# Synthesis of *N*-Substituted Diiminosuccinonitrile (DISN) and Diaminomaleonitrile (DAMN) Derivatives

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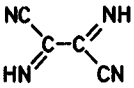
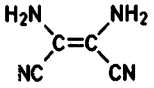
DuPont chemists have recently reported on the synthesis and reactions of diiminosuccinonitrile (DISN) and diaminomaleonitrile (DAMN)[1].



Diiminosuccinonitrile (DISN)

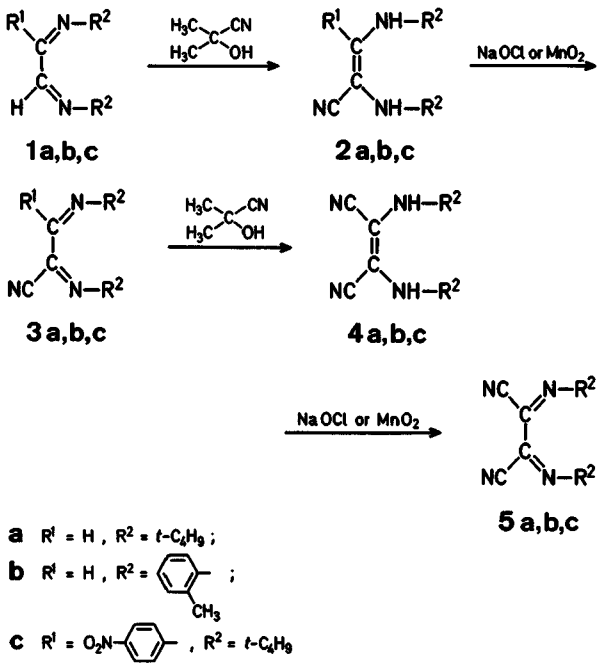


Diaminomaleonitrile (DAMN)

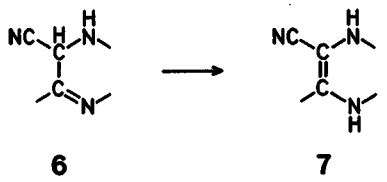
These readily available compounds owe their chemical versatility to the electron deficient character imparted by the two cyano groups. In spite of the usefulness of these compounds, there has been no report to date on the *N*-substituted analogs. Such analogs might be expected to show some of the same types of chemical properties as the parent compounds. They could also be expected to display chemistry dictated by the presence of the nitrogen substituents. *N*-substituted diiminosuccinonitrile and diaminomaleonitrile derivatives have been encountered in our studies of imine-isocyanide chemistry[2]. For purposes of structure proof as well as for further chemical study it became necessary to develop a useful synthetic procedure for their preparation.

We have found that readily available glyoxal derivatives (**1**) react smoothly with acetonecyanohydrin to give α,β-diaminoacrylonitrile derivatives (**2**)[3]. These derivatives can in turn be oxidized under mild conditions by either sodium hypochlorite or manganese dioxide to give structure (**3**). These products (when R is equal to hydrogen) can add a second molecule of hydrogen cyanide to produce (**4**).

Oxidation of **4** produces di-*N*-substituted diaminomaleonitrile derivatives (**5**).




Apparently, in each case tautomerization of the initial adduct (**6**) to the β-amino acrylonitrile (**7**) takes place more rapidly than addition of a second mole of hydrogen cyanide to **6**. As can be seen in the typical examples given in the Table, both aliphatic and aromatic nitrogen substituents are available via this route.




Preliminary investigation of the chemical properties of these compounds confirms the expected chemical utility as synthetic intermediates. The results of these investigations will be described subsequently.

**2,3-Di-*t*-butylaminoacrylonitrile (2a):**
Into a 500 ml round-bottomed flask equipped with a magnetic stirrer was placed crude glyoxylidenedi-*t*-butylamine (**1a**, 16.8 g, 0.1 mol) in methanol (300 ml). To this was added acetone cyanohydrin (12.74 g, 9.1 ml, 0.15 mol)[5] and 10% potassium cyanide solution (9.1 ml). The reaction was stirred at room temperature for 1 hour. The resultant slurry was evaporated and the extracted with chloroform from water. The residue obtained from evaporation of the chloroform extracts was crystallized from 65–110° petroleum ether to give colorless needles (**2a**); yield: 16.23 g.

**2,3-Di-*o*-toluidinacrylonitrile (2b):**
Into a 500 ml round-bottomed flask equipped with a magnetic stirrer, and reflux condenser was placed glyxoylidenedi-*o*-toluidine (**1b**, 8.75 g, 0.37 mol) in methanol (300 ml). To this was added acetone cyanohydrin (7.86 g, 5.6 ml, 0.0925 mol) and 10% potassium cyanide solution (5.6 mol). The system was flushed with nitrogen and refluxed for 1 hour in a nitrogen atmosphere. The solution was evaporated to half its original volume, dissolved in chloroform and extracted with water. The chloroform layer was separated from the water layer, dried with anhydrous magnesium sulfate, filtered, and evaporated to a white solid. Recrystallization from absolute ethanol gave white needles (**2b**); yield: 9.0 g.

**Table.** Summary of Imino- and Aminonitrile Products

| Compound | Yield (%) | m.p. | Analysis |
|---|---|---|---|
| **2a**[a] | 83 | 64–69°[h] | calc. C64.83 H9.97 N25.20 |
| | | | found 64.92 10.00 24.04 |
| **2b**[b] | 92 | 136–138°[i] | calc. C77.54 H6.51 N15.96 |
| | | | found 77.32 6.61 16.10 |
| **2c**[c] | 65 | 88–89° and | calc. C64.53 H7.65 N17.71 |
| | | 117.5–118°[j,k] | found 64.65 7.73 17.79 |
| **3a**[d] | 69 | b.p. 48°[e] | calc. C68.35 H9.91 N21.74 |
| | | | found 68.33 9.97 21.89 |
| **3b**[c] | 83 | 100–102°[i] | calc. C78.13 H5.79 N16.08 |
| | | | found 78.25 5.83 16.07 |
| **3c**[d] | 62 | 112–113°[k] | calc. C64.94 H7.05 N17.82 |
| | | | found 64.69 7.28 17.69 |
| **4a** | 57 | 63–65°[k,l] | calc. C65.42 H9.15 N25.43 |
| | | | found 65.26 9.20 25.30 |
| **4b**[f] | — | — | — |
| **5a** | 55 | 84.5–86.5°[h] | calc. C66.02 H8.31 N25.66 |
| | | | found 66.00 8.36 25.72 |
| **5b** | 44[g] | 195–196°[i] | calc. C75.51 H4.93 N19.57 |
| | | | found 75.42 4.96 19.54 |

[a] Precursor (**1a**) prepared according to J. M. Kliegman, R. K. Barnes, *Tetrahedron* **26**, 2555 (1970).
[b] Precursor (**1b**) prepared according to J. M. Kliegman, R. K. Barnes, *J. Org. Chem.* **35**, 3140 (1970).
[c] Precursor (**1c**) prepared in two successive acid ($C_7H_7SO_3H$ and $TiCl_4$) catalyzed steps from *p*-nitrophenylglyoxal hydrate.
[d] Oxidant equals NaOCl.
[e] Oxidant equals $MnO_2$.
[f] Although this product could be isolated and characterized spectrally, its susceptibility to autoxidation precluded other analytical and physical data.
[g] Overall yield from **3b**.
[h] Petroleum ether.
[i] Ethanol.
[j] Two different crystalline modifications from benzene petroleum ether.
[k] Ethanol/water.
[l] J. Honzl, P. Krivinka, *Tetrahedron Lett.* **1970**, 2357 report 77°.

**α-Cyanoglyoxylidenedi-*o*-toluidine (3b):**
Into a 250 ml round-bottomed flask equipped with a magnetic stirrer, Dean-Stark trap, and a reflux condenser was placed activated manganese dioxide[4] (6.96 g, 0.08 mol) in benzene (150 ml). The mixture was refluxed for 12 hours during which time 0.4 ml of water was collected. The reaction mixture was cooled and 2,3-di-*o*-toluidinoacrylonitrile (**2b**, 2.63 g, 0.01 mol) was added. The reaction mixture was refluxed for 12 hours during which time 0.2 ml of water was collected. The hot solution was filtered through a Celite 545 bed to remove the manganese dioxide. The manganese dioxide was washed several times with dichloromethane. The resulting black solution was evaporated to a black oil. Several recrystallizations alternating between 2-propanol and 65–110° petroleum ether gave yellow-orange needles (**3b**); yield: 2.18 g.

**α,β-Dicyanoglyoxylidenedi-*t*-butylamine (5a):**
Into a 250 ml round-bottomed flask equipped with a magnetic stirrer was placed 1,2-di-*t*-butylamino-1,2-di-cyanoethylene (**4a** 3.00 g, 0.013 mol) in methanol (130 ml). To the yellowish solution was slowly added 5% sodium hypochlorite solution (41 ml, Clorox). The solution became colorless immediately but was stirred for 5 minutes at room temperature. The solution was poured into water and extracted with chloroform to yield a pale yellow solution. The organic layer was separated form the water, layer, dried with anhydrous magnesium sulfate, filtered and evaporated to a white solid. Crystallization from 20–40° petroleum

ether or absolute ethanol gave colorless gem-like crystals of α,β-dicyanoglyoxylidenedi-*t*-butylamine (**5a**); yield: 1.63 g.

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[1] R. W. Begland, A. Cairncross, D. S. Donald, D. Hartter, W. A. Sheppard, O. Webster, *J. Amer. Chem. Soc.* **93**, 4953 (1971). W. A. Sheppard, O. W. Webster, *J. Amer. Chem. Soc.* **95**, 2695 (1973).

[2] Cf. J. A. Deyrup, M. M. Vestling, W. V. Hagen, E. J. Yun, *Tetrahedron* **25**, 1467 (1969).

[3] Structures for **3** and **5** are not meant to imply stereochemistry. Stereochemical assignments in these and related systems will be the subject of a future publication.

[4] E. F. Pratt, T. P. McGovern, *J. Org. Chem.* **29**, 1540 (1964).

[5] A larger excess of this reagent resulted in the formation of 2,3-di-*t*-butylaminosuccinonitrile.