[CONTRIBUTION FROM THE SCIENTIFIC LABORATORY, FORD MOTOR CO.]

Condensations with 1,2-Hydrazinedicarboxamidine. II.[1] 2,2′-Azoimidazoles[2]

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Ring closure of 1,2-hydrazinedicarboxamidine (I) by means of benzoins (II) leads to 2,2′-hydrazoimidazoles (III) which, in contact with air, are oxidized to 2,2′-azoimidazoles (IV). An independent synthesis of IV is the condensation of azodicarboxamidine (V) with benzoins (II). Structure proof of IV has been adduced by catalytic hydrogenation yielding 4,5-disubstituted 2-aminoimidazoles (VI). Reaction of I with anisoin accompanied by air oxidation gives a complex of 4,4′,5,5′-tetra(*p*-methoxyphenyl)-2,2′-azoimidazole with anisil (IVg). A new heterocyclic ring system, imidazo [4,5-*d*]-*v*-triazole (XI), has been obtained by the reaction of a 5-chloro-4-nitroimidazole (IX) with hydrazine.

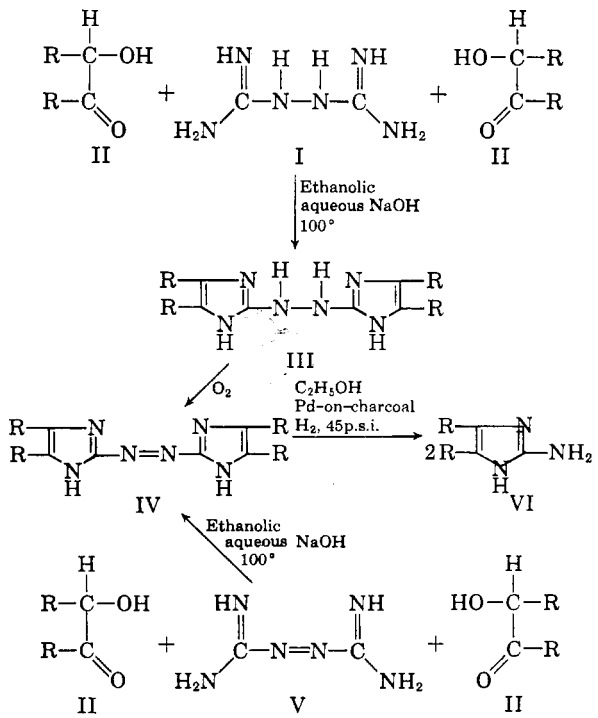
A recent development in amidine chemistry has been the demonstration that bisamidines are capable of a double ring closure, leading in the case of 1,2-hydrazinedicarboxamidine (I) to the new compound class of 2,2′-hydrazopyrimidines (VII).[1] In analogy to this ring closure by means of 1,3-bifunctional compounds, condensation with suitable 1,2-bifunctional components was expected to furnish the five-membered ring analogs of VII, *i.e.*, hydrazoimidazoles (III).

Kunckell's[3] imidazole synthesis being based on the interaction of an amidine with an α-halo ketone requires the liberation of the amidine from its salts. The free amidine must be stable enough to be extracted with chloroform and to be boiled in this solution in order to be caused to react with the α-halo ketone. However, application of this method to I was met with failure as I apparently is not stable enough to be subjected to the conditions of Kunckell's synthesis.

The dinitrate of I did not even react with typical α-halo ketones, *e.g.*, α-bromoacetophenone, upon boiling over extended periods of time. Thus, the question turned up, whether I would perhaps enter the desired reaction course as a reactive species *in situ*. As a matter of fact, a reaction did occur when sodium hydroxide was added to a suspension of I-dinitrate and an α-halo ketone. Such mixtures turned deep red to purple and its components were difficult to separate. Isolation and identification of reaction products could finally be accomplished when aromatic α-hydroxy ketones (benzoins) were substituted for α-halo ketones. The condensations were usually complete after boiling the components for two to six hours on the steam bath in the presence of sodium hydroxide.

The isolated end products are deeply colored substances which, on the basis of their properties and analyses, have been assigned the structure of 2,2′-azoimidazoles (IV). A summary of these new compounds is given along with pertinent reaction conditions in Table I. All compounds IV are insoluble in water and low-boiling organic solvents except IVa and IVf which are soluble in boiling ethanol. While most 2,2′-azoimidazoles are insoluble in aqueous 5% hydrochloric acid solution, the basicity of IVd and IVe is enhanced by the pyridyl substituents to the extent that solubility in the aforementioned agent is achieved. Generally suitable for dissolving the 2,2′-azoimidazoles (IV) are higher boiling organic solvents, *e.g.*, pyridine, *N*,*N*-dimethylformamide, nitrobenzene, glacial acetic acid, dioxane, chlorobenzene, and 1,2-dichlorobenzene.

That the formation of azo compounds of type IV is the result of air oxidation *via* the intermediate 2,2′-hydrazoimidazoles (III) may be demonstrated by the formation of the same compounds IV from II and azodicarboxamidine (V). However, the latter compound, due to the resonance stabilization of its fully conjugated system of double bonds and the decreased nucleophilic character of the terminal



(1) Previous paper in this series: A. Kreutzberger, *J. Am. Chem. Soc.*, **81**, 6017 (1959).

(2) Presented at the 140th National Meeting of the American Chemical Society, Chicago, Ill., September 1961.

(3) F. Kunckell, *Ber.*, **34**, 637 (1901).

TABLE I

SYNTHESIS OF 2,2′-AZOIMIDAZOLES (IV) FROM 1,2-HYDRAZINEDICARBOXAMIDINE (I)

Benzoin II Applied R	Reaction Product IV R	Reaction Time, Hr.	Yield, %	Purification Method	M.P. (corr.)	Color and Crystal Form	Empirical Formula	Carbon, % Calcd.	Carbon, % Found	Hydrogen, % Calcd.	Hydrogen, % Found	Nitrogen, % Calcd.	Nitrogen, % Found
C_6H_5 (IIa)	C_6H_5 (IVa)	6	71.9	Recryst. from pyridine	304–305	Red needles	$C_{30}H_{22}N_6$[a]	77.23	77.02	4.75	4.95	18.02	18.27
4-C_6H_5-C_6H_4 (4-Biphenylyl) (IIb)	4-C_6H_5-C_6H_4 (IVb)	5	88.8	Recryst. from pyridine	323–324	Reddish violet needles	$C_{54}H_{38}N_6$	84.13	83.99	4.97	5.24	10.90	10.77
2-$C_{10}H_7$ (2-Naphthyl) (IIc)	2-$C_{10}H_7$ (IVc)	3	44.2	Recryst. from pyridine	281–282	Violet needles	$C_{46}H_{30}N_6$	82.86	82.62	4.54	4.67	12.60	12.80
2-C_5H_4N (2-Pyridyl) (IId)	2-C_5H_4N (IVd)	3	40.5	Recryst. from chlorobenzene	295–296	Red scales	$C_{28}H_{18}N_{10}$	66.37	66.25	3.86	3.79	29.77	29.97
2-CH_3-6-C_5H_3N (2-Methyl-6-pyridyl) (IIe)	2-CH_3-6-C_5H_3N (IVe)	5	68.0	Recryst. from pyridine	287–288	Red prisms	$C_{30}H_{26}N_{10}$	68.42	68.19	4.98	5.19	26.60	26.48
2-C_4H_3O (2-Furyl) (IIf)	2-C_4H_3O (IVf)	3	83.9	Triturated with water	177–178	Dark blue, amorphous	$C_{22}H_{16}N_6O_4$	61.68	61.52	3.76	3.91	19.62	19.37

[a] Mol. wt. calcd.: 466, found: 457 (ebullioscopic in C_2H_5OH), 452 (ebullioscopic in C_6H_6).

nitrogen atoms, generally furnishes lower yields of IV than does I.

It is interesting to note that the facile oxidation of III contrasts sharply with the stability[1] of 2,2′-hydrazopyrimidines (VII). The latter compounds exhibit no tendency for autoxidation and remain colorless upon storing. This different behavior of the two compound types toward air may be accounted for by hydrogen bonding in VII, as well as by its much stronger resonance interaction of the unshared electrons of the hydrazo nitrogen with the pyrimidine nucleus. A comparison of molecular models shows clearly the differences in configuration of the two compound types III and VII (Fig.

Fig. 1. Dimensions in 2,2′-hydrazoimidazoles (III) and 2,2′-hydrazopyrimidines (VII)

1). Thus, pyrimidine standing in the ascending —N= containing six-membered ring series between the hexagonal[4] pyridine nucleus and the D_{3h} symmetry[5] of the *s*-triazine ring may be considered a nearly regular hexagon also. On the other hand, combination of the pertinent data of the pyridine and pyrrole rings[4] leads to an N—C—N bond angle of 108° in the imidazole ring. This bond angle in III results then in a longer distance between the "pyridine nitrogen" of the ring and the H atoms of the hydrazo group, offering thus a lesser or no chance for hydrogen bonding. In contrast to this, the larger N—C—N bond angle of 120° in VII entails a shorter distance between the ring nitrogen and the hydrazo hydrogen, the latter thus being protected against air oxidation by hydrogen bonding.

Support for this view comes from infrared spectra of VII. The hydrazo group functioning as a secondary amine is expected to give rise to an NH stretching absorption[6,7] between 3500–3300 cm.$^{-1}$ In

(4) V. Schomaker and L. Pauling, *J. Am. Chem. Soc.*, **61**, 1769 (1939).

(5) J. Goubeau, E. L. Jahn, A. Kreutzberger, and C. Grundmann, *J. Phys. Chem.*, **58**, 1078 (1954).

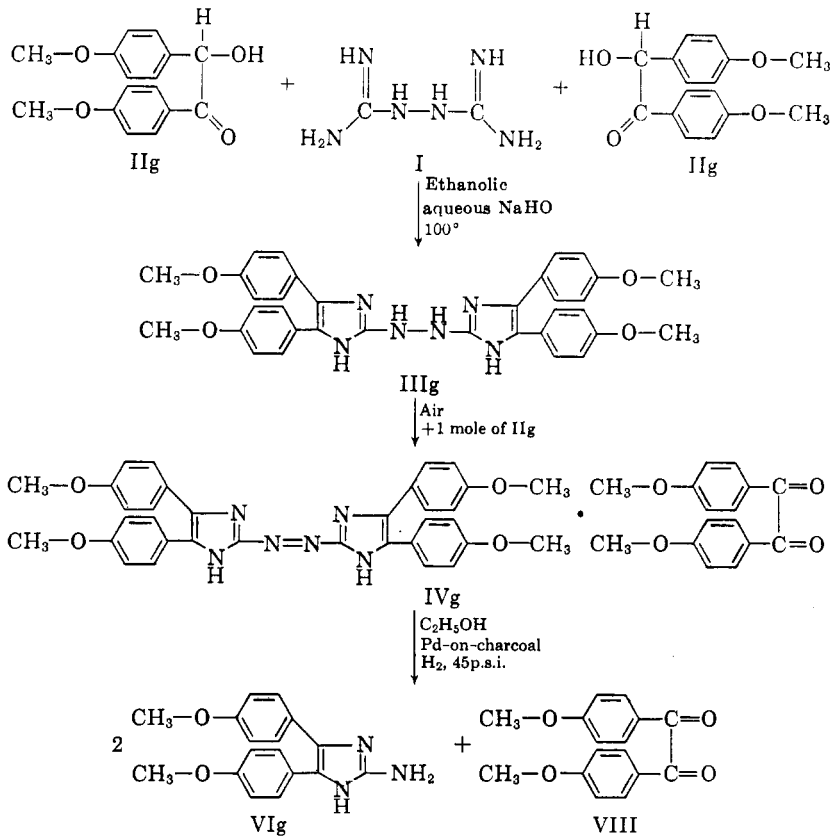
(6) N. Fuson, M. Josien, R. L. Powell, and E. Utterback, *J. Chem. Phys.*, **20**, 145 (1952).

(7) R. A. Russell and H. W. Thompson, *J. Chem. Soc.*, 483 (1955).

VII, however, this frequency has been reported[8] to occur at 3270–3230 cm.$^{-1}$ This move to lower frequencies has to be interpreted as a consequence of hydrogen bonding.[6,9]

The 2,2′-azoimidazole structure IV is also supported by the infrared spectra of representative compounds of this class. Inasmuch as the imidazole ring may best be described as a resonance hybrid, one might expect the infrared spectra of imidazoles to reflect all vibrational elements typical of known resonating systems. In analogy to the fundamental studies in the benzene series,[10] on pyrroles,[11] thiophenes,[12] and *s*-triazine,[5] the characteristic skeletal stretching mode of the substituted 2,2′-azoimidazoles (IV) can be found in the 1500–1400-cm.$^{-1}$ region. A group of three to four bands appears here which in the case of 4,4′,5,5′-tetraphenyl-2,2′-azoimidazole (IVa) are located at 1500, 1470, and 1440 cm.$^{-1}$ The N—H stretching mode due to the imidazole ring reveals itself in the bands at, respectively, 3420, 3430, 3410, 3430, and 3420 cm.$^{-1}$ in IVa, IVb, IVc, IVd, and IVe. Finally, the N—H deformation mode of the secondary amino function of the imidazole ring may be correlated to bands at, respectively, 1590, 1620, 1630, 1580, and 1570 cm.$^{-1}$ corresponding to IV-compounds in the same order as before. Thus all salient bands present in the infrared spectra of 2,2′-azoimidazoles have been shown to be in agreement with structure IV.

Conclusive proof of structure of compounds IV could be adduced by hydrogenation. The imidazole ring known to generally resist reduction, IV can be hydrogenated over a palladium-on-charcoal catalyst at 45 p.s.i. to yield the corresponding 2-aminoimidazoles (VI). Thus 4,4′,5,5′-tetraphenyl-2,2′-azoimidazole (IVa) furnishes in this reduction process 2-amino-4,5-diphenylimidazole (VI. R = C_6H_5). The latter compound[13] along with salts of its analog, 2-amino-4,5-dimethylimidazole, (VI. R = CH_3)[14]



were the only 2-aminoimidazoles carrying two like nonfunctional substituents in 4- and 5- position known at the start of the present investigations. The previous methods for preparing these compounds have in common the coupling of a diazonium salt with the particular 4,5-disubstituted imidazole followed by reduction of the azo bond. This reduc-

(8) A. Kreutzberger, *Z. physik. Chem. (Frankfurt)*, 24, 368 (1960).

(9) G. B. B. M. Sutherland, *Discuss. Faraday Soc.*, 9, 274 (1950).

(10) W. R. Angus, C. R. Bailey, J. B. Hale, C. K. Ingold, A. H. Leckie, C. G. Raisin, J. W. Thompson, and C. L. Wilson, *J. Chem. Soc.*, 966, 971 (1936); K. S. Pitzer and D. W. Scott, *J. Am. Chem. Soc.*, 65, 803 (1943).

(11) A. Kreutzberger and P. A. Kalter, *J. Phys. Chem.*, 65, 624 (1961).

(12) A. R. Katritzky and A. J. Boulton, *J. Chem. Soc.*, 3500 (1959).

(13) A. De Cat and A. Van Dormael, *Bull. soc. chim. Belges*, 59, 573 (1950).

(14) R. Burtles and F. L. Pyman, *J. Chem. Soc.*, 127, 2012 (1925).

tion step, however, results in a mixture of two different amino compounds the separation of which entails rather low yields. In contrast to this method, the catalytic reduction of IV leads to two molecules of one and the same compound (VI) obtained in high yield. Based on benzoin (IIa) and acetoin (II. R = CH_3), the synthesis of the corresponding 2-aminoimidazoles by the new reduction process is simplified by at least one step compared with the previous methods. This improvement in the synthesis of VI is the more significant as an attempt to prepare VI by condensation of guanidine with benzoins (II) met with failure. In agreement with this finding is the previously recorded failure to prepare VI from guanidine and α-halo ketones.[15] Pertinent data referring to the reduction of IV are summarized in Table II.

A modified picture is revealed in the reaction of I with anisoin (IIg), in which case a violet compound of the unexpected composition, $C_{50}H_{44}N_6O_8$ (IVg) is obtained. In deciding among several structures, including the as-yet-unknown azooxazoles, reduction furnished the conclusive clue. The catalytic hydrogenation of IVg yielded a mixture of two compounds which could be separated by boiling ethyl acetate. The insoluble compound was identified as 2-amino-4,5-di(*p*-methoxyphenyl)imidazole (VIg), while the soluble component proved to be anisil (VIII) by conversion into its monoxime.[15] This result leads logically to the conclusion that IVg is a complex of the expected 4,4′,5,5′-tetra(*p*-methoxyphenyl)-2,2′-azoimidazole with one mole of anisil. The formation of this complex IVg is explicable in terms of a double condensation of I and IIg accompanied by air oxidation of both the intermediate 2,2′-hydrazoimidazole (IIIg. R = *p*-CH_3—O—C_6H_4) and anisoin (IIg). That air oxidation of IIg in alkaline medium is possible has previously been demonstrated.[16] It is noteworthy that in the present hydrogenation procedure at room temperature (22°) in the presence of palladium no reduction of VIII to IIg takes place, whereas such reduction has been reported with platinum at the slightly increased temperature of 60°.[17]

Occasionally, other 2,2′-azoimidazoles have also been found accompanied by minor amounts of the corresponding benzils. Particularly attempts to work with higher concentrations in order to improve the yields of IV resulted in the formation of larger amounts of benzils. Air oxidation of IId is known to be even a common preparatory method for making 2-pyridil.[18] However, in all cases, with the exception of complex IVg, the benzils could easily be separated from IV due to their greater

TABLE II

REDUCTION OF 2,2′-AZOIMIDAZOLES (IV) LEADING TO 2-AMINOIMIDAZOLES (VI)

2,2′-Azoimidazole IV Used R	2-Aminoimidazole VI Obtained R	Yield, %	Solvent Used for Recrystallization	M.P. (corr.)	Empirical Formula	Carbon, %		Hydrogen, %		Nitrogen, %	
						Calcd.	Found	Calcd.	Found	Calcd.	Found
C_6H_5 (IVa)	C_6H_5 (VIa)	89.5	EtOH	233–234	$C_{15}H_{12}N_2$	76.57	76.69	5.57	5.69	17.86	17.67
2-$C_{10}H_7$ (IVc)	2-$C_{10}H_7$ (VIc)	73.0	$(CH_3)_2CO$	129–130	$C_{23}H_{17}N_3$	82.36	82.13	5.11	5.33	12.53	12.41
(2-Naphthyl) (IVc)											
2-C_5H_4N	2-C_5H_4N (VId)	86.9	$(CH_3)_2CO$	230–231	$C_{15}H_{11}N_5$	65.81	65.81	4.67	4.74	29.52	29.40
(2-Pyridyl) (IVd)											
p-CH_3O-C_6H_4[a] (IVg)	*p*-CH_3O-C_6H_4	36.2[b]	C_2H_5OH	225–226	$C_{17}H_{17}N_3O_2$	69.13	68.91	5.80	5.99	14.23	14.01

[a] As complex with anisil. [b] Based on complex IVg.

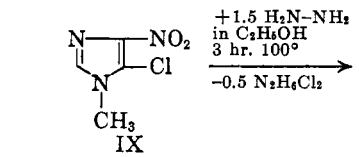
(15) R. Stierlin, *Ber.*, **22**, 379 (1889).
(16) H. Biltz and A. Wienands, *Ann.*, **308**, 8 (1899).
(17) J. S. Buck and S. S. Jenkins, *J. Am. Chem. Soc.*, **51**, 2165 (1929).
(18) W. Mathes, W. Sauermilch, and T. Klein, *Chem. Ber.*, **84**, 452 (1951).

solubility in the solvents used for recrystallizing IV.

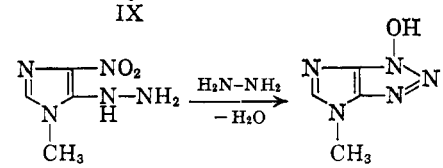
On the search for a method which would link the hydrazo group not only with the 2-, but also with the 4- or 5- position of the imidazole ring and thus produce isomeric hydrazoimidazoles, hydrazinolysis of methylmercaptoimidazoles was deemed to be applicable, since methylmercapto groups of related compounds are known to be readily replaceable by the hydrazino group, *e.g.*, in *S*-alkylthioureas[19] and methylmercaptopurines.[20] This method failed, however, in the imidazole series, 1-methyl-2-methylmercaptoimidazole not even reacting with anhydrous hydrazine at reflux temperature. As benzamidine is capable of existence in the free state in solution,[3] an attempt was made to cause it to react in situ with an appropriate bifunctional hydrazine derivative, *e.g.*, *N,N'*-bis(α-chlorophenylacetyl)-hydrazine,[21] but the desired reaction did not take place. Instead, benzamidine was converted to benzamide.

Of other functional imidazole derivatives which seemed likely to react with hydrazine, the halogen compounds held a considerable interest. Simple chloroimidazoles are accessible through Wallach's unique one-step ring closure halogenation procedure[22] involving the interaction of *N,N'*-dialkyloxamides with phosphorus pentachloride. Halogen atoms attached directly to the imidazole ring exhibit a typical aromatic behavior in that the halogen-ring bond is an extremely strong one. The inertness of halogen is modified by introduction of a nitro group in adjacent position rendering the halogen atom displaceable by nucleophilic agents.[23,24]

As a matter of fact, 5-chloro-4-nitro-1-methylimidazole (IX)[23] reacts readily with hydrazine forming the expected intermediate 5-hydrazino-4-nitro-1-methylimidazole (X). This reacts further to form a deeply purple colored compound. If this were the expected azoimidazole, it should show a molar ratio of C:N = 8:8. The fact that the analysis of the product shows a ratio of C:N = 4:5 indicates that the reaction involving X has taken an intramolecular instead of the expected intermolecular course. In analogy to carbocyclic chemistry, where numerous examples of 1-hydroxybenzo-*v*-triazole formation from *o*-nitrophenylhydrazines are known,[25] the nitrohydrazinoimidazole X is converted into 1-hydroxy-4-methylimidazo[4,5-*d*]-*v*-triazole (XI) due to the alkaline action of hydrazine. XI is even formed, if smaller than the stoichiometric amounts of hydrazine are used.

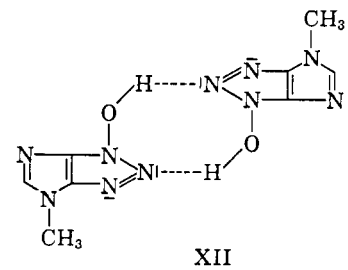


IX



X XI

Surprising is the failure of XI to produce the characteristic OH stretching band in the infrared spectrum. This behavior is reminiscent of *o*-hydroxycarbonylbenzenes and *o*-hydroxyazo compounds which, due to hydrogen bonding, do not exhibit the OH band in the infrared spectrum either.[26] Based on this analogy and in agreement with the properties of the compound, particularly its melting point of higher than 400°, it appears justified to assume that 1-hydroxy-4-methylimidazo[4,5-*d*]-*v*-triazole exists in the form of hydrogen bonding structure XII.



XII

Structure XII is supported by the capability of the compound to form metal complexes which are soluble in organic solvents but not in water.

EXPERIMENTAL[27]

1,2-Hydrazinedicarboxamidine dinitrate monohydrate (I) was prepared as described recently.[1]

Benzoins (II). The benzoins IIa, IId, IIe, IIf, and IIg used were pure grade as purchased from Matheson Coleman & Bell Division, East Rutherford, N. J.; Aldrich Chemical Co. Inc., Milwaukee, Wis., and Quaker Oats Company, Chicago, Ill., respectively. Benzoins IIb[28] and IIc[29] were prepared from the corresponding aldehydes according to known procedures.

(19) H. Schotte, German Patent **501,389** (to Schering-Kahlbaum Akt.-Ges., Berlin) (1930).

(20) J. A. Montgomery and L. B. Holum, *J. Am. Chem. Soc.*, **79**, 2185 (1957).

(21) A. Kreutzberger, *J. Org. Chem.*, **22**, 679 (1957).

(22) O. Wallach, *Ber.*, **7**, 326 (1874).

(23) J. Sarasin and E. Wegmann, *Helv. Chim. Acta*, **7**, 713 (1924).

(24) L. L. Bennett and H. T. Baker, *J. Am. Chem. Soc.*, **79**, 2188 (1957).

(25) C. Willgerodt and H. Klein, *J. prakt. Chem.*, **60**, 97 (1899); T. Curtius *et al.*, *J. prakt. Chem.*, **76**, 233, 281, 301, 369 (1907); A. Angeletti, *Gazz. chim. ital.*, **53**, 672 (1923); A. K. Macbeth and J. R. Price, *J. Chem. Soc.*, 1637 (1934); 982 (1937).

(26) S. B. Hendricks, O. R. Wulf, G. E. Hilbert, and U. Liddel, *J. Am. Chem. Soc.*, **58**, 1991 (1936).

(27) All melting points were determined in an aluminum melting point block and are corrected. Microanalyses are by Galbraith Laboratories, Knoxville, Tenn., and Spang Microanalytical Laboratory, Ann Arbor, Mich.

(28) M. Gomberg and F. J. Van Natta, *J. Am. Chem. Soc.*, **51**, 2238 (1929).

(29) J. D. Fulton and R. Robinson, *J. Chem. Soc.*, 200 (1939).

4,4′,5,5′-Tetra(4-biphenylyl)-2,2′-azoimidazole (IVb). The preparation of this compound may be given as an example typical of condensations of 1,2-hydrazinedicarboxamidine dinitrate monohydrate (I) with benzoins II.

The white suspension consisting of 2.6 g. (0.01 mole) of I and 7.3 g. (0.02 mole) of IIb[28] in 20 ml. of ethanol changed gradually in color toward violet upon the addition of 8 g. of an aqueous 10 wt. % solution of sodium hydroxide (0.02 mole). Within 30 min. of boiling on the steam bath, a transparent violet solution had formed which, after boiling for another 15 min. started to deposit dark red crystals. The quantity of these increased gradually upon extended boiling. After a total boiling time of 5 hr., the reaction appeared completed, when boiling was discontinued and the contents allowed to cool. Vacuum filtration yielded a crop of 6.8 g. (88.8%) of dark red crystalline IVb. This material was insoluble in water, 5% aqueous hydrochloric acid solution, ethanol, ethyl acetate, and acetonitrile, soluble in dioxane, chlorobenzene, 1,2-dichlorobenzene, nitrobenzene, pyridine, tetrahydrofuran, *N,N*-dimethylformamide, and glacial acetic acid and could be recrystallized best from pyridine, which furnished it in the form of reddish violet needles melting at 323–324°.

2,2′-Azoimidazoles (IV) *from azodicarboxamidine dinitrate* (V). In a typical experiment, 80 g. of an aqueous 10 wt. % sodium hydroxide solution (0.2 mole sodium hydroxide) was added to a suspension containing 24 g. of V[1] (0.1 mole) and 42.4 g. (0.2 mole) of IIa in 200 ml. of ethanol. The originally white color of the mixture turned orange within a few minutes even at room temperature. By boiling on the steam bath, a transparent deep red solution was formed within 5 min. Within the next 10 min. of boiling, a gradual deposition of red crystals set in. After a total boiling time of 3 hr., when the amount of red crystals did not seem to change any more, heating was discontinued and the mixture allowed to cool to room temperature. The red crystals being vacuum-filtered amounted to 28.2 g. of 4,4′,5,5′-tetraphenyl-2,2′-azoimidazole (IIa) (yield 60.5%). The substance was insoluble in ether, petroleum ether, ethyl acetate, benzene, toluene, acetonitrile, chlorobenzene, 5% aqueous hydrochloric acid solution, and water and soluble in ethanol, pyridine, *N,N*-dimethylformamide, dioxane, and glacial acetic acid. Recrystallization from pyridine furnished it in the form of fine red needles, m.p. 304–305°, mixed m.p. with a sample obtained from I and IIa undepressed.

Hydrogenation of 2,2′-azoimidazoles (IV). The following example describes a typical hydrogenation experiment: A suspension consisting of 2.3 g. (0.005 mole) of IVa and a catalytic amount of a 10% palladium-on-charcoal catalyst in 70 ml. of ethanol was shaken at room temperature with hydrogen under an initial pressure of 45 p.s.i. The theoretical amount of hydrogen (0.01 mole) was absorbed within 15 min., at which time the red color of the mixture had disappeared. The entire reaction contents were heated on the steam bath to boiling and filtered hot. Evaporation *in vacuo* to dryness of the clear colorless ethanolic filtrate rendered 2.1 g. (89.5% yield) of beige colored 2-amino-4,5-diphenylimidazole (VIa) which, by recrystallization from ethanol, was obtained as slightly yellowish prisms melting at 233–234°. The identity of this hydrogenation product with structure VIa was established by mixed melting point with an authentic sample.[13]

Anal. Calcd. for $C_{15}H_{13}N_3$: C, 76.57; H, 5.57; N, 17.86. Found: C, 76.69; H, 5.42; N, 18.07.

Reaction of 1,2-hydrazinedicarboxamidine dinitrate monohydrate (I) *with anisoin* (IIg). When 16 g. of a 10 wt. % aqueous solution of sodium hydroxide (0.04 mole of sodium hydroxide) was added to a suspension containing 5.2 g. of I (0.02 mole) and 15.1 g. of IIg (0.06 mole) in 100 ml. of ethanol, the originally yellowish color of the suspension changed immediately to red. A reddish purple solution was formed upon boiling on the steam bath, and soon purple solids began to deposit. After a total heating time of 3 hr., heating was discontinued and the reaction contents allowed to cool. Vacuum filtration furnished 7.7 g. of purple needles which were insoluble in water, 5% aqueous hydrochloric acid, and sodium hydroxide solutions, ether, and carbon tetrachloride, but soluble in most of the other common organic solvents. It could be recrystallized best from dioxane-water, by which procedure violet needles having a golden tinge were obtained, m.p. 134–135°. Based on the analysis and the result of the hydrogenation, this compound has been identified as a complex of 4,4′,5,5′-tetra(*p*-methoxyphenyl)-2,2′-azoimidazole and anisil (IVg). The product, 7.7 g., amounts to a yield of 45.0%.

Anal. Calcd. for $C_{34}H_{30}N_6O_4 \cdot C_{16}H_{14}O_4$: C, 70.08; H, 5.17; N, 9.81. Found: C, 69.81; H, 5.24; N, 9.88.

Hydrogenation of the 4,4′,5,5′-tetra(p-methoxyphenyl)-2,2′-azoimidazole-anisil complex (IVg). The theoretical amount of hydrogen (0.008 mole) was absorbed within 1.5 hr., when a mixture containing 3.4 g. (0.004 mole) of complex IVg, a catalytic amount of 10% palladium-on-charcoal and 25 ml. of absolute ethanol was shaken at room temperature (22°) with hydrogen at an initial pressure of 45 p.s.i. When no hydrogen was absorbed any more, the mixture was heated on the steam bath to boiling and filtered hot. On cooling, the clear ethanolic filtrate deposited yellow needles which were collected on a Büchner funnel and amounted to 0.8 g. By recrystallization from ethanol, the substance was obtained as golden yellow needles melting at 132–133°. It was identified as anisil (VIII) by mixed melting point with an authentic specimen, by analysis and by conversion into its monoxime.[15]

Anal. Calcd. for $C_{16}H_{14}O_4$: C, 71.10; H, 5.22. Found: C, 71.01; H, 5.13.

Evaporation to dryness *in vacuo* of the ethanolic filtrate yielded a solid residue whose wide melting point range indicated a mixture of compounds. The mixture was boiled with ethyl acetate and filtered hot. Upon cooling, the clear yellow filtrate furnished another crop of anisil (VIII) bringing its total amount up to 1.0 g. which is a quantitative yield based on IVg.

The white ethyl acetate-insoluble solid proved by analysis to be 2-amino-4,5-bis(*p*-methoxyphenyl)imidazole (VIg), weight 0.8 g. (yield 36.2% based on IVg). Recrystallization from ethanol furnished it in the form of colorless prisms melting at 224–225°.

Anal. Calcd. for $C_{17}H_{17}N_3O_2$: C, 69.13; H, 5.80; N, 14.23. Found: C, 68.91; H, 5.99; N, 14.01.

1-Hydroxy-4-methylimidazo[4,5-d]-v-triazole (XI). When a solution of 1.9 g. (0.06 mole) of anhydrous hydrazine in 10 ml. of absolute ethanol was added dropwise to an agitated suspension of 4.8 g. (0.03 mole) of 5-chloro-4-nitro-1-methylimidazole (IX),[22] the color of the reaction mixture turned gradually greenish and then purple. After boiling for 3.5 hr. on the steam bath, the reaction contents were allowed to cool and then vacuum-filtered. A solid of intense purple color was obtained which was freed from any accompanying hydrazine dihydrochloride and unreacted starting material IX by successive triturations with water and ethanol. The analysis of the purple solid thus obtained agreed with structure XI, weight 1.7 g. (yield 41.2%), no m.p. up to 400°.

Anal. Calcd. for $C_4H_5N_5O$: C, 34.53; H, 3.62; N, 50.35. Found: C, 34.28; H, 3.88; N, 50.06.

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