12. G. Zweifel and S. Rajagopalan, *J. Am. Chem. Soc.*, **107**, 700(1985).
13. H.A. Staab and K. Neunhoffer, *Synthesis*, 424(1974).
14. M. Rosinblum, N. Brawn, J. Papenmeier, and M. Applebaum, *J. Orgnomet. Chem.*, **6**, 173(1966).
15. W.L. Collier and R.S. Macomber, *J. Org. Chem.*, **38**, 1367(1973).
16. P.J. Kocienski, *J. Org. Chem.*, **39**, 3285(1974).
17. P.D. Bartlett and L.J. Rosen, *J. Am. Chem. Soc.*, **64**, 543(1942).
18. E.J. Corey and P.L. Fuchs, *Tetrahedron Lett.*, 3769(1972).
19. J. Villieras, P. Pierrot, and J.F. Normant, *Synthesis*, 458(1975).
20. J.B. Armitage, N. Entwistle, E.R.H. Jones, and M.C. Whiting, *J. Chem. Soc.*, 3052(1953).
21. R. Eastmond and D.R.M. Walton, *J. Chem. Soc. Chem. Commun.*, 204(1968).
22. D.R.M. Walton in "Protective Groups in Organic Chemistry", J.F.W. McOmie, Ed., Plenum Press, London, 1973, Chapter 1.
23. C.E. Castro and R.D. Stephens, *J. Org. Chem.*, **28**, 2163(1963).
24. R.D. Stephens and C.E. Castro, *J. Org. Chem.*, **28**, 3313(1963).
25. C.E. Castro, R. Havlin, V.K. Honwad, A. Malte, and S. Moje, *J. Am. Chem. Soc.*, **91**, 6464(1969).
26. R. Oliver and D.R.M. Walton, *Tetrahedron Lett.*, 5209(1972).
27. S. Takahashi, Y. Kuroyama, K. Sonogashira, H. Hagihara, *Synthesis*, 627(1980).
28. W.B. Austin, N. Bilow, W.J. Kellegham, and K.S.Y. Lau, *J. Org. Chem.*, **46**, 2280(1981).
29. A.S. Hay, *J. Org. Chem.* **27**, 3320(1962).
30. H.M. Colquhoun, J. Holton, D.J. Thompson, and M.V. Twigg, "New Pathways for Organic Synthesis", Plenum Press. New York and London, 383(1984).
31. E.J. Corey, J.O. Albright, *J. Org. Chem.*, **48**, 2114(1983).

Reactions of Aryl Organometallic Reagents with Isomers of Phthalonitriles: Triaryl Diketimines and Diketones

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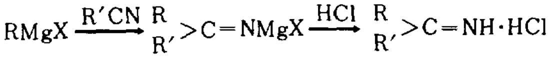
Synthesis and hydrolysis of aromatic diketimines of triaryl type were investigated by the action of aryl organometallics on the three isomers of phthalonitrile. The reactions of organometallic reagents, prepared from bromobenzene, *o*-bromotoluene and *o*-bromoanisol, with iso- and terephthalonitrile proceeded in normal way. Decomposition of the addition complex with dry ammonia, methanol or water gave six diketimines, which could be hydrolysed to the corresponding diketones. Reactions of phthalonitrile with the organometallic reagent were different from the other isomers, so that the decomposition and hydrolysis of the addition complex did not give diimines and the corresponding aromatic diketones.

Introduction

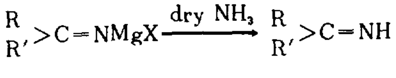
In spite of their frequent occurrence as intermediates in the synthesis of ketones from the reaction of organometallic reagents on nitriles, relatively a few ketimines appear to have been isolated and characterized. The production of ketimines as hydrochloride was described for the first time by Hantzch and Kraft,[1] in 1891, by the reaction between urethan and dihydrochlorides produced from ketones and phosphorus pentachloride. In 1920, Moureu and Mignonac[2] published a study of eleven ketimines prepared from aromatic nitriles and Grignard reagents. Other workers[3-9] also have since described the synthesis of ketimines or their salts by the action of organomagnesium reagents on nitriles. The hydrolysis of ketimines into corresponding ketones was also widely accomplished.

The systematic studies on ketimines, however, were done first by Pickard and his coworkers in early 1950s. They developed two methods for the preparation of ketimines by Grignard reaction on nitrile. The first method involves decomposition of the Grignard adduct with anhydrous hydrogen chloride to get an imine salt. This procedure, which parallels that of Moureu and Mignonac,[2] has proved feasible and afforded fair yields of products.



$$RMgX \xrightarrow{R'CN} \genfrac{}{}{0pt}{}{R}{R'}\!>C=NMgX \xrightarrow{HCl} \genfrac{}{}{0pt}{}{R}{R'}\!>C=NH\cdot HCl$$

The second involves decomposition of the Grignard adducts with anhydrous ammonia, which gives free imines. This modified procedure required less time and gave higher yield. By these methods, they prepared various ketimines of alkyl-aryl,[10,11] diaryl[12] and dialkyl types.[13-15]



$$\genfrac{}{}{0pt}{}{R}{R'}\!>C=NMgX \xrightarrow{dry\ NH_3} \genfrac{}{}{0pt}{}{R}{R'}\!>C=NH$$

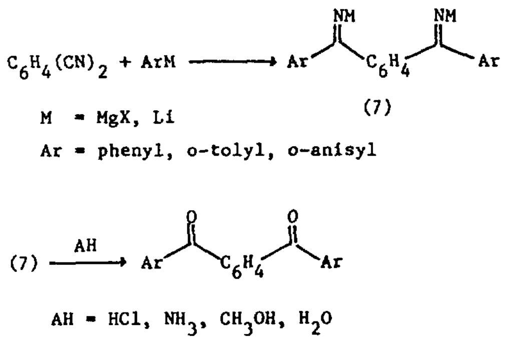
In 1961, an improved method of ketimine synthesis was reported by Pickard and Tolbert,[16] which involves the addition of nitrile solution to a Grignard reagent, followed by decomposition of the Grignard–nitrile complex with anhydrous methanol. This modified procedure have been widely applied in the synthesis of ketimines by many investigators.[17-19]

$$\begin{matrix}R\\R'\end{matrix}{>}C=NMgX\xrightarrow{\text{anhyd. MeOH}}\begin{matrix}R\\R'\end{matrix}{>}C=NH$$

On the other hand, the reaction of organolithium reagents on nitriles has been studied by some workers[20-28] as a synthetic route of ketones, without separation of intermediates, ketimines. To obtain the free ketimine, it was neccessary to hydrolyse the addition intermediate, ketiminolithium, under mild conditions,[29-31] except where further hydrolysis of the imines is prevented by steric hindrance, as in the case of pentachlorophenyl aryl ketone imine.[32,33]

The ir[18,34,35] and nmr spectrum[17] have been studied for some ketimines.

Although the studies on ketimines have been made by many investigators since the work of Moureu and Mignonac,[2] there has not been synthetic research on the aromatic diketimines. It is the object of this investigation to prepare aromatic diketimines of triaryl type and examine their properties. The authors attempted synthesizing triaryl diketimines by the reaction of aryllithium reagents with phthalo–, and isophthalo– and terephthalonitriles, respectively, followed by the decomposition of the resulting addition intermediate with appropriate acid, such as anhydrous hydrogen chloride, anhydrous ammonia, methanol, and in some cases with water.



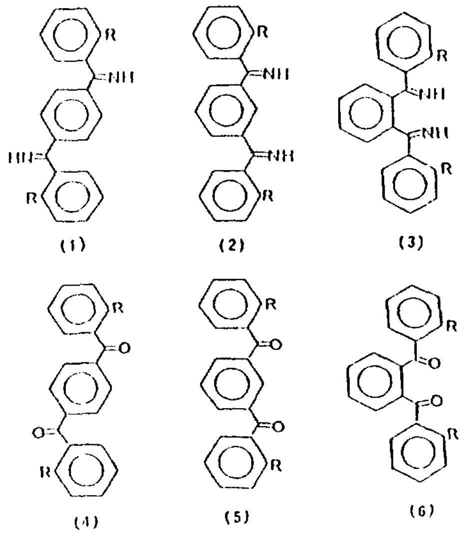
M = MgX, Li

Ar = phenyl, o-tolyl, o-anisyl

AH = HCl, NH_3, CH_3OH, H_2O

Nine aromatic diketimines were tried to prepare from the reaction of three kinds of aryl organometallic reagent with three isomers of dicyanobenzenes. But, the decomposition to diketimines of nitrile–organometallic reagent adducts obtained from the phthalonitrile was in general difficult. The hydrolysis of them into corresponding aromatic diketone was also failed. The other intermediate complexes from iso- and terephthalonitrile could be decomposed to aromatic diketimines, which could also easily be hydrolysed to corresponding aromatic diketones.

The other purpose of this investigation is to synthesize macromolecular host molecules of polycarbonyl cyclic compounds using the aromatic diketones prepared in this work as starting materials. The substituents groups, methyl and methoxy, will be converted bromo–, cyano–, and/or carbethoxy groups via several steps to give *bis*(2-bromobenzoyl)benzene, *bis* (2-cyanobenzoyl)benzene and *bis* (2-carbethoxybenzoyl)benzene. The two of these compounds may be condensed by intermolecular and then intra-molecular Grignard reaction, to give a macromolecular cyclic compound.



a: R=H b: R=CH_3 c: R=OCH_3

Experimental Section

All operations involving organometallic reagents were carried out with well-dried apparatus and solvents under nitrogen. Diethyl ether and THF were purified by refluxing it for hours in the presence of sodium metal and benzophenone, followed by distilling under nitrogen. Dichloromethane was also purified by distillation in the presence of calcium hydride. Ammonia was dried before use by passing the gas through a soda-lime tube. Phenyllithium[36-38] was prepared from bromobenzene and ether, and used as the ether solution. Melting points were uncorrected.

Ir spectra were recorded with Perkin-Elmer Model 283 spectrometer, and nmr spectra were taken on a Varian EM-360A spectrometer at 60 MHz to an internal standard of TMS. Mass spectra were obtained on a Shimazu-LKB 9000 GC/MS system. The TLC was taken with commerically available product(DC-Plastikfolien Kieselge, Art 5735 $60F_{254}$, Merck).

General Procedures for the Synthesis and Hydrolysis of Triaryl diketimines. *From the reaction of Grignard reagent on aryl dinitrile.* In a 100 ml of three-necked round-bottomed flask fitted with a reflux condenser and a dropping funnel, 0.8–1.0 g of magnesium turnings and 2–5 ml of anhydrous diethyl ether(or THF) were added. While stirring under nitrogen, a solution of 25 mmoles of aryl bromide in 10 ml of anhydrous ether was added carefully through the dropping funnel. As the reaction commences, addition was continued for a period of 30 min, and the reaction mixture was refluxed for 2–4 hr. The resulting Grignard reagent was added dropwise by cannulation to a solution of 5 mmoles of dicyanobenzene in 50–70 ml of ether contained in a 200 ml three-necked round-bottomed flask which was immersed in an ice-salt mixture. Stirred for 30 min, the reaction mixture was refluxed under nitrogen for 10–15 hr. The Grignard-nitrile complex was decomposed with anhydrous methanol or ammonia to give diketimines. If ammonia was used as a decomposing agent, the reaction mixture was cooled in a dry ice-acetone bath and dry ammonia was bubbled for 20 min through an inlet tube, when some liquid ammonia was formed in the flask. Cooling bath was removed and the mixture was allowed to warm to room temperature. Decomposed and filtered the reaction mixture, the filtrate was evaporated to give crude product which could be purified by chromatography and recrystallization.

From the reaction of aryllithium on aryldinitrile. In a 200 ml two-necked round-bottomed flask, which was completely dried for a long time in an oven, 1.0 g (0.008 mole) of dicyanobenzene was dissolved under nitrogen in 70 ml of dry ether, where usually suspension was formed. Cooling in a dry ice-acetone bath, two equivatents (or slightly excess) of aryllithium reagent in ether was added dropwise with stirring, then the suspension was dissolved, forming a red solution. Stirring was continued for a few hours, allowing the reaction mixture warm to room temperature, then usually a orange salt was precipitated forming a suspension. The aryllithium addition product was decomposed with 50-70 ml of water, stirred for 10-20 min, and the mixture was extracted three times with ether. The combined extracts were washed with water, dried over anhydrous magnesium sulfate, and filtered. The etheral solution was evaporated to give a free diketimine. If the free imine was unstable, it could be obtained as a salt by bubbling dry hydrogen chloride gas to the etheral solution, followed by filtering and washing the hydrochloride several times with ether.

Hydrolysis of the arylic diketimine. The hydrolysis of diketimines into corresponding aromatic diketone was carried out in an acid or basic solution.

Reaction of Terephthalonitrile with Phenyllithium. *1,4-Dibenzimidoylbenzene(1a).* The reaction of phenylmagnesium bromide with terepathalomitrile did not go well, and so phenyllithium was used instead of Grignard reagent. To a solution (suspension) of 1.0 g (8 mmoles) of terephthalonitrile in 50-60 ml of freshly dried diethyl ether was added dropwise by syringe, at $-78°C$, 18 mmoles of phenyllithium in ether through a rubber septum. Stirring with cooling for 30 min gave a red solution. After removing the cooling bath, the reaction mixture was allowed to warm to room temperature, when a yellow salt of diketiminolithium was precipitated. To this mixture was added with stirring 50-60 ml of water, then the red solution prompty turned to colorless, forming white precipitates at the same time which was gradually dissolved into the ether layer. The ether layer was separated, washed with saline water, dried over anhydrous magnesium sulfate, and filtered. Firstly, the ether solution was evaporated and the crude product was recrystallized from cyclohexane to give pale yellow crystals, m.p. 100-102°C. The yield was 60-75%. IR(KBr pellet): 3190 (N-H), 1580(arom. C=C), 1650 cm^{-1} (w. C=N). NMR($CDCl_3$): δ 7.3-7.8 (m. arom). MS: m/e 284(M^+). Secondly, dry HCl gas was bubbled to the ether solution to give a white crystalline salt which was washed with ether. M.p. 205-207°. IR(KBr pellet): 3300-2500(broad, N-H·HCl salt), 1650(C=N), 1600 cm^{-1}(arom. C=C).

1,4-Dibenzoylbenzene (4a). The diiminium salt(la) could easily be hydrolysed by refluxing the methanol solution in 6 N HCl for a few hours. Methanol was removed on a rotary evaporator. The residue was extracted with ether, dried over anhydrous magnesium sulfate, and was removed the solvent under reduced pressure to give a crystalline solid product. The crude product was chromatographed on silica gel column using dichloromethane as an eluent, and recrystallized from ethanol to give a colorless crystalline product, a aromatic diketone (4a), m.p. 156-158°C. The overall yield from terephthalonitrile was 35-40%. IR(KBr pellet): 1680(C=O), 1600 cm^{-1}(arom. C=C). NMR($CDCl_3$): δ 7.5$\sim$8.0(m. arom. H). MS: m/e 286(M^+).

Reaction of Terephthalonitrile with o-Tolylmagnesium bromide. *1,4-Bis (2-methylbenzimidoyl) benzene(1b).* A Grignard reagent prepared by oridinary method, as described in general procedure, from 0.8 g of magnesium turnings and 4.3 g (25 mmoles) of o-bromotoluene in ether, was added by cannulation, dropwise under nitrogen, to a solution of 0.65 g (5 mmoles) of terephthalonitrile in 70 ml of dry ether at an ice bath temperature. After stirred for 30 min, the pale yellow reaction mixture was reflux overnight. The resulting Grignard addition product was cooled in a dry ice-acetone bath and dry ammonia gas was bubbled for 30 min, when some ammonia was liquefied. Stirred for 20 min, removed the cooling bath and the mixture was warmed to room temperature to remove ammonia. The reaction mixture was filtered and the filtrate was evaporated under reduced pressure. The crude crystalline product was chromatographed on silica gel column using dichloromethane, and recrystallized from ether to give a colorless crystalline solid of triaryldiketimine(1b), m.p. 158°, yield 30-45%. IR(KBr pellet): 3220(=N-H), 1605 and 1500(arom. C=C), 1445 and 1380 cm^{-1}(CH_3). H-NMR($CDCl_3$): δ 2.13(6H, Me), δ 7.24(8H, arom.), δ 7.67(4H, arom.), δ 9.6(2H, broad, N-H).

1,4-Bis (2-methylbenzoyl) benzene (4b). The diketimine(1b) was hydrolysed almost quantitatively to corresponding diketone. The methanol solution of the diketimine was mixted with 6N hydrochloric acid, refluxed for a few hours, and extracted with dichloromethane. The extract was wash with sodium carbonate solution and water successively, dried over anhydrous magnesium sulfate, and the solvent was removed to give a crystalline solid. The crude product was chromatographed and recrystallized from petroleum ether. A pale yellow crystalline product of the corresponding diketone was obtained, m.p. 78.5° - 79.5°, yield 95%. IR(KBr pellet): 3090, 2920, 1670 (C=O), 1600 and 1500(arom. C=C), 1450 cm^{-1} (CH_3). H-NMR($CDCl_3$): δ 2.35(5H, CH_3), δ 7.28(arom. 8H), δ 7.83(arom. 4H).

Reaction of Terephthalonitrile with o-Anisylmagnesium bromide. *1,4-Bis(2-methoxybenzimidoyl)benzene (1c).* A Grignard reagnet prepared from 4.8 g (25 mmoles) of o-bromoanisole and 0.8 g of magnesium turnings in ether was added dropwise to an ice-cooled solution of 0.65 g (5 mmoles) of terephthalonitrile in 80 ml of dry ether for a period of 30 min. The mixture was refluxed overnight under nitrogen to give a yellowish Grignard-nitrile complex, which was decomposed at $-78°C$ by dry ammonia as described in general procedure. The slurry in the reaction mixture was filtered off and the solvent of the filtrate was slowly evaporated, then fine crystals of the diketimine(1c) was separated, m.p. 160-161°, yield 35-45%. Being unstable, this diketimine could not be purified by column chromatography. IR(KBr pellet): 3247 (=N-H), 3057, 2927(C-H), 1595cm^{-1}(arom. C=C). H-NMR(DMSO-d_6): δ 3.67(6H, OCH_3), δ 6.83$\sim$7.84(arom. 12H), δ 10.47(2H, NH). MS: m/e 344(M^+), 225, 210, 134, 107, 93.

1,4-Bis (2-methoxybenzoyl) benzene (4c). To a methanol solution of the diketimine(1c) was added 10-20 ml of 6N HCl, and the mixture was refluxed for a few hours. After working up the reaction mixture, as described for 4b, the crude product was chromatographed on a silica gel column using dichloromethane as eluent. Recrystallization from n-hexane-diethyl ether gave a white crystalline solid of the corresponding aromatic diketone(4c), m.p. 200.5-201.5°C, yield 95-100%. IR(KBr pellet): 3080, 2845, 1660(C=O), 1605 and 1485(arom. C=C), 1470(CH_3), 1260, 1030 cm^{-1}(C-O). H-NMR($CDCl_3$): δ 3.7(6H, OCH_3), δ 6.94~7.79(arom. 12H). MS: m/e 346(M^+), 314, 239, 211, 195.

Reaction of Isophthalonitrile with Phenyllithium. *1,3-Dibenzimidoylbenzene (2a).* To a solution(suspension) of 2.0 g(15 mmoles) of isophthalonitrile in dry ether was added dropwise by syringe, at −78°C, under nitrogen with stirring, 35 mmoles of phenyllithium. This reaction mixture was allowed to warm to room temperature while stirring for 2 hr, then a red solution was formed. To this solution about 50 ml of cold water was added, then the solution turned from red-brown to colorless and at the same same time was formed white precipitates which was gradually dissolved into the ether layer. The reaction mixture was extracted with ether, dried the filtrate, and dry HCl gas was bubble to the ether solution to give a white crysalline solid of the triaryl diketimine hydrochloride(2a), followed by washing the salt with dry ether. The diketimine being unstable, it could only be obtained as free imine by direct evaporation of the ether solution, followed by chromatography. The hydrochloride was very hydroscopic and water-sensitive, so that it could not operate further purification in the air. M.p. 194-196°C. IR(KBr pellet): 2500~3200 cm^{-1}(broad, N-H salt), 1640 cm^{-1}(C=N), 1950 cm^{-1}(arom. C=C).

1,3-Dibenzoylbenzene (5a). The diimine salt(2a) was dissolved in 3N hydrochloric acid and reflux for 1 hr. The mixture was extracted with diethyl ether, dried the filtrate on anhydrous magnesium sulfate, and removed the solvent on rotary evaporator. The crude product was recrystallized from ethanol, to give a colorless crystalline solid of the corresponding aromatic diketone(5a), m.p. 97-99°. The overall yield from isophthalonitrile was 50-60%. IR(KBr pellet): 3060, 1650(C=O), 1590 cm^{-1}(arom. C=C). NMR($CDCl_3$): δ 7.3~8.2 (m. arom. H). MS: m/e 286(M^+), 209, 181, 105, 77.

Reaction of Isophthalonitrile with *o*-Tolylmagnesium bromide. *1,3-Bis (2-methylbenzimidoyl) benzene (2b).* A Grignard reagent obtained, as ether solution, from 4.3 g (25 mmoles) of o-bromotoluene and 0.8 g of magnesium turnings was added dropwise through a cannula under nitrogen to an ice-cooled solution of 0.65 g(5 mmoles) of isophthalonitrile in 80 ml of dry ether. The mixture was refluxed for 14 hr to give a Grignard-nitrile complex, which was then decomposed by dry ammonia at low temperature as described in general procedure. After filtered the reaction mixture, the filtrate was evaporated to give a crude product, which was purified by column chromatography, obtaining a yellowish liquid product of the free diimine(2b). The yield 45-60%. IR(neat): 3242 (=N-H), 3052, 2912, 1655(C=N), 1600 cm^{-1}(arom. C=C). H-NMR (DMSO-d_6): δ 2.13(6H, CH_3). δ 7.21~8.05(arom. 12H), δ 10.33(2H, N-H). MS: m/e 312(M^+), 194, 118, 91.

1,3-Bis (2-methylbenzoyl) benzene (5b). The aromatic diimine(2b) was hydrolysed in 6N HCl and worked up after the procedure described for 4b to give a crude product, which was purified on silica gel-dichloromethane column, obtaining a yellowish liquid product. The yield 90-95%. IR(neat): 3055, 2850, 1660(C=O), 1595(arom. C=O), 1485 cm^{-1}(CH_3). H-NMR($CDCl_3$): δ 2.2(6H, CH_3), δ 7.05~8.15(arom. 12H). MS: m/e 314(M^+), 195, 165, 119, 91, 65.

Reaction of Isophthalonitrile with *o*-Anisylmagnesium bromide. *1,3-Bis (methoxybenzimidoyl) benzene (2c).* A Grignard reagent prepared from 4.7 g(25 mmoles) of *o*-bromoanisole and 0.8 g of magnesium turnings was reacted under nitrogen with 0.65 g(5 mmoles) of isophthalonitrile in 80 ml of dry ether according to the general procedure. The resultant Grignard-nitrile complex was decomposed with dry ammonia, and the reaction mixture was filtered to remove slurry. Slow evaporation of the filtrate gave a colorless crystalline solid product of the corresponding aromatic diketimine(2c). This free diimine also unstable and water sensitive, and it could not be purified on a silica gel column. M.p. 48-50°C, yield 25-35%. IR(neat): 3027-3057(=N-H, broad), 1670(C=N), 1595 cm^{-1} (arom. C=C). H-NMR(DMSO-d_6): δ 3.68(6H, OCH_3), δ 6.81~7.92 (arom. 12H), δ 10.27(2H, N-H). MS: m/e 344(M^+), 210, 134, 107.

1,3-Bis (2-methoxybenzoyl)benzene(5c). The aromatic diketimine(2c) was hydrolysed by refluxing in 6N HCl and worked up the reaction mixture according to the procedure for 4b. Recrystallization from n-hexane-dichloromethane gave a colorless crystalline product of the diketone(5c), m.p. 107.5-108.5°C, yield 90-95%. IR(KBr pellet): 3080, 2840, 1660 and 1650(C=O), 1590 and 1465(arom. C=C), 1460 cm^{-1}(CH_3). H-NMR($CDCl_3$): δ 3.65(6H, OCH_3), δ 6.8~8.2 (arom. 12H). MS: m/e 346(M^+), 314, 239, 226, 211, 195, 135, 77.

Reaction of Phthalonitrile with Organometallic Reagents. The solution of phthalonitrile in aprotic solvent was reacted with phenyllithium and Grignard reagents of o-bromotoluene and o-bromoanisole respectively. The addition complexes were worked up according to the general procedure. The products which were obtained as liquid, HCl salt or crystals, were generally unstable and difficult to purify. The expected aromatic diketimines and the hydrolytic products, diketones, could not be obtained. There seems to be little doubt that the reaction of phthalonitrile proceeds via different mechanism from the other isomers. The reaction should be examined by further experiments.

Results and Discussion

Some progress have been made in this investigation for the synthesis of aromatic diketimines of triaryl type by the action of organometallic reagents on isomers of phthalonitrile. Although dicyanobenzenes dissolve well in tetrahydrofuran, the reactions were carried out in diethyl ether in which the dinitriles still remain as a suspension because of the low solubility. When tetrahydrofuran was used as a reaction medium, dark purple coloration of reaction mixture was sometimes brought about, which was very annoying in work up contaminating the product.

The reaction of aryl Grignard reagents with aromatic dinitrile was very slow and was needed reflux for a long time. Aryllithium reagent, however, reacted very fast with the dinitrile even at −78°C, forming a red complex solution. The Grignard-nitrile addition complex could be decomposed into diketimine with water, dry ammonia or anhydrous methanol. In general, decomposition with dry (or liquid) ammonia gave better yield than with methanol in which reflux was needed for hours. Decomposition of the Grignard complex proceeded efficiently at a temperature of dry ice–acetone bath. The resultant diketimine showed comparatively low solubility in ether, and it was necessary to wash down the residue thoroughly with organic solvent on filtering the reaction mixture. By evaporating the filtrate carefully, diketimines were obtained as a crystalline or liquid product.

The aromatic diketimines could also be separated as a solid salts by passing dry HCl gas into the ether (or other aprotic organic solvent) solution of the diimine. The hydrochloride were in general hygroscopic and unstable in the air, and it was difficult to purify by recrystallization. The free diimine of triaryl type were comparatively much more stable than the hydrochloride, and could be recrystallized from appropriate organic solvents, such as dichloromethane–hexane or dichloromethane–petroleun ether. The diimines could also be purified by chromatography, but, some of them were too unstable to separate on silica gel, because they were hydrolyzed partly into corresponding diketones during the chromatography. The aromatic diketimines produced from the reaction between isophthlonitrile and phenyllithium or o-tolylmagnesium bromide melted at room temperature, so they could hardly be obtained as a crystalline solid.

We have taken for granted that phenyl–, o-tolyl– and o-anisylmagnesium bromide will show similar reaction activity on dicyanobenzenes. But, oddly enough, phenylmagnesium bromide did not react efficiently with the dinitriles, leaving starting material almost unchanged in the reaction mixture. So that, phenyllithium was used instead of the Grignard reagents. One might guess that the electron–releasing substituents, methyl and methoxy, affacted the reactivity of the Grignard reagent.

On the other hand, it was almost impossible to prepare triaryl diketimines from the reaction of phthalonitrile with organometallic reagents. It was also impossible to obtain the corresponding aromatic diketones by hydrolysing the addition complex. The reaction may proceed different way from the reaction of *iso*– and terephthalonitrile. It is likely that cyclization will occur during the reaction to form a five-membered azo ring. We have got some crystalline product from the reactions, though the structures were not determined. The reactions will be investigated further.

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References

1. A. Hantzch and F. Kraft, *Ber.* **24**, 3516(1891).
2. C. Moureu and G. Mignonac, *Ann. Chim.* [9] **14**, 322 (1920).
3. Ramart-Lucas and Salmon Legagneur, *Compt. rend.*, **184**, 103 (1927).
4. N. Easton, J. Gardner and J. Stevens, *J. Am. Chem. Soc.*, **69**, 976(1947).
5. E. Schultz, C. Robb and J. Sprague, *J. Am. Chem. Soc.*, **69**,2454(1947).
6. N. Easton, J. Gardner, M. Evanick and J. Stevens, *J. Am. Chem. Soc.*, **70**, 76(1948).
7. H. Lochte, Joe Horeczy, P. Pickard and A. Barton, *J. Am. Chem. Soc.*, **70**, 2012(1948).
8. L. Fieser and A. Seligman, *J. Am. Chem. Soc.*, **61**, 136(1930).
9. L. Fieser and D. Dowen, *J. Am. Chem. Soc.*, **62**, 2103(1940).
10. P.L. Pickard and D.J. Vaughan, *J. Am. Chem. Soc.*, **72**, 876 (1950).
11. P.L. Pickard and S.H. Jenkins, *J. Am. Chem. Soc.*, **75**, 5899(1953).
12. P.L. Pickard and D.J. Vanghan, *J. Am. Chem. Soc.*, **72**, 5017(1950).
13. P.L. Pickard and C.W. Young, *J. Am. Chem. Soc.*, **73**, 42 (1951).
14. P.L. Pickard and E.F. Engles, *J. Am. Chem. Soc.*, 4607(1952).
15. P.L. Pickard and E.F. Engles, *J. Am. Chem. Soc.*, **75**, 2148(1953).
16. P.L. Pickard and T.L. Tolbert, *J. Org. Chem.*, **26**, 4886(1961).
17. J.B. Lambert, W.L. Oliver, and J.D. Roberts, *J. Am. Chem. Soc.*, **87**, 5085(1965).
18. M.P. Doyles, W. Wierenga, and M.A. Zaleta, *J. Org. Chem.*, **37**(10), 1597(1972).
19. J. Charles, S.J. Thoman, and I. Moyer Hunsberger, *J. Org. Chem.*, **23**, 2852(1968).
20. H. Gilman and R.H. Kirby, *J. Am. Chem. Soc.*, **60**, 2336(1938).
21. F.N. Jones, R.L. Vaulx, and C.R. Hauser, *J. Org. Chem.*, **28**, 3461(1963).
22. P.L. Compagnon and M. Miocque, *Ann. Chim.*, **5**, 23(1970).
23. C.G. Screttas, J.F. Eastham, and C.W. Kamienski, *Chimina (switz.)* **24**, 109(1970).
24. V. Ramanthan and R. Levine, *J. Org. Chem.*, **27**, 1216(1962).
25. Gene Sumrell, *J. Org. Chem.*, **19**, 817(1954).
26. J. Büchi, F. Kracher, and G. Schmidt, *Helv. Chim. Acta.*, **45**, 729(1962).
27. J. Wibaut, A. De Jonge, H. Van der Voort, and P. Otto, *Rec. Trav. Chim.*, **70**, 1054(1951).
28. J. Gautier, M. Miocque, and L. Maserier, *Bull. Soc. Chim. France*, 1551(1967).
29. K. Lehmstedt and F. Dostal, *Ber.*, **72**, 804(1939).
30. I. Pattison, K. Wade, and K. Wyatt, *J. Chem. Soc.* (*A*), 837(1968).
31. J. Wibaut and J. De Jong, *Rec, Trave. Chim.*, **68**, 485(1949).
32. D.J. Berry and B.J. Wakefield, *J. Chem. Soc.* (*C*), 642(1971).
33. D.J. Berry and B.J. Wakefield, *Organometallic Chem.*, **23**, 1(1970).
34. H. Williams, P. Koenig, G. Huddleston, T. Couvillon, and W. Castille, *J. Am. Chem. Soc.*, **28**, 463(1963).
35. P.L. Pickard and G.W. Polly, *J. Am. Chem. Soc.*, **76**, 5169(1954).
36. A.I. Vogel, *"A Textbook of Practical Org. Chem."* 4th ed., p. 901, Longmans Ltd, 1978.
37. *Org. Syn. Col. Vol. II*, p. 517--518, John Wiley and Sons Inc., New York, 1973.
38. K. Zieglor and H. Colonius, *Ann.* **479**, 135(1930).
39. H. Gilman, E.A. Zoellner, and W.M. Selby, *J. Am. Chem. Soc.*, **54**, 1957(1932).