95% ethanol gave 1.75 g. (33%) of propionyltriphenylsilane, m.p. 105–106°. The infrared spectrum showed carbonyl absorption at 6.08 μ.

Anal. Calcd. for $C_{21}H_{20}OSi$: C, 79.7; H, 6.37. Found: C, 79.1; H, 6.73.

Acknowledgment.—The support of part of this research by the National Research Council of Canada is gratefully acknowledged, as is the technical assistance of D. M. MacRae.

Pyrazolidinone Oxidation. The Oxidation of 1-Phenyl-4,4-dimethyl-3-pyrazolidinone in Alkaline Solution

W. E. LEE

Research Laboratories, Eastman Kodak Company, Rochester, New York 14650

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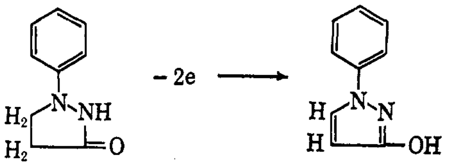
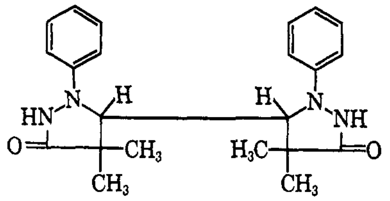
The oxidation of 1-phenyl-4,4-dimethyl-3-pyrazolidinone in alkaline solution was studied by a spectrophotometric method and also by product analysis. Under mild conditions the pyrazolidinone ring is cleaved to give benzene, nitrogen, isobutyraldehyde, CO_2, and a resinous polymeric material as major products, and small amounts of acetone, formaldehyde, and biphenyl. The reaction scheme proposed involves the formation of the pyrazolidinone semiquinone, followed by semiquinone dismutation which leads to the formation of an unstable, short-lived species which undergoes ring cleavage and produces isobutyraldehyde. The formation of other oxidation products is apparently due to further oxidation of the fragment that remains after the loss of isobutyraldehyde. The mechanism of oxidation which accounts for the major products is consistent with the observed stoichiometry, spectrochemical data, and the analytical results.

1-Phenyl-3-pyrazolidinone and its derivatives have become increasingly important as photographic developing agents. The mechanism of oxidation of the parent compound, 1-phenyl-3-pyrazolidinone, has been studied by several groups of workers.$^{1-4}$ The reaction is a two-step process in which two electrons and two protons are lost by the pyrazolidinone to form the very stable 1-phenyl-3-hydroxypyrazole (eq. 1). The existence of a resonance-stabilized semiquinone intermediate in this reaction has been shown by electrochemical[2] and by spectrophotometric measurements in the visible region of the spectrum.[5] Similar products are formed when the 4-alkyl-substituted derivatives of 1-phenyl-3-pyrazolidinone are oxidized. However, 4,4-dialkyl-substituted pyrazolidinones cannot undergo a similar transformation, since the carbon atom α to the carbonyl group carries no hydrogen atoms, although these compounds are easily oxidized by either silver ions or by other mild oxidizing agents.


(1)

No definitive study of the mechanism of oxidation of these 4,4-dialkyl-substituted compounds has appeared. Allen and Byers[6] theorized that a dimeric product, 5,5′-bis(4,4-dimethyl-1-phenyl-3-pyrazolidinone) (I) was formed upon oxidation. Jaenicke[7] has suggested that compounds of this type are oxidized in alkaline solution to a positively charged intermediate which adds water in a slow reaction to form a 5-hydroxypyrazolidinone compound, II. Recent studies in these laboratories, involving the measurement of optical properties of the steady-state condition in a flow system, have indicated that the initial steps in the oxidation of 1-phenyl-3-pyrazolidinone and 1-phenyl-4,4-dimethyl-3-pyrazolidinone are quite similar, although the subsequent reactions that follow semiquinone formation are quite different.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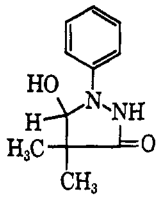
II

In this context, it was of interest to examine the products from the oxidation of the latter compound. The results are included in this paper. A detailed study of the kinetics of the oxidation of this class of compounds will be discussed in a subsequent paper.

Results

By the use of a rapid-flow technique in which the ultraviolet absorption spectrum of the steady state was recorded, the formation of a resonance-stabilized semiquinone intermediate in the oxidation of 1-phenyl-3-pyrazolidinone has been demonstrated (Figure 1). Dismutation of this semiquinone species, possibly followed by the formation of other short-lived reaction intermediates, leads ultimately to 1-phenyl-3-hydroxypyrazole as the final oxidation product. Experiments in which 1-phenyl-4,4-dimethyl-3-pyrazolidinone was oxidized under similar conditions show the formation of a semiquinone intermediate, which is even more stable than that formed from the unsubstituted compound. However, no clearly defined specific oxidation product is obvious from the examination of the ultraviolet absorption spectrum of a solution of the oxidized pyrazolidinone (Figure 2).

The oxidation of 1-phenyl-4,4-dimethyl-3-pyrazolidi-

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(1) T. H. James, *PSA J.*, **19B**, 156 (1953).

(2) S. Horrobin, L. F. A. Mason, and D. W. Ramsay, *J. Phot. Sci.*, **11**, 145 (1964).

(3) K. Honda, M. Katsuyama, and S. Kikuchi, *Bull. Soc. Sci. Phot. Japan*, **10**, 13 (1960).

(4) W. Jaenicke and H. Hoffman, *Z. Elektrochem.*, **66**, 814 (1962).

(5) G. F. VanVeelen and J. F. Willems, *Phot. Sci. Eng.*, **7**, 113 (1963).

(6) C. F. H. Allen and J. R. Byers, Jr., U. S. Patent 2,772,282 (1956).

(7) W. Jaenicke, *Phot. Sci. Eng.*, **6**, 186 (1962).

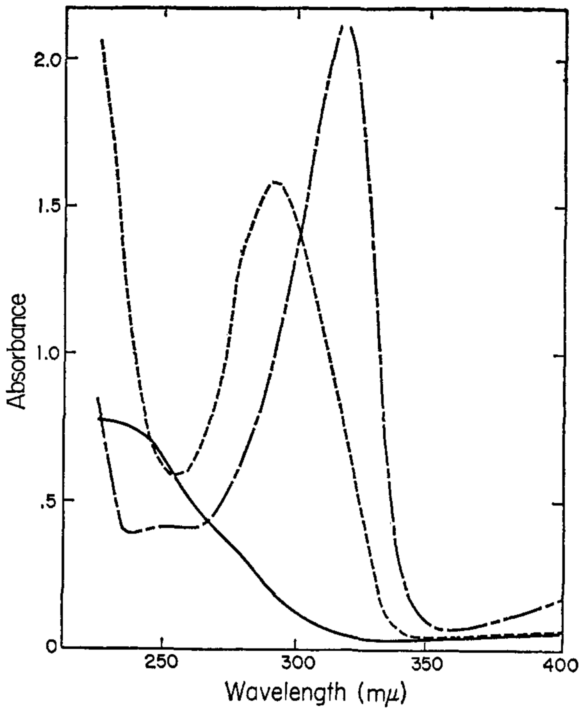

Figure 1.—The ultraviolet absorption spectrum of 1-phenyl-3-pyrazolidinone, ———; spectra after treatment with 2 equiv. of $K_3Fe(CN)_6$ in alkaline solution at pH 10.0 after a reaction time of 12 msec., – – – –; 30 sec., – – – – –.

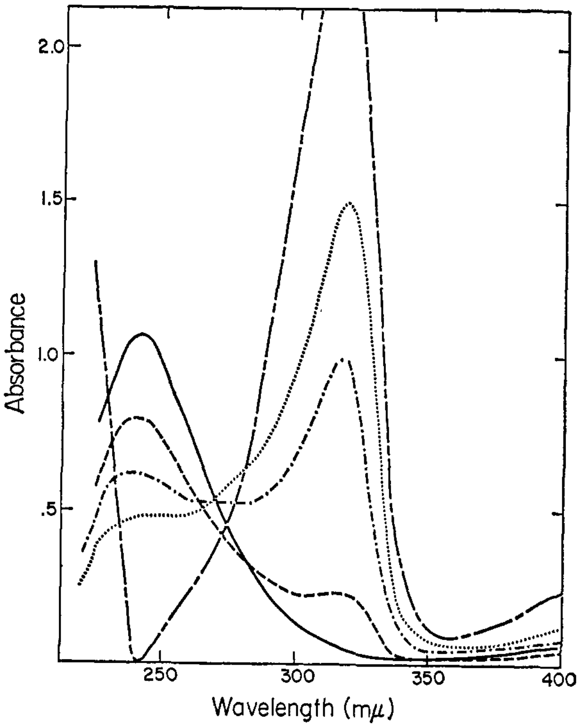

Figure 2.—The ultraviolet absorption spectrum of 1-phenyl-4,4-dimethyl-3-pyrazolidinone, ———; spectra after treatment with 2 equiv. of $K_3Fe(CN)_6$ in alkaline solution at pH 10.0 after a reaction time of 188 msec., - — -; 30 sec., ...; 60 sec., —·—·—·; 300 sec., – – – –.

none was accomplished by adding a solution of potassium ferricyanide to an alkaline solution of the pyrazolidinone under nitrogen. The decomposition products consisted essentially of benzene, isobutyraldehyde, nitrogen, CO_2, and a resinous material of unknown structure. Small amounts of phenol, formaldehyde, biphenyl, acetone, and a highly colored yellow dye were also formed. Low molecular weight carbonyl compounds were formed in moderate yield under the conditions used to effect the oxidation (Table I).

TABLE I

VOLATILE CARBONYL PRODUCTS FORMED FROM THE OXIDATION OF 1-PHENYL-4,4-DIMETHYL-3-PYRAZOLIDINONE BY SILVER CHLORIDE AND BY POTASSIUM FERRICYANIDE

Solvent and oxidant	Carbonyl product,[a] % yield[b]			
	HCHO	CH_3CHO	CH_3COCH_3	$(CH_3)_2CHCHO$
$K_3Fe(CN)_6$[c]				
H_2O, pH 10.5	0	0	0	44.6
0.1 *N* NaOH	Trace	0	2.0	36.0
C_2H_5OH + H_2O (25%) + Na_2CO_3	0.5	5.2	2.0	24.5
AgCl[c]				
H_2O, pH 10.5	0	0	0	32.6
0.1 *N* NaOH	0	0	1.0	32
C_2H_5OH, H_2O (25%) + Na_2CO_3	1.0	5.6	2.2	22.0

[a] Isolated and determined as 2,4-dinitrophenylhydrazone derivative. [b] Yields based on original pyrazolidinone present. [c] Two equivalents of oxidant used per mole of pyrazolidinone.

The nature of and the amount of the carbonyl compounds were dependent upon the solvent and the pH of the solution. Isobutyraldehyde was the major product in all the experiments and the amount ranged from 70 to 100% of the total carbonyl product. Although benzene was not quantitatively determined, it is estimated that the benzene yield was about 40 to 50% of the original pyrazolidinone present. Neither carbon monoxide nor formic acid were found as products. When aqueous ethanol was used as the reaction medium, acetaldehyde became an important product, although isobutyraldehyde was still formed in abundance. Ethanol is not converted under these conditions to acetaldehyde by ferricyanide ion in the absence of the pyrazolidinone.

Careful examination of the products failed to reveal the presence of any 1-phenyl-4,4-dimethyl-5-hydroxy-3-pyrazolidinone (I) or of any bispyrazolidinone (II).

After all the known products had been isolated from the oxidized pyrazolidinone mixture, only a resinous material remained, the nature of which could not be determined. The amount of this resin depended on the reaction conditions and, in general, ranged from 14 to about 30% of the total products. Several fractions of this material, however, were separated by chromatography and examined by mass and infrared spectrometry. The absorption spectra and the cracking patterns of these fractions were quite similar. Because of the formation of this very complex polymeric material, it was impossible to determine a mass balance for this reaction.

Experimental

All melting points were taken with a Fisher-Johns apparatus and are uncorrected. Infrared spectra were recorded on a Baird AB-1 double-beam spectrophotometer with rock salt optics. Unless otherwise noted, samples were examined by the potassium bromide disk technique.

1-Phenyl-4,4-dimethyl-3-pyrazolidinone (I) was commercially available and was further purified by several recrystallizations from aqueous ethanol. The pure compound is a white crystalline solid, m.p. 172–174°.

Oxidation of 1-Phenyl-4,4-dimethyl-3-pyrazolidinone.—Since the oxidation reaction led to volatile and nonvolatile products, several procedures were used for the oxidation in order to identify these products and to determine, where possible, the amount of these products. These experimental modifications are given below.

Method 1. Analysis for Major Volatile Products.—The oxidation was conducted in an evacuated system so that all the volatile components could be trapped and analyzed by either gas chromatography or by mass spectrometry. All of the reactions were carried out in a closed system, composed of a heavy-walled flask equipped with a dropping funnel, a magnetic stirrer, and connected to a vacuum line which contained appropriate stopcocks and gas bulbs for collecting samples of the volatile products. An alkaline solution of the pyrazolidinone was placed in the flask and the oxidant was placed in the dropping funnel. After the system had been thoroughly degassed and evacuated, the reaction was started by introducing the oxidant into the flask through the dropping funnel. The volatile products were allowed to expand into the evacuated gas bulbs and the gas samples were analyzed by gas chromatography and by mass spectrometry. In a typical experiment, 4.65 g. (0.025 mole) of 1-phenyl-4,4-dimethyl-3-pyrazolidinone dissolved in 75 ml. of 0.1 N sodium hydroxide solution was placed in the flask and 16.5 g. (0.05 mole) of potassium ferricyanide in 100 ml. of 0.1 N sodium hydroxide was placed in the dropping funnel, and the apparatus and its contents were thoroughly degassed. The oxidant was added to the pyrazolidinone and the volatile products were collected and analyzed by gas chromatography with helium as the carrier gas and columns packed with Linde 5A Molecular Sieve adsorbant. A Lovelock ionization detector was used as the sensing device.[8] Two samples were collected after 15- and 30-min. reaction time and both contained nitrogen; the second sample contained considerably more than the first sample. Gas samples were also analyzed by mass spectrometry. Nitrogen was found to be the largest component in all samples. There was no evidence for the presence of CO, CO_2, NO, or NH_3, all of which were originally suspected to be likely products. The presence of benzene was confirmed by the analysis of a gas sample by the air exhaustion method which is much more sensitive for the detection of condensable solvent vapors. When this procedure was followed, a more concentrated sample was collected by placing the gas bulb on a vacuum line and condensing the solvent vapors in a cold trap, while the noncondensable gases (N_2, O_2, etc.) were pumped off. Large amounts of benzene and isobutyraldehyde were clearly detected from the mass spectrum of this gas sample.

Carbon dioxide, which was a product of the oxidation, was soluble in the alkaline reaction medium. The CO_2 was determined by acidifying the reaction mixture, absorbing the released CO_2 in 25% KOH, and precipitating the carbonate as the barium salt. Further confirmation was obtained from the mass spectrum of a gas sample.

Method 2. Analysis for Volatile Carbonyl Products.—For these experiments, which were conducted under an atmosphere of nitrogen to eliminate the reaction with O_2, the solid reactants or thoroughly deaerated solutions were introduced into a 250-ml., heavy-walled, side-arm flask equipped with a nitrogen inlet, a magnetic stirrer, and a pressure-equalizing dropping funnel. The side arm was connected to a series of gas scrubbing bottles which contained solutions of 2,4-dinitrophenylhydrazine (4.0 g./l. in 2 N HCl). In a typical experiment, a suspension of 7.5 g. (0.052 mole) of silver chloride in 75 ml. of 1 M sodium carbonate solution was placed in the flask and allowed to react with 4.75 g. (0.025 mole) of 1-phenyl-4,4-dimethyl-3-pyrazolidinone dissolved in 150 ml. of 1 M sodium carbonate solution. A stream of nitrogen was bubbled through the reaction mixture so that the volatile products were swept into the gas scrubbing bottles where the carbonyl compounds were converted to the corresponding hydrazone derivatives. The yellow precipitate which was formed was removed, washed with water, and dried in a vacuum desiccator over concentrated sulfuric acid. The 2,4-dinitrophenylhydrazones were weighed and separated by a chromatographic procedure with columns packed with silicic acid.[9] The separated zones were removed from the columns, recrystallized from appropriate solvents, and identified by their infrared spectra, melting points, mass spectra, and in a few cases by elemental analysis.

The nature and the amount of the carbonyl compound were dependent on the solvent and the pH of the solution. Four compounds were isolated and identified by this procedure. The order of appearance of the 2,4-dinitrophenylhydrazone derivative on the chromatogram was as follows.

Zone 1.—Isobutyraldehyde 2,4-DNPH, m.p. 182–184°.

Anal. Calcd. for $C_{10}H_{12}N_4O_4$: C, 47.6; H, 4.8; N, 22.2. Found: C, 47.6; H, 4.8; N, 22.6.

Zone 2.—Acetone 2,4-dinitrophenylhydrazone, m.p. 126°.

Anal. Calcd. for $C_9H_{10}N_4O_4$: C, 45.3; H, 4.2; N, 23.5. Found: C, 44.9; H, 4.4; N, 23.3.

Zone 3.—Acetaldehyde 2,4-dinitrophenylhydrazone, m.p. 166°. The infrared spectrum and the mass spectrum of this zone were identical with those of an authentic sample.

Zone 4.—Formaldehyde 2,4-dinitrophenylhydrazone, m.p. 164°.

Anal. Calcd. for $C_7H_6N_4O_4$: C, 40.0; H, 2.9; N, 26.6. Found: C, 39.8; H, 2.9; N, 26.8.

Traces of a dicarbonyl compound, which formed an osazone derivative, were barely detectable on the chromatogram. However, the amount of this material was insignificant and it was not identified.

Optical Absorbance Measurements of Semiquinone Intermediates.—A rapid-flow technique, in which measurements of a steady-state property of a system undergoing reaction could be recorded, was used to obtain optical absorption data on the pyrazolidinone semiquinones. The jet mixer-flow equipment, which has been previously described,[10] was equipped with quartz optics so that the optical absorption in the ultraviolet region could be measured. The ultraviolet absorption spectra (225 to 400 mμ) of the oxidized compound in buffered solution were measured at predetermined times after the reaction with ferricyanide ion had begun. Solutions of the pyrazolidinone (2×10^{-4} mole), $K_3Fe(CN)_6$ (4×10^{-4} mole), and dibasic phosphate buffer (0.25 M, adjusted to the desired pH with NaOH) were mixed in the flow machine in a volume ratio of 1:1:2 and the optical absorption of the steady state was recorded. An appropriate correction was made for the absorption of the buffer and $Fe(CN)_6^{-4}$. The time of reaction could be governed by inserting the appropriate spacer in the path of flow. Reaction times of the order of 10–200 msec. generally covered the range of importance. Slow reactions requiring reaction times longer than several hundred milliseconds were studied by elapsed-time measurements and this permitted a range of from 1–300 sec. to be adequately covered. The ultraviolet absorption spectra of the transient intermediates formed from 1-phenyl-3-pyrazolidinone and the 4,4-dimethyl derivative are shown in Figures 1 and 2.

E.p.r. Spectrum of 1-Phenyl-4,4-dimethyl-3-pyrazolidinone Semiquinone.—The electron spin resonance spectrum (Figure 3) of the pyrazolidinone semiquinone was also obtained by the use of a continuous-flow system. The pyrazolidinone and the oxidant were allowed to flow into a mixing chamber, and the resulting solution containing the semiquinone was then passed directly into the cavity of a Varian V-4500 spectrometer with 100-kc. modulation. The pyrazolidinone semiquinone produced a complex symmetrical spectrum of twenty groups of lines, each group consisting of three lines ($g = 2.0040$). There was poor resolution within each group, but good resolution between the groups of lines.

Analysis of the Solid Resinous Oxidation Product.—After the oxidation had been completed and all the volatile products had been removed, the reaction mixture was neutralized with hydrochloric acid. A solid resinous material precipitated from solution. This solid was chromatographed on a column packed with silicic acid with a mixture of 5% ether–petroleum ether (b.p. 66–70°) as eluent. From this separation small amounts of phenol, biphenyl, a highly colored yellow dye, and unreacted pyrazolidinone were obtained, along with a large fraction of a white amorphous solid material. This solid material was insoluble in water and in weak acid solution but soluble in chloroform, ethanol, acetone, ethyl acetate, and aqueous alkaline solution. The material softened and melted over a wide range (72–128°).[11] This fraction was rechromatographed on a neutral alumina column with 5% ether–hexane as eluent. No clearly defined compound could be isolated by this procedure, although several

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(8) Helium contains enough easily ionizable impurities so that a standing current is obtained. The gases, nitrogen, oxygen, methane, carbon monoxide, and others, will not ionize in this atmosphere, but will cause a signal to be generated by reducing the standing current if they appear in the detector.

(9) E. W. Malmberg, *J. Am. Chem. Soc.*, **76**, 980 (1954).

(10) W. R. Ruby, *Rev. Sci. Instr.*, **26**, 460 (1955).

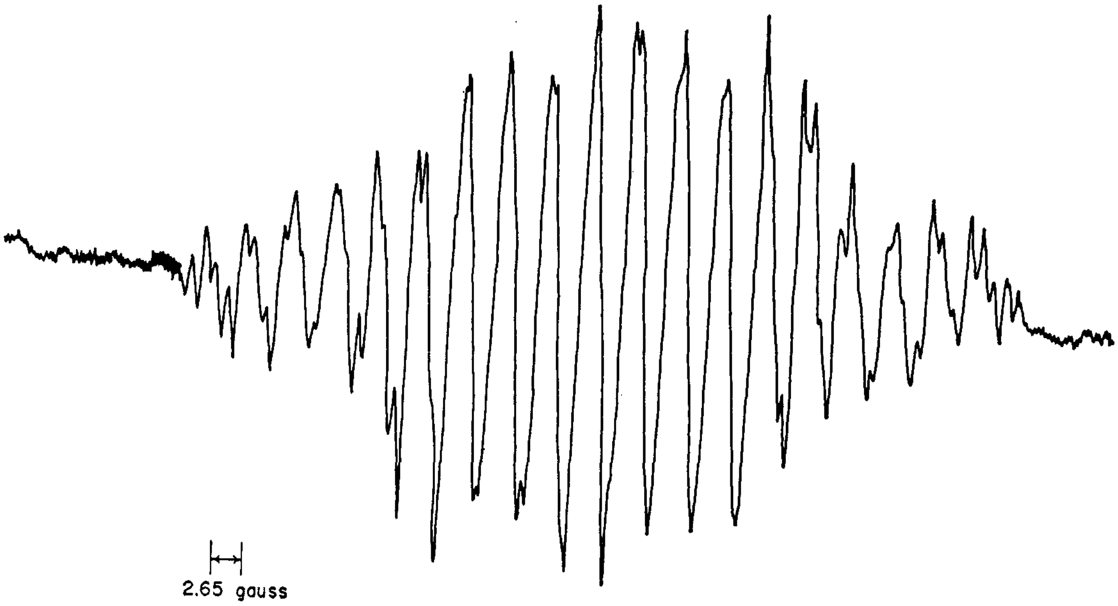

Figure 3.—The e.s.r. spectrum of 1-phenyl-4,4-dimethyl-3-pyrazolidinone semiquinone in aqueous alkaline solution at pH 10.0 ($g = 2.0004$).

fractions were clearly separated. Examination of these fractions by infrared and mass spectrometry provided the following information.

(1) Infrared spectra and mass spectral cracking patterns of these fractions are quite similar and all of these fractions retain considerable similarity to the original pyrazolidinone.

(2) At least one monosubstituted aromatic ring is present in each fraction.

(3) Although the infrared spectra of the fractions resemble those of the original material, the absorption related to the hydrogen on the nitrogen in the pyrazolidinone ring is absent in the products. The product does show a OH absorption in the normal region and this assignment suggests the possibility of CH_2OH substitution on the heterocyclic ring nitrogen.

(4) The mass spectrum of the product contains many peaks up to mass number 343 ± 1, indicating a material of molecular weight considerably above that of the original pyrazolidinone. The pattern was very complicated. However, the sample was introduced into the instrument through a heated inlet system at 230° and any thermal degradation would be expected to lead to a complex cracking pattern. One indication of at least some decomposition was the rapid decrease in the size of the peak at *m/e* 343.

Further attempts to characterize these products were abandoned.

1-Phenyl-3-hydroxypyrazole.—A solution of 16.2 g. (0.1 mole) of 1-phenyl-3-pyrazolidinone in 500 ml. of thoroughly deaerated 1 *N* sodium hydroxide was treated with a solution of 66.0 g. (0.2 mole of potassium ferricyanide in 250 ml. of water, and the mixture was stirred for 0.5 hr. The solution was neutralized to pH 7 with dilute hydrochloric acid and the solid material that precipitated was removed by filtration and washed with water. The solid was dissolved in hot aqueous ethanol, treated with decolorizing charcoal, and then recrystallized from the same solvent to white needles of constant melting point of 158–160°.

Discussion

The formation of a semiquinone intermediate from 1-phenyl-4,4-dimethyl-3-pyrazolidinone during oxidation in alkaline solution is in accord with previous data on the unsubstituted compound. Spectrophotometric measurements clearly indicate that the semiquinone, whose rate of disappearance follows a second-order kinetic process, undergoes a dismutation reaction to form an unstable species from which isobutyraldehyde, nitrogen, CO_2, and benzene are formed. No other semiquinone intermediate was apparent from the spectrophotometric curves for this reaction, even when a large excess of oxidant was used with the pyrazolidinone or when the spectrum of a solution of the partially oxidized pyrazolidinone was recorded at long reaction times, where the initially formed semiquinone had long since disappeared. Supporting evidence for the existence of a single semiquinone was obtained from the e.s.r. spectrum of the semiquinone in a continuous-flow system.

Careful examination of the oxidation products showed that the proposed dimeric product having a pyrazolidinone structure I was not formed. Nor did the oxidation proceed by a molecular rearrangement such as one involving migration of a methyl group from the 4- to the 5-position of the heterocyclic ring to form 4,5-dimethyl-1-phenyl-3-hydroxypyrazole (III). Similarly, there is no evidence for the existence of 5-hydroxypyrazolidinone product II as a stable oxidation product. However, if the 5-hydroxypyrazolidinone, or a similar species in one of several oxidation states, were formed in this reaction, then it was unstable under the conditions used and was not detected.

The high yield of isobutyraldehyde in all experiments shows that cleavage of the pyrazolidinone ring system occurs even under mild oxidation conditions. The appearance of benzene and nitrogen ensures that fragmentation is almost complete.

The oxidation of the 4,4-dimethyl pyrazolidinone is not as simple a reaction as that for the unsubstituted compound, which is completely oxidized with the addition of 2 equiv. of oxidant. Instead, more than 2 equiv. of oxidant are required for the complete loss of reducing properties of the pyrazolidinone. (In aqueous sodium carbonate solution, the reaction was completed with 4 equiv. of ferricyanide solution,

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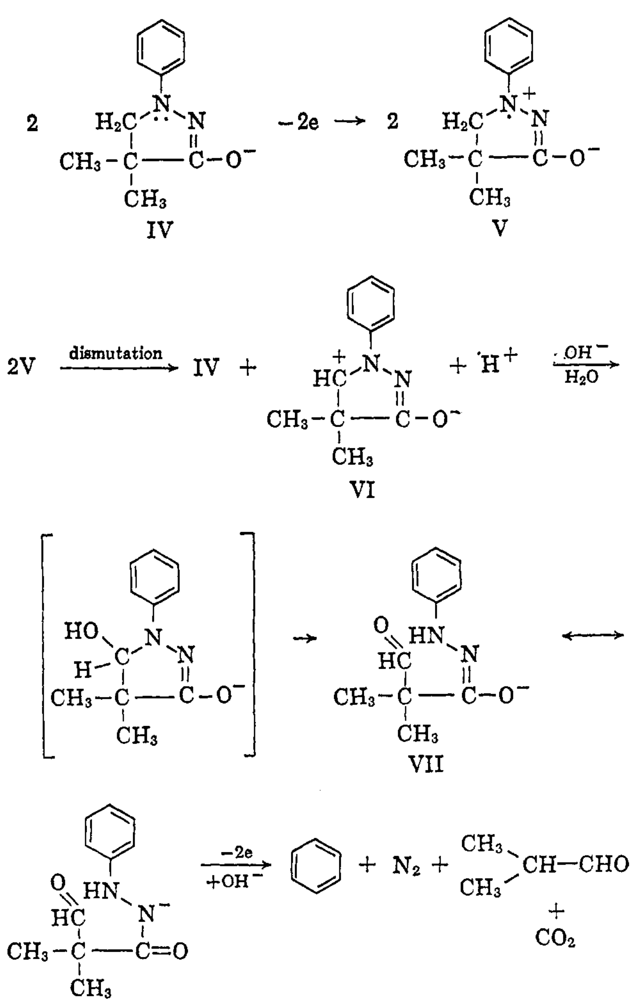
(11) The analytical results, as well as the physical properties (*i.e.*, melting point, color, etc.), were quite dependent on the conditions and the extent of reaction. A hard, solid, amorphous material which melted over a higher temperature range was obtained when a concentrated solution of the pyrazolidinone was oxidized at high pH with a large excess of the oxidant at a very long reaction time.

SCHEME I



whereas in 0.1 *N* sodium hydroxide solution, more than 5 equiv. of oxidant were required.) However, the addition of excess oxidant leads to the formation of a more resinous, polymeric material. Because of the formation of this very complex material, it was impossible to determine a mass balance for this reaction.

The steps in the oxidation reaction which follow the semiquinone dismutation are still uncertain. However, the following sequence, which is consistent with the observed stoichiometry of the reaction, accounts for the major products formed and is in agreement with the spectrochemical data. The reaction (Scheme I) can be visualized as proceeding by the loss of a single electron from the dissociated form of the pyrazolidinone IV to yield the semiquinone V. The dismutation of the semiquinone gives one molecule of IV and the electron-deficient intermediate VI, which can react with hydroxide ion to give a phenylhydrazide (VII). The major products of the reaction presumably arise by further oxidation of the hydrazide VII to the azo compound, followed by attack of hydroxide ion at the carbonyl carbon to yield benzene, nitrogen, isobutyraldehyde, and CO_2. The mode by which the minor products are formed remains obscure. However, the appearance of biphenyl, although in trace amounts, and the formation of high molecular weight polymeric materials, possibly by phenylation reactions, suggest that phenyl radicals may be formed at a relatively high concentration.

Acknowledgment.—The author should like to thank Dr. William C. Needler for his help and cooperation in providing the e.s.r. measurements and is grateful to Miss Thelma J. Davis, Mr. David P. Maier, and Dr. O. E. Schupp for infrared spectra, mass spectra, and gas chromatographic data, respectively.

Pentaoxyphosphoranes from the Reaction of Trialkyl Phosphites with α-Ketoaldehydes and with Vicinal Triketones. Condensations of α-Ketoaldehydes with α-Diketones. P^{31} and H^1 Nuclear Magnetic Resonance Spectra[1]

FAUSTO RAMIREZ,[2] A. V. PATWARDHAN, AND C. P. SMITH

Department of Chemistry, State University of New York at Stony Brook, Stony Brook, New York

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Trialkyl phosphites reacted with diphenylpropanetrione and with phenylglyoxal yielding *1:1 adducts* formulated as cyclic unsaturated pentaoxyphosphoranes on the basis of P^{31} and H^1 n.m.r. spectra and infrared and ultraviolet spectra. The trione–phosphite adduct did not react with more trione. The ketoaldehyde–phosphite 1:1 adduct reacted with a second molecule of ketoaldehyde forming a *2:1 adduct* or cyclic saturated pentaoxyphosphorane, with a new carbon–carbon bond. In this condensation, two diastereoisomers (66:34) of one type of structure were obtained. The phenylglyoxal–phosphite 1:1 adduct condensed very slowly with biacetyl to give two diastereoisomers of a pentaoxyphosphorane; the latter were obtained, very rapidly, from condensation of the biacetyl–phosphite 1:1 adduct with phenylglyoxal.

Previous papers have described the preparation of cyclic unsaturated,[3] I and II, and cyclic saturated,[1d,3] III–VIII, pentaoxyphosphoranes[4] from condensation reactions of trialkyl phosphites with α-diketones, quinones, α-keto esters, and monofunctional aldehydes.

The pentacovalent character of the phosphorus in these derivatives of the 1,3,2-dioxaphospholene and dioxaphospholane ring systems was deduced from the relatively large positive shifts of the P^{31} n.m.r. signals relative to 85% phosphoric acid, from the positions of

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[1] (a) Organic Compounds with Pentavalent Phosphorus. Part XXI; (b) Part XX: F. Ramirez, O. P. Madan, and C. P. Smith, *J. Am. Chem. Soc.*, **87**, 670 (1965); (c) Part XIX: F. Ramirez, H. J. Kugler, and C. P. Smith, *Tetrahedron Letters*, **No. 4**, 261 (1965); (d) Part XVIII: F. Ramirez, O. P. Madan, and S. R. Heller, *J. Am. Chem. Soc.*, **87**, 731 (1965).

[2] This investigation was supported by Public Health Service Research Grant No. CA-04769-05 from the National Cancer Institute, and by National Science Foundation Grant G 19509.

[3] The literature has been reviewed by (a) F. Ramirez, *Pure Appl. Chem.*, **9**, 337 (1964); (b) F. Ramirez, S. B. Bhatia, R. B. Mitra, Z. Hamlet, and N. B. Desai, *J. Am. Chem. Soc.*, **86**, 4394 (1964).

[4] For other pentaoxyphosphoranes, see (a) D. B. Denney and H. M. Relles, *ibid.*, **86**, 3897 (1964); (b) D. B. Denney and S. T. D. Gough, *ibid.*, **87**, 138 (1965).