[CONTRIBUTION FROM DEPARTMENT OF CHEMISTRY, KANSAS STATE COLLEGE]

Oxidative Cleavage of the Pyrazole Ring and the Structure of Azipyrazole

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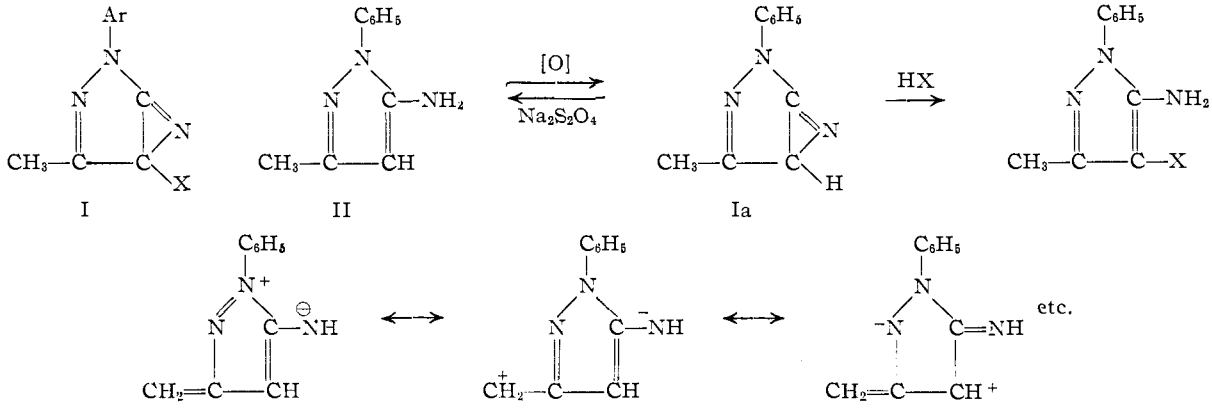
Azipyrazole, a compound formed by the action of hydrogen peroxide on 5-amino-3-methyl-1-phenylpyrazole (II), was previously assigned a structure possessing the 2,3,6-triazabicyclo[3,1,0]-3,6-hexadiene ring system, in common with several other closely related compounds. Reinterpretation of the old chemical evidence for this structure, as well as new data, leads to reformulation of the structure of azipyrazole as 3-(phenylazo)-crotononitrile. Confirmation of this structure was obtained by two independent syntheses. Evidence was obtained for two geometrical isomers. A mechanism is proposed for the oxidative cleavage of the pyrazole ring, which is apparently a new reaction. Other products of the oxidation of II are 3-(phenyl-NON-azoxy)-crotonamide and di-(3-methyl-1-phenyl-5-pyrazolyl)-amine 2,2′(?)-dioxide.

An unusual new class of compounds, called "azipyrazoles," was reported by Michaelis and associates during the period 1905–1915.[1] These compounds seem of particular interest because of the 2,3,6-triazobicyclo[3,1,0]-3,6-hexadiene ring system[2] assigned to them. The assigned structures of the compounds known in this series can be generalized as I, with X and A_2 varying but all alike with regard to the methyl group.

Such a fusion of 3- and 5-membered unsaturated rings not only is unique but would be expected to lead to extremely high internal strain. The reported properties of the compounds, however, indicate ordinary stability. Nevertheless, the assigned structures cannot be immediately dismissed, for they are supported by several lines of experimental evidence. The paradox has been recognized recently by Erickson, who has reviewed the chemistry of these compounds.[3]



Our attention has been directed in the present study to the first and simplest azipyrazole reported, which has the specific name, "azipyrazole," and which seems typical of the general class. It had been assigned the structure Ia on the following bases: (1) its synthesis from 5-amino-3-methyl-1-phenylpyrazole (II) by mild oxidation with nitrous acid or with hydrogen peroxide in aqueous acetic acid, reportedly a general method of synthesis of azipyrazoles; (2) the elemental analyses and molecular weight determinations, which were in excellent agreement with the assigned structure and showed that the synthesis had caused loss of two hydrogens; (3) the general stability of the pyrazole ring toward oxidizing agents[4]; (4) easy formation of known pyrazoles as derivatives—compound II by sodium hydrosulfite reduction and the 4-halogeno derivatives of II by treatment with aqueous hydrochloric, hydrobromic and hydriodic acids.

Erickson[3] made the interesting suggestion that the structure of azipyrazole could be more plausibly interpreted by the mesoionic formulation

A third isomeric structure for azipyrazole is also possible, as will be shown below. It was the purpose of this work to determine which formulation might be correct.

The procedure described by the previous workers[1c] for the preparation of azipyrazole gave different results in our hands, a quite different product being obtained in good yield, as described later. By carrying out the oxidation with 90% hydrogen peroxide in glacial acetic acid and using high vacuum sublimation for purification, however, a compound was isolated, which fitted the description of azipyrazole exactly, except for its having an ivory rather than light brown color. This is understandable since the previous isolation was by crystallization of the dark brown crude product. The melting point (109°) checked with the literature, as well as the facile formation of 5-amino-3-methyl-1-phenylpyrazole (II) on reduction and the corresponding 4-bromo- and 4-iodo compounds on treating with hydrobromic and hydriodic acids.

The infrared spectrum of this compound differed from that of its precursor, II, in having new bands

(1) (a) A. Michaelis and E. Brust, *Ann.*, **339**, 138 (1905); (b) A. Michaelis and L. Klappert, *ibid.*, **397**, 149 (1913); (c) A. Michaelis and A. Schafer, *ibid.*, **397**, 119 (1913); (d) **407**, 234 (1915).

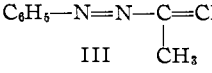
(2) R. I. no. 449, A. M. Patterson and L. T. Capell, "The Ring Index," Reinhold Publ. Corp., New York, N. Y., 1940, p. 86.

(3) J. G. Erickson in "1,2,3- and 1,2,4-Triazines, Tetrazines and Pentazines," A. Weissberger, ed., Interscience Publishers, Inc., New York, N. Y., 1957.

(4) See, for example, R. H. Wiley, "Organic Chemistry," H. Gilman, ed., Vol. IV, John Wiley and Sons, Inc., New York, N. Y., 1953, p. 777.

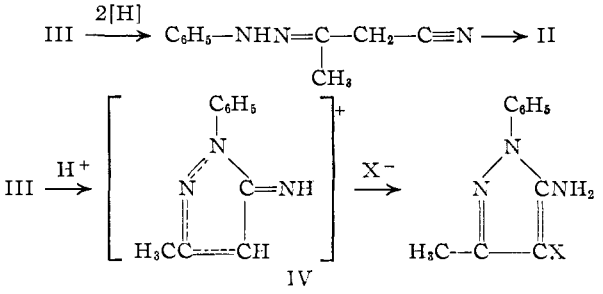
at 4.45 μ, indicative of a nitrile structure,[5] and at 6.20 and 6.25 μ, which might be assigned to a conjugated double bond and to an azo linkage. Furthermore, it lacked a band for N–H (found at 2.9 μ in II) and the bands characteristic of the pyrazole ring[6] (6.8 and 10.9 μ in II).[7] The spectrum contained bands at 7.18 and 6.76 μ which may be assigned to symmetrical and asymmetrical CH_3 deformation[5]; these would not be expected for the mesoionic formation.

It will be observed that the structure of 3-(phenylazo)-crotononitrile (III) closely fits the spectral features observed. This structure, being isomeric with Ia, fits the analytical and molecular



III

weight data, and it also provides a rational basis to explain the formation of 5-aminopyrazoles as derivatives. In the case of the reduction, conjugate addition of hydrogen may give diacetonitrile phenylhydrazone which is very easily cyclized. In the case of the reaction with the halogen acids, addition of a proton may reasonably give a hybrid cation, IV. Attack of the halide ion on this would be expected to give the observed 4-halogeno-5-amino-1-phenylpyrazole, which, of course, can exist in two tautomeric forms.



IV

Analogous ring closures have been reported with ethyl 3-(phenylazo)-crotonate: reductive ring closure by means of ammonium sulfide[8,9] or aluminum amalgam in alcohol[10] to form 3-methyl-1-phenyl-5-pyrazolone and reaction with ethereal hydrogen chloride to form 4-chloro-3-methyl-1-phenyl-5-pyrazolone.[11,12]

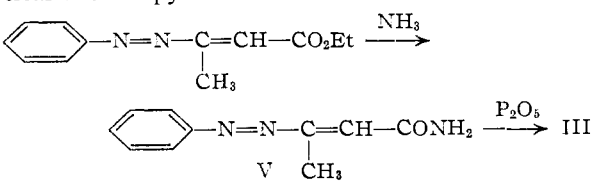
Erickson[3] has pointed out that the Michaelis formulation for azipyrazoles is inconsistent with the fact that in the presence of free halogen the phenyl group does not become halogenated, as might be expected by analogy with aniline. The new structure III is consistent with this observation, of course, because of the electron-withdrawal properties of the unsaturated nitrile side chain, due to resonance effects.

At this point it was discovered that 3-(phenylazo)-crotononitrile (III) previously had been reported in the literature as having properties distinctly different from those found for azipyrazole (orange-red color, m.p. 81°). This substance had been obtained by degradation of eulite[13] and had been synthesized also by treating the chlorination product of 5-methylisoxazole with sodium ethoxide and then with phenylhydrazine.[14] The structure III for the product of this sequence seems probable, but it was not confirmed by any supplementary work. Its *p*-nitro analog, however, was stated to react with boiling hydrochloric acid to form a compound considered to be 3-(2-chloro-4-nitrophenylhydrazino)-crotonitrile. The latter could well have been the isomeric 5-amino-4-chloro-3-methyl-1-(4-nitrophenyl)-pyrazole, which would be consistent with an azo-nitrile structure for its precursor.

It is, of course, feasible that both azipyrazole and this red compound are geometrical isomers of 3-(phenylazo)-crotononitrile, there being four such isomers theoretically possible. The lighter color of azipyrazole could reasonably be due to its configuration being more *cis* than that of the other compound, as it has been shown for polyenes that the *cis* arrangement of conjugated double bonds causes the light absorption to be less intense and to be shifted toward the low wave lengths.[15] The *cis*-configuration might be expected for azipyrazole due to its formation from a cyclic compound.

It appears that the red isomer is formed also to slight extent in the oxidation of II; it was apparently isolated, though in very small amount, and its presence would account for the orange-red color of the reaction mixture. Possibly it arises from a rearrangement of azipyrazole, though this has not been demonstrated yet.

While the discrepancy between the two reports of 3-(phenylazo)-crotononitrile thus may be due to geometrical isomerism, it seemed desirable to substantiate the structure III for azipyrazole by means of two independent syntheses. In the first of these, ethyl 3-(phenylazo)-crotonate, prepared by the mercuric oxide oxidation of the phenylhydrazone of acetoacetic ester,[9] was treated with ammonia to form 3-(phenylazo)-crotonamide (V). The reaction of this with phosphoric anhydride gave a brown solid, from which a white crystalline solid was obtained by sublimation. This proved identical with azipyrazole.



V

(5) L. J. Bellamy, "The Infrared Spectra of Complex Organic Molecules," John Wiley and Sons, Inc., New York, N. Y., 1954.

(6) C. S Rondestvedt and P. K. Chang, THIS JOURNAL, **77**, 6532 (1955).

(7) Also absent from the spectrum was any band in the 5.5 μ region, which is reported (D. J. Cram and M. J. Hatch, *ibid.*, **75**, 33 (1953)) to be characteristic of the azirine ring. The azirine ring is present, fused to the pyrrolidine ring, in the Michaelis structure.

(8) G. Bender, *Ber.*, **20**, 2747 (1887).

(9) J. U. Nef, *Ann.*, **266**, 71 (1891).

(10) J. Van Alphen, *Rec. trav. chim.*, **64**, 109 (1945), considered that aluminum amalgam reduction proceeded by conjugate addition of hydrogen to form the phenylhydrazone of acetoacetic ester, which then cyclized.

(11) P. W. Neber, G. Knoller, K. Herbst and A. Trissler, *Ann.*, **471**, 135 (1929), observed the reaction but formulated the structure of the product incorrectly.

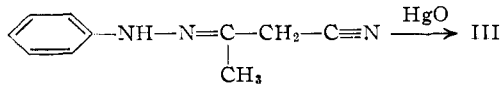
(12) J. Van Alphen, ref. 10, writes this reaction as proceeding by conjugate addition of hydrogen chloride to form an α-chlorophenylhydrazone which then cyclizes, but the cyclic transition state above seems more likely.

(13) A. Quilico, R. Fusco and V. Rosanti, *Gazz. chim. ital.*, **76**, 30 (1946).

(14) A. Quilico and R. Justoni, *Rend. inst. lombardo sci.*, **69**, 587 (1936).

(15) L. Zechmeister, *Chem. Revs.*, **34**, 267 (1944).

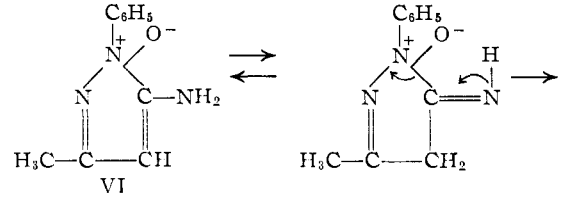
The second confirmatory synthesis of azipyrazole consisted of oxidizing diacetonitrile phenylhydrazone with mercuric oxide in alcohol. This reaction, analogous to that used for the preparation of

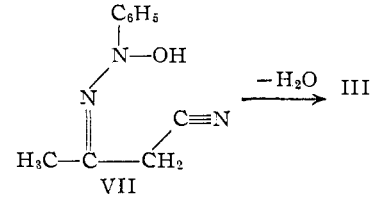


ethyl 3-(phenylazo)-crotonate, gave two crystalline products: one tan colored, m.p. 105–107°, and the other red, m.p. 82–83°. The former was identical to the azipyrazole previously obtained, and the latter appears to be the isomer described by Quilico and Justoni.[14] In view of so much evidence, there can hardly be any doubt that azipyrazole is one geometrical isomer of 3-(phenylazo)-crotononitrile.

Since oxidative cleavage of the pyrazole ring to form an unsaturated azo compound appears to be novel, one is tempted to speculate on the course of the reaction. 1-Phenylpyrazoles being actually cyclic phenylhydrazones, a formal similarity to the recently studied per-acid oxidation of acyclic phenylhydrazones is evident. The elegant study of this reaction by Lythgoe and co-workers[16] indicates that the first step in the oxidation of aldehyde phenylhydrazones is coördination of oxygen at the phenyl-substituted nitrogen, forming an N-oxide. This is followed by a tautomeric shift of hydrogen, giving the final product, an azoxy compound.

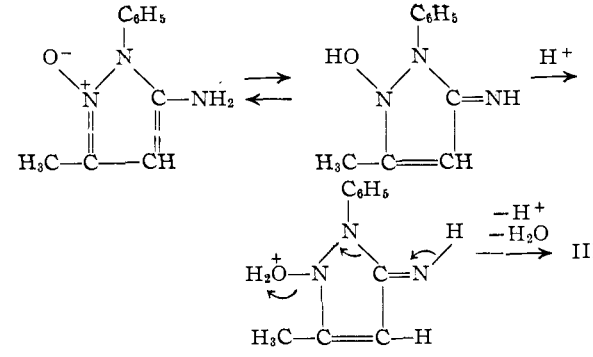
In the present case formation of the analogous pyrazole-1-oxide (VI) could be followed by an easy shift of a proton from the amino or imino group to the electro-negative oxygen and the shift of an electron pair as shown. The resulting hydroxyhydrazononitrile (VII) would be unstable in the acidic medium, losing the elements of water to form the completely conjugated azipyrazole.



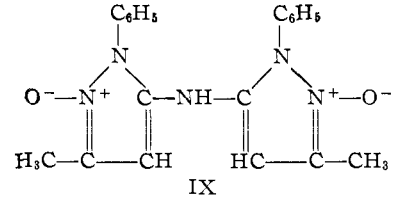


It is also possible to explain azipyrazole formation by a smooth mechanism starting with formation of the pyrazole-2-oxide (VIII).[17]

Other Products from Oxidation of II.—In the reaction of 5-amino-3-methyl-1-phenylpyrazole with hydrogen peroxide in acetic acid under all conditions used, a white crystalline compound melting at 229–230° separated quickly and could be isolated in 70% yield (pure). It seems peculiar that it was not mentioned by Michaelis and co-workers.[1] Because of its possible role as an intermediate in azipyrazole formation, its structure was investigated.



The elemental analysis and molecular weight determinations for this compound indicated an empirical formula of $C_{20}H_{19}N_5O_2$. Its infrared spectrum contained strong bands at 6.82 and 10.70 μ characteristic of the pyrazole ring,[6] at 2.85 μ characteristic of a secondary amine[5] and at 6.85 μ characteristic of an N-oxide or azoxy structure.[18,19] These data suggested that the compound was di-(3-methyl-1-phenyl-5-pyrazolyl)-amine 2,2′-dioxide (IX) or the corresponding 1,1′-dioxide.



This product may be formed by condensation of two molecules of the aminopyrazole and N-oxide formation. Although the sequence of these two steps is unknown, the presence of the N-oxide function suggests that the first reaction of the pyrazole with hydrogen peroxide is transfer of an oxygen to the ring nitrogen, just as in the case of pyridine and other nitrogen heterocycles.

The 2,2′-dioxide structure is favored over the 1,1′-analog, because the ultraviolet spectrum of the compound has its maximum at 247 mμ. This is practically the same as for 5-amino-3-methyl-1-phenylpyrazole (II) (246 mμ). If the oxygen were at N-1, there would be no unshared pairs of electrons on the nitrogen to conjugate with the benzene ring, and the bond maximum should be observed at a shorter wave length; also the N–H bond in the infrared spectrum should be shifted to a higher wave length, because of the possibility of strong hydrogen bonding to a 1-oxide function.

The 2-oxide structure for IX favors the second mechanism postulated for azipyrazole formation,

(16) J. N. Brough, B. Lythgoe and P. Waterhouse, *J. Chem. Soc.*, 4069 (1954).

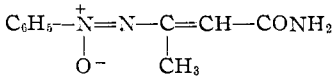
(17) It is, of course, possible to postulate other mechanisms for azipyrazole formation. A Referee has pointed out that it is conceivable that azipyrazole is formed by oxidation of the phenylhydrazone of diacetonitrile, which may be present in very small concentrations in tautomeric equilibrium with the pyrazole (II). We are planning to do further experimental work on the mechanism of oxidative cleavage of pyrazoles.

(18) B. Curnutte, Jr., S. Searles, Jr., and W. R. Hine, Jr., to be published.

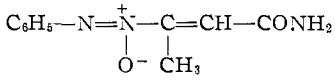
(19) Another strong band at 7.76 μ was in the region for symmetric stretching of the N=N—O group, as assigned by B. W. Langley, B. Lythgoe and L. S. Rayner, *J. Chem. Soc.*, 419 (1952).

because the intermediate VIII for the latter could give rise to IX by means of self-condensation. It is uncertain whether IX is an intermediate in azipyrazole formation, but several experiments were attempted to see if it could be converted to azipyrazole. The most interesting one was that in which the hydrochloride of IX was heated at 160°, giving a material closely resembling azipyrazole in the common physical properties. Closer examination showed it, however, to be a new compound. Since it also was a major product (38% yield) of the reaction of hydrogen peroxide with 5-amino-3-methyl-1-phenylpyrazole in hydrochloric acid, it seemed of interest to determine its structure.

The elemental analysis and molecular weight determinations showed it to have the molecular formula $C_{10}H_{11}N_3O_2$—two more hydrogens and two more oxygens than azipyrazole should have. The infrared spectrum contained the N–H and carbonyl bands of a primary amide, as well as the bands characteristic of the conjugated double bond, the phenyl group[5] and the azoxy group.[18] Significantly, the pyrazole bands were completely absent. The two oxygens are thus accounted for by the amide and the azoxy functions. It will be recognized that all the structural features, as well as the analytical data, fit 3-(phenyl-NON-azoxy)-crotonamide (Xa) as well as 3-(phenyl-NNO-azoxy)-crotonamide (Xb).[20]



Xa



Xb

In support of such an azoxyamide structure, the compound was converted to azipyrazole by heating with phosphorus trichloride in chloroform.[21] Furthermore, the reaction of 3-(phenylazo)-crotonamide (V) with perphthalic acid gave the same azoxyamide, thus providing an independent synthesis.

Comparison of the ultraviolet spectra of V and the azoxyamide then permitted assignment of the position of the N-oxide oxygen atom in the latter. The maximum for the azoamide was at 250 mμ while that for the azoxyamide was 244. This shift to shorter wave length indicates less conjugation of the benzene ring in the azoxyamide. Such would be the case with the oxygen on the phenyl-substituted nitrogen, since the oxygen would compete with the benzene ring to supply electrons to the carbonyl group. If the oxygen were on the other nitrogen, however, its unshared electrons would be able to conjugate with the benzene ring and would not compete with the latter in resonance with the conjugated chain; the result would be more conjugation of the ring and a shift of the maximum absorption to higher wave lengths. Lythgoe and associates have observed the maximum in ArN=N(O)R compounds, where R is saturated, to be at 292–300 mμ.[16] Similarity of the ultraviolet spectrum to that of nitrobenzene (λ_{max} 260 mμ) also may be used as an indication of the ArN(O)=NR structure.[25] Thus structure Xa is indicated for the azoxyamide, rather than Xb.[22]

The formation of this compound from II probably proceeded *via* azipyrozole. It is well known that hydrogen peroxide is able both to oxidize the azo group to azoxy and (due to its superior nucleophilic property)[23] to hydrolyze the nitrile group to the amide group. The formation of the azoxyamide from the (probably hydrated) hydrochloride of IX suggests that it may have first hydrolyzed to VIII and the corresponding pyrazolone-2-oxide, with VIII cleaving to azipyrazole which was subsequently oxidized by hydrogen peroxide from the pyrazolone-2-oxide and water.

Experimental[24]

5-Amino-3-methyl-1-phenylpyrazole was prepared in 75% yield by cyclizing diacetonitrile phenylhydrazone[25] with dry hydrogen chloride in absolute ethanol and treating the intermediate hydrochloride with ammonia in aqueous solution. The product was obtained as white needles from toluene, m.p. 112–114° (lit.[26] m.p. 115–116°).

Di-(3-methyl-1-phenyl-5-pyrazyl)-amine 2,2′(?)-Dioxide (IX).—A solution of 3.0 ml. of 30% hydrogen peroxide and 5.0 g. of 5-amino-3-methyl-1-phenylpyrazole in 50 ml. of 50% aqueous acetic acid was heated on a steam-bath for 5 hr. A red color developed in a few minutes and after about 30 minutes a yellow precipitate began to separate. It was removed by filtration and recrystallized from pyridine–water to give 3.57 g. (70%) of a white crystalline solid, m.p. 229–230°. The infrared and ultraviolet spectra are described in the Discussion.

Anal. Calcd. for $C_{20}H_{19}N_5O_2$: C, 66.48; H, 5.26; N, 19.39; C-methyl, 2.0; mol. wt., 361. Found: C, 66.47; H, 5.30; N, 19.38; C-methyl, 1.7; mol. wt., 339.

3-(Phenyl-NON-azoxy)-crotonamide (Xa). (A).—Addition of IX to concentrated hydrochloric acid caused precipitation of a white hydrochloride, m.p. 178–180°, which decomposed to a red oil on being heated dry at 160° for 15 minutes. On cooling the red oil solidified (m.p. 109–113°) and recrystallization from aqueous ethanol gave light tan needles, m.p. 113°. The yield was 0.2 g. from 1.0 g. of IX.

(B).—5-Amino-3-methyl-1-phenylpyrazole (5.0 g.) was dissolved in 35 ml. of concentrated hydrochloric acid, and 3 ml. of 30% hydrogen peroxide was added. The solution was evaporated on a steam-bath, leaving a red oil which was crystallized from dilute alcohol. A light tan solid, m.p. 113°, was obtained in 38% yield (2.4 g.).

(20) According to a new method of naming azoxy compounds suggested by J. N. Brough, B. Lythgoe and P. Waterhouse (ref. 16), Xb would be termed 3-(phenylazoxy)-crotonamide and Xa would have to be named 1-carbamoylpropen-2-ylazobenzene. Because the latter name seems cumbersome and screens the α,β-unsaturated amide structure, we feel the NON and NNO designation of the oxide function, used by C. S. Stevens, B. T. Gillis, J. C. French and T. H. Haskell (THIS JOURNAL, **78**, 3229 (1956)), is preferable.

(21) Use of phosphorous trichloride here was suggested by its demonstrated ability to convert pyridine N-oxides to the corresponding pyridines (E. Ochiai, *J. Org. Chem.*, **18**, 534 (1953)). The phosphorous oxychloride formed in removing the oxygen from the azoxy group may then dehydrate the amide group.

(22) The attack of hydrogen peroxide on the phenyl-substituted nitrogen seems contrary to expectation, since the reagent should be electrophilic in this reaction and the other nitrogen of the azo group should have the higher electron density. A similar result, however, has been observed on oxidation of aryl alkyl azo compounds (ref. 16).

(23) K. B. Wiberg, THIS JOURNAL, **75**, 3961 (1953). In the coiled form of the azipyrazole molecule these two groups are in close proximity, perhaps permitting both processes to go on almost simultaneously and explaining why neither azoamide nor azoxynitrile was found.

(24) Carbon–hydrogen microanalyses were performed by Weiler and Straus, Oxford, England. Melting points are uncorrected. Nitrogen analyses were by the Dumas method; molecular weight determinations by the Rast method; and C-methyl numbers by the Kuhn–Roth method (E. J. Eisenbraun, S. M. McElvain and B. F. Aycock, THIS JOURNAL, **76**, 607 (1954)).

(25) P. S. Burns, *J. prakt. Chem.*, [2] **47**, 131 (1893).

(26) R. Walther, *ibid.*, **55**, 143 (1897).

(C).—Five drops of concentrated sulfuric acid was added to a solution of 5 g. of 5-amino-3-methyl-1-phenylpyrazole and 1 ml. of 90% hydrogen peroxide[27] in 30 ml. of glacial acetic acid, cooled in ice so that the temperature remained below 40° (otherwise the reaction is very exothermic). The deep-red solution was evaporated *in vacuo*. Extraction of the red oil with 95% alcohol left a residue of 1.8–2.0 g. of compound IX. The sticky red-brown semi-solid left on evaporation of the alcohol was extracted with ether to give 0.1 g. of tan needles, m.p. 113°; mixed m.p. with products from (B) and (C) undepressed. (In one experiment 0.2 g. of orange-red needles, m.p. 70–80°, was obtained from this ether solution (lit. m.p. for Quilico and Justoni's isomer,[14] 81°). On recrystallization from dilute ethanol it was converted to light tan needles, m.p. 103–106°.) The infrared spectrum was characterized by prominent bands at 2.96, 3.15, 3.28, 3.42, 3.53, 5.9, 6.1, 6.18, 6.25, 6.54, 6.66, 6.76, 6.87, 7.18, 7.63, 10.1, 10.9, 11.9 and 13.1 μ.

Anal. Calcd. for $C_{10}H_{11}N_3O_2$: C, 58.53; H, 5.40; N, 20.5; C-methyl, 1.0; mol. wt., 205. Found: C, 58.22; H, 5.42; N, 19.8; C-methyl, 0.96; mol. wt., 188.

In the early stages of this work, when this compound was thought possibly to be "azipyrazole," its dipole moment was determined to check the possibility of a mesoionic structure. The dielectric constant of benzene solutions was determined by the standing microwave technique.[28] The calculated dipole moment was 0.86 *D*.

3-(Phenylazo)-crotononitrile (Azipyrazole). (A).—To 0.05 g. of 3-(phenyl-NON-azoxy)-crotonamide dissolved in 15 ml. of chloroform at 0°, 0.05 ml. of phosphorus trichloride was added, and the solution was refluxed 1 hr. After cooling, 25 ml. of water was added and the mixture was made alkaline with sodium hydroxide. The chloroform layer was dried with sodium sulfate and the solvent then was removed *in vacuo*. The light brown residual solid was sublimed at 90° (0.05 mm.) to give 10 mg. (30%) of ivory-white needles, m.p. 109°. The m.p. was unchanged after recrystallization from dilute alcohol.

(B).—Vacuum sublimation of the red oil described in (C) for the azoxy compound gave 20 mg. of the same product.

(C).—To a solution of 1.0 g. of diacetonitrile phenylhydrazone in 35 ml. of absolute alcohol was added 2 g. of yellow mercuric oxide, and the mixture was refluxed for 2 hr. The free mercury was filtered off and most of the alcohol distilled off, leaving a red oil. This was partially soluble in light petroleum ether; the insoluble part was then dissolved in ethyl ether. Evaporation of the solvent from the ethyl ether solution gave 0.3 g. of tan needles, m.p. 105–107°. Vacuum sublimation as described above gave 0.20 g. (26%) of ivory-colored needles, m.p. 109°. The mixed melting points of the 109° products from these three methods were undepressed and all had the same infrared spectrum. The latter was characterized by prominent bands at 4.45, 6.20 and 6.25 μ, as well as at 3.53, 3.44, 5.80, 5.87, 5.93, 6.07, 6.31, 6.65, 6.73, 7.31, 7.95 and 8.25 μ.

Anal. Calcd. for $C_{10}H_9N_3$: N, 24.55. Found: N, 24.22.

Derivatives were prepared as follows: **5-amino-3-methyl-1-phenylpyrazole**, m.p. 113–115° (lit.[26] m.p. 115–116°), when azipyrazole was boiled a few minutes in 10% sodium hydrosulfite solution and filtered. **5-Amino-4-iodo-3-methyl-1-phenylpyrazole**, m.p. 75° (lit.[1a] m.p. 75°), when azipyrazole was warmed a few minutes with concentrated hydriodic acid, followed by saturating the solution with sodium hydroxide, extracting with ether and removing the ether from the extract by evaporation. **5-Amino-4-bromo-3-methyl-1-phenylpyrazole**, m.p. 105° (lit.[1a] m.p. 106.5° and mixed m.p. with azipyrazole 83–99°), was obtained by the same procedure using 48% hydrobromic acid.

Evaporation of the solvent from the petroleum ether extract of the reaction mixture in (C) left 50 mg. of stout red needles, m.p. 73–76°; after recrystallization from alcohol they melted at 82–83°.

Anal. Calcd. for $C_{10}H_9N_3$: N, 24.55. Found: N, 24.83.

3-(Phenylazo)-crotononamide (V).—Ethyl 3-(phenylazo)-crotonate was prepared in 10% yield by the reaction of mercuric oxide on ethyl acetoacetate phenylhydrazone[9]; red crystals, m.p. 50°. A solution of 80 mg. of this azo-ester and 2 g. of dry ammonia in 10 ml. of absolute ethanol was heated in a sealed tube 10 hr. at 110°. On subsequent evaporation of the solvent 60 mg. (90%) of a black crystalline solid, m.p. 74°, remained. (In another run the yield on this reaction was 60%.)

Anal. Calcd. for $C_{10}H_{11}N_3O$: N, 22.22. Found: N, 21.92.

The above amide (40 mg.) was added to 5 ml. of an ether solution of monoperphthalic acid,[29] containing 1×10^{-3} mole of the latter. After standing two days, sodium bicarbonate was added to neutralize the acid present. The ether solution was separated, dried and evaporated *in vacuo*, leaving tan needles, melting at 113°, identical with the 3-(phenyl-NON-azoxy)-crotonamide previously described.

Azipyrazole from V.—Phosphoric anhydride (100 mg.) was added to a solution of 50 mg. of 3-(phenylazo)-crotonamide in 15 ml. of benzene. The mixture was refluxed 30 minutes, cooled and filtered. The solvent was removed from the filtrate *in vacuo*. The white needles obtained (about 15 mg.) melted at 109° and the mixed melting point with azipyrazole prepared by other methods was also 109°.

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[CONTRIBUTION FROM THE CONVERSE MEMORIAL LABORATORIES OF HARVARD UNIVERSITY]

Preparation and Thermal Rearrangement of Several Dicyclopentadiene Derivatives

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Oxidation of dicyclopentadiene with selenium dioxide in aqueous dioxane solutions has been shown to yield 1-dicyclopentadienol. The oxidation of this alcohol under Oppenauer conditions affords 1-dicyclopentadienone, and its pyrolysis leads to the formation of cyclopentadiene and 2-cyclopentenone. Treatment of 1-dicyclopentadienone with both methyl and phenyl Grignards leads to the formation of the corresponding tertiary alcohols, 1-methyldicyclopentadiene-1-ol and 1-phenyldicyclopentadiene-1-ol. Pyrolysis of 1-acetoxydicyclopentadiene, prepared by acetylation of 1-dicyclopentadienol, affords azulene in low yield.

The synthesis of oxygenated derivatives of dicyclopentadiene has hitherto been confined to the di- and tetrahydro members of the parent diene,[2] although a considerable number of polyalkyl,

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(2) *Cf.* "Elsevier's Encyclopedia of Organic Chemistry," Vol. XIII, Elsevier Publishing Co., N. Y., 1946, pp. 1018–1032.