OXIDATIVE COUPLING OF o-METHYLPHENYL ISOCYANIDES AND ITS APPLICATION TO HETEROCYCLE SYNTESES

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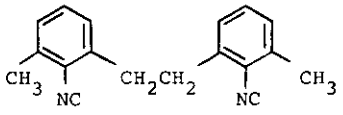
o-(Lithiomethyl)phenyl isocyanide (1), which was prepared by the treatment of o-tolyl isocyanide with 2 equiv of LDA in diglyme at -78°C, was oxidatively dimerized with 1,2-dibromoethane to give 1,2-bis(o-isocyanophenyl)ethane (2) in excellent yield. Similarly, some o-alkylphenyl isocyanides were oxidatively dimerized via the selective lithiation at the ortho-benzylic carbon to afford the corresponding bis-isocyanides.

1,2-Bis(2-isocyano-3-methylphenyl)ethane (3), coupling dimer of 2,6-xylyl isocyanide, thus prepared was treated with 4 equiv of LDA in diglyme at -78°C to give dilithiated bis-isocyanide (4), which on warming up was cyclized to 1,2-bis-(7-indolyl)ethane (5) after aq. work up.



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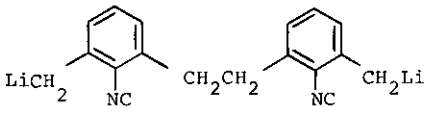

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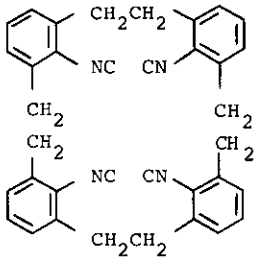
Further treatment of 4 with 1,2-dibromoethane at -78°C produced cyclic tetrakis-isocyanide (6) in 31% yield with cyclic oligomeric poly-isocyanide and insoluble poly-isocyanide.



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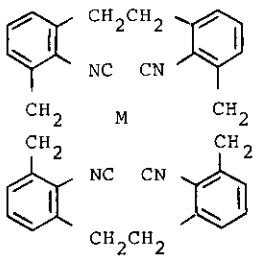

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Cyclic tetrakis-isocyanide (6) was treated with metal compounds such as CuCl, $Ni(CO)_4$, and $CoCl_2$ readily to form metal isonitrile complexes (7) in high yields. Acid hydrolysis of 6 furnished cyclic tetrakis-amine (8) in 42% yield.