.*, **19**, 1686 (1886).

(12) P. Jacobson, *Justus Liebigs Ann. Chem.*, **303**, 290 (1898).

(13) E. F. Pratt and T. P. McGovern, *J. Org. Chem.*, **29**, 1540 (1964).

(14) A. J. Papa, *J. Org. Chem.*, **31**, 1426 (1966).

low 0° over a period of 30 min. After the reaction mixture was stirred at room temperature for 30 min, it was poured into 50 ml of ice–water containing acetic acid (1 ml). The mixture was extracted with chloroform, and the extract was dried ($MgSO_4$). The extract was evaporated *in vacuo* to leave 3.3 g (88%) of crystals. Recrystallization from petroleum ether (bp 45–70°) afforded **11b**, mp 103° as colorless prisms: ir (KBr) 2180 ($N_3$), 1680 $cm^{-1}$ (C=O); mass spectrum (70 eV) *m/e* 375 ($M^+$), 305 ($M^+ - CON_3$, base peak).

*Anal.* Calcd for $C_{20}H_{14}N_5OCl$: C, 63.92; H, 3.76; N, 18.64. Found: C, 64.03; H, 3.48; N, 18.90.

Similarly, the reaction of carbamoyl chloride **10c** with tetramethylguanidium azide in dry chloroform afforded the corresponding acyl azide **11c**, mp 93.5°, as colorless prisms: yield 83%; ir (KBr) 2160 ($N_3$), 1690 $cm^{-1}$ (C=O); mass spectrum (70 eV) *m/e* 355 ($M^+$), 285 ($M^+ - CON_3$, base peak).

*Anal.* Calcd for $C_{21}H_{17}N_5O$: C, 70.96; H, 4.82; N, 19.71. Found: C, 70.87; H, 4.71; N, 19.68.

**Thermolysis of Acyl Azide 11b.**—A solution of **11b** (0.5 g) in dry xylene (5 ml) was heated at 135° for 2 hr. The reaction mixture was evaporated *in vacuo* to leave an oily substance, which on trituration with a mixture of methanol, acetone, and diethyl ether afforded crystals. Recrystallization from ethanol gave 0.18 g (39%) of triazolinone **8b**, mp 201–202°, as colorless prisms.

Similarly, thermolysis of acyl azide **11c** afforded triazolinone **5c**, mp 222–223°, in 41% yield.

**Reaction of Benzoyl Isothiocyanate (12) with 3a.**—A solution of **3a** (1.1 g) in dry benzene (20 ml) was added dropwise to a solution of **12** (1.0 g) in dry benzene (10 ml) at room temperature. Filtration afforded 1.85 g (88%) of yellow crystals, which were washed with benzene to give 1,2-diphenyl-4-benzoylthiosemicarbazide (**13**), mp 139.5–140° dec. This compound was submitted to microanalysis without further purification.

*Anal.* Calcd for $C_{20}H_{17}N_3OS$: C, 69.15; H, 4.93; N, 12.10. Found: C, 69.29; H, 4.81; N, 11.73.

**1,2-Diphenyl-1-benzoylthiosemicarbazide (14).**—A solution of **13** (0.2 g) in ethanol (10 ml) was refluxed for 5 min. The solution was concentrated to give 0.17 g (85%) of colorless crystals. Recrystallization from ethanol afforded **14**, mp 210–211° dec, as colorless prisms: nmr ($CDCl_3$) $\delta$ 6.23 (broad, 2, $NH_2$); mass spectrum (70 eV) *m/e* 347 ($M^+$).

*Anal.* Calcd for $C_{20}H_{17}N_3OS$: C, 69.15; H, 4.93; N, 12.10. Found: C, 69.38; H, 4.83; N, 12.14.

**1,2,3-Triphenyl-$\Delta^3$-1,2,4-triazoline-5-thione (15).**—Heating of **13** (0.5 g) at 160° for 10 min or treatment of **13** (0.5 g) with 15% hydrochloric acid (20 ml) at 90–95° for 30 min afforded 0.47 g (99%) or 0.45 g (95%) of **15**, mp 251°, as colorless needles: mass spectrum (70 eV) *m/e* 329 ($M^+$), 297 ($M^+ - S$), 296 ($M^+ - SH$), 180 ($PhC{\equiv}\overset{+}{N}Ph$).

*Anal.* Calcd for $C_{20}H_{15}N_3S$: C, 72.93; H, 4.59; N, 12.76. Found: C, 72.71; H, 4.37; N, 12.51.

**Reaction of 2 with Phenylhydrazine (16).**—A mixture of a standard solution of **2** and **16** (0.56 g) was stirred at −5° for 5 min. Dry diethyl ether was added to the reaction mixture, giving 1.3 g (92%) of 1-phenyl-4-thiobenzoylsemicarbazide (**17**) as yellow crystals. Compound **17** decomposed gradually under the evolution of hydrogen sulfide at room temperature: ir (KBr) 3220, 3150, 3080 (NH), 1680 $cm^{-1}$ (C=O).

Heating of **17** at 140–160° for 5 min or treatment with concentrated hydrochloric acid at room temperature for 30 min afforded 3-hydroxy-1,5-diphenyl-1,2,4-triazole (**20**)[5] in 91 or 86% yield, respectively.

**Reaction of 17 with 16.**—A solution of **17** (0.2 g) and **16** (0.18 g) in benzene (10 ml) was refluxed for 5 min. After cooling, filtration gave 0.16 g (91%) of 1,3-diphenyl-$\Delta^3$-1,2,4-triazolin-5-one (**19**),[2] mp 230–231° (lit.[15] mp 235°; lit.[16] mp 233°).

**Registry No.**—**1**, 4461-33-0; **2**, 3553-61-5; **3a**, 122-66-7; **3b**, 949-88-2; **3c**, 621-94-3; **3d**, 953-12-8; **4a**, 40587-77-7; **4b**, 40587-78-8; **4c**, 40587-79-9; **4d**, 40587-80-2; **5a**, 5378-13-2; **5b**, 40587-82-4; **5c**, 40587-83-5; **5d**, 40587-84-6; **6a**, 40587-85-7; **8b**, 40594-85-2; **8c**, 40594-86-3; **9b**, 40594-87-4; **9c**, 40594-88-5; **10b**, 40594-89-6; **10c**, 40594-90-9; **11b**, 40594-91-0; **11c**, 40594-92-1; **12**, 532-55-8; **13**, 40594-93-2; **14**, 40594-94-3; **15**, 40594-95-4; **16**, 100-63-0; **17**, 40594-96-5.

(15) J. Goerdeler and H. Schenk, *Chem. Ber.*, **99**, 782 (1966).
(16) G. Baccar and F. Mathis, *C. R. Acad. Sci.*, **261** (1), 174 (1965).

# The Reaction of Aluminum Azide with Cyano Esters. Preparation of Tetrazolo[1,5-c]pyrimidin-5(6*H*)-one and Tetrazolo[1,5-*c*]quinazolin-5(6*H*)-one

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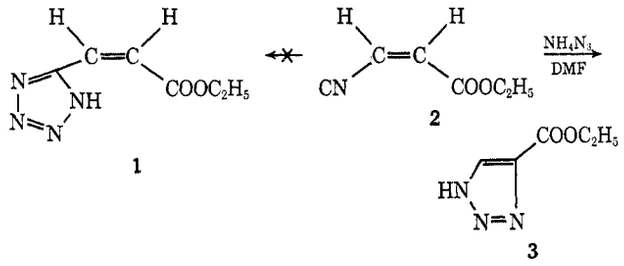
The reaction of aluminum azide and a variety of unsaturated β-cyano esters was studied. Both *cis*- and *trans*-3-cyanoacrylates gave *trans*-3-tetrazole-5-acrylate. *trans*-3-Cyanocrotonate produced *trans*-3-methyltetrazole-5-acrylate, while *cis*-3-cyanocrotonate gave a mixture consisting mainly of 1-(2-cyanopropenyl)tetrazolin-5(4*H*)-one and tetrazolo[1,5-*c*]pyrimidin-5(6*H*)-one. The reaction of aluminum azide and ethyl *o*-cyanobenzoate gave a mixture of four products: tetrazolo[1,5-*c*]quinazolin-5(6*H*)-one, 1-[*o*-(tetrazol-5-yl)phenyl]tetrazolin-5(4*H*)-one, ethyl *o*-(5-tetrazolyl)benzoate, and *o*-(5-oxo-2-tetrazolin-1-yl)benzonitrile. An explanation for the formation of the quinazolinone *via* a Curtius rearrangement is proposed. Alkaline hydrolysis of tetrazolo[1,5-*c*]-quinazolin-5(6*H*)-one produced 5-(*o*-aminophenyl)tetrazole, which could be reconverted to the tetrazolo-[1,5-*c*]quinazolinone by reaction with phosgene.

Because the previously unreported ethyl *cis*-tetrazole-5-acrylate (**1**) was required as a synthetic intermediate, an attempt was made to prepare it from the readily available ethyl *cis*-3-cyanoacrylate (**2**).[2] Several excellent methods are known for converting nitriles to tetrazoles, the most convenient being that of Finnegan, Henry, and Lofquist,[3] which employs ammonium azide in dimethylformamide. This reagent, however, caused elimination of cyanide from the cyanoacrylate




(1) Chemical Biology Research, The Dow Chemical Company, Midland, Mich. 48640.
(2) C. K. Sauers and R. J. Cotter, *J. Org. Chem.*, **26**, 6 (1961).
(3) W. G. Finnegan, R. A. Henry, and R. Lofquist, *J. Amer. Chem. Soc.*, **80**, 3908 (1958).