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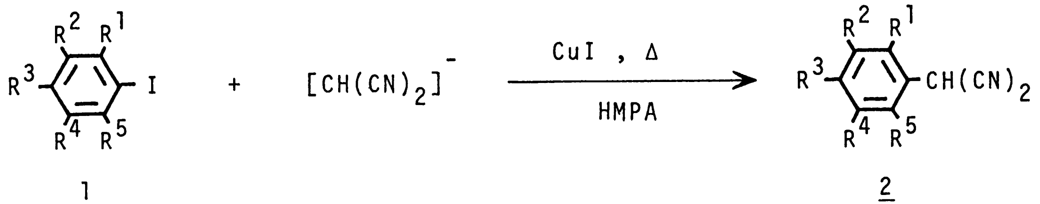
A FACILE SYNTHETIC ROUTE TO SOME ARYLMALONONITRILES

Hitomi SUZUKI,* Tsutomu KOBAYASHI, and Atsuhiro OSUKA*
Department of Chemistry, Faculty of Science,
Ehime University, Bunkyo-cho, Matsuyama 790

Copper(I) iodide-assisted reaction of aryl iodides with malononitrile anion provides a convenient route to some arylmalononitriles.

Malononitriles have been gaining increasing importance as useful intermediates for the syntheses of heterocyclic compounds.[1)] Whereas alkylmalononitriles are easily accessible by the reaction of malononitrile anion with alkyl halides, the corresponding reaction with nonactivated aryl halides does not take place under ordinary conditions. Thus the previously reported routes to arylmalononitriles involve the dehydration of arylmalonodiamides,[2)] reactions of sodiobenzyl cyanides with cyanogen chloride[3)] or N-cyano-N-methylaniline,[4)] gas-phase cyanation of arylacetonitriles with cyanogen halides,[5)] reaction of arylmethylmagnesium halides with N,N-disubstituted cyanamides,[6)] and thermal isomerization of adducts derived from arenes and dicyanocarbene.[7)] However, these methods suffer from disadvantages such as limited availability of starting materials, use of special apparatus, lack of generality, side-product formation, or low yields.

We now wish to report preliminary details of copper(I)-promoted arylation of malononitrile anion with nonactivated aryl halides, which leads to a simple one-step synthesis of arylmalononitriles under mild conditions.



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When aryl iodide 1 is heated with *in situ* generated malononitrile anion at 115-120°C in hexamethylphosphoric triamide (HMPA) in the presence of copper(I) iodide, iodine atom on the ring is readily displaced by dicyanomethyl group, giving the corresponding arylmalononitrile 2 in 42-61% yields (Table 1). The arylation proceeds quite smoothly with aryl iodides, but results are poor with aryl bromides. The reaction with aryl chlorides fails. Two equivalents of malononitrile and copper(I) iodide are required to obtain satisfactory yields. Without copper(I) salt, the arylation of carbanion does not occur. Steric congestion around reaction site

Table 1 Arylmalononitriles Obtained from the Reaction of Aryl Iodides with Malononitrile Anion

Arylmalononitrile 2[a]					Mp	Reaction	Reaction tem-	Yield[b]
R^1	R^2	R^3	R^4	R^5	(°C)	time (h)	perature (°C)	(%)
H	H	H	H	H	66-68	3	115-120	53
H	H	Me	H	H	56-57	3	115-120	55
Me	Me	Me	H	H	81-83	5	115-120	59
Me	H	Me	H	Me	90-91	4	115-120	54
Me	Me	H	Me	Me	169-170	3	115-120	51
Me	Me	Me	Me	Me	177-178	3	95-110	42[c]
H	$-OCH_2O-$		H	H	133-134	3	115-120	51
H	MeO	MeO	H	H	74-75	3	115-120	47
MeO	H	MeO	H	H	82-85	5	115-120	61

a) Spectral data and elemental analyses are in satisfactory agreement with the structures. b) Yields based on 1 refer to the isolated compounds and are not optimized. c) Accompanied by appreciable amounts of pentamethylbenzonitrile (~14%).

seems to provide no serious problem.

A general procedure is as follows: a commercial 60% sodium hydride dispersion (0.176 g; 4.4 mmol) is placed in 20 ml flask and paraffin oil is removed by washing with dry hexane (1 ml x 3). The remaining solid is covered with HMPA (1 ml) and, a solution of malononitrile (0.264 g; 4 mmol) in the same solvent (2.5 ml) is added with stirring. After 15 min, aryl iodide (1; 2.0 mmol) dissolved in HMPA (2 ml) is added, followed by copper(I) iodide (0.762 g; 4.0 mmol), and the mixture is gradually heated to 115-120°c and kept at this temperature range for several hours. The reaction is monitored by TLC analysis of small aliquots. The black mixture is then quenched with dilute hydrochloric acid (5 ml), and the organic phase is extracted with ether (20 ml x 3) and the extract washed with aqueous sodium sulfite to remove some free iodine. The solvent is evaporated under reduced pressure to leave a dark brown residue, chromatography of which on silica gel gives unchanged iodide 1 from hexane eluates and dinitrile 2 from hexane/dichloromethane eluates. The latter is further purified by recrystallization from hexane/ether.

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