TABLE III

ACETOLYSIS OF *cis*-CYCLOPENTYL-2-*d* TOSYLATE

Temp. 50.0°; [ROTs] = 0.0965; [NaOAc] = 0.1170; calcd. infinity titer, 1.762 ml.; found, 1.779 ml.

Time, min.	Titer, ml.	10^5k, sec.$^{-1a}$
0	7.609	. .
108.9	6.066	3.46
209.2	4.859	3.55
315.3	3.920	3.50
384.5	3.395	3.50
488.0	2.723	3.52
555.8	2.356	3.52
616.7	2.082	3.50
		3.51 ± 0.02^a

[a] Using equation for a first-order reaction. The least squares $k = 3.502 \times 10^{-5}$ sec.$^{-1}$.

per molecule).[45] The tosylate was prepared as above, m.p. 28–29°.

Cyclopentanol-1-*d*.—Cyclopentanone was reduced with lithium aluminum deuteride using the procedure detailed above for the reduction of IV-d_4; yield 3 g. (37%) of alcohol, b.p. 140.5–141.5°, d^{25} 0.9547 (corresponding to 1.07 deuterium atoms per molecule).[45] The tosylate prepared as above had m.p. 25.5–26°.

Kinetics.—Anhydrous acetic acid was prepared by treating reagent grade acetic acid, which had been analyzed for water by the Karl Fischer method, with an amount of acetic anhydride calculated to give a 1% excess. Freshly fused sodium acetate and dried *p*-toluenesulfonic acid were used to make up stock solutions in acetic acid. In most of the runs about 2 g. of the tosylate was dissolved in sodium acetate stock solution in a calibrated 100-ml. volumetric flask. The flask was placed in a thermostat at 50.00 ± 0.05° and aliquots were removed periodically with a calibrated 5-ml. automatic pipet and titrated potentiometrically with stock *p*-toluenesulfonic acid solution in acetic acid. The procedure for the cyclopentyl-1-*d* tosylate runs was similar except that the solution was placed in sealed tubes which were periodically withdrawn and titrated. Infinity titers generally agreed with the calculated titers within 1–2%. A typical run is shown in Table III; a summary of rate constants calculated by the method of least squares is presented in Table II.

Acknowledgment.—We are indebted to Professors W. D. Gwinn, K. S. Pitzer, H. S. Johnston, G. C. Pimentel and W. E. Doering for discussions and suggestions which greatly assisted the formulation of some of the concepts and arguments presented in this paper. We thank Professor William H. Saunders, Jr., for exchange of information in advance of publication.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF SOUTHERN CALIFORNIA]

Heterocyclic Compounds. VI. Reduction of 3-(3,4-Methylenedioxyphenyl)-4-nitro-1-phenyl-1-butanone[1]

BY MILTON C. KLOETZEL AND JACK L. PINKUS

RECEIVED NOVEMBER 11, 1957

Reduction of 3-(3,4-methylenedioxyphenyl)-4-nitro-1-phenyl-1-butanone (I) by catalytic hydrogenation over platinum black or Raney nickel, or by zinc dust and aqueous ammonium chloride, yields 4-(3,4-methylenedioxyphenyl)-2-phenyl-Δ^1-pyrroline (VI). Chemical and physical evidence clearly supports a Δ^1-pyrroline structure for VI.

Pyrrolidines and Δ^1-pyrrolines have become increasingly recognized as characteristic reduction products from aliphatic γ-nitro ketones.[2–11] However, despite the fact that aromatic nitroketones frequently have been reduced to N-oxygenated derivatives of indole or quinoline,[12] oxygen-containing reduction products from aliphatic γ-nitro ketones have remained elusive.

Kohler and Drake[2] reported the only products from catalytic hydrogenation of 3-(3,4-methylenedioxyphenyl)-4-nitro-1-phenyl-1-butanone (I), over platinum black, to be amino ketone II, pyrrolidine III and an hydroxylated pyrroline to which they ascribed structure IV or V. Prior to our reduction studies[13] this was the only instance in which an oxygenated pyrrole nucleus had been obtained by reduction of an aliphatic γ-nitro ketone.[15] For this reason it appeared of interest to include nitro ketone I in a series of nitro ketones whose behavior upon reduction we have been studying.

In our hands, reduction of I by hydrogen over platinum black or Raney nickel, or by zinc dust and aqueous ammonium chloride, yielded only 4-(3,4-methylenedioxyphenyl) - 2 - phenyl - Δ^1 - pyrroline (VI). We obtained none of the products (II-V) reported by Kohler and Drake.[2]

Pyrroline VI was characterized by formation of a crystalline picrate, hydrochloride[16] and oxalate.

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(1) Partially abstracted from a portion of the Ph.D. dissertation of Jack L. Pinkus.

(2) E. P. Kohler and N. L. Drake, THIS JOURNAL, **45**, 2144 (1923).

(3) A. Sonn, *Ber.*, **68**, 148 (1935); **72**, 2150 (1939).

(4) J. Dhont and J. P. Wibaut, *Rec. trav. chim.*, **63**, 81 (1944).

(5) M. C. Kloetzel, THIS JOURNAL, **69**, 2271 (1947).

(6) P. M. Maginnity and J. B. Cloke, *ibid.*, **73**, 49 (1951).

(7) F. G. Bordwell and M. Knell, *ibid.*, **73**, 2354 (1951).

(8) L. I. Smith and E. R. Rogier, *ibid.*, **73**, 3837 (1951).

(9) B. Witkop, *ibid*., **76**, 5597 (1954).

(10) M. L. Stein and A. Burger, *ibid.*, **79**, 154 (1957).

(11) M. C. Kloetzel, J. L. Pinkus and R. M. Washburn, *ibid.*, **79**, 4222 (1957).

(12) A. Reissert, *Ber.*, **30**, 1030 (1897); S. Gabriel and W. Gerhard, *ibid.*, **54**, 1067 (1921); K. L. McCluskey, THIS JOURNAL, **44**, 1573 (1922); S. Gabriel and R. Wolter, *Ber.*, **56**, 2445 (1923); J. Meisenheimer and E. Stotz, *ibid.*, **58**, 2334 (1925).

(13) Stein and Burger[10] recently reported the preparation of an oxygen-containing base by reduction of an aliphatic nitro ketone but did not ascribe to it a structure. Shortly thereafter, Brown, Clark and Todd[14] reported the synthesis of two alicyclic nitrones by reductive cyclization of aliphatic nitro carbonyl compounds.

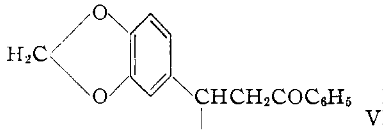
(14) R. F. C. Brown, V. M. Clark and A. Todd, *Proc. Chem. Soc.*, 97 (1957).

(15) Inconclusive evidence for a second instance was presented in the same report and has been discussed in one of our previous papers.[11]

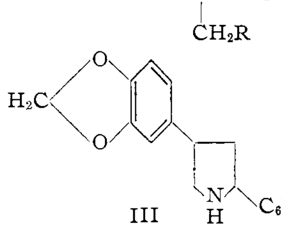
(16) The salt isolated by Kohler and Drake[2] and designated by them as the hydrochloride of III displayed melting point characteristics similar to those of our hydrochloride of VI. Since carbon and hydrogen analytical data do not permit positive differentiation between these compounds, it cannot be stated with certainty whether these salts are in fact identical. Kohler and Drake did not isolate the free base III.

The base was not oxidized by 2% potassium permanganate in cold acetone, nor did it react with phenyl isothiocyanate. As is characteristic of other Δ^1-pyrrolines,[11] VI was acetylated with concurrent cleavage of the pyrroline ring to yield the acyclic amido ketone VII. The structure of VII was established clearly by means of analytical and infrared absorption data.

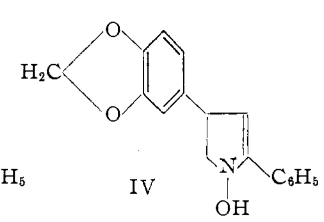
Infrared spectral characteristics of VI and its hydrochloride also are indicative of a Δ^1-structure for this pyrroline.[17] The free base exhibits the conjugated C=N absorption maximum at 6.17 μ but shows no band in the N—H region. Protonation of the nitrogen atom results in the appearance of broad ammonium absorption with a maximum at 3.89 μ, immonium absorption at 5.36 μ, and the hypsochromic shift of conjugated C=N absorption to 6.02 μ.



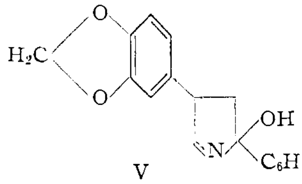
I, R = NO_2
II, R = NH_2
VII, R = $NHCOCH_3$



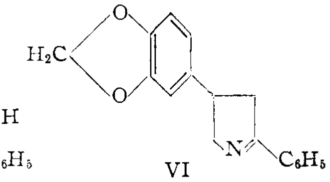
III



IV



V



VI

Acknowledgment.—The authors wish to thank Parke, Davis and Co., Detroit, Mich., for generous financial aid which made this study possible.

Experimental[18]

3-(3,4-Methylenedioxyphenyl)-4-nitro-1-phenyl-1-butanone (I).—A mixture of piperonalacetophenone[19] (63 g.), nitromethane (153 g.), dry methanol (378 ml.), dry ethanol (252 ml.) and diethylamine (18 g.) was heated barely to reflux for 4 days and the resulting orange-red solution was then allowed to stand at room temperature for 4 days. Fractional crystallization of the solid remaining after evaporation of the solvents afforded 56 g. (72%) of nitro ketone, m.p. 85–93°. Recrystallization from methanol raised the m.p. to 94°, substantially that reported previously.[2,20]

4-(3,4-Methylenedioxyphenyl)-2-phenyl-Δ^1-pyrroline (VI).—A mixture of nitro ketone I (14.5 g.), ammonium chloride (15 g.), methanol (200 ml.) and water (50 ml.) was stirred mechanically and maintained at a temperature of 5–10° while 90% zinc dust (60 g.) was added in portions over a period of 4 hours. Stirring was continued for 20 hours while the reaction mixture was gradually allowed to warm to room temperature. The paste of zinc and zinc oxide was filtered and extracted twice with 165-ml. portions of boiling ethanol. The combined extracts and filtered reaction solution were concentrated under reduced pressure to a total volume of 90 ml. and then a mixture of 30 ml. of water and 20 ml. of a commercial[21] basic solution of the tetrasodium salt of ethylenediaminetetraacetic acid (Regular Versene) was added. Extraction of the resulting basic solution 3 times with benzene (50-ml. portions) and twice with ether (50-ml. portions) afforded 8.69 g. (71%) of the pyrroline VI which remained as an oil when the dried extracts were evaporated under reduced pressure. Distillation under reduced pressure yielded 6.24 g. of nearly colorless oil, b.p. 198–202° at 3 mm., which slowly solidified. Crystallization from hexane or from a mixture of isopropyl alcohol and ether produced colorless needles, m.p. 73.5–74.5°. The infrared absorption spectrum (Nujol mull) of VI showed principal maxima at 6.17 (conjugated C=N), 6.66 and 6.72 (phenyl), 7.45 and 8.01 μ (aryl ether[22]).

Anal. Calcd. for $C_{17}H_{15}NO_2$: C, 76.96; H, 5.66; N, 5.28. Found: C, 77.29; H, 5.63; N, 5.34.

The hydrochloride of VI was prepared readily by dropwise addition of an anhydrous ether solution of hydrogen chloride to an ether solution of the pyrroline. Two crystallizations from ethanol furnished thin needles, m.p. 226–233° with slight decomposition beginning at 207°.

Anal. Calcd. for $C_{17}H_{16}ClNO_2$: C, 67.66; H, 5.35; N, 4.64. Found: C, 67.63; H, 5.32; N, 4.43.

This salt (in Nujol mull) displayed principal infrared absorption maxima at 3.89 (ammonium), 5.36 (immonium), 6.02 (conjugated C=N), 6.25, 6.64 and 6.71 (phenyl), 7.45, 7.51, 7.73, 7.91 and 8.03 μ (aryl ether).

An oxalate of VI was prepared by warming an acetone solution of pyrroline and excess oxalic acid. The crude oxalate, m.p. 166–169°, obtained in practically quantitative yield, was recrystallized from ethyl acetate and formed colorless platelets, m.p. 168–170°.

Anal. Calcd. for $C_{19}H_{17}NO_6$: N, 3.94. Found: N, 4.39.

The picrate of VI began to crystallize when a warm solution of 1.13 g. of picric acid in 25 ml. of absolute ethanol was added to a hot solution of 1.20 g. of the pyrroline in 12 ml. of absolute ethanol. Filtration of the cooled solution yielded 1.98 g. (89%) of yellow-green needles, m.p. 155.5–158°. Recrystallization from ethanol or a mixture of ethyl acetate and ether raised the m.p. to 158–159.5°.

Anal. Calcd. for $C_{23}H_{18}N_4O_9$: C, 55.87; H, 3.67; N, 11.33. Found: C, 55.70; H, 3.97; N, 11.30.

When the picrate was dissolved in hot ethyl acetate and the cooled solution was allowed to stand at 10° for 2 days, a second form of the picrate was obtained in 93% yield, m.p. 166–167°. The lower-melting form readily was converted to the higher-melting form by seeding.

Anal. Calcd. for $C_{23}H_{18}N_4O_9$: C, 55.87; H, 3.67; N, 11.33. Found: C, 55.90; H, 3.72; N, 10.91.

Acetylation of 4-(3,4-Methylenedioxyphenyl)-2-phenyl-Δ^1-pyrroline (VI).—The pyrroline (2.65 g.) was heated on a steam-bath with acetic anhydride (5 ml.) for 4 hours and the reaction mixture was then treated with water (20 ml.) containing 2 drops of 2 *N* hydrochloric acid. The oily product was extracted twice with 15 ml. of a mixture of ether and ethyl acetate (2:3) and the combined washed (with dilute hydrochloric acid, aqueous sodium carbonate and finally water), dried and decolorized extracts were evaporated at room temperature; yield 1.28 g. of colorless crystals **4-acetylamino-3-(3,4-methylenedioxyphenyl)-1-phenyl-1-butanone** (VII), m.p. 96–97°. Crystallization from a mixture of chloroform and ether (1:3) or from ethyl acetate and ether (1:3) afforded colorless needles, m.p. 99–100°. An analytical sample was allowed to crystallize at 0° for one day from a mixture of ethyl acetate and ether (1:6), whereupon the m.p. dropped to 87.5–88.5°. This m.p. did not change during storage of the compound for 2 weeks. The amide (in Nujol mull) exhibited principal infrared absorption maxima at 3.03 (N-H), 5.98 (conjugated C=O), 6.11 (amido C=O), 6.29 and 6.35 (phenyl), 6.55 (amide), 6.72

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[17] Compare spectra of 2-phenyl- and 2,4-diphenylpyrroline[11] and of myosmine.[9]

[18] Melting points are uncorrected. Except where otherwise indicated, infrared spectra (obtained with a Perkin-Elmer model 13 double beam spectrophotometer equipped with sodium chloride prism) and microanalyses are by William J. Schenck, formerly of the University of Southern California.

[19] S. v. Kostanecki and M. Schneider, *Ber.*, **29**, 1891 (1896).

[20] D. E. Worrall and C. J. Bradway, THIS JOURNAL, **58**, 1607 (1936).

[21] We wish to thank the Bersworth Chemical Co., Framingham, Mass., for a sample of this material.

[22] L. J. Bellamy, "The Infra-red Spectra of Complex Molecules," Methuen and Co., Ltd., London, 1954, p. 100.

(phenyl), 6.93, 7.08 and 7.21 (C–H) and 8.01 μ (aryl ether).[23]

Anal. Calcd. for $C_{19}H_{19}NO_4$: C, 70.14; H, 5.89; N, 4.31. Found: C, 69.99; H, 6.03; N, 4.25.

Catalytic Hydrogenation of 3-(3,4-Methylenedioxyphenyl)-4-nitro-1-phenyl-1-butanone (I).—A slurry of nitro ketone (10.63 g.), Raney nickel[24] (4 g.) and absolute methanol (233 ml.) was subjected to hydrogenation for 35 hours at an initial pressure of 48 p.s.i. Concentration of the filtered solution yielded a faintly-green oil which was dissolved in anhydrous ether and treated with ethereal hydrogen chloride in the aforedescribed manner. The crystalline hydrochloride precipitated immediately; yield 6.35 g. (62%), m.p. 205–220° dec.

The corresponding picrate formed readily when an ethanol solution of picric acid was added to an ethanol solution of the hydrochloride; m.p. 165–167° and undepressed when mixed with picrate of the pyrroline VI obtained from reduction of I by zinc and aqueous ammonium chloride.

Essentially the same results were obtained when hydrogenation of I was effected over platinum black.

LOS ANGELES, CALIFORNIA

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[23] The infrared spectrum (obtained with a Leitz recording spectrophotometer equipped with a sodium chloride prism) and microanalytical data for this compound were kindly determined by W. M. Hazenberg, Laboratory for Organic Chemistry, The University, Groningen, The Netherlands.

[24] Catalyst 113 days old; prepared according to R. Mozingo, *Org. Syntheses*, **21**, 15 (1941).

COMMUNICATIONS TO THE EDITOR

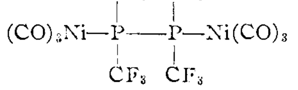
FLUOROCARBON-PHOSPHORUS-NICKEL CARBONYLS[1]

Sir:

The recent publication by Emeléus and Smith on the new compounds $(CF_3)_3PNi(CO)_3$ and $[(CF_3)_3P]_2Ni(CO)_2$[2] prompts us to report our independent (Aug. 1957) information on the latter, along with our earlier discovery of analogous materials derived from trifluoromethyl-polyphosphines.

The compound $[(CF_3)_3P]_2Ni(CO)_2$ formed from $Ni(CO)_4$ and $(CF_3)_3P$, but failed to react with excess $(CF_3)_3P$ even at 100°. It melted at −31° and its roughly measured vapor tensions (1 mm. at 0°; 3 mm. at 20°) indicated the b.p. as near 190° (Trouton const. 19 cal./deg. mole). Intense ultraviolet illumination had no effect upon its vapor or 0.001 *M.* solution in cyclohexane, but the pure colorless liquid responded to sunlight by forming an intensely purple-red solute. This was not colloidal nickel,[2] for the color accompanied the $[(CF_3)_3P]_2Ni(CO)_2$ during distillation; and the shiny black residue was soluble in acetone or sublimable on mild warming *in vacuo.*

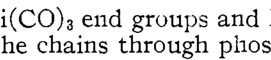
The diphosphine $P_2(CF_3)_4$ with $Ni(CO)_4$ at room temperature gave a product stoichiometrically shown to be



$$(CO)_3Ni{-}P(CF_3)_2{-}P(CF_3)_2{-}Ni(CO)_3$$

hereinafter designated as NiPPNi. Its slightly volatile (0.5 mm. at 20°) red-black crystals melted at 105°; no decomposition occurred during 100 hrs. at that temperature. NiPPNi is insoluble in water, but soluble in cyclohexane, benzene, ether, carbon tetrachloride, and methanol, with a permanganate-red color which was observed also for the vapor. Oxygen discharged the color of the solutions, but brief exposure of the solid to air was not harmful; a 12-hr. exposure converted it to a green powder.

The cyclo-tetraphosphine $(CF_3P)_4$[3] vigorously displaced CO from $Ni(CO)_4$ at 0°. In solution in toluene, the reaction gave a lively play of colors: green, gold, olive, brown, and finally an insoluble crimson. At the end, most of these colors were isolated by solvent extraction methods and filter-paper chromatography. The oily mixture of nonvolatile products (fairly stable in air) had the average composition $[Ni_{1.77}(CO)_{4.45}(CF_3P)_4]_x$, suggesting a mixture of compounds of the type $(CF_3P)_4[Ni(CO)_3]_n$ (n = 1, 2, or 3) and limited



chains with $Ni(CO)_3$ end groups and $Ni(CO)_2$ units cross-linking the chains through phosphorus. The reality of such bonding is supported by the existence of $[(CF_3)_3P]_2Ni(CO)_2$ and NiPPNi.

The absorption spectra of $[(CF_3)_3P]_2Ni(CO)_2$ and NiPPNi are shown in the table. In cyclohexane the 2370 peak of the former is only a shoulder. The vapor-phase spectrum of NiPPNi is like that in solution but shifted 50 Å. toward shorter wavelengths.

$[(CF_3)_3P]_2Ni(CO)_2$ (vapor)

λ, Å.	2,070	2,220	2,370
Shape	max.	min.	max.
Molar ext. coeff.	10,500	9,700	10,500

NiPPNi (in cyclohexane)

λ, Å.	2,470	3,100	3,490	4,050	5,300
Shape	max.	min.	max.	min.	max.
Molar ext. coeff.	14,600	1,000	11,100	570	2,850

The noumenological presence of d_π-d_π bonds in phosphine-nickel carbonyls has been mentioned.[4] We suggest that d orbitals provide a route for extensive delocalization of electrons along the angled hetero-chain O=C=Ni=P—P=Ni=C=O in NiPPNi and that this accounts for the dye-like color and relative stability of this compound.

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RECEIVED MARCH 19, 1958

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[1] This research was supported by the United States Air Force under Contract AF 33(616)-2743, monitored by the Materials Laboratory, Wright Air Development Center, Wright-Patterson Air Force Base, Ohio.

[2] H. J. Emeléus and J. D. Smith, *J. Chem. Soc.*, 527 (1958).

[3] W. Mahler and A. B. Burg, THIS JOURNAL, **79**, 251 (1957).

[4] D. P. Craig, A. Maccoll, R. S. Nyholm, L. E. Orgel, and L. E. Sutton, *J. Chem. Soc.*, 345 (1954).