Journal of Organometallic Chemistry
Elsevier Sequoia S.A., Lausanne
Printed in The Netherlands

CYCLOADDITION REACTIONS OF METAL AZIDES. FERROCENYLTETRAZOLE VIA A SILYL AZIDE

S. S. WASHBURNE AND W. R. PETERSON, JR.
Department of Chemistry, Temple University of the Commonwealth System of Higher Education, Philadelphia, Pa. 19122 (U.S.A.)

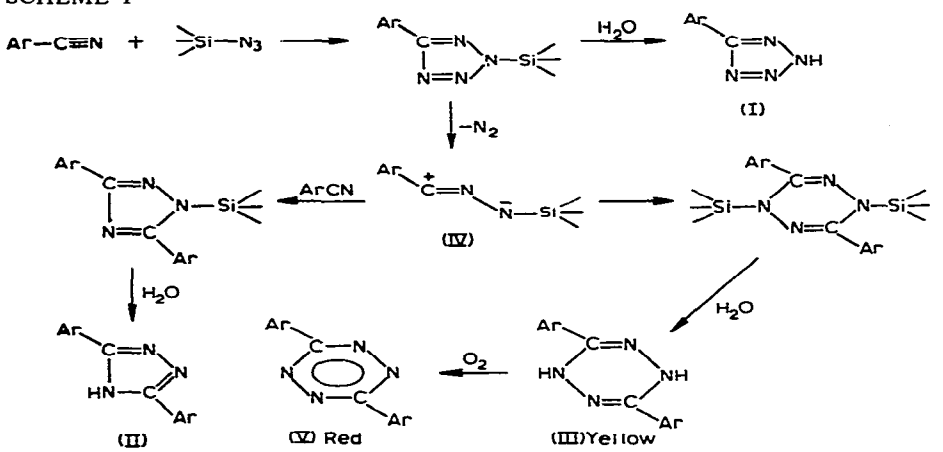
(Received July 25th, 1969; in revised form October 17th, 1969)

SUMMARY

Reaction of cyanoferrocene with trimethylsilyl azide and aluminum chloride in refluxing *o*-dichlorobenzene gave ferrocenyltetrazole as the sole organometallic product. Other aryl nitriles react with silyl azides without added aluminum chloride to give tetrazole, 3,5-diaryl-1,2,4-triazole, and 3,6-diaryl-1,2,4,5-tetrazine. Mechanisms for these transformations are proposed.

Silyl azides have been reported to react with acetylenes[1], olefins[2], and aldehydes[3]. We have found reaction of silyl azides with aryl nitriles smoothly gives mixtures of tetrazoles (I), 3,5-diaryl-1,2,4-triazoles (II), and 2,5-diaryl-1,2,4,5-tetrazines (III), according to Scheme 1. Table 1 gives product distributions from typical reactions. The nitrileimine intermediate (IV) has been invoked in the decomposition of tetrazoles previously[4].

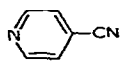
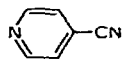
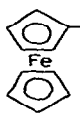
SCHEME 1



As mixtures of products more easily obtainable via other routes are produced, this is not a synthetically useful procedure. However, when a mixture of cyanoferrocene, trimethylsilyl azide, and aluminum chloride was heated at reflux in *o*-dichloroben-

TABLE 1

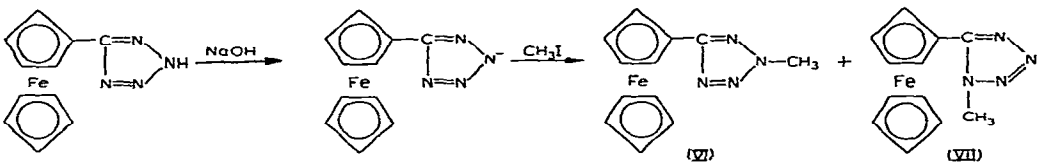
REACTION OF NITRILES WITH SILYL AZIDES

No.	Nitrile[a]		Silyl azide	Other reactant[a]	Solvent	Reaction time (h at reflux)	Yields[b] (%) (I)	(II)	(III)
1	C_6H_5CN	(3.3)	Me_3SiN_3		None	16	26[c]		14[d]
2	C_6H_5CN	(3.3)	$Ph_2Si(N_3)_2$	$AlCl_3$(2)	None	20	55[c,e]	10[e,f]	
3	C_6H_5CN	(3)	$Ph_2Si(N_3)_2$		None	8		43[e,f]	
4	C_6H_5CN	(3)	$Me_2Si(N_3)_2$		None	20		36[e,f]	
5		(1)	Me_3SiN_3		None	48	7[g]		1[h,j]
6		(1)	Me_3SiN_3		*o*-$C_6H_4Cl_2$	48	10[g]		Trace[h,j]
7		(0.8)	Me_3SiN_3	$AlCl_3$(0.8)	*o*-$C_6H_4Cl_2$	16	75		
8	CH_3CN	(1)	Me_3SiN_3	$AlCl_3$(1)	None	20	6[i]		

[a] Number in parentheses is molar ratio relative to silyl azide. [b] Melting points and elemental analyses for reported compounds were in good accord with literature values. [c] Ref. 11. [d] Ref. 12. [e] Yield assuming both azide groups are utilized. [f] Ref. 13. [g] Ref. 14. [h] Ref. 15. [i] Ref. 16. [j] Oxidized tetrazine (V) was isolated.

zene, a 75% yield of ferrocenyltetrazole, (I, Ar = π-C_5H_4Fe-π-C_5H_5) was obtained without production of triazole or tetrazine.

Ferrocenyltetrazole, previously unreported in the literature, crystallizes as shiny golden leaflets, m.p. 264–265°, and exhibits characteristic tetrazole bands[5] in the infrared at 1260 (w) and 1049 (s) cm^{-1}. It is sparingly soluble in hot water and may readily converted to a sodium salt by treatment with sodium hydroxide. Alkylation of this salt with methyl iodide affords, as expected[6], two *N*-methyl derivatives. The major product is assigned the structure 2-methyl-5-ferrocenyltetrazole, (VI), on the basis of its higher melting point, greater yield[6], and absence of an infrared band[5] in the region 1100–1000 cm^{-1}. The minor product, which absorbs in the 1100–1000 cm^{-1} region, is assumed to be 1-methyl-5-ferrocenyltetrazole, (VII).



The effect of aluminum chloride, without which no ferrocenyltetrazole is formed, is unclear, but we favor an interpretation in which a polarized $R-\overset{\delta+}{C}\equiv N-\overset{\delta-}{AlCl_3}$ intermediate, analogous to that of a Houben–Hoesch reaction[7], suffers attack by a 1,3-dipole, trimethylsilyl azide. In support of this, it may be noted that when solutions

of aluminum chloride and ferrocenyl nitrile in *o*-dichlorobenzene are mixed, a heterogenous mixture results which is redissolved when silyl azide is added. Also, acetonitrile, which does not react with sodium azide unless heated with ammonium chloride in a pressure vessel[8], or first converted to a nitrilium salt $CH_3\overset{+}{C}=N-CH_2CH_3$[9], reacts with the silyl azide/aluminum chloride reagent to produce 5-methyltetrazole in a yield of 6%. This yield could undoubtedly be increased by the use of a pressure vessel to increase the reaction temperature. Further studies exploring the scope and applicability of metal azides as azide transfer agents are in progress in these laboratories.

EXPERIMENTAL

Reaction of diphenyldiazidosilane with benzonitrile and aluminum chloride (No. 2)

A 50 ml flask was charged with 10.3 g (100 mmoles) of benzonitrile and 8.3 g (63 mmoles) of aluminum chloride, causing an exotherm and formation of white solids. The mixture was cooled to 20°, treated with 8.3 g (31 mmoles) of diphenyldiazidosilane, and heated at reflux for 20 h, during which time it slowly darkened. The cooled mixture, a brown glass, was hydrolysed with 50 ml of water (heating required). The mixture was filtered, and the residue washed with 50 ml of water, then extracted with 250 ml of ether. The remaining residue was taken up in 2 *N* NaOH, filtered, and precipitated by addition of HCl to give 3.5 g of 5-phenyltetrazole, m.p. 213–215°. The ether extract was dried ($CaCl_2$), filtered, and evaporated to dryness. Trituration with 25 ml of ether and filtration afforded an additional 1.5 g of tetrazole. The triturate was evaporated, taken up in NaOH, precipitated with HCl, filtered, and evaporated, to give 3.5 g of sticky solids. Repeated trituration of these solids with benzene gave 1.4 g of 3,5-diphenyl-1,2,4-triazole, m.p. 192° (benzene insoluble) and $(Ph_2SiO)_x$, (benzene soluble). Material insoluble in NaOH (reddish-brown) was shown by IR spectroscopy to be impure $(Ph_2SiO)_x$, possibly contaminated with traces of tetrazine (V) (bright red).

5-Ferrocenyltetrazole (No. 7)

A mixture of cyanoferrocene[10] (25 mmoles), trimethylsilyl azide[4b] (30 mmoles), and $AlCl_3$ (26 mmoles) was heated at reflux in *o*-dichlorobenzene for 16 h. The mixture was poured into water, stirred 1 h, filtered, and the residue extracted with 400 ml of hot n-heptane. The residue, taken up in hot ethanol, was concentrated to 100 ml. Crystallization at −70° afforded 4.8 g (75%) of ferrocenyltetrazole as blood-red crystals. An analytical sample (from ethanol/water), shiny golden leaflets, had m.p. 264–265° (dec.). (Found: C, 51.76; H, 3.93; N, 22.21. $C_{11}H_{10}N_4Fe$ calcd.: C, 52.00; H, 3.97; N, 22.05%.) IR (nujol mull): 2610 (broad), 1610 (s), 1260 (w), 1049 (s), 881 (w), and 752 (w) cm^{-1}. Evaporation of the heptane extracts afforded a recovery of 0.4 g (7.5%) of cyanoferrocene.

The sodium salt was prepared by dropwise addition of 10 ml of 5 *N* NaOH to a slurry of 0.51 g (2 mmoles) of 5-ferrocenyltretrazole in 20 ml of ethanol. Evaporation afforded a yellow residue, which after extraction into methanol, filtration, concentration, and precipitation by addition of benzene, gave 0.45 g (82%) of sodio-5-ferrocenyltetrazole, golden microcrystals, m.p. above 300°, darkens at 270°. IR (nujol mull); 1574 (s), 1418 (s), 1320 (m), 1166 (s), and 1141 (s) cm^{-1}.

Methyl-5-ferrocenyltetrazoles

An ethanol solution of 2 mmoles of the sodium salt from above was heated at reflux with 5 ml of methyl iodide for 15 min, then evaporated to dryness. Addition of heptane to a hot benzene extract of the crude material, filtration, and cooling to 5° overnight afforded 0.19 g (36%) of 2-methyl-5-ferrocenyltetrazole, orange rhombs m.p. 150–151.5°. (Found: C, 53.51; H, 4.39; N, 21.00. $C_{12}H_{12}N_4Fe$ calcd.: C, 53.76; H, 4.51; N, 20.90%.) IR (nujol mull): 1580 (s), 1473 (s), 1382 (w), 1134 (m), 884 (m), 750 (w), and 711 (m) cm^{-1}. Further concentration and cooling of the benzene/heptane solution gave 0.08 g (15%) of 1-methyl-5-ferrocenyltetrazole, orange crystals m.p. 115.5–117°. (Found: C, 53.49; H, 4.50; N, 21.08%.) IR (nujol mull): 1575 (s), 1327 (w), 1070 (m), 887 (m), 764 (m), and 715 (m) cm^{-1}.

REFERENCES

1 L. BIRKOFER AND P. WEGNER, *Chem. Ber.*, 99 (1966) 2512.
2 E. ZBIRAL AND K. KISCHA, *Tetrahedron Lett.*, (1969) 1167.
3 L. BIRKOFER, F. MÜLLER AND W. KAISER, *Tetrahedron Lett.*, (1967) 2781.
4 (a) R. HUISGEN, J. SAUER AND M. SEIDEL, *Chem. Ber.*, 94 (1961) 2503;
(b) L. BIRKOFER, A. RITTER AND P. RICHTER, *Chem. Ber.*, 96 (1963) 2750.
5 R. C. ELDERFIELD, *Heterocyclic Compounds*, Vol. 8, Wiley, New York, 1967, p. 4.
6 Ref. 5, pp. 54–55.
7 P. E. SPOERRI AND A. S. DUBOIS, *Org. Reactions*, 5 (1949) 387.
8 W. P. NORRIS, *J. Org. Chem.*, 27 (1962) 3248.
9 L. A. LEE, E. V. CRABTREE, J. U. LOWE, JR., M. J. CZIESLA AND R. EVANS, *Tetrahedron Lett.*, (1965) 2885.
10 A. N. NESMEYANOV, E. G. PEREVALOVA AND L. P. YUR'EVA, *Chem. Ber.*, 93 (1960) 2729.
11 R. M. HERBST AND K. R. WILSEN, *J. Org. Chem.*, 22 (1957) 1142.
12 P. SCHREINER, *J. Org. Chem.*, 34 (1969) 199.
13 R. HUISGEN, J. SAUER AND M. SEIDEL, *Justus Liebigs Ann. Chem.*, 654 (1962) 146.
14 W. J. VAN DER BERG, *Recl. Trav. Chim. Pays-Bas*, 74 (1955) 257.
15 P. CHARONNAT AND P. FABIANI, *C. R. Acad. Sci., Paris*, 241 (1955) 1783.
16 J. S. MIHINA AND R. M. HERBST, *J. Org. Chem.*, 15 (1950) 1082.