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Isolation of Primary Decomposition Products of Azides. I. 1,4-Diphenyl-5-azido-1,2,3-triazole[1]

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RECEIVED DECEMBER 30, 1963

1,4-Diphenyl-5-azido-1,2,3-triazole and substituted derivatives lose nitrogen at the exceptionally low temperature of 50° to form deep red, monomeric compounds that are easily reduced to the corresponding 5-aminotriazole. Experiments with isotopically labeled compounds show that nitrogen is lost only from the azido group and not from the ring, and that no rearrangement takes place. This and chemical evidence that no insertion reaction occurred are consistent with an unrearranged structure having a monocoordinate exocyclic nitrogen (IX), in equilibrium with a noncyclic isomer (X). The reactions of this compound lead to practical synthetic routes to acetals of α-keto amidines and diarylmaleic acid derivatives.

The cyclization of azides through reactive, electron-deficient intermediates (variously called azenes, nitrenes, imidogens, imenes, etc.[2]) has been reported by many workers.[3] Nearly all of these reactions produce five-membered rings when a choice is possible, and in the few cases where the structures force the formation of a six-membered ring instead, yields are markedly lower.[3e,4] Where two sites for cyclization are offered, each suitable for formation of a five-membered ring, some selectivity is usually shown, but the factors determining which site is preferred have not been investigated, and are not apparent from the scattered cases recorded.

With the original goal of finding out more about the factors determining the preferred site of cyclization of decomposing azides, we undertook the study of 1,4-diaryl-5-azidotriazoles (II). The corresponding amines I are easily prepared with a variety of substituents on either phenyl group by means of the base-catalyzed condensation of phenyl azides with phenylacetonitriles.[5] As reported, they are diazotizable, and thus easily convertible to azides. In such compounds, the azido group (or the fragment from its decomposition) would be presented with four sites for five-membered ring formation, all sterically nearly equivalent, but electronically widely variable by substitution and by virtue of the difference in the atom of attachment (N or C) of the two phenyl groups.

The foregoing plan was set aside when it was found that the azides decomposed instead not only without

cyclization, but without any of the other previously reported consequences[6] of azide decomposition, such as dimerization,[6a] hydrogen abstraction,[6b] rearrangement,[6c] or bimolecular insertion.[3d] This paper is the first of a group concerned with the nature and properties of the extraordinary fragmentation products of the title compound and other azidoazoles.
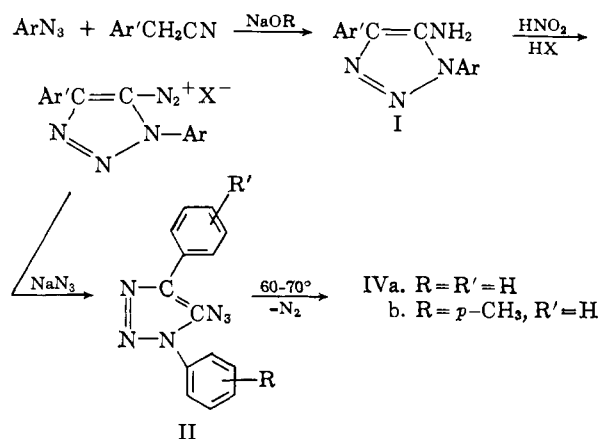
Results

1,4-Diphenyl-5-azidotriazole (IIa) was synthesized as shown, and obtained crude as nearly colorless needles. Initial attempts at purification by recrystallization led to products with erratic melting ranges and in many cases to the development of a deep red color. The azide was eventually obtained pure by precipitation with water from cold solutions in acetone or dimethylformamide, or by crystallization from cold ether. Its identity as an azide was established by its energetic decomposition on sudden heating, foaming with sulfuric acid, and strong triple-bond absorption in the infrared at 2300 cm.⁻¹. The isomeric diazotetrazole structure III was ruled out by the complete lack of color of the purified compound, and by its complete insensitivity to strong hydrochloric acid, from which it originally precipitates in preparation.

III
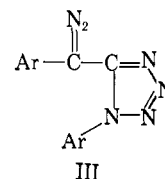
(1) Supported by Subcontract No. 26 of Prime Contract NOrd-1664 with Allegany Ballistics Laboratories. In part from the doctoral dissertation of L. O. K. Presented at the 144th National Meeting of the American Chemical Society, Los Angeles, Calif., April, 1963.

(2) In view of the wide variance in preference for these names, of which only imidogen has official standing of any sort, we are avoiding the use of any of them in this paper. In anticipation of the eventual agreement on one name, we do not wish to contribute to the existing confusion. The name "azene" has been used in previous papers from this laboratory; however, objections have been raised against all of the names quoted. The name "azylene," analogous to "methylene," which was suggested at a recent conference, appears to be free of objections, but does not seem to have been used in print yet.

(3) E.g.: (a) P. A. S. Smith and B. B. Brown, J. Am. Chem. Soc., 73, 2435 (1951); (b) P. A. S. Smith and J. H. Boyer, ibid., 73, 2626 (1951); (c) R. A. Abramovitch, D. A. H. Adams, and A. D. Notation, Can. J. Chem., 38, 2152 (1960); (d) K. H. Saunders, J. Chem. Soc., 3275 (1955); (e) G. Smolinsky, J. Am. Chem. Soc., 82, 4717 (1960); 83, 4483 (1961); (f) D. H. R. Barton and L. Morgan, Proc. Chem. Soc., 206 (1961); (g) R. A. Carboni and J. E. Castle, J. Am. Chem. Soc., 84, 2453 (1962); (h) C. Temple, Jr., R. L. McKee, and J. A. Montgomery, J. Org. Chem., 27, 1671 (1962).

(4) P. A. S. Smith, J. M. Clegg, and J. H. Hall, ibid., 23, 524 (1958); P. A. S. Smith, B. B. Brown, R. K. Putney, and R. F. Reinisch, J. Am. Chem. Soc., 75, 6335 (1953). G. Smolinsky, J. Org. Chem., 27, 3557 (1962), has reported the formation of a three-membered ring by the decomposition of α-azidostyrene, in which the only other reasonable possibility for cyclization would have led to a four-membered ring.

(5) (a) O. Dimroth and G. Werner, Ber., 35, 4058 (1902); (b) E. Lieber, C. N. R. Rao, and T. V. Rajkeemar, J. Org. Chem., 24, 134 (1959).

(6) (a) J. H. Boyer and F. C. Canter, Chem. Rev., 54, 1 (1954); (b) P. A. S. Smith and J. H. Hall, J. Am. Chem. Soc., 84, 480 (1962); (c) P. A. S. Smith in "Molecular Rearrangements," P. deMayo, Ed., John Wiley and Sons, Inc., New York, N. Y., 1963, Chapter 8; (d) W. Lwowski, T. J. Maricich, and T. W. Mattingly, Jr., J. Am. Chem. Soc., 85, 1200 (1963).

The azide melted at 70°, forming a blood-red melt with foaming; in solution in inert solvents, however, it became red and evolved gas at temperatures as low as 50°. Exactly 1 mole of pure nitrogen was evolved, and a dark red crystalline product, IV, easily soluble in petroleum ether, benzene, isopropyl alcohol, or acetone, was formed in high yield. The infrared spectrum in Nujol mull or dilute solution showed only aromatic absorptions and probable C=N and/or N=N stretching bands, none higher than 1600 cm.$^{-1}$; N—H and triple bond absorptions could not be detected. In saturated solution in chloroform, or in KBr disk, an extremely weak band at 2200 cm.$^{-1}$ appeared. An azo compound structure was ruled out by the molecular weight (cryoscopic in benzene), which was close to that calculated for the monomeric form, 28 units less than that of the parent azide. Electron paramagnetic resonance did not reveal a triplet state.[7] The red color was due to end absorption from a broad, intense absorption band in the ultraviolet (λ_{max} 343 mμ).

The nuclear magnetic resonance spectrum[8] of compound IV in carbon tetrachloride shows three apparent quadruplets, at 1.75, 2.1, and 2.4 τ, with area ratios 1 : 1 : 3. All of the hydrogens appear downfield of the parent azide, which shows a broad multiplet centered at 2.5 τ, and two of the hydrogens appear in the region usually observed for hydrogen ortho to strongly electron-withdrawing groups, such as nitro and chlorosulfonyl. The two downfield hydrogens are not para hydrogens, ·for the same relative strength signal is observed for the 1-p-tolyl analog IVb, which also shows a broad multiplet at 2.4 τ and a singlet due to methyl at 7.55 τ, area ratios 2 : 7 : 3.

Conceivable structures for the red decomposition product of the azide would be a triazolobenzimidazole (V), a triazoloindole (VI), a phenyliminotriazole (VII), a triazoloazirine (VIII), an electron-deficient system with monocoordinate exocyclic nitrogen (IX), and an α-(phenylazoimino)nitrile (X). Of these, V and VI are inconsistent with the lack of N–H absorption in the infrared, and were conclusively ruled out by the results of drastic hydrolysis, which gave benzoic acid
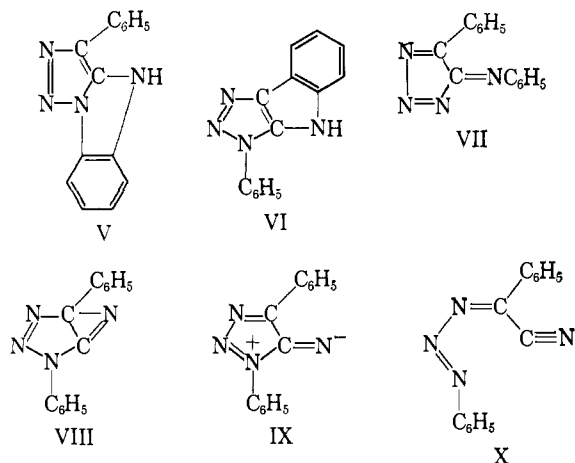

and aniline. Of the remaining possibilities, VIII is unreasonable because of the large strain that would be involved, and it does not account for the color. Structure IX (for which other electronic arrangements can also be written) seemed at first also improbable. The eminently reasonable structures VII and X, both of which could account for the deep color of the substance, remain. Structure VII was initially adopted as a guiding hypothesis for further experimentation but, as will be shown in the discussion to follow, instead we have been driven to accept a dynamic equilibrium between structures IX and X.

It was discovered during routine purification of compound IV that it effervesced when dissolved in methanol at room temperature, with complete loss of color in a few moments, even though it could be heated with impunity in benzene and other nonhydroxylic solvents. Exactly 1 mole of pure nitrogen was evolved, and a colorless, crystalline base was formed in high yield. Analysis indicated the loss of 2 atoms of nitrogen and the addition of 2 molecules of methanol. The infrared spectrum showed neither carbonyl nor O–H stretching vibrations, but did show absorption typical of amidines. A ketal–amidine structure, XI, fits these observations. Experiments with other alcohols showed that the reaction was general, but was spontaneous only with methanol. Ethanol required heating to react, and higher alcohols would react only if a trace of sodium alkoxide was present. The essential correctness of the assigned structures was supported by the example of the benzyl alcohol analog. The benzyl groups were removed by hydrogenolysis, and mandelanilide was obtained, partial hydrolysis evidently having occurred incidentally to the work-up.
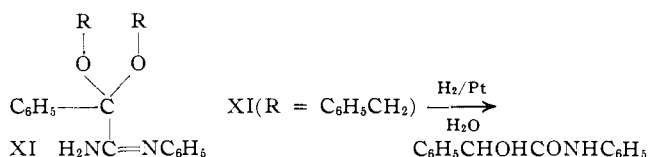
Compound IV reacted with aniline in boiling benzene with loss of nitrogen and conversion to phenylglyoxylonitrile anil in 30 to 34% yield. The source of the anil moiety in this product was revealed by a similar experiment using p-bromoaniline; the product was then phenylglyoxylonitrile p-bromoanil. When aniline hydrochloride was also present, the reaction went further to produce N,N'-diarylbenzamidines and hydrogen cyanide, the aryl groups being derived from the aniline used in each case. The same products were obtained by treatment of the isolated phenylglyoxylonitrile anils with an aniline and its hydrochloride,[9] and are thus not the result of a different mode of reaction of compound IV.
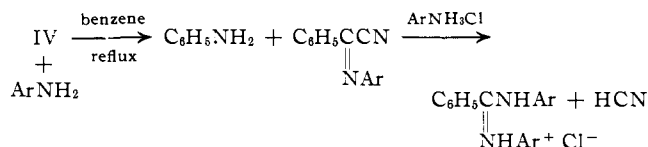

Compound IV or its 1-p-tolyl analog IVb could be converted to the amine I corresponding to the original azide by four methods. Chromatography on alumina with ethereal ethanol as eluent gave the amine I in

(9) Cf. F. Kröhnke and H. H. Steuernagel, Ber., 96, 486 (1963).

35% yield; presumably the ethanol was the source of hydrogen. Catalytic hydrogenation gave I as the only isolable product; since the yield was 45% after two recrystallizations, the amount actually formed was probably much higher. Butyl mercaptan, alone or in the presence of base, reduced IVa spontaneously and rapidly at room temperature to I. Conversion to the amine by sodium borohydride occurred with the 1-*p*-tolyl analog IVb in 65% yield. These reactions, some of which take place rapidly under very mild conditions, are difficult to reconcile with any structure but IX.

Compound IV was converted by aluminum chloride and aromatic hydrocarbons into biaryls, such as biphenyl (from benzene, 45% yield), and *o*- and *p*-methylbiphenyl (from toluene, 30% yield), accompanied by hydrogen cyanide and benzonitrile. These reactions resemble those of benzenediazonium chloride under similar conditions.[10] This substance could in principle be derived from either structure IX or X, although it is not necessary that it be formed at all, for a common reactive intermediate, such as phenyl cation, could account for the similarities.

$$IV + ArH \xrightarrow{AlCl_3} C_6H_5\text{-}Ar \; (+ \; C_6H_5CN, \; HCN)$$
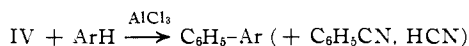
Acid hydrolysis of IV gave benzoic acid and aniline when conducted forcefully, but with a limited amount of hydrochloric acid in the cold, benzoyl cyanide was produced; the mother liquors from its isolation evidently contained benzenediazonium chloride, for it formed a vermilion azo dye when coupled with alkaline β-naphthol, and decomposed on standing. These products are consistent with both structures IX and X, although perhaps more simply derived from X, through initial hydrolysis to phenyltriazene.

$$IV \xrightarrow[HCl]{H_2O} C_6H_5COCN + [C_6H_5N{=}NNH_2] \xrightarrow{HCl} C_6H_5N_2{}^+ + NH_4{}^+$$
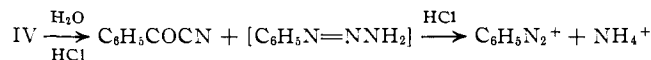
It is evident from the reactions already described that compound IV has a general susceptibility to attack by nucleophiles. Of the many possible examples, only one more will be cited in this paper, that of phenylacetonitrile, which provided additional evidence that the N^1-to-C bond is present in IV (or very easily formed from it). Reaction with IVa occurred readily in the presence of sodium, and produced two isomeric products, XII and XIII, corresponding to 1:1 addition with loss of two nitrogen atoms. Isomer XII (colorless) was converted into XIII (yellow) by boiling with strong base, and the conversion could be reversed by heating with acid. The formation of XII or XIII depended in a not clearly defined way on the experimental conditions. The infrared spectra of both showed absorption attributable to an amidine structure. Whereas XIII was isomerized to XII by concentrated hydrochloric acid at steam bath temperatures, boiling acid brought about hydrolysis of XIII to diphenylmaleimide. These observations imply the diphenylmaleimidine structural assignments given.

In order to determine which nitrogen atoms were eliminated in the reactions of the azide II and its primary decomposition product IV, and to determine whether migration of the N-attached phenyl might have occurred at any stage, samples of 1,4-diphenyl-5-

(10) R. Möhlau and R. Berger, *Ber.*, **26**, 1994 (1893).

$$IV + C_6H_5CH(Na)CN \longrightarrow$$
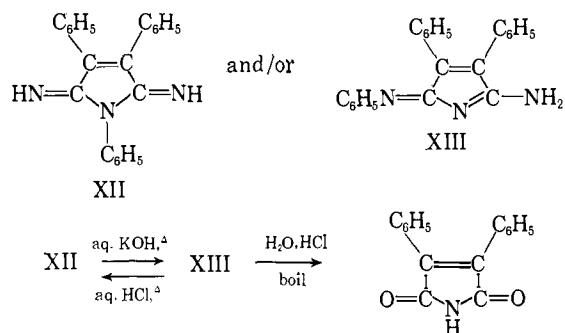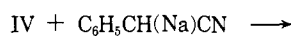
azidotriazole separately labeled by N^{15} enrichment at one of five (those numbered in Chart I) of the six possible N-positions were prepared. The syntheses, which employed conventional reactions, are shown in Chart I. The reactions by which the azido groups are built up stepwise have already been studied in the same or in closely analogous cases[11]; while the positional specificity in the azide-forming reactions is not 100%, it is high, and more than sufficient for the present purposes. The results of the reactions of the labeled compounds are shown in Chart II. They can be summarized by the statement that the azide decomposes by loss of nitrogen only from the azido group, compound IV loses the nitrogen atoms corresponding to positions 2 and 3 (the unsubstituted nitrogens) of the original azido triazole, and the N-phenyl group remains attached to the same nitrogen throughout the transformations (the actual enrichment figures observed for each nitrogen-producing step in the reactions of the five labeled samples are given in the Experimental section).

The choice between the phenyliminotriazole structure VII, the charge-separated structure IX, and the open structure X appears to be in the large part determined by the experiments in which compound IV is reduced to the amine I; the phenyliminotriazole would yield 4-phenyl-5-anilinotriazole (XIV) on reduction. Although 4-phenyl-5-anilinotriazole has been shown by Dimroth[12] to be interconvertible with I, XIV is the favored form at equilibrium, and the equilibrium proportion of I is <17% at 132°, still less at lower temperatures.[13] The equilibration is negligibly slow at ordinary temperatures (the rate constant for XIV → I is only 2.6 × 10⁻³ min.⁻¹ at 132°).[13] Since compound I was formed from IV under very mild conditions, in higher than equilibrium amounts, and free of isolable amounts of XIV, it is clear that compound I could not have arisen from IV by initial reduction to XIV followed by isomerization. The argument is even more
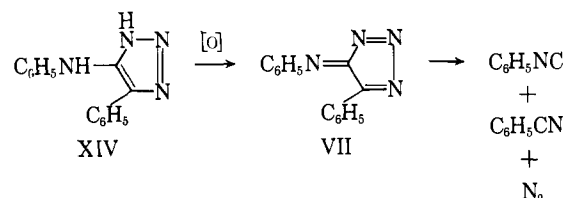
(11) K. Clusius and K. Schwarzenbach, *Helv. Chim. Acta*, **42**, 739 (1959).

(12) O. Dimroth, *Ann.*, **364**, 183 (1908).

(13) E. Lieber, C. N. R. Rao, and T. S. Chao, *J. Am. Chem. Soc.*, **79**, 5962 (1957); E. Lieber, T. S. Chao, and C. N. R. Rao, *J. Org. Chem.*, **22**, 654 (1957).
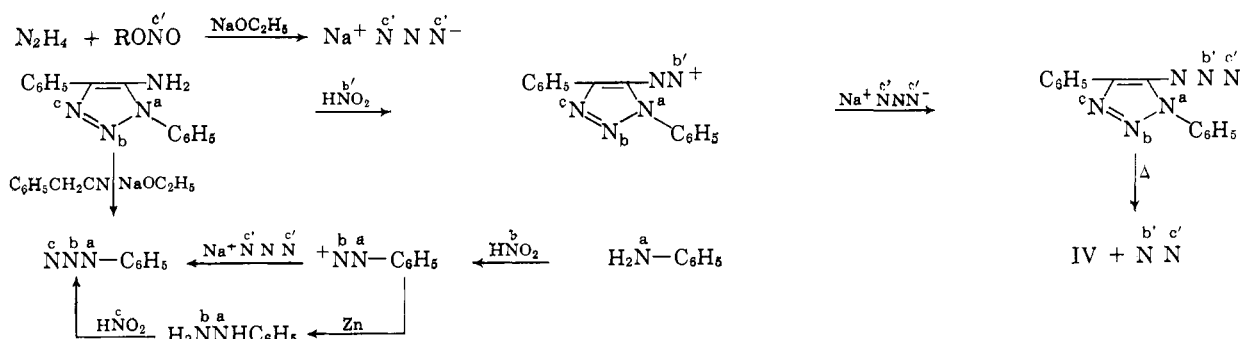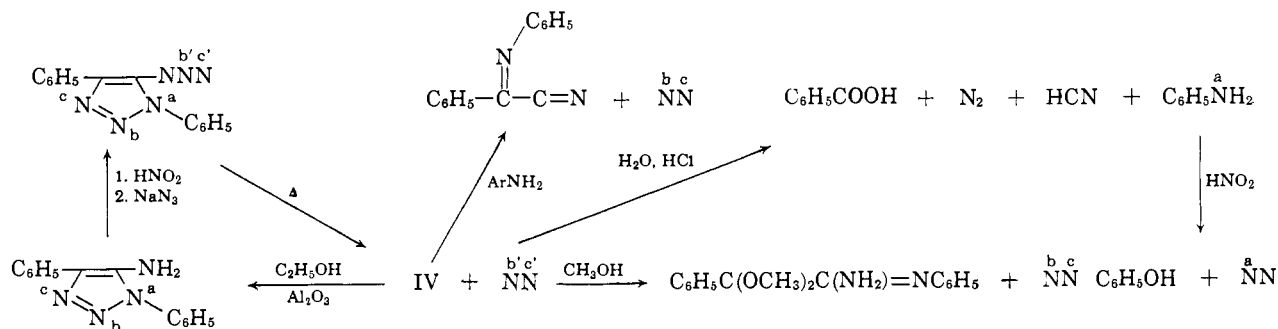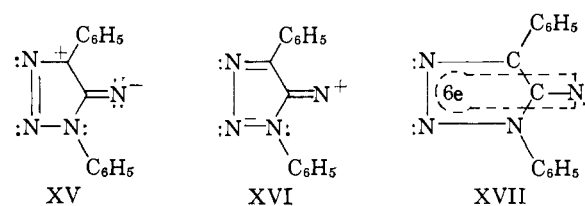
CHART I

CHART II

decisive in the case of IVb, from which the yield of amine (65%) exceeds even more greatly the equilibrium amount (<27% at 132°).
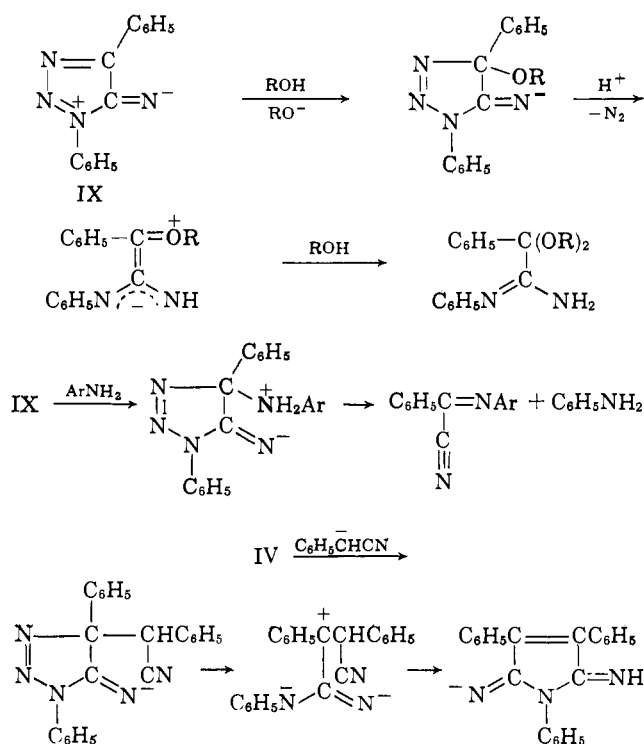
Additional support for the conclusion that compound IV does not have structure VII was obtained from oxidation experiments with the anilinotriazole XIV. Oxidative removal of two hydrogen atoms should give a product with structure VII. Treatment of XIV with various oxidizing agents, such as hypohalites, mercuric oxide, etc., converted it to a wine-red substance that could not be purified for characterization because of its instability. The color, however, was qualitatively different from that of compound IV, which, in addition, would have been stable under the reaction conditions. The detection of both benzonitrile and phenyl isocyanide as decomposition products provided further evidence that we had structure VII in hand, and that it was distinct from compound IV.

Structure IX can be written in charge-separated forms closely related to the mesoionic systems defined by Baker and Ollis[14]; two arbitrary forms are shown (XV and XVI). Stabilization in this way is presumably responsible for the lower reactivity of compound IV compared to the primary decomposition products of most azides,[15] and for the preference for the singlet-state structure. However, a truly mesoionic system (according to the Baker and Ollis definition), with six electrons in "aromatic" π-orbitals, is not possible with the five atoms of the ring alone; one can have either the conventional delocalized triazole system with electron-deficient exocyclic nitrogen, or a larger delocalized π-system, XVII, embracing six atoms (i.e., including the exocyclic nitrogen), analogous to fulvenes.

The reactions of compound IV can be reasonably interpreted in terms of structure IX as arising from attack

(14) W. Baker and P. D. Ollis, *Quart. Rev.* (London), **11**, 15 (1957).
(15) G. Smolinsky, E. Wasserman, and W. A. Jager, *J. Am. Chem. Soc.*, **84**, 3220 (1962).

XV   XVI   XVII

of nucleophiles at the carbon atom at position 4 of the triazole ring, or, in the case of reduction, by acquisition of hydrogen atoms, hydride, or an electron pair by the exocyclic nitrogen atom. The reactions beginning by nucleophilic attack at position 4 must then

proceed by expulsion of nitrogen followed by proton migration, and ring closure if appropriate, as shown in the accompanying equations.

The behavior of IV so far described points somewhat inconclusively to structure IX. On the one hand there is a group of reactions in which the N^1–C^5 bond is found intact in the products, thus implying structure IX, while on the other hand there are certain reactions in which the N^1–C^5 bond is broken. The reactions leading to retention of the N^1–C^5 bond, such as the exceptionally mild reductions, are not those typical of any of the functional moieties present in structure X (azo, ketimine, nitrile), and one must accept abnormal behavior of at least one of these functions in in order to account for the formation of cyclic products from structure X.

The appearance of infrared absorption at 2200 cm.$^{-1}$, however, is not easily accounted for except by structure X. The weakness of the absorption is inconclusive for the intensity of nitrile absorption is very variable.[16] While it may be intrinsically weak in structure X, it can also be accounted for in terms of a dynamic equilibrium between IX and X, in which the equilibrium concentration of X is the smaller. This concept has the happy feature of additionally accounting for the chemical evidence favoring structure IX, and for this reason we consider it the best explanation on the basis of the evidence so far available. The position of the ultraviolet absorption maximum changes somewhat among different solvents, a fact that could be due in part to differing equilibrium positions. Changes in form of the absorption band, which would be more revealing, would unfortunately be obscured by the broad, intense background.

Other reactions of compound IV and of differently substituted derivatives of the same ring system will be reported in a forthcoming communication. Analogous reactions of azido derivatives of several other heterocyclic systems have already been accomplished, and will be reported upon the completion of further logical extensions of the reaction.

The ease of decomposition of the 5-azidotriazoles and the stability of the initial product are very probably closely connected. There is, however, the possibility that the stabilized electron-deficient intermediates isolated in this case may actually be only moderately rather than exceptionally more stable than those derived from other aryl azides, such as the phenyl azides. Compound IV is not stable at temperatures above 150°, which are required for the decomposition of most phenyl azides, and had it been necessary to resort to such temperatures in the present case, such an intermediate as compound IV would not have been found. Some additional stability must, of course, be conceded to compound IV, to account, *inter alia*, for the fact that it does not dimerize to an azo compound. The transformation products of compound IV at temperatures above 150° have not been investigated yet; they are dark colored, not obviously crystalline, and their formation involves further loss of nitrogen.

It appears that analogous decompositions may have been observed in the past by others, without the true nature of the products having been realized. Several azidoazoles have been reported[17] to decompose at relatively low temperatures to give bright red, frothing melts, and Forster and Müller[18] actually isolated a red substance from the decomposition of 1,5-dimethyl-2-phenyl-4-azidopyrazolone-3 at 74°, but were unable to obtain it pure. We are now reinvestigating these reports.

Experimental[19]

1,4-Diphenyl-5-azidotriazole.—1,4-Diphenyl-5-aminotriazole[6a] (5.0 g.) was diazotized by slow addition of 2.5 g. of sodium nitrite in 10 ml. of water to a well stirred suspension in 150 ml. of concentrated hydrochloric acid solution at 0°. After 1.5 hr. at 0°, the mixture was filtered, and the yellow filtrate added to excess sodium azide solution; gas was evolved and a yellow precipitate formed. This product was filtered off, washed with water, and purified by trituration with ether; wt. 5.0 g. (90%), m.p. 70° dec. The infrared spectrum showed strong absorption at 2140 and lower frequency absorptions beginning at 1595 cm.$^{-1}$.

Anal. Calcd. for $C_{14}H_{10}N_6$: C, 64.11; H, 3.84; N, 32.01. Found: C, 64.23; H, 4.01; N, 31.90.

Decomposition of 1,4-Diphenyl-5-azidotriazole. Compound IV.—A solution of 4.0 g. of 1,4-diphenyl-5-azido-1,2,3-triazole in 150 ml. of petroleum ether (b.p. 60–75°) was heated under reflux for 2 hr., filtered hot, and the solvent removed by distillation. The red residue was first recrystallized from petroleum ether (b.p. 60–75°) and then from isopropyl alcohol, yielding 2.8 g. (78%) of compound IV, dark red crystals, m.p. 115–116°. In a similar experiment in which the evolved gas was collected from 2.62 g. (0.01 mole) of azide, 235 ml. was obtained (calcd. for 0.01 mole of N_2, 224 ml.): ultraviolet spectrum: λ_{max} 3430 Å., ϵ 2.28 × 10^4 (3 × 10^{-5} M in heptane); λ_{max} 3510 Å., ϵ 2.8 × 10^4 (in 1,2-dichloroethane); λ_{max} 3500 Å., ϵ 2.0 × 10^4 (in dimethylformamide). The infrared spectrum in carbon tetrachloride and in carbon disulfide solutions as well as in Nujol mull showed no absorption attributable to NH and no absorption between 2800 and 1590 cm.$^{-1}$; in saturated solution in chloroform, a weak band at 2200 cm.$^{-1}$ appeared.

Anal. Calcd. for $C_{14}H_{10}N_4$: C, 71.78; H, 4.31; N, 23.90; mol. wt., 234. Found: C, 71.96; H, 4.54; N, 23.74; mol. wt. (cryoscopic in benzene), 222, 229; (cryoscopic in 2,4,6-tribromophenol), 180, 199, 220.

Decomposition of 1,4-Diphenyl-5-azidotriazole in Ethanol.—A stirred suspension of 1.0 g. of 1,4-diphenyl-5-azidotriazole was refluxed in 50 ml. of dry ethanol for 18 hr.; 171 ml. (corrected to STP) of gas was collected (theoretical for evolution of 2 moles of gas is 171 ml.). The alcohol was removed and the residue was recrystallized from petroleum ether (b.p. 60–75°), giving 0.5 g. (39%) of N-phenyl-α,α-diethoxyphenylacetamidine, m.p. 97°.

Reduction of Compound IV to Amine I. A. Chromatography.—A solution of 2.0 g. of compound IV, m.p. 114–116°, in benzene was placed on an alumina chromatographic column and eluted with 95% ether–5% ethanol. The first band eluted was 1,4-diphenyl-5-aminotriazole, 0.7 g. (35%), m.p. 170–171°, mixture m.p. 170–171°. All other eluates were uncrystallizable gums.

B. Catalytic Hydrogenation.—A solution of 5.5 g. of compound IV in 200 ml. of isopropyl alcohol was hydrogenated on a Parr shaker at 50 p.s.i. with 1 g. of 5% palladium-on-charcoal. The solution was then heated and filtered from catalyst while hot. Removal of the solvent by distillation left a yellow solid, which was recrystallized twice from ethanol, giving 2.5 g. (54%) of 1,4-diphenyl-5-aminotriazole, m.p. 166–168°, mixture m.p. 167–168°.

C. With Butyl Mercaptan.—A suspension of 0.50 g. of compound IV in 12 ml. of isopropyl alcohol was mixed with 0.6 ml. of butyl mercaptan and allowed to stand at room temperature with occasional swirling until the red solid had all dissolved (about 10 min.). Dilution with ligroin (b.p. 90–100°) precipitated 0.21 g.

(16) R. M. Silverstein and G. C. Bassler, "Spectrometric Identification of Organic Compounds," John Wiley and Sons, Inc., New York, N. Y., 1963, pp. 67–68; L. J. Bellamy, "The Infrared Spectra of Complex Molecules," 2nd Ed., John Wiley and Sons, Inc., New York, N. Y., 1958, p. 265.

(17) L. Cramer, *Ber.*, **27**, 3089 (1894); G. T. Morgan and J. Reilly, *J. Chem. Soc.*, **105**, 435 (1914).

(18) M. O. Forster and R. Müller, *ibid.*, **95**, 2072 (1909).

(19) Melting points are corrected, boiling points uncorrected. Microanalytical Laboratory, Ann Arbor, Mich., or by Micro-Tech Laboratories, Skokie, Ill.

(42%) of I in three crops, m.p. 165–168°, mixture melting point with an authentic sample undepressed.

N-Phenyl-α,α-dimethoxyphenylacetamidine.—When a mixture of 1.6 g. of compound IV and methanol was prepared, gas evolution began immediately and within 1 min. the solution had faded to yellow. The methanol was then removed by distillation and the residue taken up in petroleum ether (b.p. 60–75°) and treated with Norit. Upon cooling, 1.25 g. (87%) of N-phenyl-α,α-dimethoxyphenylacetamidine, m.p. 94–97°, crystallized. An analytical sample was obtained by recrystallizing several times from petroleum ether (b.p. 60–75°); m.p. 97–98°.

Anal. Calcd. for $C_{16}H_{18}N_2O_2$: C, 71.08; H, 6.71; N, 10.37. Found: C, 71.14; H, 6.66; N, 10.35.

The infrared spectrum had bands at 3280–3300 (NH), 1635 and 1600 (amidine), plus many peaks from 1540 cm.$^{-1}$ downward. This compound was recovered unchanged from attempted hydrogenation at 40 p.s.i. for 18 hr., in benzene solution over 5% palladium-on-charcoal.

N-Phenyl-α,α-diethoxyphenylacetamidine.—A solution of 2.0 g. of compound IV in 50 ml. of dry ethanol underwent no apparent reaction until it was refluxed for 2 hr. The alcohol was removed and the residue taken up in petroleum ether (b.p. 60–75°) and treated with Norit, yielding 1.9 g. (75%) of N-phenyl-α,α-diethoxyphenylacetamidine, m.p. 96–97°. An analytical sample was obtained by recrystallization several times from petroleum ether (b.p. 60–75°); white crystals, m.p. 97.0–97.5°; mixture m.p. with the methyl analog, 78–88°. The infrared spectrum was almost the same as that of the methyl analog. This compound was soluble in dilute acid, but was recovered in 60% yield after refluxing for 24 hr. with 1.5 N hydrochloric acid and then neutralizing.

Anal. Calcd. for $C_{18}H_{22}N_2O_2$: C, 72.54; H, 7.44; N, 9.40. Found: C, 72.22; H, 7.59; N, 9.46.

In a similar experiment in which the evolved gas was collected, its volume from 1.0 g. of compound IV was 127 ml. (corrected to STP); theoretical for evolution of one molecular equivalent of H_2, 134 ml.

In a similar experiment in which 0.5 g. of compound IV was heated with 22 ml. of ethanol in the presence of 3 ml. of triethylamine, the red color of compound IV faded in about 3 min.; the product and yield were similar.

N-Phenyl-α,α-diisopropoxyphenylacetamidine.—Compound IV did not visibly react with isopropyl alcohol when refluxed in it for 36 hr., alone or in the presence of triethylamine; unchanged IV was recovered. When 3.0 g. of compound IV was added to 25 ml. of isopropyl alcohol in which 0.1 g. of sodium had been dissolved, an immediate reaction took place. In much the same way as in the foregoing examples, there was obtained 1.8 g. (43%) of N-phenyl-α,α-diisopropoxyphenylacetamidine, m.p. 97–98°.

Anal. Calcd. for $C_{20}H_{26}N_2O_2$: C, 73.68; H, 8.04; N, 8.59. Found: C, 73.81; H, 8.08; N, 8.67.

N-Phenyl-α,α-dibenzyloxyphenylacetamidine.—Refluxing benzyl alcohol converted IV only to a red gum that could not be crystallized, but in the presence of a little dissolved sodium, N-phenyl-α,α-dibenzyloxyphenylacetamidine was formed normally, and obtained in 45% yield, m.p. 113.0–113.5°.

Anal. Calcd. for $C_{28}H_{26}N_2O_2$: C, 79.59; H, 6.20; N, 6.63. Found: C, 79.33; H, 6.21; N, 6.72.

Catalytic Hydrogenation of N-Phenyl-α,α-dibenzyloxyphenylacetamidine.—A solution of 6.9 g. of N-phenyl-α,α-dibenzyloxyphenylacetamidine in ethanol was hydrogenated over 5% palladium-on-charcoal on a Parr shaker. The catalyst and solvent were removed and an oil remained. Part of the oil was chromatographed on alumina; a 75% ether–25% alcohol solution eluted 0.3 g. of mandelanilide, m.p. 149–151° (reported[20] m.p. 152°), mixture m.p. 149–151°.

Hydrolysis of IV.—A chilled mixture of 2.0 ml. of concentrated hydrochloric acid and 10 ml. of glacial acetic acid was poured into 2.34 g. of IV. Frothing of the pasty mixture became noticeable after a few seconds; after 45 min., the red color had become brown, and most of the solid had dissolved. After 15 min. more, at room temperature, the solution was filtered from a small amount (50 mg.) of white solid, later identified as ammonium chloride, and diluted with ice. A copious, crystalline precipitate soon formed; it was filtered off and washed with ice water. It was identified as benzoyl cyanide by its m.p., 31–32° (reported[21]

m.p. 33–34°), and strong bands in its infrared spectrum at 2220 (C≡N) and 1685 cm.$^{-1}$ (C=O); wt. 0.85 g. (67.5%).

A portion of the filtrate was added to an alkaline solution of β-naphthol; a heavy, bright vermilion precipitate of azo dye formed.

In another experiment in which IV was heated with dilute hydrochloric acid, only benzoic acid, m.p. 122°, and aniline hydrochloride, m.p. 195–196°, undepressed by mixture with authentic samples, could be isolated from the tarry reaction mixture, and in only poor yield.

Reaction of IV with Aromatic Hydrocarbons. A. IVb with Benzene.—A mixture of 1.0 g. of IVb, 1.0 g. of aluminum chloride, and 30 ml. of benzene was allowed to stand at room temperature for 24 hr. Gas was slowly evolved, and hydrogen cyanide was detected by odor, the Prussian Blue reaction, and the isopurpuric acid reaction. The dark reaction mixture was then shaken with 30 ml. of water and filtered; the dark brown residue, wt. 15 mg., m.p. >320°, was discarded.＊ The benzene layer showed clear nitrile absorption at 2220 cm.$^{-1}$. Vapor phase chromatography showed three principal components, which were identified by their retention times as benzonitrile, p-chlorotoluene, and p-methylbiphenyl; biphenyl was absent in detectable amounts. Chromatography of the dried (Na_2SO_4) benzene layer on an alumina column yielded 0.15 g. (22%) of p-methylbiphenyl, m.p. 45°, on elution with benzene; recrystallization from aqueous ethanol gave a product, m.p. 47–48° (reported[22] m.p. 47–48°).

B. IVb with Toluene.—In a similar experiment, 0.10 g. (13.5%) of crude p-bitolyl, m.p. 105–107°, was obtained. Recrystallization gave a pure sample, m.p. 121° (reported[23] m.p. 122°).

C. IVa with Benzene.—In a similar experiment, 0.20 g. (35%) of biphenyl, m.p. 69° (reported[10] m.p. 70.5°), was obtained.

D. IVa with Toluene.—An analogous experiment produced 0.20 g. (29%) of a colorless oil, which was shown by comparison of retention times in vapor phase chromatography to contain o- and p-methylbiphenyl in a ratio of about 1:2.

Reaction of Compound IV with Aniline and Aniline Hydrochloride. A.—A mixture of 5.0 g. of compound IV, 0.5 g. of aniline hydrochloride, and 125 ml. of benzene was refluxed for 24 hr. The solvents were then removed under vacuum, the residue extracted with petroleum ether (b.p. 90–100°), and the extracts treated with Norit. Evaporation left orange crystals, wt. 2.5 g., which were then dissolved in benzene and passed through an alumina column. The benzene was removed and the yellowish crystals recrystallized several times from ligroin (b.p. 90–100°), yielding 1.25 g. (20%) of N,N'-diphenylbenzamidine, m.p. 145° (reported[9] m.p. 146°), mixture m.p. with an authentic sample 144–145°. The infrared spectrum of N,N'-diphenylbenzamidine obtained from this experiment was identical with that of an authentic sample.

B.—A mixture of 8.0 g. of compound IV, 24 ml. of aniline, 0.2 g. of aniline hydrochloride, and 200 ml. of benzene was refluxed for 10 hr. The solvents were then removed and the residue chromatographed on alumina. A mixture of 90% benzene and 10% petroleum ether eluted 0.9 g. (13%) of phenylglyoxylonitrile anil, m.p. 72°. Benzene eluted 3.0 g. (31%) of N,N'-diphenylbenzamidine, m.p. 145°.

Reaction of Compound IV with Pyridine. Phenylglyoxylonitrile Anil.—A solution of 2.0 g. of compound IV and 25 ml. of pyridine was refluxed for 6 hr. and the solvents removed under vacuum. The dark residue was chromatographed on alumina. Benzene eluted the first band (0.2 g.), which was recrystallized several times from petroleum ether (b.p. 60–75°), yielding 0.1 g. (6%) of phenylglyoxylonitrile anil, m.p. 72° (reported[24] m.p. 72°), mixture m.p. 72°. No other compounds could be isolated.

Anal. Calcd. for $C_{14}H_{10}N_2$: C, 81.62; H, 4.89; N, 13.60. Found: C, 81.60; H, 4.92; H, 13.39.

In a similar experiment, 0.1 g. of phenylglyoxylonitrile anil, m.p. 72°, was sublimed from the concentrated reaction mixture without prior chromatography.

A solution of phenylglyoxylonitrile anil in chloroform showed the expected infrared absorption at 2400 cm.$^{-1}$, characteristic of nitriles, but a Nujol mull of it failed to show this absorption.

(20) C. A. Bischoff and P. Walden, *Ann.*, **279**, 118 (1894).

(21) H. Hübner and K. Buchka, *Ber.*, **10**, 479 (1877).

(22) L. Gattermann, *Ann.*, **347**, 381 (1906).

(23) F. Ullmann and G. M. Meyer, *ibid.*, **332**, 40 (1904).

(24) F. Kröhnke, *Ber.*, **71**, 2583 (1938).

Reaction of Compound IV with Aniline. Phenylglyoxylonitrile Anil.—A mixture of 2.0 g. of compound IV, 3 ml. of aniline, and 25 ml. of *p*-xylene was heated on the steam bath for 4 hr. The solvents were removed and the residue chromatographed on alumina. A mixture of 90% benzene and 10% petroleum ether eluted the only compound isolated. This band, after recrystallization from petroleum ether (b.p. 60–75°), gave 0.5 g. (29%) of phenylglyoxylonitrile anil, m.p. 72°. Similar results were obtained from reaction in benzene solution.

In a similar experiment the product was removed from the reaction mixture with hot petroleum ether (b.p. 60–75°) after removal of the solvents. After several treatments with Norit and recrystallizations, 0.2 g. of phenylglyoxylonitrile anil, m.p. 72°, was isolated.

Small amounts of N,N'-diphenylbenzamidine could sometimes be isolated from experiments on a larger scale.

Isotopically Enriched Potassium Nitrite.—Following the procedure of Vaughan, *et al.*,[25] isotopically enriched potassium nitrate manufactured by Isomet Corporation was reduced with lead to potassium nitrite. The product was treated with ammonium chloride and the nitrogen evolved was collected: found, $^{29}N_2/^{28}N_2 = 0.1196$ ($^{29}N_2/^{28}N_2$ natural is 0.0073).

Purification and Collection of Nitrogen for Mass Spectrometric Analysis.—The nitrogen evolved from the labeled systems was collected and purified for mass spectrometric analysis by a modification of the procedure described by Vaughan, *et al.*[25] The apparatus consisted of a four-necked standard taper flask equipped with a magnetic stirrer, a reflux condenser, a thermometer, a gas inlet, and a serum bottle stopper fitted in one neck. The reflux condenser was connected with a stopcock (A) and a mercury seal to the bottom of a nitrometer which was filled with 50% potassium hydroxide solution. The nitrometer was closed at the top by a stopcock (B) fitted with a ball joint which connected to a cold finger trap of approximately 25-ml. capacity that could be closed off from the system by two stopcocks (C and D). The exit from the cold finger trap was connected by a short piece of heavy hose to a three-way stopcock (E) fitted on one arm with a 10/30 standard taper joint to which the sample bottle was attached. The other arm was connected to a vacuum pump.

The solvent was first degassed by boiling and the system flushed with carbon dioxide; then the solvent was allowed to cool to the desired temperature in a carbon dioxide atmosphere. The nitrometer was completely filled with potassium hydroxide solution, stopcock B closed, and the remaining part of the system evacuated for at least 1 hr. During this time the sample was introduced into the reaction vessel with a hypodermic syringe. The gas evolved was transferred to the nitrometer by periodic flushings with carbon dioxide. When the reaction was over and all the gas collected in the nitrometer, the cold finger trap was immersed in liquid nitrogen, stopcocks A and D were closed, and the gas was transferred from the nitrometer to the cold finger trap by opening stopcock B. When sufficient gas had transferred, stopcock C was closed and the gas in the cold finger was left at liquid nitrogen temperature for at least 1 hr. to ensure that all solvent vapor was frozen out. The vacuum pump was then closed off from the system at E. With the cold finger trap still in liquid nitrogen, stopcock D was opened and the nitrogen allowed to enter the evacuated sample bottle.

The carbon dioxide used to flush the system was generated from Dry Ice in a dewar flask.

Only the nitrogen evolved from the decomposition and occasionally a very small amount of air could be detected with the mass spectrometer.

1,4-Diphenyl-5-(3-^{15}N-azido)triazole.—Potassium azide randomly enriched with ^{15}N at the terminal position of the azide ion was prepared from ^{15}N-enriched potassium nitrite and hydrazine.[26] A solution of 3.0 g. of 1,4-diphenyl-5-aminotriazole was diazotized in the usual manner, and then treated at 0° with 0.7 g. of enriched potassium azide extended with 0.3 g. of ordinary sodium azide. The precipitated product was triturated with petroleum ether (b.p. 40–60°), and then had m.p. 71–73°, wt. 2.4 g. A 0.5-g. sample of the enriched azide was decomposed at 70° in ligroin solution (b.p. 90–100°), and the evolved gas collected. The mass spectrometric ratio found was $^{29}N_2/^{28}N_2 = 0.0214$ (2.9 × standard ratio), but this figure is inaccurate owing to contam-

(25) W. R. Vaughan, W. T. Boyd, D. L. McCane, and G. L. Sloan, *Anal. Chem.*, **23**, 508 (1951).

(26) J. Thiele, *Ber.*, **41**, 2681 (1908); R. Stollé, *ibid.*, **41**, 2811 (1908).

ination by traces of solvent. The compound IV isolated had m.p. 112–114°, wt. 0.4 g.

1,4-Diphenyl-5-(2-^{15}N-azido)-1,2,3-triazole with presumed approximate ^{15}N/^{14}N ratio of 0.240 at the labeled position was prepared by diazotizing 1,4-diphenyl-5-aminotriazole as already described, but using isotopically enriched potassium nitrite, followed by coupling the diazonium salt with ordinary sodium azide.

Decomposition of 1,4-Diphenyl-5-(2-^{15}N-azido)-1,2,3-triazole.—A solution of 0.5 g. of labeled 1,4-diphenyl-5-(2-^{15}N-azido)-1,2,3-triazole was dissolved in warm di-*n*-butyl ether and introduced with a hypodermic syringe into the reaction vessel, which contained methylcyclohexane heated to 70°. The vessel was kept at 70 ± 2° for several hours. After the reaction was over, the purified nitrogen collected was found to have $^{29}N_2/^{27}N_2 = 0.1151$. The compound IV produced was isolated and recrystallized; m.p. 113–115°. Using the same apparatus, this product was dissolved in hot isopropyl alcohol and introduced into hot methanol. The purified nitrogen evolved was found to have $^{29}N_2/^{28}N_2 = 0.0073$.

1,4-Diphenyl-5-azido-1,2,3-triazole-3-^{15}N.—Terminally labeled phenyl azide was prepared by treating phenylhydrazine in dilute hydrochloric acid with isotopically enriched potassium nitrite solution. The product was condensed in the usual manner with phenylacetonitrile to give 1,4-diphenyl-5-amino-1,2,3-triazole-3-^{15}N. The labeled triazole was then diazotized and coupled with sodium azide.

This labeled azide triazole was decomposed and the gas purified as already described; found $^{29}N_2/^{28}N_2 = 0.0075$. The IV produced in this decomposition was recrystallized (m.p. 113–115°) and then treated with methanol in the previously described manner. The evolved gas had $^{29}N_2/^{28}N_2 = 0.1160$.

Part of the IV obtained was treated with alumina to convert it to 1,4-diphenyl-5-aminotriazole, which was then diazotized and converted back to the azide with a now unknown position of isotopic labeling. This azide was decomposed in exactly the same manner, and the nitrogen analyzed; found $^{29}N_2/^{28}N_2 = 0.0075$. The IV produced was treated with methanol as before and the evolved nitrogen analyzed; found $^{29}N_2/^{28}N_2 = 0.120$.

1,4-Diphenyl-5-azido-1,2,3-triazole-2-^{15}N.—Phenyl azide-2'-^{15}N was made by diazotizing aniline with enriched potassium nitrite, followed by coupling with sodium azide. The labeled phenyl azide was converted to compound IV as before. Part of the labeled product was treated with methanol as before, and the nitrogen evolved analyzed; found $^{29}N_2/^{28}N_2 = 0.110$.

Another portion of the labeled IV was chromatographed on alumina and the resulting amine converted to the corresponding azide. This azide was again converted to compound IV, which was recrystallized and treated with methanol as before; the evolved nitrogen had $^{29}N_2/^{28}N_2 = 0.0996$.

Reaction of Aniline with Compound IV Enriched at N^3.—A solution of compound IV prepared from phenyl azide-3-^{15}N in 5 ml. of hot benzene was added to a mixture of 75 ml. of refluxing benzene and 5 ml. of aniline. The nitrogen evolved was collected and purified as before; found $^{29}N_2/^{28}N_2 = 0.115$. A repetition of the experiment, using *p*-xylene instead of benzene, gave a similar result: $^{29}N_2/^{28}N_2 = 0.106$.

Nitrobenzene-^{15}N.—To a well stirred solution of 35 ml. of sulfuric acid and 5 ml. of water cooled to 10° in an ice bath, 10 g. of ^{15}N-enriched potassium nitrate was added. The mixture was then cooled to 10° and 25 ml. of benzene was added rapidly. An exothermic reaction occurred upon addition of the benzene, during which the mixture was kept below 30° with an ice bath. The temperature was then slowly raised to 60° and kept there for 1 hr. The product was then steam distilled from the solution made basic with sodium hydroxide, the distillate extracted with ether, dried over sodium sulfate, and distilled, giving 10 g. (82% based on nitrate) of nitrobenzene-^{15}N.

Compound IV Enriched at N^1.—A mixture of 4.0 g. of ^{15}N-labeled nitrobenzene, 100 ml. of ethanol, and 1.0 g. of 5% palladium-on-charcoal was hydrogenated on a Parr shaker. The catalyst was filtered off, the alcohol removed, and the ^{15}N-labeled aniline dissolved in 30 ml. of water and 10 ml. of hydrochloric acid. The solution was diazotized and coupled with sodium azide, yielding phenyl azide-1-^{15}N. The product was extracted with ether, dried over sodium sulfate, treated with Norit, and then condensed with phenylacetonitrile and converted to compound IV as before, yielding 2.5 g., m.p. 111–112°.

Hydrolysis of Compound IV Enriched at N^1.—A mixture of 2.5 g. of compound IV enriched at N^1, 100 ml. of water, and 30 ml. of concentrated hydrochloric acid was refluxed for 3 hr. The solution was then made basic with sodium hydroxide and steam distilled. The distillate was extracted with ether, the extracts dried over sodium sulfate, and the ether removed. The residue was dissolved in benzene, and hydrogen chloride gas bubbled in, yielding 0.25 g. of aniline hydrochloride, m.p. 196°.

The aniline was then diazotized in dilute sulfuric acid at 5°, and then slowly warmed to 50°. The evolved nitrogen was collected and purified as before; found $^{29}N_2/^{28}N_2 = 0.116$.

Analysis of Gaseous Products from Reaction of Compound IV with Aniline.—A mixture of 2.0 g. of analytically pure compound IV, 5 ml. of aniline, and 25 ml. of benzene was placed in a three-necked flask which had a gas inlet apparatus and reflux condenser. The reflux condenser was connected to another flask by a tube which led beneath the surface of approximately 20 ml. of very dilute sodium hydroxide. The sodium hydroxide trap was closed off by a mercury bubbler. The system was flushed with nitrogen, refluxed 10 hr., and flushed with nitrogen again. When a portion of the trap solution was made acidic with nitric acid and silver nitrate added, a white precipitate was produced. Another portion was made slightly acidic with nitric acid and ferric nitrate was added. The solution did not develop the red color of the ferric azide complex, but did so afterward when a very small quantity of sodium azide was added as a control. Another portion of the trap solution, made acidic with nitric acid, gave a positive Prussian blue test for cyanide.

Phenylglyoxylonitrile p-Methylanil.—A mixture of 2.0 g. of compound IV, 5 g. of p-toluidine, and 50 ml. of benzene was refluxed for 12 hr. and the reaction mixture chromatographed on alumina. With a 90% benzene–10% petroleum ether solution, 1.0 g. (53%) of phenylglyoxylonitrile p-methylanil, m.p. 91–92° (reported[27] m.p. 96°), was obtained after recrystallization from petroleum ether (b.p. 60–75°).

Anal. Calcd. for $C_{15}H_{12}N_2$: C, 81.89; H, 5.50; N, 12.73. Found: C, 81.63; H, 5.71; N, 12.79.

Phenylglyoxylonitrile p-Bromoanil.—A mixture of 4.0 g. of compound IV, 6 ml. of p-bromoaniline, 0.5 g. of p-bromoaniline hydrochloride, and 100 ml. of benzene was refluxed for 4 hr. and the mixture chromatographed on alumina. The first band was eluted with a 90% benzene–10% petroleum ether mixture. The eluate was evaporated and the residue was recrystallized from petroleum ether (b.p. 60–75°), giving 1.0 g. (20%) of phenylglyoxylonitrile p-bromoanil, m.p. 115° (reported[28] m.p. 118°).

Anal. Calcd. for $C_{14}H_9N_2Br$: C, 59.00; H, 3.18; N, 9.83; Br, 28.04. Found: C, 59.28; H, 3.26; N, 9.89.

Reaction of Compound IV with m-Toluidine.—A mixture of 4.0 g. of compound IV, 6 ml. of m-toluidine, 0.5 g. of m-toluidine hydrochloride, and 75 ml. of benzene was refluxed for 4 hr. and the solvent was removed. The residue was chromatographed on alumina. The only compound isolated was eluted with benzene. This fraction, after repeated recrystallization from petroleum ether (b.p. 90–100°), gave 0.8 g. (16%) of N,N'-di-m-tolylbenzamidine, m.p. 128–129° (reported[29] m.p. 133–134°), mixture m.p. with an authentic sample 128–129°.

Reaction of Phenylglyoxylonitrile Anil with Aniline.—A solution of 1.0 g. of phenylglyoxylonitrile anil, 3 ml. of aniline, and 25 ml. of p-xylene was heated for 15 hr. on the steam bath. The solvents were then removed under vacuum and the residue chromatographed on alumina. A mixture of 90% benzene–10% petroleum ether eluted 0.85 g. of starting material. No other compound was isolated.

Reaction of Phenylglyoxylonitrile Anil with Aniline and Aniline Hydrochloride.—A mixture of 1.0 g. of phenylglyoxylonitrile anil, 3 ml. of aniline, 0.1 g. of aniline hydrochloride, and 25 ml. of benzene was refluxed for 20 hr. The solvents were removed under vacuum and the residue chromatographed on alumina. A mixture of 90% benzene–10% petroleum ether eluted 0.15 g. of phenylglyoxylonitrile anil, m.p. 72°. A 90% benzene–10% diethyl ether mixture eluted 0.7 g. (60%) of N,N'-diphenylbenzamidine, m.p. 145–146°, mixture m.p. 145–146°.

Attempted Exchange between Phenylglyoxylonitrile Anil and p-Toluidine.—A solution of 1.0 g. of phenylglyoxylonitrile anil, 3.0 g. of p-toluidine, and 25 ml. of p-xylene was heated on the

steam bath for 18 hr. The solvents were then removed and the residue chromatographed on alumina. A mixture of 90% benzene and 10% petroleum ether eluted 0.6 g. of phenylglyoxylonitrile anil, m.p. 72°. Benzene eluted p-toluidine, which was the only other compound isolated.

Attempted Exchange between Phenylglyoxylonitrile p-Methylanil and Aniline.—A solution of 0.8 g. of phenylglyoxylonitrile p-methylanil, 25 ml. of benzene, and 5 ml. of aniline was refluxed for 24 hr., the solvents removed, and the residue recrystallized from petroleum ether (b.p. 60–75°), yielding 0.65 g. of recovered phenylglyoxylonitrile p-methylanil, m.p. 90–92°, as the only isolated product.

Attempted Exchange between Compound IV and p-Toluidine. —A solution of 2.0 g. of compound IV, 50 ml. of benzene, and 6 g. of p-toluidine was stirred at room temperature for 1 hr. The solution was then extracted with 5% citric acid solution and dried over calcium chloride. When the benzene was removed, only pure compound IV (0.4 g.), m.p. 112°, remained.

1-p-Tolyl-4-phenyl-5-azidotriazole.—A solution of 4.0 g. of sodium nitrite in 10 ml. of water was added dropwise to a well stirred suspension of 10.0 g. of 1-p-tolyl-4-phenyl-5-aminotriazole in 100 ml. of concentrated hydrochloric acid cooled to 0°. The solution was kept at 0° for 1 hr. and filtered. The orange filtrate was added to a solution of 10 g. of sodium azide in 200 ml. of water. The resulting mixture was extracted with ether and the ethereal solution was dried over sodium sulfate. The ether was removed under water aspirator pressure at a temperature of 20° or less. The residue was then triturated with cold petroleum ether (b.p. 40–60°), and 8.3 g. (76%) of orange crystals of partially decomposed 1-p-tolyl-4-phenyl-5-azidotriazole was collected. An analytical sample was prepared by recrystallization and trituration from diethyl ether, yielding yellow crystals which rapidly became light orange and melted with decomposition at 75°.

Anal. Calcd. for $C_{15}H_{12}N_6$: C, 65.27; H, 4.38; N, 30.45. Found: C, 65.35; H, 4.43; N, 30.39.

The 1-p-Tolyl Analog of Compound IV (IVb).—A mixture of 4.1 g. of 1-p-tolyl-4-phenyl-5-azidotriazole and 100 ml. of petroleum ether (b.p. 90–100°) was refluxed for 2 hr. The resulting solution was cooled and 3.4 g. (92%) of garnet-red crystals, m.p. 130–135°, was filtered off. An analytical sample, m.p. 138.0–138.5°, was prepared by recrystallization from isopropyl alcohol.

Anal. Calcd. for $C_{15}H_{12}N_4$: C, 72.64; H, 4.88. Found: C, 72.57; H, 4.92.

Reaction of IVb with p-Toluidine.—A solution of 2.0 g. of IVb, 5 g. of p-toluidine, and 50 ml. of benzene was refluxed for 14 hr. and chromatographed on alumina. A mixture of 90% benzene and 10% petroleum ether eluted 1.0 g. (56%) of phenylglyoxylonitrile p-methylanil, m.p. 91–92°. The only other compound isolated was p-toluidine.

Reaction of IVb with Aniline.—A solution of 2 g. of IVb, 50 ml. of benzene, and 5 ml. of aniline was refluxed for 14 hr. The solvents were then removed under vacuum and the residue chromatographed on alumina. A solution of 90% benzene and 10% petroleum ether yielded 0.7 g. of yellow crystals, m.p. 50–68°. Several recrystallizations from petroleum ether (b.p. 60–75°) raised the m.p. range to 62–68°.

Reduction of IVb.—A total of 0.05 g. of sodium borohydride was added in portions at room temperature to a solution of 0.245 g. of IVb in 5 ml. of tetrahydrofuran and 0.5 ml. of isopropyl alcohol. After 15 min. the color had faded to light yellow; only very mild warming was noticed. Dilution to *ca.* 30 ml. with water containing a little sodium bicarbonate caused the formation of a yellow, crystalline precipitate, which was filtered off and washed with water. A very little methanol washed out the yellow color, leaving 0.16 g. (65%) of 1-p-tolyl-4-phenyl-5-aminotriazole, m.p. 177–178°, undepressed by an authentic sample.

Condensation of IV with Phenylacetonitrile.—A small piece of sodium was stirred with 12 ml. of phenylacetonitrile for about 10 min. in order to form a small amount of sodium salt, and the sodium was then removed. Compound IV was added slowly in portions up to a total of 1.50 g., the mixture was heated at 100° for 5 min., and then allowed to cool. Rubbing with a glass rod brought about crystallization of 0.60 g. of a nearly colorless product, m.p. 160°, which was augmented by a second crop, wt. 0.20 g., m.p. 155°, by treating the filtrate with petroleum ether. After washing with 1:1 benzene–petroleum ether and one recrystallization from aqueous ethanol, colorless needles (XII), m.p. 191°, were obtained. An analytical sample had m.p.

(27) F. Sachs and E. Bry, *Ber.*, **34**, 494 (1901).

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191.5°. The infrared spectrum showed strong bands at 1590 and 1640 cm. $^{-1}$ (amidine). This compound was insoluble in cold water, and was converted by hydrochloric acid into a sparingly soluble salt, m.p. 248°, which we were not able to obtain analytically pure.

Anal. Calcd. for $C_{22}H_{17}N_3$: C, 81.80; H, 5.32; N, 13.01. Found: C, 81.68; H, 5.39; N, 12.88.

In another experiment, 0.470 g. of IV was added slowly to 5 ml. of phenylacetonitrile in which 0.046 g. of sodium had been dissolved. There was lively gas evolution. When the dark red reaction mixture had become quiet, it was heated at 100° for about 10 min., cooled, and diluted with petroleum ether. The oil that separated soon became a yellow solid (XIII). It was slurried with alcohol and sucked dry; wt. 0.40 g., m.p. 254–258° dec. It was insoluble even in boiling water, but dissolved in cold hydrochloric acid to give an orange solution, and slightly in hot alcohol, from which an analytical sample, yellow needlets, m.p. 258°, was obtained. The infrared spectrum was similar to that of XII.

Anal. Calcd. for $C_{22}H_{17}N_3$: C, 81.80; H, 5.32; N, 13.01. Found: C, 81.63; H, 5.33; N, 12.85.

Interconversion of Compounds XII and XIII.—When 100 mg. of XIII was heated for an hour on a steam bath with concentrated hydrochloric acid, in which it dissolved, and the solution then concentrated, 70 mg. of a yellow hydrochloride, m.p. 240° dec., was obtained. There was no depression of melting point when mixed with XII hydrochloride, and XII itself was obtained by treatment with sodium bicarbonate solution.

When 0.10 g. of XII was boiled for *ca.* 5 min. with a solution of 3 g. of potassium hydroxide in 12 ml. of 50% ethanol and then cooled, 80 mg. of yellow solid, m.p. 200–210°, was obtained. Recrystallization from ethanol gave pure XIII, m.p. and mixture m.p. 254°.

Hydrolysis of XII and XIII.—When a solution of 0.20 g. of XIII in 10 ml. of concentrated hydrochloric acid was boiled for 2 min., the orange color faded and a yellow-green solid began to separate before cooling. After cooling, the solid was filtered off, washed well with water, and recrystallized from benzene; yellow-green needles, m.p. 218° (reported[30] for diphenylmaleimide, m.p. 217°), wt. 0.11 g. (72%). A portion was boiled briefly with 25% potassium hydroxide solution for a few minutes, and then acidified. The colorless substance, m.p. 156°, that separated[31] was identified as diphenylmaleic anhydride (reported m.p. 156–157°).

Attempts to hydrolyze XII by boiling it with concentrated hydrochloric acid alone, or in ethanol or acetic acid, or by heating it with sirupy phosphoric acid, yielded only starting material or its hydrochloride.

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Electrical Effects of *ortho*-Substituents in Pyridines and Quinolines

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Received November 21, 1963

Correlation of the σ_0 constants proposed by various workers to represent the electrical effects of *o*-substituents with σ_I, σ_m, and σ_p constants shows that in general $\sigma_0 = m\sigma_p + c$ (1) represents the "normal" electrical effect of *o*-substituents. By contrast, *o*-substituted pyridines, quinolines, and isoquinolines show an "abnormal" electrical effect. Correlation of rate and equilibrium data for these systems with σ_I, σ_m, and σ_p constants shows that σ_m and/or σ_I generally give the best results. This behavior is in accord with the electrical effect of *o*-substituents on deuterium–protium exchange at the *o*-position in substituted benzenes. It is proposed that this behavior is due to a short range localized electrostatic effect. These results invalidate the use of the 2-substituted pyridines as a reference series for the "normal" *ortho* electrical effect.

Brown and McDaniel[1] have suggested that ionization constants of 2-substituted pyridines represent a good reference series for the electrical effects of *o*-substituents as, of course, steric effects in this series are minimal. This approach has been criticized by Roberts and Carboni,[2] who felt that the electrical effects in this series would not be equivalent to those generally found in *o*-substituted reaction series. Hall, Piccolini, and Roberts[3] found that rates of deuterium–protium exchange in substituted benzenes are dependent on a localized electrostatic effect which they believed to be a combination of inductive and field effects. They found no significant resonance effect. Shatenstein[4] noted that these data, combined with some of his own work, when plotted against σ_I constants[5] gave a linear relationship.

The analogy between exchange reactions in benzene and the ionization of pyridine and quinoline bases is obvious. Thus, for example, Huisgen and co-workers[6]

report a linear relationship between partial rate factors for benzyne formation of 2-, 3-, or 4-substituted bromobenzenes with the pK_a's of the corresponding pyridinium ions. It therefore seemed reasonable to determine whether substituent effects in *o*-substituted pyridines and quinolines resemble those observed for deuterium–protium exchanges in the 2-position in substituted benzenes, or whether they resemble those usually found in *o*-substituted benzene reaction series. In view of the proposal that the pyridines be used as a reference series for the electrical effects of *o*-substituents, this question is certainly significant.

The "Normal" Electrical Effects of *o*-Substituents.— Our study of the application of the Hammett equation[7–9] to *o*-substituted series[10] in which the reaction site is joined to the ring by some intervening group has shown that in these series the σ_p constants provide adequate representation of the electrical effects of *o*-substituents. To verify this point with regard to series in which the reaction site is directly joined to the ring, the σ_0 values proposed by a number of authors to re-

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