[CONTRIBUTION FROM MCNEIL LABORATORIES, INC.]

2-Alkoxy-2-imidazolines and Related Compounds[1]

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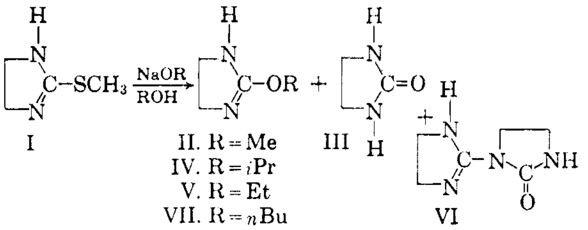
The preparation of several of 2-alkoxy-2-imidazolines by treating 2-methylmercapto-2-imidazoline with strong bases in the appropriate alcohol is described. A side-product, which was isolated in several cases, was shown to be 1-(2'-imidazolin-2'-yl)-2-imidazolidinone (VI). Further proof for the correct structure of Jaffe's base (IX, the thio analog of VI) is presented. Attempts to improve the yield of side-product VI or obtain it by an alternate method were unsuccessful.

The reaction of amines with 2-methylmercapto-2-imidazoline (I) hydroiodide gives 2-substituted amino-2-imidazolines.[2] In a study of this reaction using secondary amines and mercuric oxide in methanol solvent,[3] we isolated 2-methoxy-2-imidazoline (II) as the fumarate in very low yield. Since 2-alkoxy-2-imidazolines had not been previously reported,[4] we decided to investigate their preparation and properties. Although many examples are known of the replacement of the methylmercapto group in heterocycles by amino, substituted amino, and hydroxyl groups, we are unaware of any reports of replacement by alkoxyl.

The use of triethylamine with mercuric oxide, I-hydriodide, and methanol did not appreciably increase the yield of II despite the fact that the tertiary amine could not form a 2-amino-2-imidazoline. We then turned our attention to stronger bases. When heated under reflux with sodium methoxide in methanol, 2-methylmercapto-2-imidazoline slowly liberated methyl mercaptan. After 18 hours, mercaptan evolution had practically ceased. Work-up of the reaction gave a 75 to 80% recovery of organic material. This mixture of products was conveniently separated by differential ether solubility; the ether-insoluble part proved to be ethyleneurea (III) which was obtained in 5 to 20% yield. The ether-soluble product was crude 2-methoxy-2-imidazoline which was present in 50 to 70% yield. Conversion to a salt such as the fumarate or chromatography on alumina of the free base provided pure products in 40–50% yield.



As the free base, 2-methoxy-2-imidazoline proved to be a rather low-melting, fairly volatile crystalline solid. It tended to become oily on standing, which may have been due to the somewhat hygroscopic nature of II. When pressed into potassium bromide pellets for a study of the infrared spectrum, medium intensity bands appeared at 5.8 and 5.9 μ that were absent in solution or Nujol mull spectra and suggested that chemical changes occurred in the pelleting process. However, it was recovered unchanged after standing overnight in normal sodium hydroxide solution as well as 24 hours at 40° in normal hydrochloric acid.

A number of unsuccessful attempts were made to obtain a reasonable yield of II by other routes. Methods known to *O*-methylate caprolactam[5] and urea[6] when applied to ethyleneurea yielded only the *N*-methylated product (1-methyl-2-imidazolinone). Since the conversion of I to II by alkoxides bears some formal resemblance to ester interchange,[7] 2-methylmercapto-2-imidazoline was subjected to acid-catalyzed interchange conditions. With hydrogen chloride in dry methanol, I was recovered unchanged. When I was heated in methanol with a catalytic amount of *p*-toluenesulfonic acid hydrate, only ethyleneurea could be isolated. The appearance of a report by Behringer and Meier[8] describing several methods for converting cyclic thioureas and ureas to the corresponding methyl isourea prompted our investigation of them in the five-membered ring case. We repeated Behringer and Meier's[8] attempted reaction of ethylenethiourea and mercuric oxide in methylene chloride–methanol in the hope of detecting a small amount of 2-methoxy-2-imidazoline but found only unchanged ethylenethiourea, confirming their result. However, heating ethyleneurea with methyl *p*-toluenesulfonate did give us about 1.5% of II, isolated and identified as the picrate. These results

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[1] Part of this work has been published in preliminary form; C. K. Cain, J. Kleis, and G. I. Poos, *J. Org. Chem.*, **22**, 1283 (1957).

[2] S. R. Aspinall and E. J. Bianco, *J. Am. Chem. Soc.*, **73**, 602 (1951).

[3] C. K. Cain, U. S. Patent **2,742,481** (1956).

[4] Recently, A. F. McKay, M. E. Kreling, G. Y. Paris, R. O. Braun, and D. J. Wittingham, *Can. J. Chem.*, **35**, 843 (1957), reported a compound for which they write a 1-substituted-2-ethoxy-2-imidazoline structure.

[5] R. E. Benson and T. L. Cairns, *J. Am. Chem. Soc.*, **70**, 2115 (1948); *Org. Syntheses*, **31**, 72 (1951).

[6] E. A. Werner, *J. Chem. Soc.*, **105**, 923 (1914).

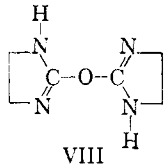
[7] Very recently the first successful interchange of thiol to alcohol esters was reported to occur under both acidic and basic conditions: G. S. Sasin, P. R. Shaeffer, and R. Sasin, *J. Org. Chem.*, **22**, 1183 (1957).

[8] H. Behringer and H. Meier, *Ann.*, **607**, 67 (1957).

made it apparent that the 2-alkoxy-2-imidazoline system is relatively difficult to form. We find its stability to acid and base somewhat surprising.

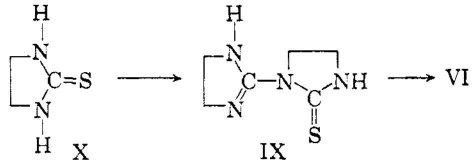
The behavior of 2-methylmercapto-2-imidazoline in several other alkanols with the sodium alkoxide was investigated. After 63 hours' heating of I in isopropanol with sodium isopropoxide, methyl mercaptan continued to evolve slowly. The reaction was worked up giving 66% of unchanged I and, after chromatography over alumina, 11% of 2-isopropoxy-2-imidazoline (IV). With sodium ethoxide in ethanol, about 45 hours under reflux was required to complete the reaction. In this case, 2-ethoxy-2-imidazoline (V) was obtained in crude yields of 30 to 85%. It was conveniently isolated as the fumarate which was obtained pure in yields up to 65%. In addition, this reaction gave up to 40% of a mixture from which up to 17% of a new base VI was isolated. The structure and formation of VI is discussed in greater detail below. When *N*-butyl alcohol was used, a 22-hour reflux period provided 47% of pure 2-*n*-butoxy-2-imidazoline (VII) and about 10% of product VI. With benzyl alcohol and sodium benzylate, 23 hours' heating at 100° completed the reaction. No 2-benzyloxy-2-imidazoline could be found in the mixture of products. Small amounts of ethyleneurea and compound VI were separated from this mixture.

Microanalyses of compound VI and its normal fumarate showed the formula $C_6H_{10}N_4O$. Only two structures, VI and VIII, can be reasonably written for this formula. Since VI is a monoacidic base and VIII would have two basic nitrogens, a potentiometric titration of compound VI which showed a single break in the curve (pK_a 6.0, neut. equiv. 160) allowed us to choose structure VI. This structure was supported by the infrared spectrum which showed an intense carbonyl absorption band at 5.82 μ. Although ethyleneurea itself shows its carbonyl absorption band at 6.0 μ, the proximity of the C=N function to the carbonyl group in VI would be expected to lead to a vibrational interaction between the two groups which would result in the observed lowering of the carbonyl absorption wave length.[9]



VIII

In seeking additional support for structure VI, we have prepared the known thioanalog IX [1 (2′-imidazolin-2′-yl)-2-imidazolidinethione; "Jaffé's base"] and converted it to VI by heating in aqueous ethanol with mercuric oxide. Since both the original[10] and a subsequent[11] assignment of structure to Jaffé's base (IX) were in error,[12] we have provided additional evidence for the correctness of IX. Structure IX was first suggested by Lecher and Gubernator[13] by analogy to some of their results with *N*-alkylthioureas but without carrying out experimental work. Later Chase and Walker[14] prepared Jaffé's base, investigated its ultraviolet spectrum and concluded that Lecher and Gubernator were correct in assigning structure IX. Initially we prepared Jaffé's base by Johnson and Edens' method *via* ethylenethiourea disulfide hydroperiodide. Analysis of the base and its hydroiodide, potentiometric titration of the base and ultraviolet and infrared spectra of the base and its salts provided convincing evidence for assignment of the 1-(2′-imidazolin-2′-yl)-2-imidazolidinethione structure. These data together with the conversion of IX to VI mutually support both structures as written.



The reported conversion of 1,1,3-trimethyl-2-thiourea into 1-(trimethylguanyl)-1,3,3-trimethyl-2-thiourea by reaction with mercuric oxide in benzene[13] prompted us to try the reaction with ethylenethiourea (X). With benzene as a solvent, we recovered only a trace of organic material. However, by heating ethylenethiourea with mercuric oxide in xylene, a 25% recovery of organic product was realized from which 9% of pure Jaffé's base IX was obtained by recrystallization.

An effort was made to determine the source of 1-(2′-imidazolin-2′-yl)-2-imidazolidinone (VI). Although many experiments designed to shed light on a logical pathway to VI were carried out, the results have been disappointing.

Particularly frustrating was the variability in the amount of this compound obtained from one run to the next. Variations in concentration of 2-methylmercapto-2-imidazoline or of the base, in the presence or absence of water, air, and peroxide, and in the methods of working up the reaction

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[9] We have observed a 0.15 μ lowering of the carbonyl band in several 2-benzoxazolinones substituted on the nitrogen atom with a doubly bound carbon; see J. Sam, J. N. Plampin, and G. I. Poos, *J. Org. Chem.*, **23,** 1500 (1958).

[10] M. Jaffé and B. Kühn, *Ber.*, **27,** 1663 (1894).

[11] T. B. Johnson and C. O. Edens, *J. Am. Chem. Soc.*, **63,** 1058 (1941); T. B. Johnson and C. O. Edens, *J. Am. Chem. Soc.*, **64,** 2706 (1942).

[12] The second incorrect assignment persists in several authoritative books on heterocycles: (a) E. S. Schipper and A. R. Day in Elderfield, *Heterocyclic Compounds*, Vol. 5, John Wiley & Sons, Inc., New York, N. Y. (1957), p. 251. (b) K. Hofmann, *The Chemistry of Heterocyclic Compounds, Imidazole and Its Derivatives (Part I)*, Interscience Publishers, Inc., New York, N. Y. (1953), p. 237.

[13] H. Z. Lecher and K. Gubernator, *J. Am. Chem. Soc.*, **75,** 1087 (1953).

[14] B. H. Chase and J. Walker, *J. Chem. Soc.*, 4443 (1955).

mixtures could not be correlated with variations in the yield of VI.

An attempt to react ethyleneurea (III) with 2-methylmercapto-2-imidazoline (I) in potassium *t*-butoxide/*t*-butyl alcohol led to the recovery of I and III. Equimolar quantities of I and III heated in methanolic sodium methoxide gave only II and III. Equal amounts of the S- and O-methyl compounds I and II were heated under reflux in toluene for many hours without reaction. When I and ethylenethiourea (X) with 0.5 mole of sodium hydroxide in ethanol were heated until methyl mercaptan evolution had ceased, an estimated 55% of X was recovered, Jaffé's base (IX) was formed in 45% yield (based on I and X), and 2-ethoxy-2-imidazoline (V) in 45% yield. No VI was found. The reaction of V and X under similar conditions gave a complex mixture but no VI could be detected by infrared. With sodium hydroxide in ethanol, III and X failed to react.

EXPERIMENTAL[15]

2-Methoxy-2-imidazoline (II). Freshly liberated 2-methylmercapto-2-imidazoline (I, 11.5 g., m.p. 102–107°, from 24.5 g., 0.1 mole, of the hydroiodide[16]) was added to a solution of 0.1 mole of sodium methoxide in 85 ml. of reagent grade methanol. The colorless solution was heated under reflux for 23 hr. Methyl mercaptan began to evolve after 1 hr. and appeared to have ceased after 20 hr. The solution was concentrated to dryness under vacuum, ice and water were added, and the resulting aqueous solution was continuously extracted for 6 hr. with methylene chloride. Evaporation of the extract provided 7.6 g. of a low-melting residue. Care had to be taken to prevent loss of product by volatilization. The residue was triturated with anhydrous ether and the insoluble part was separated by filtration; 0.46 g. (5.3%), m.p. 128–132°. After recrystallization from ethanol, this minor product melted at 132–134° and was shown to be ethyleneurea by mixed melting point and infrared spectrum (λ_{max} 3.03, 6.0, 6.61, 6.71 μ).

Evaporation of the ethereal filtrate provided 7.0 g. (70%) of crude crystalline product, m.p. 57–69°. Purification by recrystallization from heptane gave water-soluble, somewhat volatile, colorless crystals melting at 67–70°. When adsorbed on alumina, eluted with 1:4 ether–petroleum ether and then recrystallized from ether–petroleum ether, the resulting pure 2-methoxy-2-imidazoline showed m.p. 70–72°; λ_{max} 3.16, 6.11, 6.59 μ; pK_a 5.8 (neut. equiv. 101). Ultraviolet spectra in methanolic, acidic, and basic solution showed only end absorption. On standing in the atmosphere, 2-methoxyimidazoline became oily and liquefied. A single attempt at microanalysis gave low values for carbon, hydrogen, and nitrogen.

The *acid fumarate* from methanol had m.p. 136–139°; λ_{max} 3.23, 3.67, 5.90, 6.09, 6.33, 6.70 μ.

Anal. Calcd. for $C_8H_{12}N_2O_5$: C, 44.44; H, 5.60; N, 12.96. Found: C, 44.70; H, 5.52; N, 13.27.

Picrate from methanol, m.p. 168–170°.

Anal. Calcd. for $C_{10}H_{11}N_5O_8$: C, 36.48; H, 3.37; N, 21.27. Found: C, 36.53; H, 3.23; N, 20.86.

2-Isopropoxy-2-imidazoline (IV). One-tenth mole quantities of sodium and then I were dissolved in 150 ml. of anhydrous 2-propanol and the solution heated under reflux. After 63 hr., methyl mercaptan continued to evolve slowly so the solution was concentrated *in vacuo*, the residue dissolved in ice water, and the resulting solution was extracted with ether and methylene chloride. From the combined extracts there was obtained 10 g. of an oily solid that appeared to be a mixture of I and IV by infrared.

Chromatography over 200 g. of alumina using ether–petroleum ether gave crude IV first followed by recovered I (7.3 g., 66%, m.p. 104–105°). Rechromatography of the product provided 1.3 g. (10%), m.p. 65–67°; λ_{max} 3.16, 6.16, 6.63, 6.74 μ.

Anal. Calcd. for $C_6H_{12}N_2O$: N, 21.87. Found: N, 21.20.

Picrate from methanol, m.p. 131–133°.

Anal. Calcd. for $C_{12}H_{15}N_5O_8$: C, 40.34; H, 4.23; N, 19.60. Found: C, 40.62; H, 4.23; N, 19.36.

2-Ethoxy-2-imidazoline (V) *and 1-(2'-imidazolin-2'-yl)-2-imidazolidinone* (VI). Absolute ethanol (75 ml.) containing sodium ethoxide (0.1 mole) and methylmercapto compound I (0.1 mole) was heated under reflux until the evolution of methyl mercaptan had ceased (47 hr.) and worked up as described for II. The total crude product amounted to 10.5 g. of oily solid which was separated into ether-insoluble [0.40 g. (5%), m.p. 145–160°] and ether-soluble [9.6 g. (84%), m.p. 30–40°] fractions. The amount of ether-insoluble material, which proved to be crude VI, varied in a series of experiments from a mere trace up to about 3 g. (40%).

Purification of the ether-soluble product by chromatography over alumina using ether–petroleum ether to elute the product gave pure 2-ethoxy-2-imidazoline, m.p. 50–51.5°; λ_{max} 3.23, 6.14, 6.57, 6.73 μ.

When the entire ether-soluble fraction was combined in methanol with an equimolar quantity of fumaric acid, the acid fumarate of V was precipitated with ether in 70% yield; m.p. 116–121°. Recrystallization from ethanol-ether gave the pure salt, m.p. 123–125°; λ_{max} 3.25, 3.70, 5.15–5.25, 5.88, 6.12, 6.20, 6.34, 6.68 μ.

Anal. Calcd. for $C_9H_{14}N_2O_5$: N, 12.17. Found: N, 12.16, 12.23.

Recrystallization of the ether-insoluble fraction from acetone-heptane and finally from benzene provided pure VI, m.p. 200–204° (dec.); λ_{max} 3.00, 3.18, 5.82, 6.22, 6.64, 6.70 μ, pK_a 6.0.

Anal. Calcd. for $C_6H_{10}N_4O$: C, 46.74; H, 6.54; N, 36.34; neut. equiv. 154. Found: C, 46.77; H, 6.51; N, 36.31; neut. equiv. 160.

The normal *fumarate* of VI was recrystallized from methanol-ether, melted at 232–234° (dec.) and showed λ_{max} 3.02, 3.65, 5.70, 6.14, 6.30, 6.65, 6.73 μ.

Anal. Calcd. for $C_{16}H_{24}N_8O_6$: C, 45.28; H, 5.70; N, 26.40. Found: C, 45.22; H, 5.70; N, 26.42.

2-n-Butoxy-2-imidazoline (VII). Tenth-molar quantities of sodium *n*-butoxide and I were heated under reflux in *n*-butyl alcohol for 22 hr. and the reaction mixture was worked up as described for II. From acetone-heptane, the total crude product yielded 1.0 g. (13%) of VI, m.p. 187–197°, identified by infrared spectrum. Chromatography on alumina of the remainder of the material provided 6.7 g. (47%) of pure VII, m.p. 56–58°; λ_{max} 3.16, 6.13, 6.58, 6.71 μ. The acid fumarate of VII was prepared, m.p. 126–128°; λ_{max} 3.26, 3.72, 5.20, 5.88, 6.01, 6.12, 6.39 μ.

Anal. Calcd. for $C_{11}H_{18}N_2O_5$: N, 10.85. Found (K): N, 10.73, 10.82.

1-(2'-Imidazolin-2'-yl)-2-imidazolidinethione (IX). *A. By the method of Johnson and Edens.*[11] Ethylenethiourea disulfide hydroperiodide was obtained in 80% yield from ethylenethiourea, iodine, and KI as purple crystals which decomposed at about 100°; λ_{max} 2.99, 3.07, 6.14, 6.23, 6.48, 6.55 μ. Boiling the hydroperiodide in water gave the hydroiodide of IX as white needles, m.p. 220–260° (dec.) in 50% yield. A sample recrystallized from water decomposed at 296–299° and showed λ_{max} 3.17, 6.15, 6.27, 6.52, 6.72 μ; λ_{max} 222 mμ, ϵ_{max} 25,000, λ_{max} 263 mμ, ϵ_{max} 11,700.

Anal. Calcd. for $C_6H_{11}IN_4S$: C, 24.17; H, 3.72; N, 18.95. Found: C, 24.14; H, 3.60; N, 18.90.

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[15] Melting points were determined with a Kofler micro hot-stage. Infrared spectra were determined in mineral oil mull and ultraviolet spectra in methanol solution.

[16] W. Schacht, *Arch. Pharm.*, **235**, 441 (1897).

Liberation of the base from an aqueous solution of the hydroiodide with ammonia gave crude IX melting at 218–222° (dec.). Recrystallization from ethanol to constant melting point provided prisms, m.p. 236–238° (dec.); λ_{max} 3.05, 3.25, 6.21, 6.45–6.52, 6.60, 6.74 μ; λ_{max} 234 mμ, ϵ_{max} 11,600, λ_{max} 262 mμ, ϵ 12,600 (literature[14] 232 and 264 mμ in methanol, ϵ_{max} 13,500).

Anal. Calcd. for $C_6H_{10}N_4S$: C, 42.33; H, 5.92; N, 32.91; S, 18.83. Found: C, 42.46; H, 5.80; N, 33.07; S, 18.71.

B. From ethylenethiourea and mercuric oxide. A suspension of 10 g. of yellow mercuric oxide and 5.0 g. of ethylenethiourea in 50 ml. of xylene was heated under reflux for 4 hr. and filtered hot. The dark insolubles were continuously extracted with chloroform and the combined xylene filtrate and chloroform extract was concentrated to dryness providing 1.21 g. of yellow solid, m.p. 155–190°. Two recrystallizations from ethanol resulted in 0.37 g. (9%) of IX, identified by mixed melting point [236–238° (dec.)] and infrared spectrum.

Conversion of IX *to* VI. A mixture of 3.00 g. of IX, 9.0 g. of yellow mercuric oxide, and 55 ml. of 50% ethanol was heated under reflux for 4.5 hr., was then filtered hot, and the dark insoluble part was washed thoroughly with hot ethanol. The combined solution was concentrated to dryness and the gummy residue (1.15 g.) was dissolved in acetone and the solution was filtered. Concentration to low volume provided 0.14 g. (5%), m.p. 188–202°, which after recrystallization from acetone-benzene amounted to 0.11 g. of VI, m.p. and mixed m.p. 200–204° (dec.), further identified by infrared spectrum.

O-Methylation of ethyleneurea. A mixture of 8.6 g. (0.10 mole) of ethyleneurea and 18.6 g. (0.10 mole) of methyl *p*-toluenesulfonate was heated at 100° for 4 hr. by the method of Behringer and Meier.[8] The cooled mixture was distributed between ether and dilute hydrochloric acid and the acid layer was made basic and extracted with ether. From the dried ether extract there was obtained a small amount of oily solid which gave an infrared spectrum very similar to that of 2-methoxy-2-imidazoline (II). A picrate was obtained from methanol, which after one recrystallization amounted to 0.50 g. (1.5%) of II-picrate, m.p. 164–166°, identified by mixed melting point and infrared spectrum.

1-Methyl-2-imidazolinone. The procedure known to *O*-methylate caprolactam[5] was applied to ethyleneurea. In this case, a heterogeneous reaction mixture was obtained. From 17.2 g. (0.2 mole) of ethyleneurea and 25.2 g. (0.2 mole) of dimethylsulfate, there was obtained 15.9 g. of organic material after work-up. Fractional crystallization from ethyl acetate provided 2.8 g. (16%) of unchanged starting material, identified by melting point (128–131°) and infrared spectrum. The remainder was chromatographed over alumina. No 2-methoxy-2-imidazoline could be detected. The first material to be eluted (with mixtures of ether–petroleum ether and with ether) was crystalline 1-methyl-2-imidazolinone, melting first at 100–110° and then at 110–112° in later fractions. Purification by recrystallization from benzene and benzene-ether gave 2.3 g. (11%), m.p. 115–116°; λ_{max} 3.07, 3.22, 5.95, 6.60 μ.

Anal. Calcd. for $C_4H_8N_2O$: C, 47.98; H, 8.05; N, 27.98. Found: C, 48.14; H, 7.93; N, 27.60.

Heating ethyleneurea with methylsulfate by the method used to make methylisourea[6] gave very similar results.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF DELAWARE]

1,3-Disubstituted Indeno[1,2-*c*]pyrazol-4-ones[1]

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The reaction of hydrazine with 2-pivalyl, 2-benzoyl, and 2-*p*-methoxy-1,3-indandiones give the corresponding 3-substituted indeno[1,2-*c*]pyrazol-4(1*H*)-ones in good yields. These compounds give *N*-sodium and potassium salts which react readily with active halogen compounds to give a new class of fluorescent compounds, 1,3-disubstituted indeno[1,2-*c*]pyrazol-4-ones. The infrared absorption spectra are discussed.

In connection with our earlier work on the Wolff-Kishner reduction of 2-acyl-1,3-indandiones,[3] we showed that 3-substituted indeno[1,2-*c*]pyrazol-4(1*H*)-ones were intermediates in the reduction. The primary purpose of the investigation reported here was to study 3-substituted-indeno[1,2-*c*]pyrazol-4(1*H*)-ones and their reactions, with emphasis on the new compounds, 1,3-disubstituted indeno[1,2-*c*]pyrazol-4-ones.

The cyclization of β-diketones with hydrazine to give pyrazoles has been studied extensively,[4] but prior to our work there has been no report of the cyclization reaction of 2-acyl(aroyl)-1,3-indandiones with hydrazine. A somewhat related reaction was studied by Ruhemann[5] and later by Leucks and Kowalski.[6] They found that ethyl-1-hydrindone-2-oxalate reacted with phenyl hydrazine to give ethyl-1-phenylindeno[1,2-*c*]pyrazole-3-carboxylate.

In our study of the monohydrazones of 2-acyl-(aroyl)-1,3-indandiones we observed that certain indandiones did not give monohydrazones, but cyclized very rapidly. 2-Pivalyl, 2-benzoyl, or 2-*p*-methoxybenzoyl-1,3-indandione reacts with one equivalent of hydrazine in refluxing alcohol to give white crystalline compounds resulting from the elimination of two moles of water, as shown by elemental analyses and molecular weight de-

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(1) From the dissertation submitted by Robert A. Braun in partial fulfillment of the requirements for the Ph.D. degree, University of Delaware.

(2) To whom inquiries should be addressed.

(3) R. A. Braun and W. A. Mosher, *J. Am. Chem. Soc.*, **80**, 4919 (1958).

(4) H. Gilman, *Organic Chemistry, An Advanced Treatise*, John Wiley & Sons, Inc., New York, N. Y., 1953, Vol. IV, p. 774.

(5) S. Ruhemann, *J. Chem. Soc.*, **101**, 1731 (1912).

(6) H. Leucks and G. Kowalski, *Ber.*, **58B**, 2288 (1958).