# 214. iso*Cyanates. Part III.* Benzoyl* iso*Cyanate.*

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Addition reactions of benzoyl *iso*cyanate are reported which indicate this compound to be among the most reactive of *iso*cyanates.

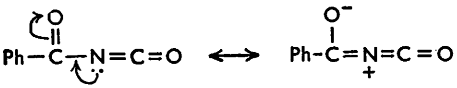
4-Benzoyl-1-phenyl- and 4-benzoyl-1-*p*-nitrophenyl-semicarbazide, derived from benzoyl *iso*cyanate, have been cyclised to 3-hydroxy-1 : 5-diphenyl- and-1-*p*-nitrophenyl-5-phenyl-1 : 2 : 4-triazole.

In connection with an investigation of the Hofmann reaction with *C*-benzoylformamide (Part II) it was observed that benzoyl *iso*cyanate undergoes vigorous hydrolysis with aqueous alkali, yielding benzamide. Billeter [1] found benzoyl *iso*cyanate to react with ammonia, aniline, benzamide, benzenesulphonamide, and ethanol to yield, respectively, benzoyl-, *N*-benzoyl-*N'*-phenyl-, dibenzoyl-, and *N*-benzenesulphonyl-*N'*-benzoyl-urea, and ethyl benzoylcarbamate; with urea it yields 1-benzoylbiuret.[2] Benzoyl *iso*cyanate appeared, therefore, to be a markedly reactive *iso*cyanate, and further reactions of this compound, together with its use in ring-closure, have been investigated.

Benzyl, *iso*propyl, *tert.*-butyl, and 1-methyl-1-α-naphthylpropyl benzoylcarbamate, Ph·CO·NH·CO·OR, have been prepared by the reaction of the corresponding alcohol with benzoyl *iso*cyanate. Since difficulty is, in some instances, experienced in the preparation of urethanes from tertiary alcohols, it is noteworthy that satisfactory derivatives were obtained from the two tertiary alcohols above.

From benzylamine there was obtained *N*-benzoyl-*N'*-benzylurea, Ph·CO·NH·CO·NH·$CH_2$Ph. Both the $NH_2$-groups of hydrazine reacted with benzoyl *iso*cyanate, yielding 1 : 2-bisbenzoylcarbamoylhydrazine, $(Ph{\cdot}CO{\cdot}NH{\cdot}CO{\cdot}NH)_2$. The arylhydrazines Ar·NH·$NH_2$ [Ar = Ph, *p*-$C_6H_4{\cdot}NO_2$, 2 : 4-$C_6H_3(NO_2)_2$] yielded the corresponding 1-aryl-4-benzoylsemicarbazides, Ar·NH·NH·CO·NH·COPh. (Phenylhydrazine reacts with phenyl *iso*cyanate to yield 1 : 4-diphenylsemicarbazide,[3] whence it is known that the $NH_2$ rather than the NHPh group reacts with an *iso*cyanate).

The presence of an electron-attracting (*—I*, *—M*) *p*-nitro-group in *p*-nitrophenyl *iso*cyanate has been found by Baker and Holdsworth [4] to increase the rate of reaction with methanol by a factor of 130 (under the stated conditions) in comparison with that of phenyl *iso*cyanate. Attempts were made to compare the rates of reaction of *p*-nitrophenyl and benzoyl *iso*cyanate with the same alcohol, by devising conditions under which both urethanes, but neither *iso*cyanate, could be precipitated and collected, but no satisfactory procedure was found. However, it is considered, in view of the reactions which it undergoes, that benzoyl *iso*cyanate is among the most reactive of *iso*cyanates; this is ascribed to (*a*) inductive electron-attraction by the carbonyl and phenyl constituents of the benzoyl group adjacent to the *iso*cyanate group, and (*b*) conjugation of the lone-pair on the nitrogen atom with the benzoyl-carbonyl group; both effects render the carbon atom of the *iso*cyanate group exceptionally prone to attack by an electron-donor. In each of the reactions above the donor is either $-\ddot{\text{O}}-$ or $>\ddot{\text{N}}-$.



Derivatives of benzoyl *iso*cyanate of type (I), in which either one or two atoms separate

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* Part II, *J.*, 1954, 4018.

[1] Billeter, *Ber.*, 1903, **36**, 3218.

[2] Hill and Degnan, *J. Amer. Chem. Soc.*, 1940, **62**, 1595.

[3] Freund and Goldsmith, *Ber.*, 1888, **21**, 2464.

[4] Baker and Holdsworth, *J.*, 1947, 716.

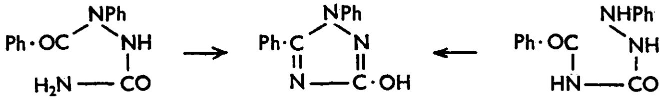
XH from the nearest carbonyl group, are potentially convertible, by elimination of the elements of water, into rings of type (II).

(I)

(II)

From 4-benzoyl-1-phenyl- and -*p*-nitrophenyl-semicarbazide the corresponding ring-compounds have been prepared; it has not been found possible to cyclise the derivatives of benzyl alcohol, benzylamine, and 2 : 4-dinitrophenylhydrazine.

By the action of aqueous sodium hydroxide followed by acidification with acetic acid, Widman [5] cyclised 1-benzoyl-1-phenylsemicarbazide (III). Similar treatment of 4-benzoyl-1-phenylsemicarbazide (IV) has been found to yield the same compound, 3-hydroxy-1 : 5-diphenyl-1 : 2 : 4-triazole (V).



(III) (V) (IV)

The formation of this from the isomeric compound (IV) provides additional evidence for the structure of the latter; were the compound the isomeric 4-benzoyl-2-phenylsemicarbazide, $NH_2$·NPh·CO·NH·COPh, then the product would be 5-hydroxy-1 : 3-diphenyl-1 : 2 : 4-triazole. This compound has m. p. 229—230°,[6] whereas (V) has m. p. 288—289°.

The relatively mild procedure above did not effect ring closure of the other semicarbazides. A number of examples of cyclisation by the use of polyphosphoric acid have been reported,[7] and on being heated with this reagent the compound (IV) yielded the triazole (V). On similar treatment 4-benzoyl-1-*p*-nitrophenylsemicarbazide gave 3-hydroxy-1-*p*-nitrophenyl-5-phenyl-1 : 2 : 4-triazole, but 4-benzoyl-1-(2 : 4-dinitrophenyl)semicarbazide was not changed.

## EXPERIMENTAL

M. p.s are corrected.

Benzoyl *iso*cyanate was prepared as described in Part II. The reactions below were carried out in a flask fitted with a condenser and, where required, a dropping funnel, to each of which was attached a calcium chloride tube; heating was by an oil-bath; all solvents were dried, and benzoyl *iso*cyanate was exposed as little as possible to moist air.

*Reactions with Alcohols.*—To benzyl alcohol (1·1 g.) in benzene (5 ml.) was added benzoyl *iso*cyanate (1·5 g.) in benzene (8 ml.); the solution was heated for ½ hr. at 70°, and on cooling yielded *benzyl benzoylcarbamate* (2·4 g.), m. p. 113—114°, which after recrystallisation from aqueous ethanol (1 : 1) had m. p. 115—115·5° (Found : C, 70·3; H, 5·0; N, 5·85. $C_{15}H_{13}O_3N$ requires C, 70·6; H, 5·15; N, 5·5%).

To *iso*propyl alcohol (15 ml.) was added benzoyl *iso*cyanate (1·5 g.); the solution was heated for ¾ hr. at 65°; iso*propyl benzoylcarbamate* (0·9 g.) separated on cooling, and on recrystallisation from benzene formed needles, m. p. 99—100° (Found : C, 63·85; H, 6·45; N, 6·9. $C_{11}H_{13}O_3N$ requires C, 63·75; H, 6·3; N, 6·75%).

To *tert.*-butyl alcohol (30 ml.) was added benzoyl *iso*cyanate (3·0 g.). An immediate reaction occurred; the flask was thereafter heated for 10 min. at 90°. On cooling there separated tert.*-butyl benzoylcarbamate* (2·9 g.), needles, m. p. 146—147°, unchanged by recrystallisation from aqueous ethanol (1 : 1) (Found : C, 65·45; H, 6·9; N, 6·1. $C_{12}H_{15}O_3N$ requires C, 65·15; H, 6·85; N, 6·35%).

To 1-methyl-1-α-naphthylpropanol (2·0 g., m. p. 50°) in ether (10 ml.), benzoyl *iso*cyanate (1·5 g.) in ether (8 ml.) was added; the ether was allowed to evaporate, yielding a product (2·9 g.), m. p. 119—121°, which on recrystallisation from ethanol gave 1-*methyl*-1-α-*naphthylpropyl benzoylcarbamate*, needles, m. p. 122° (decomp.) (Found : C, 75·7; H, 6·15; N, 4·1. $C_{22}H_{21}O_3N$ requires C, 76·05; H, 6·1; N, 4·05%).

[5] Widman, *Ber.*, 1896, **29**, 1951.

[6] Wheeler and Stratiropoulos, *Amer. Chem. J.*, 1905, **34**, 128.

[7] Birch, Jaeger, and Robinson, *J.*, 1945, 585; Koo, *J. Amer. Chem. Soc.*, 1953, **75**, 1891.

*Reactions with Amines.*—Reaction of benzylamine (1·1 g.) and benzoyl *iso*cyanate (1·5 g.), as for benzyl alcohol, gave *N*-benzoyl-*N*′-benzylurea (1·95 g.), m. p. 160—162°, which after recrystallisation from ethanol formed needles, m. p. 165—166° (Found : C, 70·65; H, 5·45; N, 11·25. Calc. for $C_{15}H_{14}O_2N_2$ : C, 70·85; H, 5·55; N, 11·0%). Wheeler and Johnson [8] record m. p. 165—166°.

To a stirred suspension of hydrazine hydrate (1·0 g.; 100%) in ether (10 ml.) was added benzoyl *iso*cyanate (2·4 g.) in ether (24 ml.). Immediate reaction occurred, and there separated a product (2·5 g.), m. p. 240—241° (decomp.), for which no satisfactory solvent was found. It was heated at 80°/1 mm. in a sublimation apparatus, when a relatively small amount of a lower-melting by-product sublimed; there remained 1 : 2-*bisbenzoylcarbamoylhydrazine*, m. p. 250° (Found : C, 58·6; H, 4·7; N, 17·2. $C_{16}H_{14}O_4N_4$ requires C, 58·95; H, 4·3; N, 17·15%).

To phenylhydrazine (3·9 g.) in benzene (20 ml.) was added benzoyl *iso*cyanate (5·9 g.) in benzene (20 ml.); the solution was heated for 10 min. at 70°; on cooling there separated 4-*benzoyl*-1-*phenylsemicarbazide* (7·2 g.), needles, m. p. 191—192°, which after recrystallisation from methanol had m. p. 194—195° (Found: C, 66·15; H, 5·05; N, 16·4. $C_{14}H_{13}O_2N_3$ requires C, 65·8; H, 5·15; N, 16·45%).

To *p*-nitrophenylhydrazine (6·0 g.) in dioxan (100 ml.), benzoyl *iso*cyanate (6·0 g.) in dioxan (30 ml.) was added; the solution was heated for ½ hr. at 70°. On cooling there separated 4-*benzoyl*-1-p-*nitrophenylsemicarbazide* (10·1 g.), m. p. 224—226·5°, which on recrystallisation from 2-ethoxyethanol formed yellow needles, m. p. 226—227° (Found : C, 56·1; H, 3·95; N, 18·35. $C_{14}H_{12}O_4N_4$ requires C, 56·0; H, 4·05; N, 18·65%).

Similar interaction of 2 : 4-dinitrophenylhydrazine (8·0 g.) in dioxan (125 ml.) and benzoyl *iso*cyanate (6·0 g.) in dioxan (30 ml.) gave a product (10·6 g.), m. p. 204—205°, which after recrystallisation from 2-ethoxyethanol yielded 4-*benzoyl*-1-(2 : 4-*dinitrophenyl*)*semicarbazide*, yellow needles, m. p. 210·5—211·5° (Found: C, 48·9; H, 3·25; N, 19·95. $C_{14}H_{11}O_6N_5$ requires C, 48·7; H, 3·2; N, 20·3%).

*Ring-closure.*—4-Benzoyl-1-phenylsemicarbazide (4·2 g.) was dissolved in 10% aqueous sodium hydroxide (63 ml.) at 50°, and the solution was poured into aqueous acetic acid (50%; 70 ml.). The product (2·5 g.) was heated with ethanol (175 ml.), and the solution filtered; the filtrate yielded 3-hydroxy-1 : 5-diphenyl-1 : 2 : 4-triazole (1·6 g.), m. p. 288—289°, unaltered by further recrystallisation (Found : C, 70·35, 70·1; H, 4·5, 4·6; N, 17·3. Calc. for $C_{14}H_{11}ON_3$ : C, 70·65; H, 5·0; N, 17·65%). Recorded m. p.s : 288—290°.[5, 9]

To 4-benzoyl-1-phenylsemicarbazide (0·5 g.) was added polyphosphoric acid (5 g.; $P_2O_5$ content, 83%); the mixture was heated at 65° for ¾ hr., a clear solution being obtained. It was poured into ice-water; there immediately separated 3-hydroxy-1 : 5-diphenyl-1 : 2 : 4-triazole (0·35 g.), having m. p. 285—287° and, after recrystallisation from ethanol, m. p. 288—289° alone and when mixed with the above specimen.

Similar reaction of 4-benzoyl-1-*p*-nitrophenylsemicarbazide (1·1 g.) with polyphosphoric acid (10 g.), but at 105° for 1 hr., yielded 3-*hydroxy*-1-p-*nitrophenyl*-5-*phenyl*-1 : 2 : 4-*triazole* (1·1 g.), m. p. 263—265°, which on recrystallisation from chlorobenzene formed yellow needles, m. p. 265—266° (Found : C, 59·6; H, 3·9; N, 19·5. $C_{14}H_{10}O_3N_4$ requires C, 59·55; H, 3·55; N, 19·85%).

Similar treatment did not cyclise 4-benzoyl-1-(2 : 4-dinitrophenyl)semicarbazide, which was recovered.

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[8] Wheeler and Johnson, *Amer. Chem. J.*, 1902, **27**, 218.

[9] Young, *J.*, 1895, **67**, 1064.