Reactions of Polychloroaryl-lithium Compounds with Nitriles

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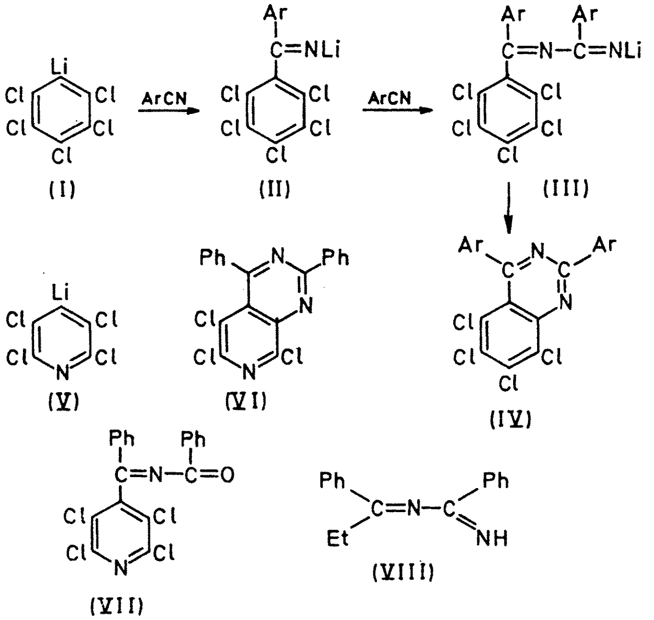
Summary Aromatic nitriles react with pentachlorophenyl-lithium to give 2,4-diaryl-5,6,7,8-tetrachloroquinazolines, and with tetrachloro-4-pyridyl-lithium to give 2,4-diaryl-5,6,8-trichloro-1,3,7-triazanaphthalenes.

WE report reactions of polyhalogenoaryl-lithium compounds with aromatic nitriles which lead to cyclised products by a route which involves addition of two moles of the nitrile, followed by intramolecular nucleophilic aromatic substitution. These reactions provide a novel and convenient route to fused pyrimidine systems, and will be capable of adaptation to a variety of heterocyclic syntheses. In a typical experiment, the reaction of an ethereal solution of pentachlorophenyl-lithium (I)[1] with an excess of benzonitrile under reflux led to 5,6,7,8-tetrachloro-2,4-diphenylquinazoline† (IV) (42%), m.p. 251—252°. Similarly, tetrachloro-4-pyridyl-lithium (V)[2] gave 5,6,8-trichloro-2,4-diphenyl-1,3,7-triazanaphthalene (VI), m.p. 180—181° (11%). The evidence that the cyclised products arise by the route, shown in the Scheme for the case of pentachlorophenyl-lithium (I), is as follows. (a) Reaction of the lithium compound with one mole of benzonitrile, followed by hydrolysis, gave the ketimine corresponding to the intermediate (II) (or the corresponding tetrachloropyridyl derivative). (b) Besides the triazanaphthalene derivative, the reaction of tetrachloro-4-pyridyl-lithium (V) with benzonitrile gave *N*-benzoyl(tetrachloro-4-pyridyl)phenylketimine (VII) (30·5%), m.p. 157—158°, the hydrolysis product from the pyridine analogue of intermediate (III). Attempts to isolate hydrolysis products of compound (III) were unsuccessful, and in this series cyclisation is evidently faster than the addition of the second molecule of nitrile.

It is at first sight surprising that an *N*-lithio-ketimine should be sufficiently reactive to add to a nitrile. We are aware of only one previous report of an analogous reaction, in which a small amount of the ketimine (VIII) was obtained as a by-product from the reaction of diethylmagnesium with benzonitrile.[3] Addition reactions of metal ketimides clearly warrant further investigation, which we are now undertaking.



(*Received, September 11th,* 1969; *Com.* 1376.)

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† Correct elemental analyses and molecular weights (from mass spectra), and appropriate n.m.r. spectra, were obtained for all new compounds.

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