nmr tube. The spectra were then run immediately. Tautomer ratios were estimated by integration of the respective spectra.

cis-**1,3-Diphenyl-2,3-dihydro-1H-naphth[1,2-*e*][1,3]oxazine (7A).**—As described previously,[2b] 2-naphthol was condensed with ammonia and benzaldehyde in 95% ethanol. After recrystallization from 95% ethanol, **7A** (71%) had mp 144–145°, ir $\nu_{max}^{CHCl_3}$ 1650 cm^{-1} (lit.[2b] mp 148–150°).

1-(α-Aminobenzyl)-2-naphthol.—Using the reported procedure,[2b] **7** was hydrolyzed with 20% hydrochloric acid. After recrystallization from ether–methanol 1-(α-aminobenzyl)-2-naphthol hydrochloride (85%) had mp 196–198° dec (lit.[2b] mp 190–220° dec).

The hydrochloride was decomposed in the usual way.[2b] The free base (98%) had mp 120–122°; nmr 5.68 (broad hump, 2 H, NH_2), 5.87 ppm (singlet, 1 H, methylidyne proton) (lit.[2b] mp 124–125°).

Condensation of 1-(α-Aminobenzyl)-2-naphthol with Aldehydes.—To *ca.* 0.03 mol of the free base in 75 ml of warm 95% ethanol was added a 10% molar excess of the aldehyde in 50 ml of warm 95% ethanol. The mixture was allowed to stand at room temperature overnight. The crystals which separated were collected by filtration and recrystallized to a constant melting point from an appropriate solvent. The reported yield was calculated on the basis of the weight of material with the constant melting point. A sample for elemental analysis was dried overnight at 56° (0.02 mm).

cis-**3-(*p*-Nitrophenyl)-1-phenyl-2,3-dihydro-1H-naphth[1,2-*e*][1,3]oxazine (3A)** resulted: light yellow needles (88%) from 95% ethanol, mp 174–175° (lit.[6b] mp 196° for an optically active isomer).

Anal. Calcd for $C_{24}H_{18}N_2O_3$: C, 75.38; H, 4.74. Found: C, 75.24; H, 5.10.

cis-**3-(3,4-Dichlorophenyl)-1-phenyl-2,3-dihydro-1H-naphth[1,2-*e*][1,3]oxazine (4A)** resulted: microscopic, white needles (48%) from benzene, mp 193°.

Anal. Calcd for $C_{24}H_{17}Cl_2NO$: C, 70.94; H, 4.22. Found: C, 71.34; H, 4.20.

cis-**3-(*p*-Bromophenyl)-1-phenyl-2,3-dihydro-1H-naphth[1,2-*e*][1,3]oxazine (5A)** resulted: microscopic, white needles (68%) from benzene, mp 181–182°, ir $\nu_{max}^{CHCl_3}$ 1650 cm^{-1}.

Anal. Calcd for $C_{24}H_{18}BrNO$; C, 69.24; H, 4.36. Found: C, 69.47; H, 4.50.

cis-**3-(*p*-Chlorophenyl)-1-phenyl-2,3-dihydro-1H-naphth[1,2-*e*][1,3]oxazine (6A)** resulted: microscopic, white needles (64%) from benzene, mp 173°, ir $\nu_{max}^{CHCl_3}$ 1660 cm^{-1} (lit.[6c] mp 158° for an optically active isomer).

Anal. Calcd for $C_{24}H_{18}ClNO$: C, 77.52; H, 4.88. Found: C, 77.49; H, 4.56.

cis-**3-(*p*-Isopropylphenyl)-1-phenyl-2,3-dihydro-1H-naphth[1,2-*e*][1,3]oxazine (8A)** resulted: white needles (57%) from 95% ethanol, mp 134–135°, ir $\nu_{max}^{CHCl_3}$ 1650 cm^{-1} (lit.[6a] mp 155–156° for an optically active isomer).

Anal. Calcd for $C_{27}H_{25}NO$: C, 85.45; H, 6.64. Found: C, 84.96; H, 6.69.

cis-**3-(*p*-Dimethylaminophenyl)-1-phenyl-2,3-dihydro-1H-naphth[1,2-*e*][1,3]oxazine (9A)** resulted: yellow needles (58%) from ethylene chloride, mp 192–193° (lit.[6c] mp 219–220° for an optically active isomer).

Anal. Calcd for $C_{26}H_{24}N_2O$: C, 82.07; H, 6.36. Found: C, 81.57; H, 6.06.

Registry No.—**3A**, 24609-72-1; **3B**, 24609-73-2; **4A**, 24609-74-3; **5A**, 24609-75-4; **6A**, 24609-76-5; **6B**, 24609-77-6; **6C**, 24605-71-8; **7A**, 24609-78-7; **7B**, 24609-79-8; **7C**, 24609-80-1; **8A**, 24609-81-2; **8B**, 24609-82-3; **8C**, 24609-84-5; **9A**, 24609-85-6; **9C**, 24609-86-7.

Acknowledgment.—This work was supported in part by the American Cancer Society through an Institutional Cancer Grant (IN-25-K-5) to Vanderbilt University for which we are very grateful.

Isolation of Primary Decomposition Products of Azides. II. Azidopyrazoles[1]

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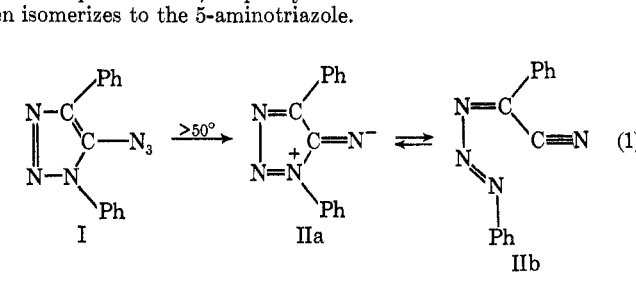
Received September 8, 1969

Variously substituted 5-aminopyrazoles have been converted into the azides, which lose nitrogen above room temperature to form red, monomeric products analogous to those from 5-azidotriazoles. The same or isomeric substances are formed by oxidations of 5-aminopyrazoles, along with variable quantities of 5,5′-azopyrazoles. Both are converted back into 5-aminopyrazoles by reducing agents, in some instances through an isolable open-chain β-hydrazono nitrile. The overall behavior of the fragmentation products of 5-azidopyrazoles indicates a β-azoacrylonitrile structure, which may equilibrate with a kinetically significant concentration of a cyclic form. Whereas some of them are identical with the β-azoacrylonitriles obtained by oxidizing the hydrazones of β-ketopropionitriles, many are geometrical isomers, such as the product from 1-phenyl-3-methyl-5-azidopyrazole, which is distinct from the known β-phenylazocrotononitrile, into which it can be converted by acid, and from the "azipyrazole" of Michaelis and Schäfer. The fragmentation product of 1,4-diphenyl-5-azidotriazole can be reduced to 1-phenyl-3-(α-cyanobenzyl)triazene, which then isomerizes to the 5-aminotriazole.

We recently reported[2] the fragmentation of 5-azido-1,4-diphenyltriazole, which loses 1 mol of nitrogen at temperatures above about 50° to form a deep red, monomeric compound (II), whose chemical and physical characteristics suggested a mobile equilibrium in solution between an open-chain and a cyclic structure (eq 1). Most of the reactions of this substance involved further loss of nitrogen, which added complications to the investigation although at the same time giving



(1)

interesting information. In order to reduce such complications and to gain further information about fragmentation products of heterocyclic azides, we have now investigated the analogous pyrazole systems.

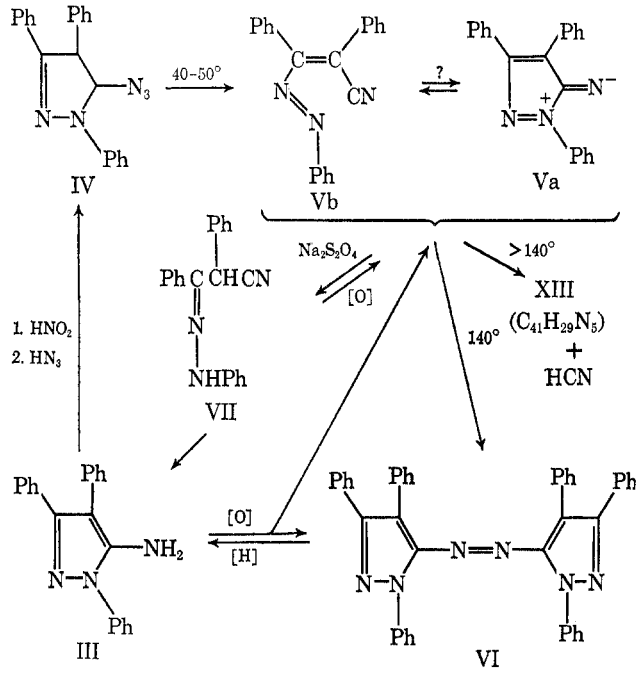
(1) Presented in part at the 153rd National Meeting of the American Chemical Society, Miami Beach, Fla., March 1967. Address correspondence to P. A. S. S.

(2) P. A. S. Smith, L. O. Krbechek, and W. Resemann, *J. Amer. Chem. Soc.*, **86**, 2025 (1964).

Results

The analogous azidopyrazole (IV) was prepared from the known[3] 5-amino-1,3,4-triphenylpyrazole (III). It decomposed in solution slightly above room temperature, losing 1 mol of nitrogen, and forming a deep red product (V) nearly quantitatively (Scheme I). The

SCHEME I



infrared spectrum of V in concentrated solution showed only a very weak nitrile band at 2150 cm^{-1}.

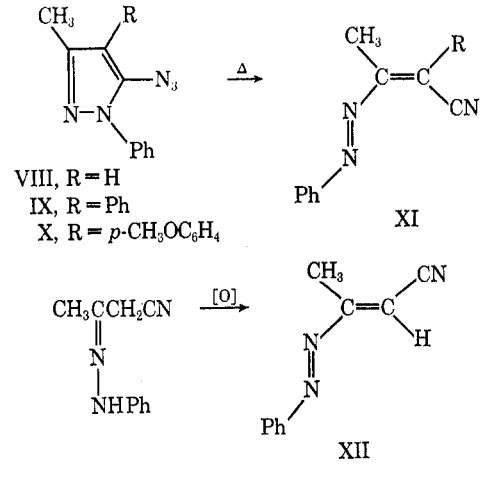
The same substance, V, was obtained by treating the amine (III) with oxidizing agents, such as dilute aqueous permanganate; the equivalent of two hydrogen atoms was consumed. The formation of V by permanganate oxidation was always accompanied by a yellow substance (VI) having the same analysis; under certain conditions, notably in solutions of low acidity, VI was overwhelmingly the major product. Molecular weight determinations were only approximate, owing to the low solubility of VI, but indicated a dimer of V. Both V and VI could be reduced to the original amine in high yield, but V was not converted to VI under the conditions of the oxidation experiments. The infrared spectrum of VI was similar to those of III and IV and was compatible with an azopyrazole structure.

Although reduction of V ordinarily gave back the aminopyrazole III, with sodium dithionite an intermediate stage could be isolated. When the reactants were mixed in aqueous alcoholic solution at room temperature, the red color of V disappeared at once. If the solution was drowned in water promptly, a colorless solid was precipitated whose melting behavior indicated a mixture, and whose infrared spectrum was consistent with an open-chain β-hydrazono nitrile structure, VII, contaminated with III. On standing, this product was converted completely to III.

The crude β-hydrazono nitrile VII was oxidized back to V (free of VI) very rapidly by treatment with N-bromosuccinimide. The cyclic isomer, III, was oxidized relatively slowly under the same conditions and gave rise to both V and VI. The chemistry of the fragmentation products of the 1-*p*-tolyl and 4-*p*-chlorophenyl analogs of IV was completely parallel to that of the triphenyl system. The permanganate oxidation of the 1-*p*-tolyl analog of III, however, gave only the azoxypyrazole rather than the azopyrazole, whereas phenyliodoso acetate gave, very slowly, the analog of V.

Three 5-azidopyrazoles bearing a methyl group in the 3 position [1-phenyl-3-methyl- (VIII), 1,4-diphenyl-3-methyl- (IX), and 1-phenyl-3-methyl-4-*p*-anisyl-5-azidopyrazole (X)] each gave rise to red substances analogous to V in high yields at mild temperatures. However, oxidation of the corresponding β-hydrazono nitriles gave substances isomeric with, but functionally similar to, the fragmentation products of the azides, and only in one case, the phenylhydrazone of α-anisylacetoacetonitrile, was any of the fragmentation isomer formed as well.

Azide VIII lost nitrogen to form a red substance, mp 61°, whose nmr and ultraviolet spectra were distinct from, although similar to, those of the oxidation product, mp 81°, of the phenylhydrazone of acetoacetonitrile. These isomers could not be interconverted by heating in various solvents, but brief exposure of the 61° compound to hydrochloric acid converted it to the 81° compound. The small differences in their spectra are consistent with their formulation as geometrical isomers (XI and XII). Permanganate oxidation of 5-amino-1-phenyl-3-methylpyrazole gave the azo dimer accompanied by products of more deep-seated changes, which were not further investigated. Oxidation with hydrogen peroxide in acetic acid gave only the oxygenated dimer reported by Searles and Hine.[4] In hydrochloric acid, oxidation by peroxide gave instead 4,4-dichloro-3-methyl-1-phenylpyrazol-5-one, and oxidation



with N-bromosuccinimide in the presence of pyridine gave 2-bromo-3-phenylazocrotononitrile. The cleanest oxidation was with phenyliodoso acetate, which gave XI in high yield. In no case were we able to detect formation of the phenylazocrotononitrile of mp 109° reported by Searles and Hine[4] and Michaelis and Schäfer.[5] The thermolysis product of IX and the oxidation product of the phenylhydrazone of α-phenylacetoacetonitrile showed similar differences.

(3) R. Walter and P. G. Schickler, *J. Prakt. Chem.*, [II] **55**, 305 (1897).

(4) S. Searles, Jr., and W. R. Hine, Jr., *J. Amer. Chem. Soc.*, **79**, 3175 (1957).

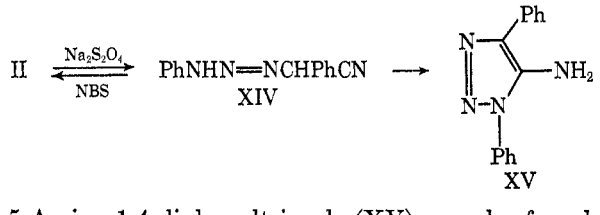
(5) A. Michaelis and A. Schäfer, *Ann.*, **397**, 119 (1913); **407**, 234 (1915).

The *p*-methoxy analog of IX, 1-phenyl-3-methyl-4-*p*-anisyl-5-azidopyrazole (X), gave a single product upon thermolysis, which could be reduced to the phenylhydrazone of α-anisylacetoacetonitrile. Oxidation of the phenylhydrazone gave a mixture of two isomers, the nmr spectrum of which corresponded to that of the product from thermolysis of the azide plus an isomer in smaller amount with methyl resonances slightly shifted from those of the other in the ratio 3:1.

In none of the foregoing three systems could interconversion of the isomeric products be observed under the conditions of the thermolyses or oxidations. The β-hydrazono nitriles, however, readily cyclized to the aminopyrazoles. No conditions could be found that would accomplish partial reduction to the intermediate hydrazopyrazole stage.

Although the fragmentation product V did not show detectable conversion to the azo dimer VI under the experimental conditions used to produce V and/or VI, other ways to bring about such a conversion were found. Heating at temperatures below 100° left V unchanged, and heating at 170° formed XIII, $C_{41}H_{29}N_5$ (dimerization with loss of hydrogen cyanide, a study that will be reported separately), but heating under vacuum at intermediate temperatures, such that sublimation took place, converted V slowly and incompletely to its azo dimer (with concurrent formation of some XIII). The fragmentation products of the other triaryl-5-azidopyrazoles also dimerized under these conditions. In another investigation, dealing with the reaction of Grignard reagents with V and analogs, dimerization was also encountered quite unexpectedly. Treatment of V with phenylmagnesium bromide (among others) resulted in rapid reaction (change of color, qualitative disappearance of Grignard reagent); work-up produced the azo dimer VI in high yields. The function of the Grignard reagent in this conversion has not been fully elucidated, but it is not reduction followed by oxidation by air. Treatment with strong sodium hydroxide solution also caused dimerization.

The isolation of β-hydrazono nitrile intermediates in the reduction of V and its analogs was found to be paralleled by the reduction of the fragmentation product (II) of the azidotriazole I which we had earlier observed[2] to result in formation of the aminotriazole (XV). Treatment of II with sodium dithionite under the same mild conditions as used with V formed a highly labile, colorless, crystalline substance isomeric with the aminotriazole XV, to which it could be isomerized. This substance was easily oxidized back to II and must possess the triazene structure XIV or a tautomer thereof.



5-Amino-1,4-diphenyltriazole (XV) was also found to undergo oxidation in a manner analogous to the aminopyrazoles. The azo dimer predominated in oxidation by permanganate, the amount depending on the acidity of the medium.

Discussion

The foregoing results show that decomposition of 5-azidopyrazoles and 5-azidotriazoles results in fragmentation with ring opening to form nitriles such as Vb, IIb, and XI. The observations that the first stage in reduction has an open-chain structure, which is more easily reoxidized than is the cyclic tautomer (*e.g.*, III), neutralize the earlier argument that exceptionally easy reduction to cyclic products implied the electronically stabilized, cyclic, singlet nitrene structure (Va, etc.).

On the other hand, dimerization of the fragmentation products upon heating is not so simply reconciled with an open-chain structure and is best explained by equilibration with a significant (although perhaps quite small) concentration of the cyclic, nitrenoid form such as Va. The structure of the dimers as symmetrical azo compounds is well supported by spectrographic similarity between them and compounds of known pyrazole (or triazole) structure, by the fact that, when aliphatic protons are present, a symmetrical dimer is indicated by the nmr spectrum and by the observation that the chemistry of the dimers parallels that of aromatic azo compounds.

The observations on oxidation of the amines (*e.g.*, III) and hydrazono nitriles (*e.g.*, VII) raise two important questions: why were the monomeric products in some cases isomeric with those from fragmentation of the corresponding azides, and how did the dimeric products arise under conditions where the monomers were stable? Three explanations of the first question suggest themselves. One possible answer, that the conditions of the oxidation experiments were sufficient to catalyze conversion to a more stable geometrical isomer, is not tenable. The oxidations were for the most part carried out in neutral or mildly basic media in which the isomers, such as X and XI, were observed to be quite stable to interconversion.

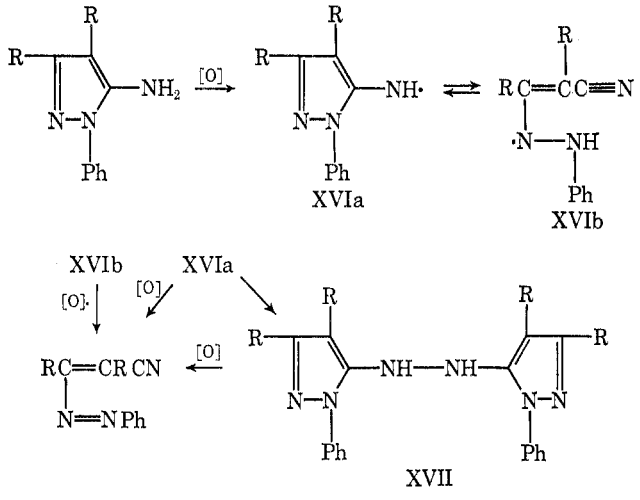
A more likely explanation is a consequence of the fact that the geometry about the α,β carbon–carbon bond in β-hydrazono nitriles is not fixed as it is in the cyclic tautomers. The geometry of the oxidation product, whether kinetically or thermodynamically determined, need not then be the same as that from the azide. Ring–chain tautomerism in certain amino azoles is well established,[6] and it is reasonable to assume that it can occur with the amino pyrazoles. The fact that oxidation of the open-chain forms is demonstrably much faster than oxidation of the cyclic tautomers is consistent with the hypothesis that ring opening to the β-hydrazono nitrile structure may precede the oxidation step for amino azoles.

Lastly, oxidation may proceed in two stages through an amino radical (XVI) which may also undergo ring–chain tautomerization before further oxidation to the isolated product. This possibility provides an explanation for the second question. Dimerization of amino radicals to form hydrazopyrazoles (XVII) (or hydrazotriazoles) provides a reasonable route to the observed azo dimers.[7] Further oxidation of the amino radicals would, of course, be competitive with dimerization and would be influenced by conversion to their

(6) For example, see F. R. Benson, "Heterocyclic Compounds," Vol. 8, R. C. Elderfield, Ed., John Wiley and Sons, Inc., New York, N. Y., 1967, p 63.

(7) L. Horner and J. Dehnert, *Ber.*, **96**, 786 (1963).

conjugate acids with the result that the proportion of monomer to dimer in the products would vary with the oxidation conditions, as observed. An alternative explanation is that the azo compounds may arise by reaction of a nitroso compound with unchanged amine



XVIa XVIb XVII

(Mills reaction) as demonstrated by Konaka, Koruma, and Terabe for basic oxidation of primary arylamines.[8] This path would not, of course, be available in thermolysis of azides. Although the fact that no nitroso compounds or derived oxygenated functional groups could be detected with most of the amines does not encourage the view that nitroso compounds are involved in our oxidations (which were mostly carried out in neutral to acidic medium); the fact that one example (1-*p*-tolyl-3,4-diphenyl-5-aminopyrazole) did give an azoxy compound demands that involvement of a nitroso intermediate be taken seriously. Unfortunately, the nitrosopyrazoles could not be prepared for investigation, but in other situations it has been shown[8] that azoxy compounds may arise from N-hydroxyhydrazine intermediates in the Mills reaction.

The two isomeric, orange-red β-phenylazocrotononitriles that we have obtained, mp 61 and 81°, do not correspond with the one obtained by Searles and Hine,[4] mp 109°, "ivory" in color from the peroxide oxidation of 1-phenyl-3-methyl-5-aminopyrazole followed by sublimation and from oxidation of acetoacetonitrile phenylhydrazone, and which they felt to be the same as "azipyrazole" obtained by Michaelis and Schäfer.[5] Since we were not able to obtain this substance by any procedure, we have not been able to compare it with our substances. The isomer of mp 81° is presumably the same one reported by Quilico and coworkers[9] and also obtained by Searles and Hine. It sublimed unchanged without detectable conversion to the substance of mp 109°. There are, of course, four possible geometrically isomeric β-phenylazocrotononitriles, whose electronic spectra would vary with the effectiveness of conjugation.

The isomer obtained from the azide must have a *trans*-azo configuration with the methyl group *trans* to the cyano group (XI) as fixed by the ring structure from which it is derived. Since the isomer of mp 81° is thermodynamically more stable, it, too, must have the *trans*-azo configuration and consequently must have the methyl group *cis* to the cyano group (XII). Isomerization of XI to XII would reduce interference and lower energy only when R = H; it is thus understandable that only in this instance was isomerization observed. The "azipyrazole" of Michaelis, which Searles and Hine[4] have convincingly deduced to be a β-phenylazocrotononitrile, would then have to have a *cis*-azo configuration.

There is no compelling reason not to accept a concerted fragmentation process for thermolysis of the foregoing 5-azido azoles to unsaturated nitriles, but it should be noted that the bicyclic azirine structure assigned to "azipyrazole" by Michaelis and Schäfer[5] is analogous to the cyclohexadienoazirine that has been proposed as an intermediate in certain reactions of arylnitrenes,[10] perhaps in equilibrium with the singlet nitrene.

A number of examples of the analogous opening of pyrazole, indolizine, and pyrrolopyrimidine rings by an alternative nitrene-forming reaction, deoxygenation of nitro and nitroso azoles, have recently been reported.[11]

Experimental Section[12]

α-*p*-Chlorophenylbenzoylacetonitrile was prepared by adding 8 g of potassium *t*-butoxide to 10 g of ethyl benzoate and 10 g of *p*-chlorophenylacetonitrile in 50 ml of dimethylformamide. After the initial exothermic reaction, the mixture was stirred for 2 hr and then poured into ice water with stirring. After extraction of insoluble material with ether, the aqueous solution was acidified, precipitating 7.0 g (30%) of a cream-colored solid, mp 100°. Recrystallization from aqueous ethanol gave an analytical sample, mp 102–104°.

Anal. Calcd for $C_{15}H_{10}ClNO$: C, 70.49; H, 3.94; N, 5.45. Found: C, 70.63; H, 4.04; N, 5.39.

α-*p*-Anisylacetoacetonitrile.—This substance was prepared in 60% yield from *p*-anisylacetonitrile and ethyl acetate in dimethylformamide solution in the presence of 1 equiv of potassium *t*-butoxide, as described for the foregoing compound. It formed cream-colored needles, mp 83–85°.

Anal. Calcd for $C_{11}H_{11}NO_2$: C, 69.82; H, 5.86; N, 7.40. Found: C, 69.99; H, 5.78; N, 7.35.

Aminopyrazoles. 5-Amino-3,4-diphenyl-1-*p*-tolylpyrazole.—An aqueous solution of 5.0 g of *p*-tolylhydrazine hydrochloride was added to a warm solution of 7.5 g of α-benzoylphenylacetonitrile in 100 ml of glacial acetic acid, and the mixture was heated on a steam bath for 25 hr. Drowning the mixture in 300 ml of ice-cold water precipitated 7.0 g (65%) of the pyrazole. Recrystallization from chloroform–ethanol mixture gave an analytical sample, pale yellow needles, mp 183–185°.

Anal. Calcd for $C_{22}H_{19}N_3$: C, 81.20; H, 5.89; N, 12.91. Found: C, 80.96; H, 6.11; N, 12.76.

5-Amino-4-*p*-anisyl-3-methyl-1-phenylpyrazole was prepared in a similar manner, colorless needles, mp 137–139°.

Anal. Calcd for $C_{17}H_{17}N_3O$: C, 73.09; H, 6.13; N, 15.04. Found: C, 72.85; H, 6.03; N, 15.02.

5-Amino-4-*p*-chlorophenyl-1,3-diphenylpyrazole, mp 149–150°, was also prepared in this way.

Anal. Calcd for $C_{21}H_{16}N_3Cl$: C, 72.93; H, 4.66; N, 12.15; Cl, 10.26. Found: C, 73.05; H, 4.64; N, 12.10; Cl, 10.26.

5-Azido-1,3,4-triphenylpyrazole.—Benzoylphenylacetonitrile was treated with phenylhydrazine to obtain 5-amino-1,3,4-triphenylpyrazole, mp 168–169°, originally reported[3] as the phenylhydrazone of the keto nitrile, mp 169°. Diazotization of

(8) R. Konaka, K. Koruma, and S. Terabe, *J. Amer. Chem. Soc.*, **90**, 1801 (1968).

(9) A. Quilico and R. Justoni, *Rend. Ist. Lomb. Sci. Lett.*, **69**, 587 (1963); A. Quilico, R. Fusco, and V. Rosanti, *Gazz. Chim. Ital.*, **76**, 30 (1946).

(10) R. A. Abramovitch and B. A. Davis, *Chem. Rev.*, **64**, 149 (1964).

(11) (a) J. B. Wright, *J. Org. Chem.*, **34**, 2474 (1969); (b) W. J. Irwin and D. G. Wibberley, *Chem. Commun.*, 878 (1968); (c) H. Dounchis, doctoral dissertation, University of Michigan, 1968.

(12) Melting points are corrected. Infrared spectra were taken on a Perkin-Elmer Model 237B instrument. Nmr spectra were determined with a Varian Model A60 instrument. Ultraviolet spectra were measured with a Cary Model 11 spectrophotometer. Microanalyses were performed by Spang Microanalytical Laboratories, Ann Arbor, Mich., and Micro-Tech Laboratories, Skokie, Ill.

TABLE I
5-AZIDOPYRAZOLES AND THEIR THERMOLYSIS PRODUCTS

5-Azidopyrazole	Mp, °C	Thermolysis product: Yield, %	Thermolysis product: Mp, °C	Thermolysis product: Color
1-Phenyl-3-methyl[a] (a)	Oil	50[b]	59.5–61	Deep red
1-*p*-Tolyl-3,4-diphenyl[c] (b)	110 dec	87[d]	135–137	Red
1,4-Diphenyl-3-methyl[e] (c)	73–74 dec	60[f]	102–104	Deep red
1-Phenyl-3-methyl-4-*p*-nitrophenyl[g] (d)	108 dec	88[h]	167–169	Bronze-red
1,3-Diphenyl-4-*p*-chlorophenyl[g] (e)		*i*	157–158	Red
1-Phenyl-3-methyl-4-*p*-anisyl[g] (f)		80[i]	126–127	Red
1,4-Diphenyl[g] (g)	68–69 dec	90[k]	100	Garnet

[a] Accompanied by 10–15% of 1-phenyl-3-methyl-4-nitroso-5-aminopyrazole, mp 202° (lit. 200°), and not obtained pure. [b] Nmr ($CDCl_3$) δ 2.13 ppm (C-CH_3); uv max (ethanol) 323 (ϵ 38,900), 238 (3000) and 232 mμ (3000); ir (Nujol) 2220, 1820 (w), 1620, 1595, 1585, 1485 cm^{-1}. *Anal.* Calcd for $C_{10}H_9N_3$: C, 70.15; H, 5.30; N, 24.55. Found: C, 70.40; H, 5.40; N, 24.60. [c] *Anal.* Calcd for $C_{22}H_{17}N_5$: C, 75.19; H, 4.88; N, 19.93. Found: C, 75.25; H, 5.06; N, 19.79. Yield, 80%. [d] Nmr ($CDCl_3$) δ 2.40 (s, 3), 7.0–7.6 (m, 12), 7.77 (s, 1), and 7.92 ppm (s, 1); ir (Nujol) 2230 (w) 1610, 1595 (w), 1575 (w) cm^{-1}. *Anal.* Calcd for $C_{22}H_{17}N_3$: C, 81.71; H, 5.30; N, 13.00. Found: C, 81.63; H, 5.37; N, 13.06. [e] Attempts at recrystallization resulted in decomposition; estimated yield 60%. [f] Based on amine. Nmr (CCl_4) δ 2.33 (s, 3), 7.3–7.7 (m, 8), and 7.9–8.2 ppm (m, 2); ir (Nujol) 2210, 1575–1600, 1445, and 1430 cm^{-1}. *Anal.* Calcd for $C_{16}H_{13}N_3$: C, 77.71; H, 5.30; N, 16.99. Found: C, 77.62; H, 5.44; N, 16.91. [g] Not purified or analyzed. [h] Based on amine. Nmr ($CDCl_3$) δ 2.20 (s, 3), 7.4–8.4 (m, 7), 8.25 (s, 1), and 8.4 ppm (s, 1); ir (Nujol) 2220 (w), 1610, 1600, 1520–1530, 1410 cm^{-1}. *Anal.* Calcd for $C_{16}H_{12}N_4O_2$: C, 65.75; H, 4.14; N, 19.17. Found: C, 65.82; H, 4.21; N, 19.10. [i] Ir (Nujol) 2220 (w), 1595, 1490, 1445, 1435 cm^{-1}. *Anal.* Calcd for $C_{21}H_{14}N_3Cl$: C, 73.35; H, 4.11; N, 12.22. Found: C, 73.34; H, 4.13; N, 12.16. [j] Based on amine. Nmr ($CDCl_3$) δ 2.25 (s, 3, C-CH_3), 3.81 (s, 3, O-CH_3), 6.87 (s, 1), 7.03 (s, 1), 7.3–7.7 (m, 5), and 7.05–8.05 ppm (m, 2); ir (Nujol) 2220, 1610, 1590, 1515, 1420 cm^{-1}. *Anal.* Calcd for $C_{17}H_{15}N_3O$: C, 73.63; H, 5.45; N, 15.15. Found: C, 73.59; H, 5.47; N, 15.17. [k] Based on amine. *Anal.* Calcd for $C_{15}H_{11}N_3$: C, 77.24; H, 4.76; N, 18.02. Found: C, 77.36; H, 4.82; N, 18.00.

1.56 g (0.01 mol) of amine dissolved in 100 ml of concentrated hydrochloric acid with the help of *ca.* 25 ml of glacial acetic acid was accomplished by adding a concentrated solution of 0.38 g of sodium nitrite all at once to the chilled solution, which became red. After 15 min, a little urea was added, followed by 0.4 g of sodium azide dissolved in a little water; some gas was evolved slowly. Addition of water in portions (total *ca.* 50 ml) precipitated a cream-colored, crystalline substance. The mixture was filtered after 3 hr and the solid was washed with water; wt 1.55 g (89%), mp 90° with gas evolution and formation of a red melt. Recrystallization from cold acetone by addition of water gave an analytical sample: mp 93–96° dec; ir (Nujol) 2128, 2080 (w) cm^{-1} (-N_3).

Anal. Calcd for $C_{21}H_{15}N_5$: C, 74.76; H, 4.48; N, 20.76. Found: C, 74.80; H, 4.20; N, 20.70.

The other 5-azidopyrazoles were prepared similarly; they are listed in Table I.

Thermolysis of 5-Azido-1,3,4-triphenylpyrazole.—A solution of 1.19 g of the azide in 30 ml of ligroin was heated near the boiling point for 30 min. The blood-red solution deposited clusters of deep red needles of V on cooling; they were collected by filtration and washed with light petroleum ether: wt 1.00 g (96%); mp 140–141° after partial liquefaction and resolidification over the range 125–135°; uv max (hexane) 359 mμ (ϵ 2.13 × 10^4); ir (Nujol) 2220 (w), 1610 (w), 1595 (w), 1570 (w), and 1305 cm^{-1}; nmr ($CDCl_3$) δ 8.7 (m, 13) and 9.45 ppm (m, 2). An analytical sample recrystallized from isopropyl alcohol had mp 141–142° (softened 125–130°).

Anal. Calcd for $C_{21}H_{15}N_3$: C, 81.53; H, 4.89; N, 13.58. Found: C, 81.78; H, 4.95; N, 13.50.

The thermolysis products of the other 5-azidopyrazoles are listed in Table I.

Reduction of V. A. With Mercaptoacetic Acid.—A suspension of 0.35 g of V in 6 ml of isopropyl alcohol was mixed with 0.3 ml of 80% aqueous mercaptoacetic acid. The red color disappeared in a few moments after slight warming was applied without apparent gas evolution. Filtration of the cooled mixture left pale, cream-colored crystals of amine III which were washed with methanol, wt 0.19 g (55%), mp 168° (undepressed by an authentic sample). From the filtrates, a further 0.11 g was obtained (total yield 85%).

B. With Sodium Dithionite.—When samples of V were shaken in ethereal solution with aqueous sodium dithionite, the red color took nearly 30 min to disappear, and the product obtained was amine III. When 0.3 g of V was dissolved in 50 ml of ethanol and added all at once to 50 ml of a concentrated aqueous solution of sodium dithionite, the color disappeared at once. The resulting mixture was immediately poured into 250 ml of cold water (total elapsed time ~30 sec), and the off-white precipitate was filtered off and washed with water: mp 60–80°, with resolidification at *ca.* 100° and remelting at 168–169° (mp of amine III); ir (Nujol) 3300 (s) (NH) and 2200 (s) (-C≡N) cm^{-1}. All attempts at purification by recrystallization or sublimation gave only amine III, and the spectrum of freshly prepared solutions corresponded to a mixture containing 50% or more of amine III. Thin layer chromatography showed two components, one of which was amine III and the other a more mobile substance. Treatment of the crude reduction product with 1.3 mol equiv of N-bromosuccinimide and twice its weight of pyridine in methylene chloride resulted in immediate formation of a deep red color. Evaporation of the solvent, extraction of the residue with ether, washing of the ether with dilute hydrochloric acid and with water, drying, evaporating, and crystallizing from ethanol gave pure V, mp 150°; no dimer (VI) could be detected.

Thermolysis of V.—A flask containing 100 mg of V was repeatedly evacuated and flushed with nitrogen, after which the pressure was reduced to 20 mm and the vessel was heated at 140° for 18 hr. When the cooled residue was stirred with acetone and then filtered, 15 mg (15%) of VI, mp 269°, was obtained. Addition of water to the filtrate precipitated a red substance (XIII), the major product, in varying but substantial yields. Recrystallization from aqueous acetone gave an analytical sample as bright red plates: mp 149–151°; uv max (ethanol) 262 mμ (ϵ 17,000), 387 (7000), 430 (shoulder, 5000).

Anal. Calcd for $C_{41}H_{29}N_5$: C, 83.22; H, 4.94; N, 11.84; mol wt, 591.68. Found: C, 83.07; H, 4.79; N, 12.11; mol wt (mass spectroscopy), 591.

Similar results were obtained from experiments in which the residual atmosphere was oxygen instead of nitrogen. At higher temperatures (*e.g.*, 145°), no VI was produced, and the only product was XIII in yields up to 80%; at lower temperatures, little or no reaction occurred in a reasonable time.

Similar results were obtained with the 1-*p*-tolyl analog of V (the thermolysis product of 1-*p*-tolyl-3,4-diphenyl-5-azidopyrazole) which at 115° gave rise in 20% yield to the azopyrazole dimer. At temperatures of 130° and above, this substance was not detected; instead, a red compound was formed, analogous to that from the triphenyl derivative: mp 170–172°; uv max (ethanol) 251 mμ (ϵ 15,000), 356 (6000), 380 (shoulder, 3500).

Anal. Calcd for $C_{43}H_{33}N_5$: C, 83.33; H, 5.37; N, 11.30. Found: C, 83.32; H, 5.31; N, 11.41.

Reaction of V with Sodium Hydroxide.—A suspension of 500 mg of V in 25% sodium hydroxide solution was overlaid with tetrahydrofuran and allowed to stand for 20 hr. The residual solid was collected and extracted with warm ethanol which left 50 mg (10%) of the dimer VI, mp 270°. The filtrate deposited crystals of 5-amino-1,3,4-triphenylpyrazole on cooling, wt 200 mg (40%), mp 170°.

Oxidation of Aminopyrazoles.—The various aminopyrazoles were oxidized in a manner similar to the experiments described here for the representative example, 5-amino-1,3,4-triphenylpyrazole (III). A solution of 0.50 g (1.6 mmol) of III in 10 ml of benzene was stirred briefly with a solution of 0.20 g (1.25 mmol) of potassium permanganate in 10 ml of water; no visible reaction took place until *ca.* 1 ml of glacial acetic acid was added, whereupon the benzene layer gradually became vermilion, and a sludge of manganese dioxide formed. After 18 hr, the mixture was filtered, and the filter cake was washed well with hot benzene. The combined benzene solutions were washed with water, filtered through cotton, and evaporated, leaving a vermilion powder, wt 0.41 g (82%), mp 214–218°. Washing with boiling isopropyl alcohol removed the red color and left a bright yellow powder, mp 269–270°. Recrystallization from benzene or glacial acetic acid gave an analytical sample of VI: mp 271–272°; nmr (CF_3COOH) δ 8.3–9.3 ppm (m); ir (Nujol) 1650, 1600, and 1500 cm^{-1}.

Anal. Calcd for $C_{42}H_{30}N_6$: C, 81.53; H, 4.89; N, 13.59. Found: C, 81.13; H, 4.84; N, 13.85.

A similar experiment in which the reaction medium was 30 ml of 5% of sulfuric acid and 10 ml of acetone produced VI in 30% yield and V in 10% yield (separated by extracting the latter with chloroform or benzene and recrystallizing from 2-propanol). The actual yield of V was presumably somewhat higher for there were evident losses in separation. Experiments carried out in glacial acetic acid gave VI in approximately 80% yields accompanied by ~5% of V. The addition of about 2 ml of 2% sulfuric acid per gram of amine accelerated the disappearance of the permanganate color and caused small increases in the yield of V at the expense of VI.

Oxidation of 5-amino-4-*p*-chlorophenyl-1,3-diphenylpyrazole in a similar manner gave orange-yellow **4,4′-bis-*p*-chlorophenyl-1,1′,3,3′-tetraphenyl-5,5′-azopyrazole** in 70% yield: mp 282°; ir (Nujol) 1600, 1545, 1500, 1420 cm^{-1}.

Anal. Calcd for $C_{42}H_{28}Cl_2N_6$: C, 71.72; H, 4.10; N, 12.25. Found: C, 72.02; H, 3.95; N, 12.01.

Similarly, oxidation of 5-amino-1,4-diphenylpyrazole in glacial acetic acid gave **1,1′,4,4′-tetraphenyl-5,5′-azopyrazole**, orange needles, in 60% yield: mp 209–211°; nmr ($CDCl_3$) δ 7.25 (s, 10) and 7.72 ppm (s, 1).

Anal. Calcd for $C_{30}H_{22}N_6$: C, 77.23; H, 4.75; N, 18.02. Found: C, 77.01; H, 4.94; N, 18.06.

5-Amino-3-methyl-4-*p*-nitrophenyl-1-phenylpyrazole in glacial acetic acid when treated with aqueous potassium permanganate at ambient temperature gave **4,4′-bis-*p*-nitrophenyl-3,3′-dimethyl-1,1′-diphenyl-5,5′-azopyrazole**, orange needles, in 40% yield: mp 278–280°; ir (Nujol) 1605, 1525, 1505, 1355 cm^{-1}.

Anal. Calcd for $C_{32}H_{24}N_8O_4$: C, 65.75; H, 4.14; N, 19.17. Found: C, 65.57; H, 4.11; N, 19.20.

Oxidation of 5-Amino-3-methyl-1-phenylpyrazole. A. With Permanganate.—A solution of 0.50 g of the amine in 40 ml of glacial acetic acid and 20 ml of chloroform was titrated with aqueous potassium permangante and was then diluted with water and extracted with chloroform. The extracts were concentrated to a yellow-brown oil after washing successively with solutions of sodium bicarbonate, sodium bisulfite, and sodium chloride. Trituration with methanol gave 100 mg (21%) of **3,3′-dimethyl-1,1′-diphenyl-5,5′-azopyrazole**, yellow needles: mp 205–206° after recrystallization from ethanol; nmr ($CDCl_3$) δ 2.37 (s, 3) and 6.32 ppm (s, 1).

Anal. Calcd for $C_{20}H_{18}N_6$: C, 70.15; H, 5.30; N, 24.55. Found: C, 70.14; H, 5.24; N, 24.58.

When the oxidation was attempted in a mixture of glacial acetic acid and acetone, or in 5% aqueous sulfuric acid, only reddish oils and gums were obtained, sometimes accompanied by up to 5% of the substance $C_{20}H_{19}N_5O_2$, mp 228–229°, obtained by Searles and Hine[4] from oxidation with hydrogen peroxide. The infrared spectra of the oils and gums were consistent with mixtures of this substance and the foregoing azopyrazole.

B. With Hydrogen Peroxide.—Treatment of 2.00 g of the aminopyrazole in 15 ml of 50% acetic acid with 3 ml of 30% hydrogen peroxide and with warming for 5 hr caused precipitation of 1.14 g (60%) of a cream-colored solid: mp 228–229° dec, red melt (lit.[7] mp 229–230°); nmr (CF_3COOH) δ 2.21 (s, 1.3), 2.31 (s, 2.5), and 7.2–7.9 ppm (m, 5); ir (Nujol) 3425, 3330, 1715, 1620, 1600 cm^{-1}.

Anal. Calcd for $C_{20}H_{19}N_5O_2$: C, 66.48; H, 5.26; N, 19.39. Found: C, 66.50; H, 5.44; N, 19.49. No other product could be isolated.

C. With Hydrogen Peroxide and Hydrochloric Acid.—To a solution of 2.00 g of 5-amino-3-methyl-1-phenylpyrazole in 15 ml of concentrated hydrochloric acid was added 3 ml of 30% hydrogen peroxide. Heat was evolved and a yellow oil separated. After 2 hr of heating on a steam bath, the mixture was diluted with water and extracted with ether. Concentration of the extracts left an oil which crystallized on standing. Two recrystallizations from aqueous ethanol gave 0.35 g (12%) of yellow prisms of 4,4-dichloro-3-methyl-1-phenylpyrazol-5-one: mp 61.5–63° (lit.[13] mp 65°); nmr ($CDCl_3$) δ 2.30 (s, 3) and 7.1–8.0 ppm (m, 5).

Anal. Calcd for $C_{10}H_8N_2Cl_2O$: C, 49.42; H, 3.29; N, 11.53. Found: C, 49.12; H, 3.25; N, 11.44.

D. With NBS.—A mixture of 3.0 g of N-bromosuccinimide and 1.0 g of 5-amino-3-methyl-1-phenylpyrazole dissolved in 80 ml of methylene chloride and 2 ml of pyridine was stirred for 2 hr, during which time it became red. Water was added, and the heavy layer was washed with water, dried, and evaporated. Crystallization of the red residue from aqueous ethanol gave 0.40 g (28%) of red plates of **2-bromo-3-phenylazocrotononitrile**: mp 73–76°; nmr ($CDCl_3$) δ 2.25 (s, 3) and 7.2–7.9 ppm (m, 5).

Anal. Calcd for $C_{10}H_8N_3Br$: C, 48.01; H, 3.22; Br, 31.96. Found: C, 47.97; H, 3.32; Br, 31.89.

E. With Phenyliodoso Acetate.[14]—A solution of 0.40 g of phenyliodoso acetate in 15 ml of methylene chloride was added dropwise to a solution of 0.22 g of the aminopyrazole in 15 ml of methylene chloride with ice-cooling, and the resulting orange mixture was stirred overnight. The solution was washed with sodium bicarbonate solution and water, and concentrated at the aspirator. The residual red oil crystallized over 2 days to give massive red prisms of phenylazocrotonitrile: mp 61–62° undepressed with the thermolysis product of 5-azido-3-methyl-1-phenylpyrazole; ir spectra superimposable; wt 0.16 g (70%).

Oxidation of 5-Amino-3,4-diphenyl-1-*p*-tolylpyrazole. A. With Permanganate.—A solution of 1.0 g of the aminopyrazole in 50 ml of glacial acetic acid was titrated with 4% aqueous potassium permanganate until the purple color persisted, whereupon the mixture was diluted with 200 ml of water and treated with enough 2% aqueous sodium bisulfite to destroy the precipitate manganese dioxide. The residual yellow solid (0.78 g, 75%) was recrystallized from chloroform–ethanol mixture to give an analytical sample of **1,1′-bis-*p*-tolyl-3,3′,4,4′-tetraphenyl-5,5′-azoxypyrazole**: mp 293–295°; ir (Nujol) 1605 (w), 1540 (w), 1520 (azoxy N=N?) cm^{-1}.

Anal. Calcd for $C_{44}H_{34}N_6O$: C, 79.73; H, 5.17; N, 12.68. Found: C, 79.45, 79.83; H, 5.07, 5.00; N, 12.46, 12.65.

B. With Phenyliodoso Acetate.—A solution of 52 mg of the aminopyrazole and 52 mg of phenyliodoso acetate in 20 ml of methylene chloride was stirred for 19 hr at ambient temperature; it became orange. Concentration on a steam bath left a vermilion oil containing a few crystals; trituration with light petroleum ether left 35 mg of crude starting material, mp 173–181°. Concentration and refrigeration of the filtrate yielded red crystals: wt, 4 mg (12%); mp 138–140°; ir identical with that of the thermolysis product of the azide.

Under the same conditions, 5-amino-1,3,4-triphenylpyrazole (III) gave the corresponding product (V) in 95% yield in only 1.5 hr, and 5-amino-4-*p*-chlorophenyl-1,3-diphenylpyrazole gave the corresponding α-*p*-chlorophenyl-β-phenylazocinnamonitrile in 90% yield after 18 hr.

Oxidation of 5-Amino-1,4-diphenyltriazole.—A 4% aqueous solution of potassium permanganate was added to a solution of 1.0 g of 5-amino-1,4-diphenyltriazole in 30 ml of glacial acetic acid until the permanganate color persisted. Sodium bisulfite was added to dissolve the manganese dioxide, and the mixture was then diluted with much water, precipitating a brown material. The precipitate was collected and washed and taken up in chloroform, from which red needles of **1,1′,4,4′-tetraphenyl-5,5′-azotriazole**, mp 226–228°, slowly formed after addition of ethanol, wt 0.30 g (30%). The mother liquors yielded only brown gum on evaporation.

Anal. Calcd for $C_{28}H_{20}N_8$: C, 71.78; H, 4.30; N, 23.92. Found: C, 71.64; H, 4.30; N, 23.92.

Reduction of 1,1′,4,4′-Tetraphenyl-5,5′-azotriazole.—A solution of 300 mg of the azotriazole in 30 ml of chloroform was stirred with 3 ml of 98% hydrazine hydrate while 300 mg of 5%

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palladium on charcoal was added. After 1 hr, the mixture was filtered, and the filtrate was washed with water and brine, and was dried over magnesium sulfate. Evaporation left 270 mg (91%) of 5-amino-1,4-diphenyltriazole, mp 168° alone and when mixed with an authentic sample.

Reduction of II.—Saturated aqueous sodium dithionite was added to a solution of 2.0 g of II in 100 ml of 95% ethanol until the red color was discharged, and the resulting mixture was poured at once into a large volume of ice water. The resulting nearly colorless solid **1(3)-phenyl-3(1)-α-cyanobenzyltriazene** (XIV) was collected, washed with water, and dried: wt 1.8 g (91%); mp 138° with violet decomposition. An analytical sample was prepared by extraction with hot alcohol and recrystallization from aqueous tetrahydrofuran: mp 155° dec alone and 145–146° dec when mixed with 5-amino-1,4-diphenyltriazole (mp 178–180°); ir (Nujol) 3240, 2260 (w), 1610, 1535, 1495 cm^{-1}.

Anal. Calcd for $C_{14}H_{12}N_4$: C, 71.16; H, 5.12; N, 23.72. Found: C, 71.27; H, 5.08; N, 23.73.

Oxidation of Acetoacetonitrile Phenylhydrazone.—This substance was dissolved in methanol or ethanol and refluxed for 2 hr with mercuric oxide from various commercial batches. The cooled mixtures were filtered with the aid of Celite and the components were separated by column chromatography on alumina or by thin layer chromatography. In the several experiments without added base, only two significant substances were found: unreacted phenylhydrazone, and a red substance, mp 80–81°, apparently identical (ir and nmr) with the phenylazocrotononitrile (XII) reported by Quilico and coworkers,[9] and by Searles and Hine.[4] Yields varied from low to moderate. In other experiments sodium hydroxide, potassium hydroxide, triethylamine, or pyridine were added to the reaction mixtures. The only products in significant quantities were 1-phenyl-3-methyl-5-aminopyrazole (50 to 80% of the mixture) and the phenylazocrotononitrile (XII) of mp 80–81°: ir (Nujol) 2210, 1615 (w), 1505 (w), 1585 (w), cm^{-1}; nmr (CCl_4) δ 2.28 (d, 3, J = 0.8 Hz) (q, 1, J = 0.8 Hz) and 7.3–8.0 ppm (m, 5). In no case could any substance of mp 109° (isomeric phenylazocrotononitrile) be obtained. Sublimation of the material of mp 80–81° alone or when mixed with the aminopyrazole produced only unchanged substrate.

Isomerization of Phenylazocrotononitrile XI.—A dilute ethereal solution of 150 mg of XI was refluxed with 5 drops of 10 N HCl for 5 hr. Concentration and cooling caused crystallization of the isomer XII essentially quantitatively: mp 80° undepressed by admixture with XII obtained by oxidation of acetoacetonitrile phenylhydrazone; ir spectrum identical with that of XII. No isomerization was observed without the addition of acid or when ammonium hydroxide was used.

Oxidation of α-Acetylphenylacetonitrile Phenylhydrazone.—A solution of 0.8 g of the phenylhydrazone[15] in 30 ml of ethanol was refluxed for 5 hr with 1.5 g of yellow mercuric oxide. Thin layer chromatography showed the resulting mixture to contain 5-amino-1,4-diphenyl-3-methylpyrazole and another red substance. The filtered and concentrated mixture was digested with light petroleum ether, which left the aminopyrazole behind. The chilled and filtered extracts left a red oil on evaporation; crystallization from aqueous ethanol gave brilliant red plates of an **α-phenyl-β-phenylazocrotononitrile:** mp 110–111° (mp 80–84° when mixed with the thermolysis product of 5-azido-1,4-diphenyl-3-methylpyrazole); nmr ($CDCl_3$) δ 2.47 (s, 3) and 7.3–7.9 ppm (m, 10).

Anal. Calcd for $C_{16}H_{13}N_3$: C, 77.71; H, 5.30; N, 16.99. Found: C, 77.55; H, 5.28; N, 17.00.

Oxidation of α-Acetyl-p-methoxyphenylacetonitrile Phenylhydrazone.—A suspension of 2.5 g of yellow mercuric oxide in ethanol was heated to boiling and 1.0 g of the phenylhydrazone was added in portions over 5 min after which refluxing was continued for 2 hr. Filtration and concentration gave a red gum which was taken up in benzene and filtered through a short column of silica gel; 380 mg (40%) of red needles, mp 100–110°, separated from the filtrate on standing. Recrystallization from aqueous ethanol did not change the mp which was not depressed by admixture with the thermolysis product of 5-azido-1-phenyl-4-p-methoxyphenyl-3-methylpyrazole (mp 126–127°), and the infrared spectra of the two substances were essentially the same: nmr ($CDCl_3$) δ 2.77 (s, 2.25, C–CH_3), 2.48 (s, 0.75, C–CH_3), 3.87 (s, 3, O–CH_3), and 6.85–8.1 ppm (m, 9) (C–CH_3 intensities correspond to a 3:1 mixture).

Registry No.—Table I—a, 24515-19-3; a (cyclic product),[16] 24514-90-7; a (noncyclic product), 24515-82-0; b, 24514-91-8; b (cyclic product), 24515-20-6; b (noncyclic product), 24515-83-1; c, 24514-92-9; c (cyclic product), 24515-21-7; c (noncyclic product), 24515-84-2; d, 24514-93-0; d (cyclic product), 24515-22-8; d (noncyclic product), 24515-85-3; e (cyclic product), 24514-94-1; e (noncyclic product), 24515-86-4; f (cyclic product), 24515-23-9; f (noncyclic product), 24515-87-5; g, 24514-95-2; g (cyclic product), 24515-24-0; g (noncyclic product), 24515-88-6; Va, 24514-96-3; Vb, 24514-99-6; VI, 24514-97-4; XII, 24514-98-5; XIV, 24515-14-8; α-p-chlorophenylbenzoylacetonitrile, 5415-05-4; α-p-anisylacetoacetonitrile, 5219-00-1; 5-amino-3,4-diphenyl-1-p-tolylpyrazole, 24515-02-4; 5-amino-4-p-anisyl-3-methyl-1-phenylpyrazole, 24515-03-5; 5-amino-4-p-chlorophenyl-1,3-diphenylpyrazole, 24515-04-6; 5-azido-1,3,4-triphenylpyrazole, 24515-05-7; 4,4′-bis-p-chlorophenyl-1,1′,3,3′-tetraphenyl-5,5′-azopyrazole, 24515-06-8; 1,1′,4,4′-tetraphenyl-5,5′-azopyrazole, 24515-07-9; 4,4′-bis-p-nitrophenyl-3,3′-dimethyl-1,1′-diphenyl-5,5′-azopyrazole, 24515-08-0; 3,3′-dimethyl-1,1′-diphenyl-5,5′-azopyrazole, 24515-09-1; 4,4-dichloro-3-methyl-1-phenylpyrazol-5-one, 24515-10-4; 2-bromo-3-phenylazocrotonitrile, 24515-11-5; 1,1′-bis-p-tolyl-3,3′,4,4′-tetraphenyl-5,5′-azoxypyrazole, 24523-23-7; 1,1′,4,4′-tetraphenyl-5,5′-azotriazole, 24515-12-6; α-phenyl-β-phenylazocrotononitrile, 24515-13-7.

Acknowledgment.—We are grateful for support of this work by grants from the National Science Foundation (GP 3536, GP 6463).

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(16) Cyclic product refers to structure type Va and noncyclic product refers to structure type Vb (Scheme I).