THE REACTION OF α-BROMODIPHENYLACETONITRILE AND POTASSIUM *p*-CHLORO-*N*-CYANOANILIDE*

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α-Bromodiphenylacetonitrile reacts with potassium *N*-cyanoanilide in anhydrous DMSO to yield, after work-up by pouring the reaction mixture into water, 61% of *N*-(cyanoanilino)-diphenylacetonitrile (**1a**) [1]. When α-bromodiphenylacetonitrile was allowed to react under similar conditions with potassium *p*-chloro-*N*-cyanoanilide, a compound **A** was obtained in 15% yield which contained two atoms of hydrogen and one atom of oxygen more than the expected **1b**. The IR spectrum of **A** exhibited a broad NH band at 3400—2700 cm^{-1} with local maxima at 3300 and 2900, and a C=0 and C=N band at 1705 and 1665 cm^{-1}, respectively; no bands were present in the 2300—2100 cm^{-1} region. Considering these data as well as the conceivable pathways leading to the formation of compound **A**, four alternative structures, **7—10**, have been tentatively derived for the latter. The probable modes of formation of compounds **7—10** are shown Scheme 1. The initial product of the reaction should be either **1b** (by analogy to the formation of **1a** [1]) or the isomeric carbodiimide **2**. (For aralkylations of monosubstituted cyanoamide anions to furnish disubstituted carbodiimides, see Ref. [2].) Hydration of one or the other of the functional groups of the initial product and subsequent cyclization should lead through the intermediates **3—6** to **7—10**, respectively.** (The cyclizations could, in principle, furnish oxazolidine derivatives as well, but the presence of a C=O band in the IR spectrum of compound **A** precludes the oxazilidine structure).

In order to be able to make a decision between the alternative structures **7—10** for **A**, the latter was subjected to acid hydrolysis to yield a compound **B** whose elemental composition and IR spectrum (ν $O{=}\underset{|}{C}{-}\overset{|}{N}{-}\underset{|}{C}{=}O$ 1760 +

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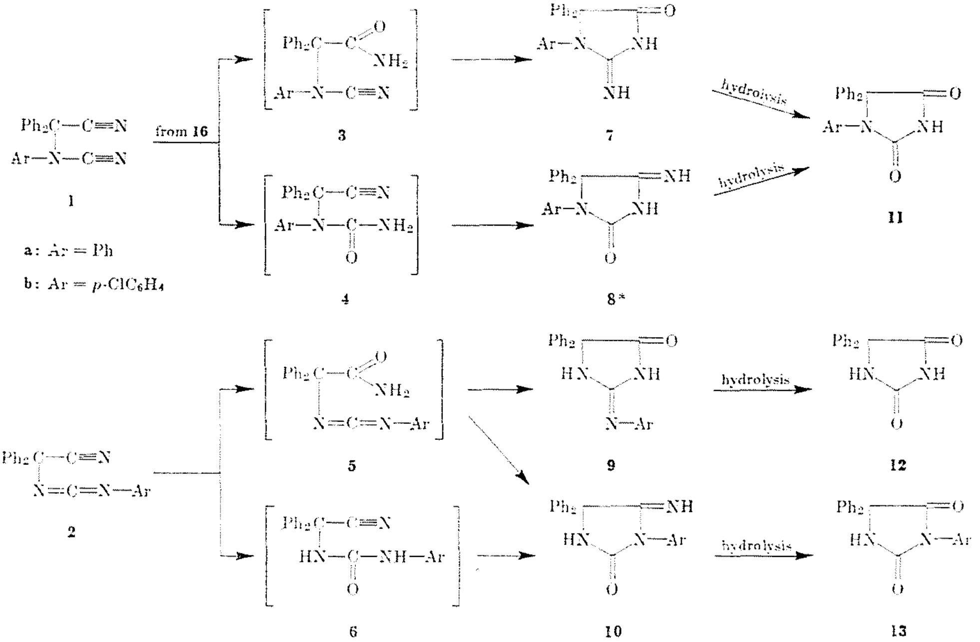
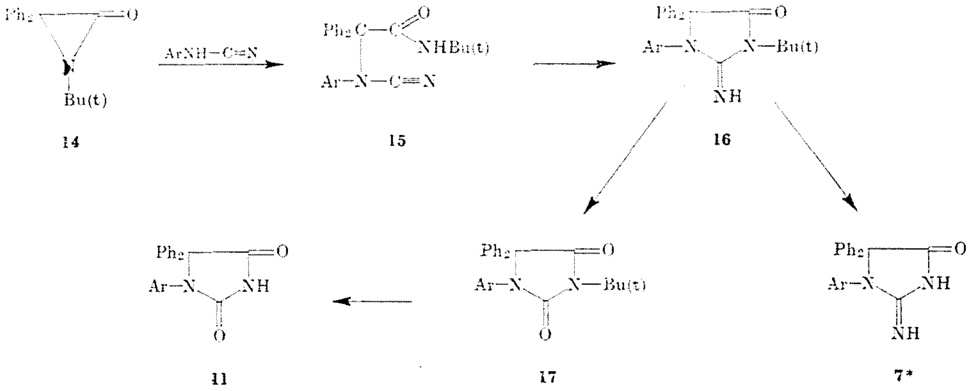
** The reaction of α-chloro-α,α-diphenylacetamide with potassium *N*-cyanoanilide to yield 5-imino-1,4,4-triphenyl-2-imidazolidinone (**10**, Ar = Ph] [3] may be considered as analogous to the presumed conversion **5** → **10**.



2—11 and **13**: Ar = p-ClC_6H_4



Ar = p-ClC_6H_4

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* Potentially tautomeric compound. The tautomeric structure has not been established.

+ 1710 cm^{-1}) were consistent with the structure of an *N*-(*p*-chlorophenyl)-5,5-diphenylhydantoin (**11** or **13**). Thus, structures **12** and **9** for **B** and **A**, respectively, were ruled out. The site of attachment of the *p*-chlorophenyl group in **B** (and therefore also in **A**) was established by comparison of **B** with an authentic sample of **11** which was synthesized, by the adaptation of a method described in Ref. [4], as shown in Scheme 2. Since **B** proved identical with **11**, only two alternative structures, **7** and **8**, remained for **A**. Comparison of **A** with an authentic sample of **7**, obtained as shown in Scheme 2, proved that these two compounds were different and, therefore, that the correct structure of **A** is **8**.

Experimental

Reaction of α-bromodiphenylacetonitrile with potassium p-chloro-N-cyanoanilide

A mixture of α-bromodiphenylacetonitrile (3.0 g; 11 mmole), potassium *p*-chloro-*N*-cyanoanilide (6.3 g; 33 mmole) and anhydrous DMSO (20 ml) was kept for a month at r.t. and, subsequently, poured into water (100 ml). The amorphous precipitate was washed with water and, while still wet, triturated with benzene (50 ml) to yield 0.6 g (15%) of **8**, m.p. 297—8 °C (from *i*-PrOH).

$C_{21}H_{16}ClN_3O$ (361.83), calc. Cl 9.80, N 11.61; found Cl 9.56, N 11.45%.

Hydrolysis of 1-(p-chlorophenyl)-4-imino-5,5-diphenyl-2-imidazolidinone (**8**)

A mixture of **8** (0.20 g; 0.6 mmole), EtOH (3 ml) and conc'd HCl (4 ml) was refluxed for 20 hrs and diluted with water to yield 0.08 g (41%) of **11**, m.p. 194—5 °C (from aqu. EtOH), identical, according to m.p's, mixed m.p. and IR spectra, with an authentic sample (see below).

N-(t-Butyl)-2-[N-cyano-N-(p-chloro-anilino)]-2,2-diphenylacetamide (**15**)

1-(*t-Butyl*)-3,3-diphenylaziridinone (**14**) [5] (2.5 g; 9.5 mmole) was added to the suspension of *p*-chloro-*N*-cyanoaniline [6] (1.5 g; 9.8 mmole) in dry benzene (20 ml). A clear solution resulted immediately which was stirred for 2 hrs at r.t. and allowed to stand overnight to yield 2.2 g (56%) of **15**, m.p. 157—8 °C (from EtOH).

$C_{25}H_{24}ClN_3O$ (417.94), calc. C 71.85, H 5.79, Cl 8.48, N 10.05; found C 71.59, H 5.76, Cl 8.72, N 10.32%

IR (KBr): ν NH 3400, $\nu C{=}N$ 2230, amide I 1690 cm^{-1}

3-(t-Butyl)-1-(p-chlorophenyl)-5,5-diphenylglycocyamidine (**16**)

A mixture of **15** (0.89 g; 2.1 mmole), EtOH (9 ml) and Et_3N (0.9 ml) was refluxed for 2 hrs and poured into water (80 ml) to yield 0.8 g (90%) of **16**, m.p. 135 °C (from EtOH).

$C_{25}H_{24}ClN_3O$ (417.94), calc. C 71.85, H 5.79, N 10.05; found C 71.76 H 5.71, N 10.16%

IR (KBr): $\nu C{=}O$ 1740, $\nu C{=}N$ 1630 cm^{-1}

3-(*t-Butyl*)-1-(*p-chlorophenyl*)-5,5-*diphenylhydantoin* (**17**)

To a solution of **16** (0.22 g; 0.5 mmole) in AcOH (5 ml) a conc'd aqueous solution of $NaNO_2$ (1.0 g) was added under continuous stirring at about 80 °C within 1/2 hr. Water (20 ml) was added to the hot mixture to yield 0.19 g (87%) of **17**, m.p. 132 °C (from aqueous AcOH).

$C_{25}H_{23}ClN_2O_2$ (418.91), calc. C 71.68, H 5.53, Cl 8.64, N 6.69; found C 71.77, H 5.19, Cl 8.55, N 6.89%

IR (KBr): $\nu\ O{=}\underset{|}{C}-\overset{|}{N}-\underset{|}{C}{=}O$ 1760 + 1710 cm^{-1}

1-(*p-Chlorophenyl*)-5,5-*diphenylhydantoin* (**11**)

A mixture of **17** (90 mg; 0.2 mmole), AcOH and 48% aqueous HBr (2 ml, each) was refluxed for 30 hrs and, subsequently, diluted with water to yield 64 mg (82%) of **11**, m.p. 193—4 °C (from aqueous EtOH).

$C_{21}H_{15}ClN_2O_2$ (362.81), calc. Cl 9.77, N 7.72; found Cl 10.05, N 8.14%

IR (KBr): $\nu\ O{=}\underset{|}{C}-\overset{|}{N}-\underset{|}{C}{=}0$ 1765 + 1710 cm^{-7}

1-(*p-Chlorophenyl*)-5,5-*diphenylglycocyamidine* (**7**)

A mixture of **16** (0.3 g; 0.7 mmole) and 20% HCl (6 ml) was refluxed for 2 hrs and evaporated to dryness. The crystalline residue was dissolved in EtOH, and the solution was made slightly alkaline with N/1 NaOH. Water was added to precipitate 0.18 g (69%) of **7**, m.p. 294—5 °C (from EtOH).

$C_{21}H_{16}N_3O$ (361.83) calc. Cl 9.80, N 11.61; found Cl 9.83, N 11.42%.

IR (KBr): $\nu\ C{=}O$ 1700, $\nu\ C{=}N$ 1665 cm^{-1}

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Summary

The reaction of the title compounds has been shown to yield 1-(*p*-chlorophenyl)-4-imino-5,5-diphenyl-2-imidazolidinone [8].

References

1. SIMIG, GY.—LEMPERT, K.—TAMÁS, J.: Tetrahedron **29**, 3571 (1973)
2. LEMPERT, K.—PUSKÁS, J. and BÉKÁSSY, S.: Periodica Polytechn. Chem. Eng. **12**, 123 (1968)
3. SIMIG, GY.—LEMPERT, K.: Tetrahedron **31**, 983 (1975)
4. SIMIG, GY.—LEMPERT, K.: Tetrahedron **31**, 1195 (1975)
5. BAUMGARTEN, H. E.—CLARK, R. D.—ENDRES, L. S.—HAGEMEIER, L. D.—ELIA, V. J.: Tetrahedron Letters **1967**, 5033
6. BAMI, H. L.—IYER, B. H.—GUHA, P. C.: Science and Culture **12**, 448 (1947); Chem. Abstr. **41**, 4463i (1947)

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