Notes

The Formation of a Dimer of N-Vinylcarbazole

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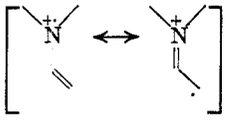
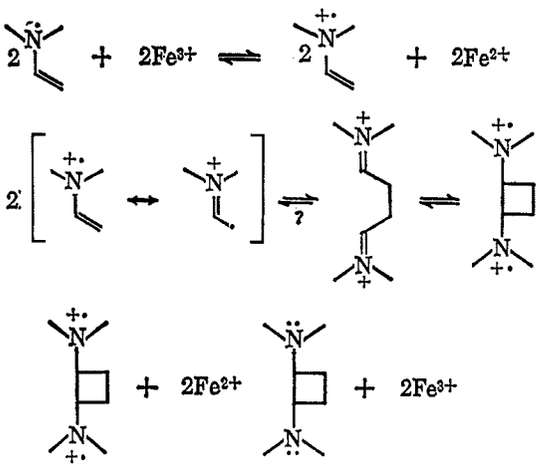
There have been a number of recent studies on the polymerization of N-vinylcarbazole either by ionic or free-radical mechanisms. Scott[2] and co-workers and Ellinger[3] observed that π-complex electron acceptors such as *p*-chloranil and tetracyanoquinodimethane initiated the polymerization of N-vinylcarbazole. Scott indicated that the polymerization process was qualitatively unaffected by the presence of thiophene, a potent retarder of conventional cationic propagation, and acrylonitrile, a radical or anionically readily polymerized monomer. In the presence of water and certain amines, however, Scott reported the retardation of polymerization of this monomer. The atypical nature of N-vinylcarbazole polymerization with respect to either ionic or radical mechanisms is further complicated by the observation that oxygen[3] and hindered phenols[4] have relatively little or no effect on this process. Scott, *et al.*, suggested that this is a cationic polymerization initiated by a Wurster radical cation formed by oxidation of N-vinylcarbazole. Ellinger indicated that there is a "partial transfer" of one electron from N-vinylcarbazole to the electron acceptor as the initiation mechanism. However, where ferric ion is used as the oxidant instead of π-complex-forming electron acceptors, N-vinylcarbazole as well as 4-vinylpyridine was polymerized in methanol solution.[5] Since it is not easy to visualize a "partial electron transfer" with ferric ion, we believe that there is oxidation–reduction by complete electron transfer between the metal ion and N-vinylcarbazole or 4-vinylpyridine. The resulting radical cation from such oxidation–reduction initiated the polymerization of the monomer. Scott, *et al.*, suggested that the initiation and propagation probably do not involve intermediates with independent radical and ionic functions which implies that the Wurster ion of N-vinylcarbazole does not exist with a localized carbon-radical function, *e.g*, the following. It may not be completely relevant to compare the mechanism of ferric ion and π-complex electron acceptors in initiating polymerization of N-vinylcarbazole. However, in our more recent experiments with ferric ion as the oxidant, we obtained evidence for the existence of a localized carbon-radical intermediate by isolation of a dimer of N-vinylcarbazole wherein the formation of a new carbon–carbon bond is involved.



The Structure of the Dimer.—With a high concentration of ferric ion (ferric nitrate, anhydrous or hydrate) in methanol–water medium (90:10), there was almost immediate dimerization of N-vinylcarbazole in good yield. The white crystalline compound melts at 191–193°. It does not decolorize bromine in carbon tetrachloride or potassium permanganate in acetone–water solution. The infrared spectrum showed neither the N–H stretching frequency near 3600 cm^{-1} nor the C=C vibration frequency near 1670 cm^{-1} characteristic of N-vinylcarbazole.

Elementary, mass spectral, and nmr analyses correspond to the dimer, *trans*-1,2-dicarbazylcyclobutane, previously reported by Ellinger[6] as a by-product from the reaction of N-vinylcarbazole with chloranil or tetranitromethane.

Mechanism of the Formation of the Dimer.—The simplest possible mechanism for the formation of such a dimer with a cyclobutane skeleton should be a four-center-type reaction. It will give 1,3-dicarbazylcyclobutane as the chief product. However, ferric ion is essential for the rapid formation of the dimer. It is not reasonable that the function of ferric ion is only to facilitate the delocalization of the olefinic π bond in the N-vinylcarbazole. The nature of Fe^{+3}–Fe^{+2} oxidation–reduction, as well as the chemistry of N-vinylcarbazole, is by no means simple either in the dark or under photolysis. Thus, it is quite feasible to account for the participation of ferric ion in this process as an oxidation–reduction reaction leading to a carbon-free radical which then dimerizes.



This mechanism is consistent with the observation that the rate of formation of the dimer increases with

(1) Participant in the Wellesley College Institute of Chemistry supported by the National Science Foundation.

(2) H. Scott, G. A. Miller, and M. M. Labes, *Tetrahedron Letters*, **No. 17**, 1073 (1963).

(3) L. P. Ellinger, *Chem. Ind.* (London), 1982 (1963).

(4) C. H. Wang, unpublished result.

(5) C. H. Wang, *Chem. Ind.* (London), 751 (1964).

(6) L. P. Ellinger, J. Fenney, and A. Ledwith, *Monatsh. Chem.*, **96**, 131 (1965).

the concentration of ferric ion present, and can also account for the absence of any isomeric 1,3-dicarbazylcyclobutane.

Experimental Section[7]

Hydrolysis of N-Vinylcarbazole.—To a solution of 1 g (5×10^{-3} mole) of N-vinylcarbazole (Matheson Coleman and Bell, mp 67°) in 44 ml of 9:1 methanol–water, 0.01 g (2.5×10^{-5} mole) of ferric nitrate (Mallinckrodt, $Fe(NO_3)_3 \cdot 9H_2O$) was added. The mixture was stirred at room temperature and a white precipitate gradually appeared. At the end of 4 days, 0.7 g of white solid was collected. This material was identified as carbazole by melting point and mixture melting point determinations with known samples of carbazole, mp 238–241°, and by comparison of their infrared spectra. The mother liquor furnished acetaldehyde in about 50% yield based on the isolation of acetaldehyde 2,4-dinitrophenylhydrazone, mp 145–147°, lit.[8] mp 148°. Comparable results were obtained when the same molar concentrations of hydrochloric acid were used instead of ferric nitrate.

Formation of the Dimer.—To a solution of 2 g (0.01 mole) of N-vinylcarbazole in 88 ml of 9:1 methanol–water, 0.2 g (5×10^{-4} mole) of ferric nitrate was added. The mixture was stirred and a white precipitate was observed within 10 min. At the end of 1 hr, the solid was collected by filtration. The yield was 0.4 g (20%), mp 189–193°. Recrystallization from an ethanol–acetone (1:1) solution raised the melting point to 191–193.5°.

Anal. Calcd for $C_{28}H_{22}N_2$: C, 87.01; H, 5.74; N, 7.25; mol wt, 386.5. Found: C, 86.74; H, 5.80; N, 7.31; mol wt, 373 (Rast method), 386 (mass spectrum).

Acknowledgment.—We are indebted to Dr. G. Dudek of Harvard University and Mrs. G. Dudek of this department for the mass spectral and nmr analyses.

(7) Analysis was by Dr. M. S. Nagy, Massachusetts Institute of Technology, Cambridge, Mass. Melting points are not corrected. The nmr spectrum was recorded by using a Varian A-60 spectrometer, and mass spectral analysis was done by using a mass spectrophotometer, A.E.I. MS9.

(8) G. R. Clemo and W. H. Perkin, Jr., *J. Chem. Soc.*, **125**, 1804 (1924).

3-Hydroxy-4-Substituted 1,2,5-Thiadiazoles. A New Synthesis

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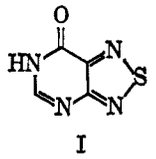
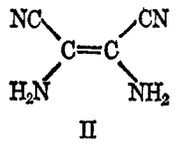
Although 2,1,3-benzothiadiazole bicyclic systems have been known since the last century,[1] 1,2,5-thiadiazoles were not described until 1957. The monocyclic system has been obtained by oxidation of 2,1,3-benzothiadiazole derivatives[2-4] to 1,2,5-thiadiazole-3,4-dicarboxylic acid and also by basic cleavage of 1,2,5-thiadiazolo[3,4-*d*]pyrimidin-7(6H)-one (I) to 4-amino-1,2,5-thiadiazole-3-carboxamide.[5]

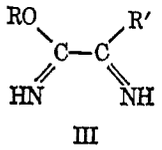
Carmack and associates have synthesized 3,4-dicyano-1,2,5-thiadiazole[6] by ring closure from thionyl chloride and hydrogen cyanide tetramer (II) and have developed a general synthesis from substituted oxalimidates (III).[7]



I



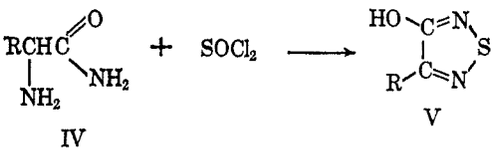
II



III

Two other interesting approaches have led to 3-cyano-4-hydroxy-1,2,5-thiadiazole,[8] obtained from the reaction of potassium cyanide and sulfur dioxide in the absence of hydroxylic solvents, and to 3-phenyl-1,2,5-thiadiazole,[9] formed by refluxing S_4N_4 with ethylbenzene.

α-Amino acid amides undergo condensation with 1,2-dicarbonyl compounds to give 2-hydroxypyrazines.[10] We are indebted to Dr. R. G. Jones of these laboratories for calling to our attention the fact that this demonstrated similarity of α-amino acid amides (IV) to aromatic vicinal diamines suggests a route for the direct synthesis of substituted monocyclic hydroxythiadiazoles[11] (V).

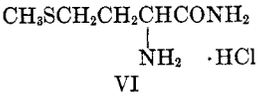


IV V

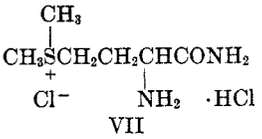
The initial experiments were carried out in chloroform with thionyl chloride and alaninamide hydrochloride. Very low yields of a product were isolated that had the characteristics expected of 3-hydroxy-4-methyl-1,2,5-thiadiazole. Improved results were obtained when the α-amino acid amides were allowed to react with thionylaniline[12] in pyridine. A number of 3-hydroxy-4-substituted 1,2,5-thiadiazoles were thus prepared in yields usually ranging from 20 to 60% (Table I).

The stable aromatic character of the ring system is demonstrated by the marked phenolic properties of the hydroxyl function.[8] The pK_a values determined were generally in the range 6.4–7.3.

A large-scale preparation of methioninamide (VI),[10,13] without purification of the ester intermediate, allowed the isolation of a methylsulfonium chloride by-product (VII) in about 30% yield.



VI



VII

(1) O. Hinsberg, *Ber.*, **22**, 2895 (1889).

(2) (a) A. M. Khaletskiĭ, V. G. Pesin, and T. Chou, *Dokl. Akad. Nauk SSSR*, **114**, 811 (1957); *Chem. Abstr.*, **52**, 4605*i* (1958); (b) V. G. Pesin, A. M. Khaletskiĭ, and T. Chou, *Zh. Obshch. Khim.*, **28**, 2089 (1958); English translation, *J. Gen. Chem. USSR*, **28**, 2126 (1958), Consultants Bureau, Inc., New York, N. Y.

(3) (a) M. Carmack, L. M. Weinstock, and D. Shew, Abstracts of Papers, 136th National Meeting of the American Chemical Society, Atlantic City, N. J., Sept 1959, p 37P; (b) M. Carmack, D. Shew, and L. M. Weinstock, U. S. Patents 2,990,408 and 2,990,409 (June 27, 1961); *Chem. Abstr.*, **56**, 4775 (1962).

(4) I. Sekikawa, *Bull. Chem. Soc. Japan*, **33**, 1229 (1960).

(5) Y. F. Shealy and J. D. Clayton, *J. Org. Chem.*, **28**, 1491 (1963).

(6) D. Shew, *Dissertation Abstr.*, **20**, 1593 (1959).

(7) R. Y. Wen, *ibid.*, **23**, 4121 (1963).

(8) J. M. Ross and W. C. Smith, *J. Am. Chem. Soc.*, **86**, 2861 (1964).

(9) V. Bertini and P. Pino, *Angew. Chem.*, **77**, 262 (1965).

(10) R. G. Jones, *J. Am. Chem. Soc.*, **71**, 78 (1949).

(11) Personal communications with Dr. Carmack, of Indiana University, indicate that he has prepared the 1,2,5-thiadiazole in the same manner.

(12) A. Michaelis, *Ann.*, **274**, 173 (1893); *Ber.*, **24**, 745 (1891).

(13) The α-amino acid esters were prepared according to the procedure of T. Curtius and F. Goebel, *J. Prakt. Chem.*, [2] **37**, 150 (1888). The α-amino acid amides were prepared as methioninamide described in ref 10.