

Heterocycles from Ketenimines. X. *Bis*(5-Iminoisoxazolidines) (1a)

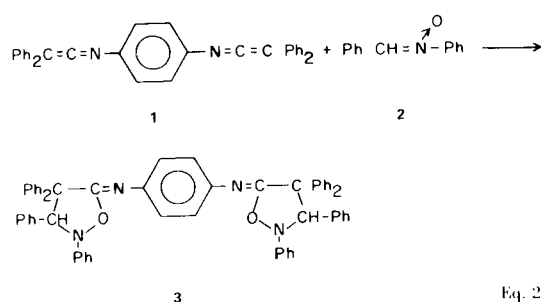
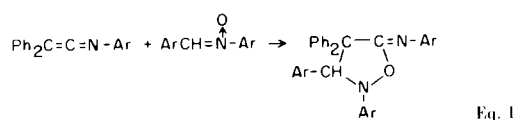
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The utility of the ketenimine moiety as a precursor to a series of heterocycles with exocyclic unsaturation has been the subject of several investigations (2,3,4,5,6). In general, this heterocumulene has been found to undergo both 2+2 and 2+3 cycloadditions, and the heterocycles so produced are usually obtained in good yields. More recently, two studies to determine if *bis*-heterocycles could be achieved through bicycloadditions to *bis*-ketenimines have been reported (1a, 7). Both of these studies involved 2+2 cycloadditions and demonstrated that *bis*-heterocycles were available by this route. This report concerns observations on the 2+3 bicycloadditions of *bis*-ketenimines.

Earlier work from this laboratory (5) has shown that ketenimines and nitrones undergo cycloaddition to yield iminoisoxazolidines (Eq. 1). Structure proof for the adducts was obtained through analysis, ir (characteristic absorption for the exocyclic imine), and ms data. If *bis*-ketenimines behave similarly, then treatment of ketenimine **1** with nitron **2** should result in the production of a *bis*(iminoisoxazolidine) (**3**) (Eq. 2).

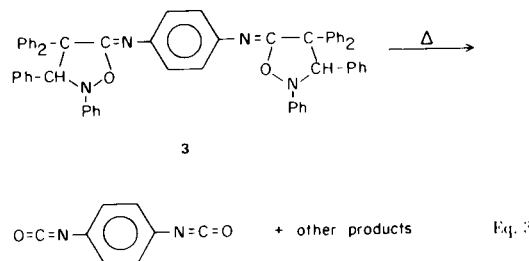


To test this postulate, a 1:2 molar ratio of *bis*-ketenimine **1** and nitron **2** was dissolved in dry tetrahydrofuran and the solution was heated to reflux. The progress of the reaction was monitored by following the disappearance of the ketenimine absorption in the ir at 2000 cm^{-1} . This

absorption had completely disappeared in 24 hours, and the isolated product had an elemental analysis consistent with a 2:1 adduct (the *bis*-heterocycle). The adduct exhibited a strong absorption in the unsaturated region of the ir (1710 cm^{-1}) indicative of structure **3**. However, supporting evidence from mass spectroscopy (for comparison with Barker and Gardner's iminoisoxazolidine (**5**)), could not be obtained from the available instruments because of the high molecular weight of the adduct.

Fortunately, chemical evidence for structure **3** is readily available. This adduct and the others listed in the Experimental section decompose near their melting points. Thermolysis of a sample of **3** and trapping of the volatile material on a cold finger gave a chloroform soluble compound which was identical with *p*-phenylene diisocyanate prepared by an alternate route (8). Only structure **3** for the adduct could account for this observation (Eq. 3). The other *bis*(iminoisoxazolidines) produced differed from **3** in that different nitrones were used. These adducts, however, should yield the same diisocyanate on thermolysis, and this was observed experimentally.

This work demonstrates that *bis*-ketenimines undergo 2+3 bicycloaddition reactions as well as 2+2 bicycloadditions to yield 5 membered as well as 4 membered *bis*-heterocycles. The natural sequence for this study is the development of syntheses for important *bis*-heterocycles employing the bicycloaddition reactions. This will be the subject of future reports.



EXPERIMENTAL

Melting points were determined on a Mel-Temp apparatus and are corrected. Infrared spectra were determined in chloroform on Perkin-Elmer Model 137 and 137 G Infracords. Analysis were per-

formed by Galbraith Laboratories, Inc., Knoxville, Tennessee and by the Heterocyclic Chemical Corporation, Harrisonville, Missouri.

5,5'-(*p*-Phenylenedinitrilo)bis[2,3,4,4-tetraphenylisoxazolidine] (**3**).

In a 100 ml. round bottom flask equipped with a reflux condenser fitted with a drying tube were placed 2.30 g. (0.005 mole) of *N,N'*-bis(diphenylethenylidene)-1,4-benzenediamine (**1**), 1.97 g. (0.01 mole) of α -*N*-diphenylnitron (**2**), and 50 ml. of dry tetrahydrofuran. The solution was refluxed for 24 hours, then allowed to stand overnight. The tetrahydrofuran was removed under reduced pressure without heating. An oily material remained which was triturated with cyclohexane. The solid adduct was removed by vacuum filtration and dried overnight. A yield of 2.76 g. (64.6%) of crude material was obtained. Recrystallization of the crude adduct from tetrahydrofuran-cyclohexane gave an analytical sample, m.p. 176-178° dec.; ir 1710 cm^{-1} (s).

Anal. Calcd. for $\text{C}_{60}\text{H}_{46}\text{N}_4\text{O}_2$: C, 84.48; H, 5.20; N, 6.57. Found: C, 84.51; H, 5.49; N, 6.64.

5,5'-(*p*-Phenylenedinitrilo)bis[3,4,4-triphenyl-2-*p*-tolylisoxazolidine].

Fifty ml. of dry tetrahydrofuran, 2.30 g. (0.005 mole) of **1**, and 2.10 g. (0.01 mole) of α -phenyl-*N-p*-tolylnitron were treated as described to yield 3.67 g. (83.4% yield) of crude adduct which was then recrystallized from chloroform-cyclohexane to give an analytical sample, m.p. 151-152° dec.; ir 1710 cm^{-1} (s).

Anal. Calcd. for $\text{C}_{62}\text{H}_{50}\text{N}_4\text{O}_2$: C, 84.32; H, 5.71; N, 6.34. Found: C, 84.19; H, 5.95; N, 6.64.

5,5'-(*p*-Phenylenedinitrilo)bis[3,4,4-triphenyl-2-*p*-chlorophenylisoxazolidine].

Fifty ml. of dry tetrahydrofuran, 2.30 g. (0.005 mole) of **1** and 2.32 g. (0.01 mole) of α -phenyl-*N-p*-chlorophenylnitron were treated as described to yield 3.52 g. (79.1% yield) of crude adduct which when recrystallized from chloroform-cyclohexane gave an analytical sample, m.p. 183-185° dec.; ir 1715 cm^{-1} (s).

Anal. Calcd. for $\text{C}_{60}\text{H}_{44}\text{N}_4\text{O}_2\text{Cl}_2$: C, 78.00; H, 4.80; N, 6.06. Found: C, 78.09; H, 4.69; N, 6.38.

5,5'-(*p*-Phenylenedinitrilo)bis[2,4,4-triphenyl-3-*p*-methoxyphenylisoxazolidine].

Fifty ml. of dry tetrahydrofuran, 2.30 g. (0.005 mole) of **1**, and 2.27 g. (0.01 mole) of α -*p*-methoxyphenyl-*N-p*-phenylnitron were treated as described to yield 3.77 g. (82.5% yield) of crude adduct. The adduct was recrystallized from chloroform-cyclohexane to give an analytical sample, m.p. 190-191° dec.; ir 1710 cm^{-1} (s).

Anal. Calcd. for $\text{C}_{62}\text{H}_{50}\text{N}_4\text{O}_4$: C, 81.37; H, 5.51; N, 6.12. Found: C, 81.12; H, 5.66; N, 5.93.

5,5'-(*p*-Phenylenedinitrilo)bis[4,4-diphenyl-2-*p*-chlorophenyl-3-*p*-tolylisoxazolidine].

Fifty ml. of dry tetrahydrofuran, 2.30 g. (0.005 mole) of **1** and 2.46 g. (0.01 mole) of α -*p*-tolyl-*N-p*-chlorophenylnitron were treated as described to yield 4.00 g. (84.0% yield) of crude adduct which when recrystallized from chloroform-cyclohexane gave an analytical sample, m.p. 144-145° dec.; ir 1715 cm^{-1} (s).

Anal. Calcd. for $\text{C}_{62}\text{H}_{48}\text{N}_4\text{O}_2\text{Cl}_2$: C, 78.22; H, 5.08; N, 5.89. Found: C, 78.51; H, 4.92; N, 5.92.

Proof of Structure of the Bis(5-Iminoisoxazolidines).

Into a 250 ml. erlenmeyer flask equipped with a cork stopper through which a test tube (20 cm. long) has been fitted was placed approximately 0.1 g. of adduct. The test tube was filled with dry ice and acetone and the entire apparatus was placed on a hot plate which had been heated to about 300°. After ten minutes, the apparatus was removed from the hot plate, the dry ice-acetone mixture dumped from the test tube, and the outside of the test tube washed with chloroform. The chloroform washings were immediately placed in the sample cell of the ir and a spectrum was determined. In each case the infrared absorption (2250 cm^{-1} and 1710 cm^{-1}) was similar to that of *p*-phenylene diisocyanate which had been prepared by an alternate method (8). Some discrepancy occurred in the finger print region because of the impurities present in the diisocyanate. However, in each sample decomposed, the fundamental region of the ir was identical with *p*-phenylene diisocyanate.

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