Preparation of 1-Aryl-5-(*N*-aryl-*N*-benzoylamino)tetrazoles

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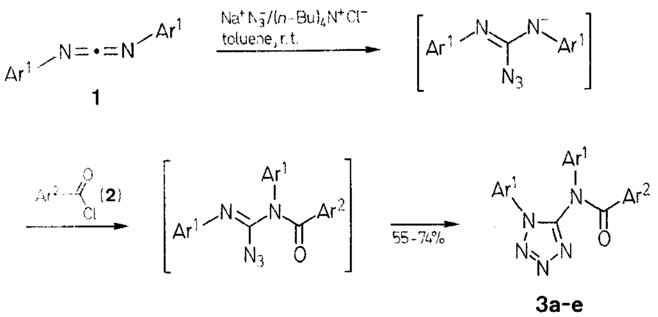
The synthesis of 1-aryl-5-(*N*-aryl-*N*-benzoylamino) tetrazoles from diarylcarbodiimides, azide ion, and benzoyl chloride using solid-liquid phase-transfer catalysis is reported.

We should like to report the direct formation of 1-aryl-5-(*N*-aryl-*N*-benzoylamino)tetrazoles by the solid-liquid phase-transfer catalyzed (PTC) reaction of diarylcarbodiimides, aroyl chlorides, and sodium azide in toluene. With both sodium and potassium azide, in the absence of PTC catalyst the reaction gave recovered diarylcarbodiimides and aryl isocyanates. It should be noted that while there are numerous successful liquid-liquid PTC reactions, solid-liquid PTC reactions are still quite rare.[1,2,3] Tetrabutylammonium chloride (Q^+/Cl^-) was used as the PTC catalyst. We believe that a sequence of reactions begins by migration of the Q^+/Cl^- ion pair to the surface of the solid sodium azide where anion exchange occurs resulting in formation of a toluene soluble tetrabutylammonium cation/azide anion pair and precipitation of sodium chloride. Nucleophilic addition of azide anion to the central carbon of the carbodiimide **1** yields an amide anion which reacts with aroyl chloride **2** to give an *N*-aryl-*N*-aroyl-*N*′-arylcarbamimidic azide and simultaneously regenerates a Q^+/Cl^- ion pair. Migration of the Q^+/Cl^- ion pair to the surface of sodium azide starts the reaction cycle again. Intramolecular reaction of the azide with the C=N double bond of the *N*-aryl-*N*-aroyl-*N*′-arylcarbamimidic azide yields the tetrazole product **3**.

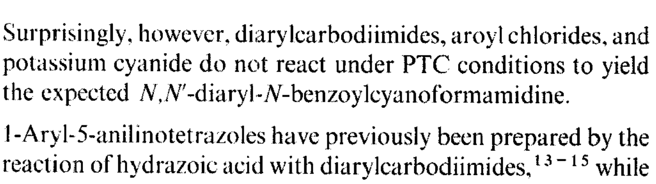


3a-e

3	Ar¹	Ar²
a	C_6H_5	C_6H_5
b	C_6H_5	3-ClC_6H_4
c	4-$CH_3C_6H_4$	3-ClC_6H_4
d	4-$CH_3C_6H_4$	C_6H_5
e	C_6H_5	4-$CH_3C_6H_4$

While aroyl chlorides have been found to react with azide ion under PTC conditions to yield aroyl azides[4,5] which will decompose on heating to yield aryl isocyanates,[6] we do not believe that our reaction involves the intermediacy of aroyl azides since reaction of diarylcarbodiimides, aroyl azides and sodium azide under similar PTC conditions only gave aryl isocyanates and recovered diarylcarbodiimides as products. In fact, under our reaction conditions small amounts of aryl isocyanates are isolated. Apparently, under PTC conditions the addition of azide anion to one of the C=N double bonds of diarylcarbodiimides **1** is faster than the competing nucleophilic acyl substitution reaction with aroyl chlorides **2**. The reaction, however, is unsuccessful with dialkylcarbodiimides such as dicyclohexylcarbodiimide.

This new reaction is related mechanistically to several PTC reactions: the formation of cyanohydrin esters by reaction of aromatic aldehydes, benzoyl chlorides, and sodium cyanide;[7,8,9] the preparation of cyanohydrin carbonates by the reaction of aromatic aldehydes with alkyl carbonochloridates and sodium cyanide;[10,11] the synthesis of aroyl cyanide dimers by the PTC reaction of aroyl cyanides with aroyl chloride and potassium cyanide,[4] and finally perhaps most closely to the Reissert reaction of quinolines with aroyl chlorides and potassium cyanide.[12]



Surprisingly, however, diarylcarbodiimides, aroyl chlorides, and potassium cyanide do not react under PTC conditions to yield the expected *N*,*N*′-diaryl-*N*-benzoylcyanoformamidine.

1-Aryl-5-anilinotetrazoles have previously been prepared by the reaction of hydrazoic acid with diarylcarbodiimides,[13-15] while 1-aryl-5-(*N*-trimethylsilylanilino)tetrazoles have been prepared by the reaction of azidotrimethylsilane with diarylcarbodiimides.[16]

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Table. 1-Aryl-5-(*N*-aryl-*N*-benzoylamino)tetrazoles **3** Prepared

3	Yield (%)	m.p. (°C) (solvent)	Molecular Formula[a]	MS (70 eV)[b] m/e (%)	IR ($CHCl_3$)[c] ν(cm^{-1})	UV (hexane)[d] λ_{max} (nm) (log ε)	^{1}H-NMR ($CDCl_3$)[e] δ	^{13}C-NMR ($CDCl_3$)[e] δ
a	64	134–136 (benzene/heptane)	$C_{20}H_{15}N_5O$ (341.35)	341 (M^+, 7.1) 105 (100), 77 (63)	1675	228 (4.23)	7.0–7.5 (m)	123.6, 126.2, 127.7, 128.0, 128.5, 129.3, 129.5, 130.3, 131.6, 132.4, 132.7, 139.6 (C_{arom}); 153.5 (C=N); 169.1 (C=O)
b	74	125–126.5 (EtOH)	$C_{20}H_{14}ClN_5O$ (375.8)	377 (M^+, 1.1), 375 (M^+, 3.3), 141 (43%), 139 (100), 113 (22), 111 (64), 105 (67), 77 (96), 76 (19), 75 (25)	1685	221 (4.23)	7.0–7.5 (m)	123.9, 126.4, 127.8, 128.2, 128.6, 128.8, 129.4, 129.7, 129.8, 130.5, 130.6, 131.8, 134.5, 139.3 (C_{arom}); 152.8 (C=N); 167.8 (C=O)
c	65	113–115 (Et_2O)	$C_{22}H_{18}ClN_5O$ (403.85)	405 (M^+, 0.5), 403 (M^+, 1.3), 141 (21), 139 (65), 113 (10), 111 (32), 105 (100), 91 (43), 77 (66)	1700	222 (4.34)	2.305 (s, 3H); 2.41 (s, 3H); 7.01–7.25 (m, 12H)	21.0 (CH_3); 21.3 (CH_3); 123.8, 126.4, 128.2, 128.9, 129.0, 129.4, 130.3, 131.7, 133.0, 134.6, 138.1, 138.5, 140.9, 141.1 (C_{arom}); 153.13 (C=N); 167.8 (C=O)
d	55	129.5–131	$C_{22}H_{19}N_5O$ (369.4)	369 (M^+, 4.1), 105 (100), 91 (36), 77 (96)	1680	226 (4.28)	2.25 (s, 3H); 2.36 (s, 3H); 7.02–7.24 (m, 13H)	20.8 (CH_3); 21.1 (CH_3); 123.6, 126.2, 128.1, 128.6, 130.0, 130.1, 130.5, 131.5, 132.7, 137.2, 137.9, 140.8 (C_{arom}); 153.1 (C=N); 169.30 (C=O)
e	70	145–157 (Et_2O)	$C_{21}H_{17}N_5O$ (355.4)	355 (M^+, 0.4), 119 (100), 91 (57), 77 (42.5)	1680	229 (4.185)	2.28 (s, 3H); 6.8–7.8 (m, 14H)	21.47 (CH_3); 119.96, 123.92, 126.41, 127.87, 128.95, 129.60, 129.71, 130.47, 130.25, 131.98, 140.11, 142.67 (C_{arom}); 153.39 (C=N); 169.24 (C=O)

[a] Satisfactory microanalyses obtained: C ±0.30, H ±0.10, N ±0.2.
[b] Hewlett Packard 5985.
[c] Perkin-Elmer 281.
[d] Shimadzu-UV 260.
[e] JEOLCO FX-90Q.

Diphenylcarbodiimide and 4,4′-ditolylcarbodiimide are prepared by literature methods and have properties in complete agreement with those previously reported.[17] Microanalyses were performed by Galbraith Laboratories, Knoxville, TN.

1-Aryl-5-(*N*-aryl-*N*-benzoylamino)tetrazoles (3); General Procedure:
To a stirred solution of the diarylcarbodiimide **1** (10 mmol), sodium azide (975 mg, 15 mmol), and tetrabutylammonium chloride (278 mg, 1 mmol) in dry toluene (40 mL) is slowly added over 1 h a solution of the aroyl chloride **2** (0.01 mol) in toluene (10 mL). The reaction is carried out at room temperature under an N_2 atmosphere. After 3–4 h, the mixture is heated to 95 °C for 30 min. In this manner, any benzoyl azide which has been formed is converted to the corresponding aryl isocyanate. The mixture is cooled and filtered and toluene is evaporated under reduced pressure. The product **3** is purified by dry-column chromatography on silica gel with hexane/EtOAc (4:1)[18,19] and recrystallized from the solvents given in the Table.

This work was supported by Air Force Office Scientific Research, Grant No. 86-0042.

Received: 22 November 1986; revised: 12 January 1987

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