

Heterocycles from Ketenimines. IX. *Bis*(Diazetidines) (1a)

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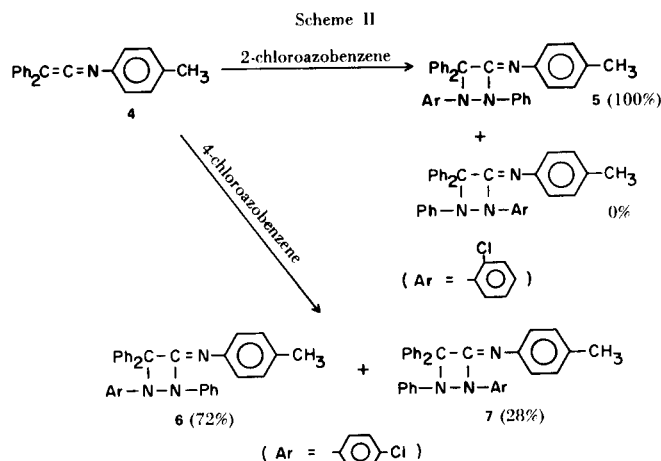
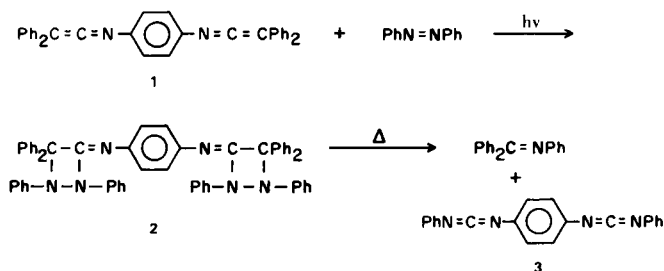
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Received February 6, 1974

Ketenimines (nitrogen analogs of ketenes) have been shown to be general precursors to heterocycles through simple 2 + 2 and 2 + 3 cycloaddition reactions. Heterocycles produced by these routes include oxetanes (2), oxazetidines (3), diazetidines (4), azetidines (5), oxazolines (6), isoxazolidines (7), and triazoles (8). More recently *bis*(oxazetidines) have been shown to be available through the cycloaddition reactions of nitrosoarenes and *bis*(ketenimines) (1a). We wish to report the preparation of another *bis*-heterocycle through a cycloaddition reaction of *bis*-ketenimines.

In a mechanistic study of the reaction of azobenzenes and monoketenimines, Barker and Jones state that the cycloaddition is concerted and that the need for light is to ensure the presence of the *cis* isomer of the azobenzene - the demonstrated reactive form of the azobenzene in the concerted cycloaddition (9). We have studied the reaction of *bis*-ketenimine 1 (*N,N'*-*bis*(diphenylethenylidene)-1,4-benzenediamine) with various azobenzenes under the conditions described for the monoketenimine reaction to ascertain if *bis*(diazetidines) could be realized by this route and to determine if a similar mechanism is operative. When 1 and azobenzene are irradiated in a Srinivasan-Griffin photochemical reactor equipped with 3500 Å lamps for 48 hours, a 65% yield of a 2:1 adduct is obtained. Proof of structure of the *bis*-heterocycle (2) is based on elemental analysis, ir (a 1712 cm^{-1} absorption which is characteristic of imines on a strained rings (3,4)), and thermal degradation studies (Scheme I). The observation of only an imine and the *bis*-carbodiimide 3 upon degradation establishes the heterocycle structure to be a *bis*(3-iminodiazetidines). No other mode of addition would yield a product which could

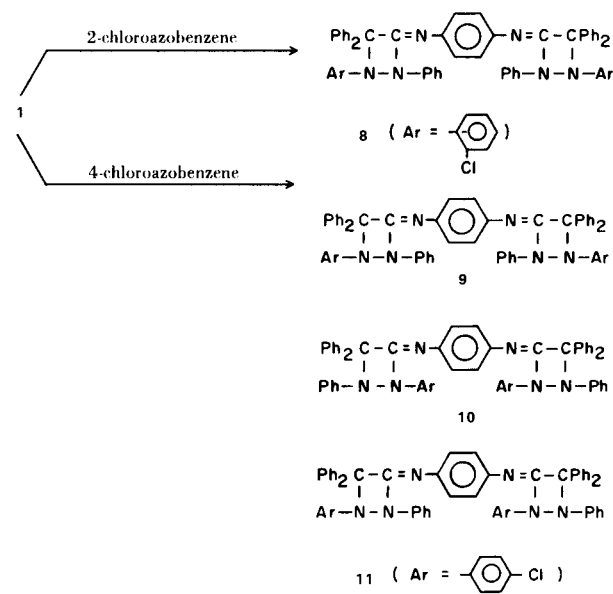
Scheme I



degrade to 3. Similar results were obtained with 1 and symmetrically substituted azobenzenes (see Experimental).

In the original study of the production of 1,2-diazetidines from ketenimines and azobenzenes, Barker and Jones also observed a pronounced steric effect (9). For instance 4 and 2-chloroazobenzene yielded only one of the two possible isomeric products while 4-chloroazobenzene and 4 gave both isomers in a ratio of 72:28 (Scheme II).

Scheme III



Similar results were obtained with other *o* and *p* mono-substituted azobenzenes regardless of the electron donating or withdrawing character of the substituent. To determine if this same steric effect after alignment would be observed in the production of *bis*(1,2-diazetidines), **1** was treated with 2-chloroazobenzene and with 4-chloroazobenzene. Analysis by thermal degradation of the adducts to the corresponding *bis*-carbodiimides and anils (**9**) was utilized to obtain the isomer ratio. The results obtained (Scheme III) are in accord with the observations on the monoketenimines. The *o*-substituted azobenzene yielded an adduct (**8**) analogous to **5**. This adduct constituted 97% of the product. Thermal degradation of the product from **1** and the *p*-substituted azobenzene gave a ratio of 68% benzophenone *p*-chloroanil to 32% benzophenone anil. Three adducts (**9**, **10**, and **11**) are possible, but from this ratio of anils **9** must be the predominate product. These results are in agreement with expectations if a steric effect after alignment is operative (**9**).

In summary, the reaction of *bis*-ketenimine **1** and symmetrical azobenzenes yields *bis*(1,2-diazetidines). The same reaction with unsymmetrical azobenzenes yields adducts indicative of steric control on the cycloaddition.

EXPERIMENTAL

Melting points were determined on a Mel-Temp apparatus and are corrected. Infrared spectra were determined in carbon tetrachloride, chloroform, potassium bromide, and neat on Perkin-Elmer Model 137 and 137G Infracords. The gas chromatographic analyses were made on a Hewlett-Packard Model 5750 instrument using a six foot column of 10% UCW 98 on Chromosorb W. Analyses were performed by Galbraith Laboratories, Inc., Knoxville, Tennessee.

3,3'-(*p*-Phenylenedinitrilo)*bis*[1,2,4,4-tetraphenyl-1,2-diazetidine] (**2**).

A solution of 2.30 g. (0.005 mole) of **1** and 1.82 g. (0.01 mole) of azobenzene in 50 ml. of dry benzene was irradiated in a pyrex tube in the Srinivasan-Griffin photochemical reactor equipped with 3500 Angstrom lamps for 48 hours. At the end of this time, the adduct had precipitated from the solution and was separated by filtration to give 2.68 g. (65.0% yield) of tan crystals. The solid adduct was extracted three times with hot tetrahydrofuran and then washed with hot methanol to prepare the analytical sample, m.p. 250-251°; ir: 1712 cm⁻¹ (s).

Anal. Calcd. for C₅₈H₄₄N₆·H₂O: C, 82.63; H, 5.50; N, 9.97. Found: C, 82.80; H, 5.36; N, 9.79.

3,3'-(*p*-Phenylenedinitrilo)*bis*[4,4-diphenyl-1,2-di-*p*-tolyl-1,2-diazetidine].

Fifty milliliters of dry benzene 2.30 g. (0.005 mole) of **1**, and 2.10 g. (0.01 mole) of 4,4'-dimethylazobenzene were treated as described to yield 3.50 g. (79.5% yield) of crude adduct which when extracted and washed as described gave the analytical sample, m.p. 238-239°; ir: 1709 cm⁻¹ (s).

Anal. Calcd. for C₆₂H₅₂N₆: C, 84.51; H, 5.95; N, 9.54. Found: C, 84.53; H, 6.12; N, 9.35.

3,3'-(*p*-Phenylenedinitrilo)*bis*[4,4-diphenyl-1,2-di-*p*-bromophenyl-1,2-diazetidine].

One hundred milliliters of dry benzene, 2.30 g. (0.005 mole) of **1** and 3.40 g. (0.01 mole) of 4,4'-dibromoazobenzene were treated as described to yield 0.94 g. (17% yield) of tan crystals which when extracted and washed as described gave the analytical sample, m.p. 249-250°; ir: 1704 cm⁻¹ (s).

Anal. Calcd. for C₅₈H₄₀Br₄N₆: C, 61.07; H, 3.53; N, 7.37. Found: C, 61.25; H, 3.64; N, 7.21.

3,3'-(*p*-Phenylenedinitrilo)*bis*[4,4-diphenyl-1,2-di-*p*-chlorophenyl-1,2-diazetidine].

One hundred milliliters of dry benzene, 2.30 g. (0.005 mole) of **1**, and 2.51 g. (0.01 mole) of 4,4'-dichloroazobenzene were treated as described to yield 2.41 g. (50.1% yield) of crude adduct which when extracted and washed as described gave the analytical sample, m.p. 233-235°; ir: 1704 cm⁻¹ (s).

Anal. Calcd. for C₅₈H₄₀Cl₄N₆: C, 72.35; H, 4.19; N, 8.73. Found: C, 72.40; H, 4.16; N, 8.57.

3,3'-(*p*-Phenylenedinitrilo)*bis*[2,4,4-triphenyl-1-*p*-chlorophenyl-1,2-diazetidine].

Fifty milliliters of dry benzene, 2.30 g. (0.005 mole) of **1** and 2.17 g. (0.01 mole) of 2-chloroazobenzene were treated as described to give 3.03 g. (67.7% yield) of crude adduct which when extracted and washed as described gave the analytical sample, m.p. 237-237.5°; ir: 1712 cm⁻¹ (s).

Anal. Calcd. for C₅₈H₄₂Cl₂N₆: C, 77.93; H, 4.74; N, 9.40. Found: C, 77.78; H, 5.00; N, 9.18.

Reaction of **1** with 4-Chloroazobenzene.

Fifty milliliters of dry benzene, 2.30 g. (0.005 mole) of **1** and 2.17 g. (0.01 mole) of 4-chloroazobenzene were treated as described to give 2.92 g. (65.3% yield) of crude adduct which when extracted and washed as described gave the analytical sample, m.p. 241-242°; ir: 1709 cm⁻¹ (s).

Anal. Calcd. for C₅₈H₄₂Cl₂N₆: C, 77.93; H, 4.74; N, 9.40. Found: C, 78.11; H, 4.92; N, 9.13.

Proof of Structure of the *Bis*-heterocycles.

Each purified adduct was heated at its melting point for 10 seconds. The benzophenone-anil formed was soluble in cold chloroform while the carbodiimide was sparingly soluble and would remain behind.

The identity of the anil was shown in each case by comparison of the infrared of the anil produced by degradation with the authentic anil. The retention time of the anil produced by degradation and the authentic anil were determined to be identical by gc also (**10**).

The adducts from **1** with *o* and *p*-chloroazobenzene were analyzed the same way except relative peak areas of the two possible anils were used to determine how much of each adduct was present (**10**).

Acknowledgements.

We wish to thank the Vice President for Research and the Biological and Physical Sciences Institute of Mississippi State University for partial support of this work.

REFERENCES

- (1a) Part VIII. M. W. Barker and C. John Wierengo, *J. Heterocyclic Chem.*, accepted. (b) On leave from Mississippi State

College of Women, Columbus, Mississippi 1973-1974.

(2) L. A. Singer, G. A. Davis, and R. L. Knutsen, *J. Am. Chem. Soc.*, **94**, 1188 (1972) and references cited therein.

(3) M. W. Barker and J. T. Gill, *J. Heterocyclic Chem.*, **7**, 1203 (1970).

(4) M. W. Barker and M. E. Coker, *ibid.*, **4**, 155 (1967).

(5) M. W. Barker and J. D. Rosamond, *ibid.*, **9**, 1147 (1972).

(6) W. J. Kauffman, *J. Org. Chem.*, **35**, 4244 (1970).

(7) M. W. Barker and J. H. Gardner, *J. Heterocyclic Chem.*, **5**, 881 (1968).

(8) *op cit.*, **6**, 251 (1969).

(9) M. W. Barker and R. H. Jones, *ibid.*, **9**, 555 (1972).

(10) Authentic benzophenone anil gave a gc retention time of 295 seconds under the following conditions: sample size, 2 μ l; flow rate, 2 ml./min. of He; column temperature, 285 $^{\circ}$; injection port temperature, 190 $^{\circ}$; and flame detector temperature, 310 $^{\circ}$. The substituted benzophenone anils always had longer retention times (i.e. for $(C_6H_5)_2C=NC_6H_4pCl$, 440 seconds) and the relative peak areas were used to determine the amounts of each anil present and, hence, the amount of each *bis*(diazetidine) present in the original reaction mixture.