with sodium ethylate using phenolphthalein as an indicator. The precipitated sodium chloride was removed by filtration and 2.5 g. (0.016 mole) of methyl α-pyridylacetate added. The mixture was heated gradually in a 50-cc. round-bottomed flask to 200° by allowing the alcohol to escape through a short air-cooled reflux condenser. The mixture was heated at 200° for twenty minutes. On cooling, a thick red-brown resin was obtained which was soluble in benzene, alcohol, or chloroform, but insoluble in ether or petroleum ether. A number of attempts to crystallize the amide were unsuccessful. Some of this sirupy material was dissolved in ethyl alcohol, and an alcoholic solution of picric acid was added. A resinous precipitate formed which could not be made to solidify. An anhydrous alcoholic solution of hydrogen chloride was added to an anhydrous alcoholic solution of the amide. Upon the addition of dry ether a sirupy hydrochloride precipitated which did not crystallize even at −80°. The solvent was decanted and the hydrochloride placed in a vacuum desiccator. The material gradually crystallized but on exposure to the atmosphere immediately became a sticky mass. The dried hydrochloride melted with decomposition at 105–110°. No analysis was made.

Attempts to cyclize the crude free base by the procedures of Clemo, McIlwain and Morgan,[2] of Pictet and Gams,[3] or of Bruckner and Fodor,[27] gave tars from which only α-picoline could be isolated as the picrate.

Absorption Spectra.—Absorption spectra not previously reported were obtained with a Beckman Quartz Spectrophotometer, Model DU, using 1-cm. quartz cells, a hydrogen discharge lamp for the ultraviolet light source, and a tungsten filament lamp for wave lengths above 325 mμ. The concentrations were from 1 to 2×10^{-5} molar in 95% ethyl alcohol or alcohol containing dry hydrogen chloride or sodium hydroxide. In each case freshly recrystallized material was used, and the absorption determined immediately without allowing the solutions to stand. If these precautions were not taken, inconsistent results sometimes were obtained. The spectra for styrene,[5] stilbene[4] and α-stilbazole[4] were taken from the literature.

Summary

It is concluded from their absorption spectra that the cyclization products of N-acetyl- and N-phenylacetylhomopiperonylamine are 1-methyl- and 1-benzyl-3,4-dihydro-6,7-methylenedioxyisoquinoline, respectively, whereas the cyclization product of N-(α-pyridylacetyl)-homopiperonylamine is 1-(α-picolal)-1,2,3,4-tetrahydro-6,7-methylenedioxyisoquinoline. Reaction of the last compound with hydrochloric acid converts it into 1-(α-picolyl)-3,4-dihydro-6,7-methylenedioxyisoquinoline hydrochloride. It is further concluded that 1-benzal-1,2,3,4-tetrahydro-2-methyl-6,7-methylenedioxyisoquinoline has the structure corresponding to this name when in solution, only in the presence of strong bases, and that when dissolved in alcohol alone it is largely in the form of the quaternary hydroxide. Further attempts to synthesize 1-(α-picolyl)-isoquinolines have been unsuccessful.

STANFORD UNIVERSITY, CALIFORNIA
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[27] Bruckner and Fodor, *Ber.*, **71**, 547 (1938).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF STANFORD UNIVERSITY]

The Reaction of 2,5-Dimethylfuran with *p*-Nitrobenzenediazonium Chloride

BY RICHARD H. EASTMAN AND FRANCIS L. DETERT[1]

The ease with which the furan nucleus undergoes typical aromatic substitution reactions is well known[2] and suggested to us that alkylated furans, as analogs of mesitylene,[3] should undergo a coupling reaction with reactive dizonium halides. Both Gilman and Ochaiai[4] have reported that furan reacts with diazonium halides. Johnson[5] has reported formation of 2-(and some 3-)arylfurans by interaction of furan with a diazotate. Recently, a report[6] of the coupling of sodium *anti-p*-nitrobenzenediazotate with ethyl 2-furylcarbamate has appeared.

We chose for our study of this reaction an available furan with unsubstituted β-positions, 2,5-dimethylfuran and the reactive *p*-nitrobenzenediazonium chloride. These components were combined in an ice-cold aqueous alcoholic solution that contained an excess of potassium acetate as a buffer.[7] The initial coupling product separated as a semi-solid red mass which could not be crystallized to a state of assured purity. When the initial coupling product was heated *in vacuo* or hydrolyzed with dilute acid it was converted in good yield to a substance $C_{12}H_{11}O_3N_3$ which is formulated as 1-*p*-nitrophenyl-3-acetyl-5-methylpyrazole (II) on the basis of its giving a positive iodoform reaction and its smooth oxidation to an acid, $C_{11}H_9O_4N_3$ shown to be identical with 1-*p*-nitrophenyl-5-methyl-3-pyrazolecarboxylic acid (III), m. p.[8] 216–217°, prepared by an unequivocal synthesis.

Consideration of the properties and easy transformation to II of the initial, red coupling product (*cf.* Experimental Part) suggests the tentative structual assignment I for this material.

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[1] Part of the work described in this article is taken from a thesis presented to Stanford University by Francis L. Detert in partial fulfillment of the requirements for the degree of Master of Science.

[2] Gilman and Towne, *Rec. trav. chim.*, **51**, 1054 (1932); Gilman, Calloway and Burtner, THIS JOURNAL, **57**, 906 (1935).

[3] Meyer and Tochtermann, *Ber.*, **54**, 2283 (1921).

[4] Gilman, Wooley and Vanderwal, *Proc. Iowa Acad. Sci.*, **29**, 176 (1932); Ochaiai, *J. Pharm. Soc., Japan*, **58**, 1025 (1938).

[5] A. W. Johnson, *J. Chem. Soc.*, 895 (1946).

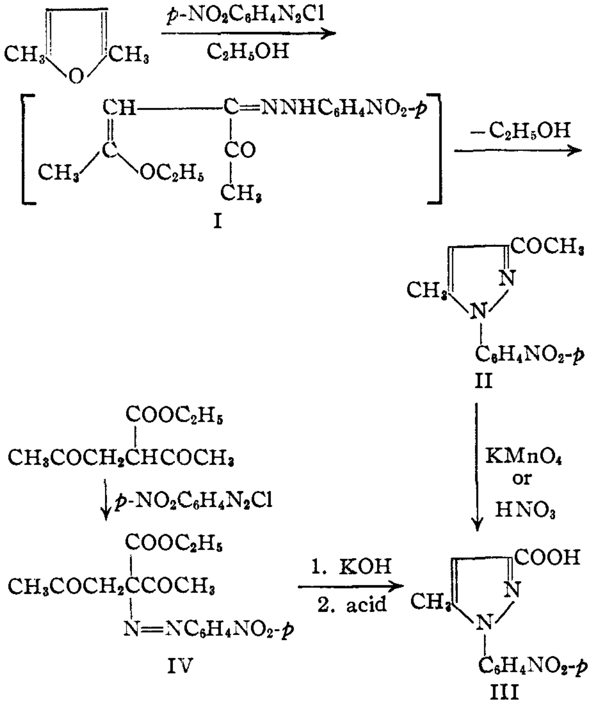
[6] Hurd and Priestley, THIS JOURNAL, **69**, 859 (1947).

[7] Similar reaction conditions were employed by Fischer and Hepp (*Ber.*, **19**, 2251 (1886)) in the successful coupling of pyrrole with diazonium halides, and by Johnson (Ref. 5).

[8] An isomer of this compound, but reported in Beilstein, 4th ed., **25**, 120, as this compound, was prepared by Knorr and Macdonald, *Ann.*, **279**, 224 (1894). It melted at 122° and was prepared by reaction of 1-phenyl-5-methyl-3-pyrazolecarboxylic acid with fuming nitric acid. On repeating this work we obtained an acid of m. p. 153–154° without establishing its identity.

Synthesis of III was accomplished by reaction of ethyl 2-acetyl-2-*p*-nitrophenylazolevulinate (IV) with alcoholic alkali followed by acidification. IV, prepared by the coupling of ethyl acetonylacetoacetate with *p*-nitrobenzenediazonium chloride changed spontaneously into the ethyl ester of III on standing.

The pyrazolecarboxylic acid III was also obtained as one product of the condensation of *p*-nitrophenylhydrazine with the sodium derivative of oxalacetone followed by alkaline hydrolysis and acidification.



Experimental

Reaction of 2,5-Dimethylfuran with *p*-Nitrobenzenediazonium Chloride.—To an ice-cold solution of 4.8 g. of 2,5-dimethylfuran, 250 ml. of ethanol and 15 g. of potassium acetate was added all at once the diazonium salt solution prepared from 7.0 g. of *p*-nitroaniline in 150 ml. of water, 30 ml. of 10% hydrochloric acid, and 3.5 g. of sodium nitrite. The reaction mixture was kept in ice for three hours and then poured into twice its volume of water, giving a gummy, orange solid that was crystallized from benzene to yield 3.9 g. of golden yellow plates which melted at 129–131° with gas evolution. Attempts to prepare sharply melting samples of assured purity failed. When a sample was heated *in vacuo* at 100°, quantitative conversion to **1-*p*-nitrophenyl-3-acetyl-5-methylpyrazole** (II) of m. p. 134–135° occurred. This initial coupling product is tentatively formulated as I.

When the coupling reaction was carried out under the same conditions but using methanol as solvent the initial product was obtained in the form of a gummy, red solid which could not be purified but which, on acid hydrolysis underwent conversion to II in good yield (see below).

Hydrolysis of Initial Coupling Product.—The above described red product (4.0 g.) from the coupling reaction carried out in methanol was boiled for a few minutes in 25 ml. of alcohol which contained 3 ml. of 6 *N* hydrochloric acid. When the hydrolysis mixture was poured into an excess of water a red solid separated that on crystallization from aqueous alcohol and treatment with decolorizing carbon yielded pale-yellow needles (2.2 g.) of m. p. 134–135°. The substance was 1-*p*-nitrophenyl-3-acetyl-5-methylpyrazole and readily gave iodoform, m. p. 115–118°, with sodium hypoiodite.

Anal. Calcd. for $C_{12}H_{11}O_3N_3$: C, 57.8; H, 4.52. Found: C, 57.9; H, 4.68.

Under the same conditions of hydrolysis the initial deep-yellow coupling product of m. p. 129–131° (1.5 g.) from the coupling reaction carried out in ethanol yielded 0.90 g. of pale-yellow needles of m. p. 134–135° that showed no depression when mixed with the materials of the same melting point obtained as described above.

Anal. Found: C, 58.0; H, 5.00.

Oxidation of 1-*p*-Nitrophenyl-3-acetyl-5-methylpyrazole (II).—To 2.5 g. of II suspended in 200 ml. of water containing 5 ml. of 5% sodium hydroxide solution was added a solution of 3.2 g. of potassium permanganate in water. The mixture was heated at 60° until the permanganate color had disappeared, and after the precipitated manganese dioxide had been destroyed by the addition of sodium bisulfite, the tan solid which remained was separated, extracted with ether, and dissolved in dilute sodium hydroxide. The alkaline solution was filtered, and from the filtrate there was obtained on acidification a gelatinous greenish precipitate which was separated and crystallized from aqueous alcohol to yield 0.4 g. of white micro-crystals of m. p. 216–217°.

Anal. Calcd. for $C_{11}H_9O_4N_3$: C, 53.4; H, 3.67. Found: C, 53.5, 53.9; H, 3.75, 3.61.

The identity of this material and **1-*p*-nitrophenyl-5-methyl-3-pyrazolecarboxylic acid** (III), the synthesis of which is described below, was established in a mixed melting point determination (m. p. 216–217°).

When 1.5 g. of II was boiled with 15 ml. of concentrated nitric acid until brown fumes were no longer evolved there resulted after crystallization of the crude acid product from aqueous alcohol 0.8 g. of white micro-crystals of m. p. 216–217°, taken alone or mixed with the material of the same melting point described above.

Ethyl 2-Acetyl-2-*p*-nitrophenylazolevulinate (IV).—To an ice-cold solution of 17.0 g. of ethyl acetonylacetoacetate[9] and 65 g. potassium acetate in 250 ml. of alcohol was added all at once the filtered diazonium salt solution prepared from 13.8 g. of *p*-nitroaniline in 100 ml. of 6 *N* hydrochloric acid and 7.0 g. of sodium nitrite. The mixture became deep orange immediately and after fifteen minutes at ice temperature the addition of 500 ml. of water threw down a heavy, red-orange precipitate that was separated and crystallized from alcohol to yield 17.0 g. of ethyl 2-acetyl-2-*p*-nitrophenylazolevulinate (IV) of m. p. 80–81°.

Anal. Calcd. for $C_{15}H_{17}O_6N_3$: C, 53.8; H, 5.11. Found: C, 53.7, 53.8; H, 5.70, 5.31.

Both the analytical sample and the less highly purified samples of the red-orange IV after two weeks had decomposed with loss of acetic acid to yield a pale-yellow crystalline solid, 3.0 g. of which on two crystallizations from alcohol yielded 1.5 g. of straw-colored needles of m. p. 96–97° which proved to be **ethyl 1-*p*-nitrophenyl-5-methyl-3-pyrazolecarboxylate** (V).

Anal. Calcd. for $C_{13}H_{13}O_4N_3$: C, 56.7; H, 4.74. Found: C, 56.8; H, 4.93.

1-*p*-Nitrophenyl-5-methyl-3-pyrazolecarboxylic Acid (III): (a) **From Condensation of *p*-Nitrophenylhydrazine with Sodium Oxalacetone.** To 3.06 g. of *p*-nitrophenylhydrazine in 35 ml. of glacial acetic acid was added 3.60 g. of sodium oxalacetone dissolved in 10 ml. of water. The reaction mixture was heated for fifteen minutes on the steam-bath and poured into an excess of water. The tan crystalline precipitate which appeared was separated and one-half of it was hydrolyzed by boiling for fifteen minutes with a solution of 6.0 g. of potassium hydroxide in 10 ml. of water and 30 ml. of methanol. The hot hydrol-

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[9] Ossipow and Korschun, *Chem. Zentr.*, **74**, II, 1281 (1903). Our material had b. p. 97–104° at 2 mm. and d. 1.061 at 21°.

ysis mixture was diluted with an equal volume of water, decolorized with carbon and acidified. The precipitate which appeared was removed from the hot solution by filtration and the filtrate on being cooled deposited 0.14 g. of tan solid which after three crystallizations from glacial acetic acid yielded yellowish-white crystals of m. p. 215–217° taken alone or mixed with the oxidation product (III) of 1-*p*-nitrophenyl-3-acetyl-5-methylpyrazole (II).

(b) **By Hydrolysis of Ethyl 1-*p*-Nitrophenyl-5-methyl-3-pyrazolecarboxylate** (V).—Five-tenths of a gram of the ester (V) was heated on the steam-bath with a mixture of 1 ml. of concentrated hydrochloric acid and 3 ml. of glacial acetic acid for four hours. The hydrolysis mixture was cooled, the solid which crystallized therefrom was separated and crystallized three times from aqueous alcohol to yield 0.15 g. of pure-white, crystalline 1-*p*-nitrophenyl-5-methyl-3-pyrazolecarboxylic acid of m. p. 216.5–217.5° taken alone or mixed with III.

Anal. Found: C, 53.5; H, 4.14.

(c) **By Hydrolysis of Ethyl 2-Acetyl-2-*p*-nitrophenylazolevulinate** (IV).—To one gram of the dye IV in 20 ml. alcohol and 5 ml. water at the boiling point was added 0.4 g. of potassium hydroxide in 5 ml. of water. After three hours of heating, the dark reaction mixture was acidified, and on being cooled the acidic solution deposited a gelatinous yellowish precipitate that was separated and treated with warm dilute solution bicarbonate solution. The cloudy bicarbonate solution was filtered and acidified to yield a yellowish-white precipitate that gave after separation and three crystallizations from glacial acetic acid 0.10 g. of 1-*p*-nitro-phenyl-5-methyl-3-pyrazole carboxylic acid in the form of white needles of m. p. 215.5–216.5° taken alone or mixed with III.

Summary

The furan nucleus of 2, 5-dimethylfuran on reaction with *p*-nitrobenzenediazonium chloride followed by acid hydrolysis of an initial, unstable coupling product is cleaved with the formation of 1-*p*-nitrophenyl-3-acetyl-5-methylpyrazole.

RECEIVED AUGUST 25, 1947

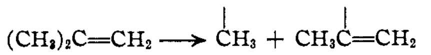
[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE CATHOLIC UNIVERSITY OF AMERICA]

The Thermal Decomposition of Mono-olefins: Isobutylene

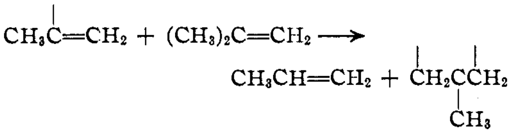
BY FRANCIS OWEN RICE AND W. STUART HAYNES[1]

The mechanism of the thermal decomposition of paraffin hydrocarbons from the free radical standpoint[2] has already been studied in considerable detail and appears to give a satisfactory interpretation of the complicated chemical changes that occur in the pyrolysis of saturated, open chain hydrocarbons. Even when this picture is applied to the decomposition of paraffins as high as the octanes, the amounts of products calculated are in reasonable agreement[3] both qualitatively and quantitatively with the amounts found experimentally.

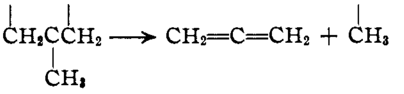
In contrast with the decomposition of paraffin hydrocarbons, the mechanism of olefin decompositions is not well understood in spite of a considerable amount of study. This is surprising because the predictions made on the basis of the free radical theory proposed by Rice[2] are rather straightforward and are shown for example in the case of isobutylene by the equations



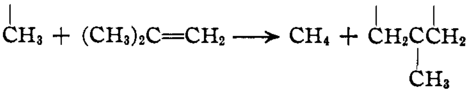
$$(CH_3)_2C{=}CH_2 \longrightarrow \overset{|}{C}H_3 + CH_3\overset{|}{C}{=}CH_2 \quad (1)$$



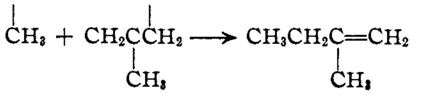
$$CH_3\overset{|}{C}{=}CH_2 + (CH_3)_2C{=}CH_2 \longrightarrow CH_3CH{=}CH_2 + \overset{|}{C}H_2\underset{\overset{|}{CH_3}}{\overset{|}{C}}H_2 \quad (2)$$



$$\overset{|}{C}H_2\underset{\overset{|}{CH_3}}{\overset{|}{C}}H_2 \longrightarrow CH_2{=}C{=}CH_2 + \overset{|}{C}H_3 \quad (3)$$



$$\overset{|}{C}H_3 + (CH_3)_2C{=}CH_2 \longrightarrow CH_4 + \overset{|}{C}H_2\underset{\overset{|}{CH_3}}{\overset{|}{C}}H_2 \quad (4)$$



$$\overset{|}{C}H_3 + CH_2\underset{\overset{|}{CH_3}}{\overset{|}{C}}H_2 \longrightarrow CH_3CH_2\underset{\overset{|}{CH_3}}{C}{=}CH_2 \quad (5)$$

The initial step produces radicals and the final step removes them. Reactions (3) and (4) constitute the chain which yields equal molecular quantities of methane and allene. If the chain is fairly long (50 or more chain cycles), we would expect methane and allene to be the predominant products and to be accompanied by only negligible amounts of other compounds. If, however, the chain is short and consists of only a few cycles, the amount of propylene, methane and other molecules resulting from the non-chain radical reactions would be increased. There are several other non-chain radical reactions that can be written but we have omitted them since they should produce only a small proportion of the decomposition products.

The pyrolysis of isobutylene has been the subject of a number of investigations.[4] Methane, hydrogen, ethylene and propylene were found to constitute the bulk of the gaseous products. Although the conditions were varied widely, allene was found to be completely absent or, at most, present in traces. In all cases the decomposition was accompanied by considerable quantities of oily and tarry material, containing benzene and

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[1] This is taken from the dissertation presented by W. Stuart Haynes for the degree of Doctor of Philosophy in The Catholic University of America.

[2] F. O. Rice and K. K. Rice, "The Aliphatic Free Radicals," The John Hopkins Press, Baltimore, Md., 1935.

[3] A. Kossiakoff and F. O. Rice, THIS JOURNAL, **65**, 590 (1943).

[4] (a) Hurd and Spence, *ibid*, **51**, 3561 (1929); (b) Hurd and Eilers, *Ind. Eng. Chem.*, **26**, 776 (1934); (c) Tropsch, Parrish and Egloff, *ibid.*, **28**, 581 (1936); (d) Hurd and Blunck, THIS JOURNAL, **59**, 1869 (1937).