are observed.[41] As a radical trap, cupric chloride in acetonitrile is as good or better than molecular oxygen which reportedly[42] is able to trap 85% of the radicals produced in benzene solution. The product appeared mainly as acetone cyanohydrin, though in *p*-xylene a 46% yield of 2-cyano-2-propyl hydroperoxide was isolated. The scavenging efficiencies toward the 2-cyano-2-propyl radical of a number of effective scavengers, among which are iodine,[22] galvinoxyl,[43] mercaptans,[22c] and diphenylpicrylhydrazyl,[41] have been studied. Present results[44] are encouraging enough to pursue these efficiencies with metal salt inhibitors.

Acknowledgment. We wish to thank the National Science Foundation for a generous grant which supported the work.

(41) G. S. Hammond, E. S. Wu, and O. D. Trapp, *J. Am. Chem. Soc.*, in press.
(42) Talat-Erben and N. Onal, *Can. J. Chem.*, **38**, 1154, 1157 (1960).
(43) P. D. Bartlett and T. Funabashi, *J. Am. Chem. Soc.*, **84**, 2596 (1962).
(44) Until actual competition experiments are conducted, relative efficiencies are not relevant since radical-pair production may vary substantially in different solvents.

The Diazapentalene System. 1-Benzoyl-2-phenylpyrazolo 1,2-*a* pyrazole Derivatives

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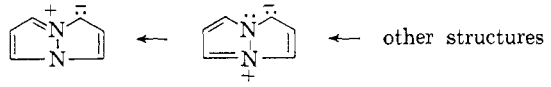
Contribution from the Chemistry Department, University of South Florida, Tampa, Florida. *Received August 7, 1964*

Pyrazole has been converted to 1,2-diphenacylpyrazolium salts by reaction with 2 moles of phenacyl bromide, p-bromo-, p-chloro-, and m-nitrophenacyl bromide. The salts undergo cyclization to 1-benzoyl-2-phenylpyrazolo-[1,2-a]pyrazole derivatives (IV) when heated with aqueous sodium bicarbonate. Heating one of these derivatives (X = H) with concentrated hydrochloric acid has been found to result in cleavage of the benzoyl group.

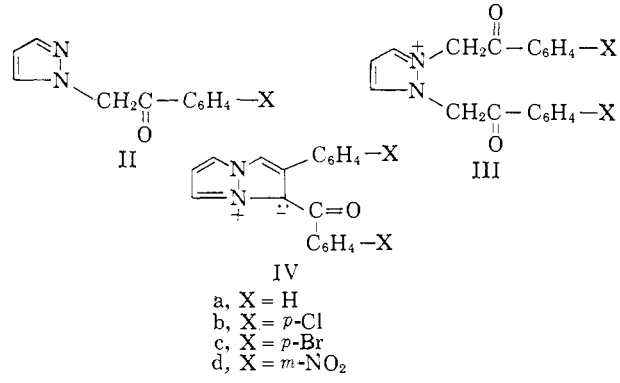
The pyrazolo[1,2-*a*]pyrazole (I) ring system has been of interest to us because of the steric and electronic analogies that can be drawn between it, pentalene,[2] and naphthalene. Our interest in this system was increased by the synthesis of the pentalene dianion,[3] a structure with which I is isosteric and isoelectronic.



I

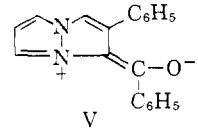
In an earlier communication[4] we reported the synthesis of 1-phenyl-2-benzoylpyrazolo[1,2-*a*]pyrazole. We now record the details of that synthesis and report an extension of it to three other phenyl-substituted derivatives.

Pyrazole reacted with phenacyl bromide in 1,2-dimethoxyethane to give a salt which on treatment with aqueous ammonia gave 1-phenacylpyrazole (IIa) in 48% yield. Alkylation of compound IIa by a second mole of phenacyl bromide in dimethylformamide produced 1,2-diphenacylpyrazolium bromide (IIIa) in 86% yield. This dialkylated salt was a colorless water-soluble substance; its infrared spectrum was lacking in N–H absorption and showed a strong carbonyl band at 5.90 μ.



The salt IIIa was treated with 10% aqueous sodium bicarbonate and heated to 50°.[5] After a few minutes yellow crystals began to deposit, and after 3 hr. a 98% yield of compound IVa was obtained.

The infrared and n.m.r. data are in accordance with our structure for IVa. No N–H, O–H, or aliphatic C–H bonds are indicated in the infrared; indeed, in this region the only peaks that appear are those normally assigned to aromatic C–H. A strong absorption at 6.58 μ is assigned to the carbonyl group and suggests that such canonical forms as V are important. The n.m.r. spectrum shows a complex series of peaks in the region τ 2.4–3.3 only.

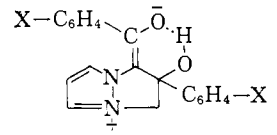


V

(1) National Science Foundation Undergraduate Participant (1962–1963); American Chemical Society–Petroleum Research Fund Scholar (1963–1964).
(2) For a review see the chapters by E. D. Bergmann and D. Craig in "Non-Benzenoid Aromatic Compounds," D. Ginsberg, Ed., Interscience Publishers, Inc., New York, N. Y., 1959.
(3) T. J. Katz, M. Rosenberger, and R. K. O'Hara, *J. Am. Chem. Soc.*, **86**, 249 (1964).
(4) T. W. G. Solomons and F. W. Fowler, *Chem. Ind* (London), 1462 (1963).
(5) These are the conditions used in the Chichibabin pyrrocoline synthesis; *cf.* A. E. Chichibabin, *Ber.*, **60**, 1607 (1927).

Comparison of Hückel LCAO–MO calculations carried out on compound I[6] with those for the pentalene dianion indicates that the increased coulombic attraction of the nitrogen atoms lowers the energy of certain of the molecular orbitals. The energy difference between the highest occupied orbital and lowest unoccupied orbital is indicated to be less for I than for the colorless pentalene dianion. This suggests that compound I should absorb at somewhat longer wave lengths. The ultraviolet absorption spectrum of IVa shows a broad absorption band at 400 mμ which correlates well with this prediction.

The three other substituted 1,2-diphenacylpyrazolium salts (IIIb, c, and d) were prepared and subjected to the same cyclization conditions. When the reactions were carried out for a short time the products that were obtained were unstable and did not appear to be of the same nature as IVa. Analysis of these intermediates from the *m*-nitro and *p*-bromo derivatives indicated that the molecule had not yet been dehydrated. The infrared spectrum of these showed no carbonyl absorption and a strongly hydrogen-bonded OH consistent with VI. When these reactions were carried out for much longer periods (120 hr. to 7 days) the fully de-



VI

hydrated derivatives (IVb, c, and d) were obtained. These products showed visible, ultraviolet (Table I), and infrared absorbances similar to IVa.

Table I. Ultraviolet Absorption Spectra of 1-Benzoyl-2-phenylpyrazolo[1,2-*a*]pyrazoles

Compd.	λ_{max}	Log ε	λ_{min}	Log ε
IVa	231	4.44	264	4.08
	275	4.14	287	4.02
	291	4.02	326	3.59
	400	4.45		
IVa	277	4.27	243	4.11
(in 6 *N* HCl)	330[a]	3.96		
IVb	230	4.22	330	3.27
	275[a]	3.90		
	400	4.10		
IVc	235	4.22	335	3.38
	405	3.95		
IVd	220	4.45	330	3.51
	260[a]	4.32		
	400	4.16		

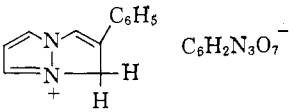
[a] Shoulder.

All of these cyclized derivatives (IV) are weakly basic. Compound IVa is insoluble in 0.1 *N* hydrochloric acid but dissolves readily in 6 *N* hydrochloric acid to give a colorless solution. When dissolved in concentrated sulfuric acid, IVa gives a red solution from which it can be recovered unchanged. Compounds IV all react rapidly with more than 1 mole of bromine, in water or carbon tetrachloride, to yield dark, intractable gums. An attempted nitration of IVa gave an oxidized product which has not been identified.

(6) E. Hückel, *Z. Physik*, 70, 204 (1933). The nitrogen atoms were assigned coulomb integrals of $\alpha + 2\beta$.

Compound IVa has considerable thermal stability in that it can be sublimed *in vacuo* at 160°.

A cleavage reaction of IVa occurred when it was refluxed with concentrated hydrochloric acid. Benzoic acid (62% yield) sublimed into the condenser and after evaporation of the acid a picrate was obtained which analyzed correctly for the hydropicrate of 2-phenylpyrazolo[1,2-*a*]pyrazole (VII).



VII

The chemistry of VII is now being investigated. It appears to be quite unstable when treated with bases suggesting that much of the stability of the derivatives IV derives from the electron-withdrawing benzoyl group in the 1-position.

Experimental[7]

Spectroscopy. All visible and ultraviolet spectra were determined in 95% ethanol solution using a Beckman DU spectrophotometer. The infrared data were determined on a Perkin-Elmer Model 137G spectrophotometer using Nujol and hexachlorobutadiene mulls in the appropriate regions. The n.m.r. spectrum was determined on a Varian A-60 spectrometer.

1-Phenacylpyrazole (IIa). A solution of pyrazole (2.04 g., 0.03 mole) and phenacyl bromide (6.0 g., 0.03 mole) in 50 ml. of 1,2-dimethoxyethane was allowed to stand at room temperature for 24 hr. and then boiled under reflux for 1 hr. The solvents were removed *in vacuo* and the residue was crystallized by triturating with chloroform and ethyl acetate. The yield of crude 1-phenacylpyrazole hydrobromide was 5.10 g. (64%), m.p. 190–193° dec. A mixture of 3.00 g. of this hydrobromide and 30 ml. of concentrated aqueous ammonia was stirred for 30 min. at room temperature. The free base was extracted into chloroform (three 20-ml. portions). The combined extracts were dried over sodium sulfate, and then evaporated to yield 1.95 g. of yellow-brown crystals. These were dissolved in ethyl acetate and chromatographed over a column (20 × 250 mm.) of Merck acid-washed alumina. Yellow needles, 1.83 g., m.p. 89–92°, were obtained in the second 25-ml. fraction. Trituration of these with hexane and ether removed the yellow impurity and gave 1.69 g. (81%) of pure 1-phenacylpyrazole, m.p. 90–91°.

Anal. Calcd. for $C_{11}H_{10}N_2O$: C, 70.95; H, 5.41; N, 15.05. Found: C, 71.34; H, 5.54; N, 15.28.

The picrate, m.p. 147–148°, was prepared in ethanol.

Anal. Calcd. for $C_{17}H_{13}N_5O_8$: C, 49.16; H, 3.15; N, 16.87. Found: C, 48.90; H, 3.44; N, 16.49.

1,2-Diphenacylpyrazolium Bromide (IIIa). A solution of 1-phenacylpyrazole (1.57 g.) and phenacyl bromide (1.70 g.) in 2 ml. of dimethylformamide was allowed to stand at room temperature for 4 days. The salt was crystallized by the addition of ethyl acetate as colorless prisms, yield 2.81 g. (86%), m.p. 173.5–174°.

(7) All melting points were taken in a Mel-Temp block and are not corrected. Analyses were by Galbraith Laboratories, Knoxville, Tenn.

The analytical sample, m.p. 176.5–177.5°, was obtained from methanol–ethyl acetate.

Anal. Calcd. for $C_{19}H_{17}BrN_2O_2$: C, 59.22; H, 4.44; N, 7.27. Found: C, 59.56; H, 4.55; N, 7.27.

1-Benzoyl-2-phenylpyrazolo[1,2-a]pyrazole (IVa). One gram of the salt IIIa was dissolved in 10 ml. of distilled water to form a yellow solution. A saturated solution of sodium bicarbonate (40 ml.) was added and the resulting mixture was heated to 50–60°. Yellow crystals began to deposit almost immediately. Heating was continued for 3 hr. to give after drying *in vacuo* 0.728 g. (98%) of a yellow solid, m.p. 192–193° dec.

The analytical sample was obtained from acetone–methylcyclohexane as orange prisms, m.p. 193–194° with darkening and decomposition at 186°: infrared 3.15 (w), 3.17 (w), 3.21 (w), 3.27 (w), 6.25 (w), 6.33 (w), 6.42 (w), 6.58 (s), 6.68 (w), 6.73 (w), 6.82 (w), 6.88 (w), 6.95 (s), 7.05 (m), and 7.47 μ (m); n.m.r. complex pattern in the region τ 2.4–3.3 only.

Anal. Calcd. for $C_{19}H_{13}N_2O$: C, 79.98; H, 4.60; N, 9.83; mol. wt., 285. Found: C, 80.02; H, 4.67; N, 9.40; mol. wt., 304.

1-(p-Chlorophenacyl)pyrazole (IIb). *p*-Chlorophenacyl bromide (11.4 g.) and pyrazole (3.4 g.) were dissolved in 70 ml. of 1,2-dimethoxyethane. This solution was stirred at room temperature for 116 hr. during which time a colorless solid deposited. Ether was added at the end of the reaction period to complete the precipitation of the salt. The yield was 12.3 g. (83%) of the hydrobromide of IIb, m.p. 171–172° dec. Concentrated aqueous ammonia (50 ml.) was added to a suspension of all the hydrobromide in 10 ml. of water. The reaction was stirred for 35 min. after which 8.22 g. (95%) of yellow crystals, m.p. 140–146° dec., was collected. The analytical sample was obtained as colorless plates, m.p. 154–155° dec., from ethanol–ether.

Anal. Calcd. for $C_{11}H_9ClN_2O$: C, 59.84; H, 4.10; N, 12.69. Found: C, 59.80; H, 4.13; N, 12.51.

1,2-Di-(p-chlorophenacyl)pyrazolium Bromide (IIIb). A solution of 5.91 g. of 1-(*p*-chlorophenacyl)pyrazole and 6.25 g. of *p*-chlorophenacyl bromide in 70 ml. of dry acetone was boiled under reflux for 66 hr. The solid that precipitated was collected and dried *in vacuo*, yielding 6.97 g. (57%) of a tan powder, m.p. 194° dec. The analytical sample was obtained from methanol–ethyl acetate as a colorless solid, m.p. 204° dec.

Anal. Calcd. for $C_{19}H_{15}BrCl_2N_2O_2$: C, 50.24; H, 3.33; N, 6.17. Found: C, 49.98; H, 3.52; N, 6.48.

1-(p-Chlorobenzoyl)-2(p-chlorophenyl)pyrazolo[1,2-a]pyrazole (IVb). The salt IIIb (1.00 g.) was heated at 60° for 44 hr. with 20 ml. of 10% aqueous sodium bicarbonate. The solid which was formed was collected and dried *in vacuo*, yielding 0.80 g. of a yellow powder, m.p. 145–150° with decomposition beginning at 143°. The analytical sample, m.p. 151–152° dec., was prepared from methanol–water. During recrystallization of this material a dark substance that precipitated first was discarded.

Anal. Calcd. for $C_{19}H_{12}Cl_2N_2O$: C, 62.00; H, 3.38; N, 7.89. Found: C, 62.13; H, 3.60; N, 7.65.

1-(p-Bromophenacyl)pyrazole (IIc) was prepared in the same way as the *p*-chloro derivative in 61% yield. The analytical sample was a colorless solid, m.p. 162–164°.

Anal. Calcd. for $C_{11}H_9BrN_2O$: C, 49.83; H, 3.43; N, 10.57. Found: C, 49.53; H, 3.42; N, 10.21.

1,2-Di-(p-bromophenacyl)pyrazolium bromide (IIIc) was prepared in dimethylformamide in the same way as IIIb, yielding 53.4% of colorless prisms, m.p. 201.5°.

Anal. Calcd. for $C_{19}H_{15}Br_3N_2O_2$: C, 42.02; H, 2.79; N, 5.16. Found: C, 41.89; H, 2.78; N, 5.29.

1-(p-Bromobenzoyl)-2-(p-bromophenyl)pyrazolo[1,2-a]pyrazole (IVc) was prepared by bicarbonate cyclization at 60° for 7 days, yielding 85% of an orange-yellow powder, m.p. 120° dec. The analytical sample was prepared from methanol–water.

Anal. Calcd. for $C_{19}H_{12}Br_2N_2O$: C, 51.38; H, 2.72; N, 6.31. Found: C, 51.16; H, 2.90; N, 6.10.

Short-Time Cyclization of 1,2-Di-(p-bromophenacyl)-pyrazolium Bromide. When the above reaction was carried out for only 2 hr., a water-insoluble orange solid, m.p. 130° dec., was obtained in nearly quantitative yield. This material showed peaks at 2.90, 3.14, 3.18, and 3.22 μ, with broad background absorption in the region 2.4–3.6 μ. The carbonyl region showed a weak shoulder at 5.90–6.0 μ. Recrystallization from 2-butanone and pentane yielded an analytical sample, m.p. 151° dec.

Anal. Calcd. for $C_{19}H_{14}Br_2N_2O_2$: C, 49.37; H, 3.05; N, 6.06. Found: C, 49.89; H, 2.96; N, 6.20.

1-(m-Nitrophenacyl)pyrazole (IId). A solution of pyrazole (3.4 g.) and *m*-nitrophenacylpyrazole (12.20 g.) in 75 ml. of 1,2-dimethoxyethane was stirred at room temperature for 142 hr. The precipitate was collected, yield 11.57 g. (74%) of the hydrobromide of IId, m.p. 215–216° dec. This was treated with aqueous ammonia to yield 5.31 g. (63%) of the free base, m.p. 135–136°. The analytical sample was obtained from methanol–ethyl acetate as colorless needles, m.p. 135.5–136°.

Anal. Calcd. for $C_{11}H_9N_3O_3$: C, 56.89; H, 3.93; N, 18.17. Found: C, 56.92; H, 4.16; N, 17.98.

1,2-Di-(m-nitrophenacyl)pyrazolium Bromide (IIId). This compound was prepared in the same way as the corresponding *p*-chloro derivative in 40% yield. The analytical sample was obtained as tan plates, m.p. 199–200°.

Anal. Calcd. for $C_{19}H_{15}BrN_4O_6$: C, 48.01; H, 3.18; N, 11.78. Found: C, 48.04; H, 3.19; N, 11.44.

1-(m-Nitrobenzoyl)-2-(m-nitrophenyl)pyrazolo[1,2-a]pyrazole (IVd). The salt IIId (0.95 g.) was heated at 60° with 30 ml. of 10% aqueous sodium bicarbonate for 120 hr. to give 0.137 g. of an orange solid which decomposed slowly from 174 to 204°.

Anal. Calcd. for $C_{19}H_{12}N_4O_5$: C, 60.64; H, 3.22; N, 14.89. Found: C, 60.47; H, 3.26; N, 14.56.

Short-Time Cyclization of 1,2-Di-(m-nitrophenacyl)-pyrazolium Bromide. Reaction of this salt with 10% sodium bicarbonate for 2 hr. furnished a near-quantitative yield of an orange solid, m.p. 140–150° dec. The infrared spectrum of this substance showed sharp C–H absorption at 3.18, 3.20, 3.24, and 3.30 μ with a broad background peak from 3.0 to 4.0 μ. It showed no

absorption in the 5.0–6.0-μ region. All attempts at crystallization from a variety of solvents resulted in decomposition with the appearance of a band at 5.95 μ. Analysis of the material directly from the reaction mixture after drying at 55° for 48 hr. *in vacuo* gave the following result.

Anal. Calcd. for $C_{19}H_{14}N_4O_5$: C, 57.9; H, 3.56. Found: C, 57.9; H, 3.50.

This material could be converted to IVd by heating with aqueous bicarbonate for an additional 120 hr.

Reaction of 1-Benzoyl-2-phenylpyrazolo[1,2-a]pyrazole with Hydrochloric Acid. Two hundred milligrams of IVa was treated with 6 ml. of concentrated hydrochloric acid. The resulting solution was heated under reflux for 10 hr. during which time 0.039 g. of benzoic acid (identified by infrared and melting point) sublimed into the condenser. On cooling the solution, an additional 0.012 g. of benzoic acid (61% over-all) was obtained. The filtrate was evaporated *in vacuo* to yield 0.241 g. of a brown hygroscopic solid. This was treated with picric acid to give what appeared to be the *hydropicrate* of 2-phenylpyrazolo[1,2-*a*]pyrazole, yield 0.230 g. (82%), as a yellow solid, m.p. 174–178°. This material was unstable in solution and was analyzed directly.

Anal. Calcd. for $C_{18}H_{13}N_5O_7$: C, 52.55; H, 3.19; N, 17.02. Found: C, 52.54; H, 3.19; N, 16.80.

Acknowledgment. Acknowledgment is made to the National Science Foundation and to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this research.

The Reaction of Aliphatic Diamines with Phenyl Acetate

Thomas C. Bruice[1] and Roland G. Willis[2]

Contribution From the Department of Chemistry, Cornell University, Ithaca, New York. *Received July 27, 1964*

The reactions of the aliphatic primary amines n-propylamine and n-butylamine, the diamines $NH_2(CH_2)_nNH_2$, and their conjugate acids $NH_2(CH_2)_nNH_3^+$ (where n = 2–6), with phenyl acetate are kinetically first order in amine and first order in ester. The lack of detectable termolecular terms provides evidence that intermolecular general base and general acid catalysis is not significant in the aminolysis of phenyl acetate by alkyl amines. The positive deviations of the log k_r values for the diamines from a Brønsted plot for the reaction of simple amines with phenyl acetate suggest that some contribution from intramolecular general base and general acid catalysis might occur or alternatively that the diamines form a separate Brønsted series. The reactions of 2-dimethylaminoethylhydrazine and 3-dimethylaminopropylhydrazine with phenyl acetate were also found to be first order in nucleophile and first order in ester. This result is in marked contrast to the importance of general base and/or general acid assistance in the reaction of hydrazine and N-methylhydrazine with phenyl acetate. The rate constants for the reaction of dimethylaminoalkylhydrazines with phenyl acetate are about 10^3 greater than predicted from a Brønsted plot and the dependence of the rate constants on the mole fraction of the dimethylamino group in the free-base form suggests a very significant intramolecular general base catalysis.

Previous reports of investigations of the aminolysis, ammonolysis, hydrazinolysis, etc., of phenyl acetate (PA) have shown these reactions to be subject to general base and general acid catalysis. Bruice and Mayahi[3] found the ammonolysis of PA to follow the rate expression (30°, H_2O, μ = 1.0 *M*)

$$\frac{+d(P)}{dt} = [0.245(NH_3) + 0.722(NH_3)^2](PA) = [k_n(NH_3) + k_{gb}(NH_3)^2](PA) \quad (1)$$

where k_n and k_{gb} represent rate constants for second-order nucleophilic attack of ammonia and third-order general base assisted nucleophilic attack of ammonia, respectively. Jencks and Carriuolo[4a] reported the following rate laws for the aminolysis of PA by several simple aliphatic amines (25°, H_2O, μ = 1.0 *M*).[4b]

$$\frac{+d(P)}{dt} = [4.5(n\text{-BuNH}_2) + 5.0(n\text{-BuNH}_2)^2 + 1900(OH^-)(n\text{-BuNH}_2)](PA) \quad (2)$$

$$\frac{+d(P)}{dt} = [4.5(Me_2NH) + 14.0(Me_2NH)^2 + 2430(OH^-)(Me_2NH)](PA) \quad (3)$$

In addition it was found by Jencks and Carriuolo[4a] that the hydroxylaminolysis of PA exhibited general acid as well as general base catalysis, *viz.*

$$\frac{-d(PA)}{dt} = [0.70(NH_2OH) + 6.0(NH_2OH)^2 + 1.7(NH_2OH)(NH_3^+OH)](PA) = [k_n(NH_2OH) + k_{gb}(NH_2OH)^2 + k_{ga}(NH_2OH)(NH_3^+OH)](PA) \quad (4)$$

where k_{ga} is the rate constant for the termolecular

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(2) Postdoctoral Fellow of the Department of Chemistry, Cornell University.

(3) T. C. Bruice and M. F. Mayahi, *J. Am. Chem. Soc.*, **82**, 3067 (1960).

(4) (a) W. P. Jencks and J. Carriuolo, *ibid.*, **82**, 675 (1960). (b) We were unable to detect a k_{gb} term for either *n*-butyl- or *n*-propylamine reacting with PA (see Results).