m.p. 143–146°. A sample was recrystallized from ether–hexane for analysis and had m.p. 147–148°; $[\alpha]^{22}D$ +37° (*c* 1.0); ν_{max} 3450 (OH) cm.$^{-1}$.

Anal. Calcd. for $C_{25}H_{37}NO$: C, 81.69; H, 10.15; N, 3.81. Found: C, 81.81; H, 10.15; N, 4.01.

3β-Acetoxy-5α-17-azapregnan-20-one (11) from 9.—The solution of 300 mg. of the N-benzyl compound (9) in 10 ml. of methanol containing a few drops of acetic acid was added to 50 mg. of platinum oxide, and the mixture was reduced with hydrogen for 18 hr. at 40 p.s.i. The catalyst was filtered off and washed with some ethanol. Evaporation of solvent gave 250 mg. of an oil which crystallized from ether. The crystals were too hygroscopic for isolation and the amine, therefore, was acetylated at room temperature with 2 ml. of acetic anhydride in 5 ml. of pyridine for 18 hr. Usual work-up yielded 270 mg. of an oil which was chromatographed on a silica gel column. Elution with 30–35% ethyl acetate in benzene yielded 200 mg. of crystalline 17-azapregnanolone acetate (11), m.p. 175–176°. A portion was recrystallized from ether for analysis and had m.p. 180–182°; $[\alpha]^{22}D$ +24° (*c* 0.63); ν_{max} 1740 (3-acetate), 1660 (C=O of N-acetate), and 1245 (3-acetate) cm.$^{-1}$.

Anal. Calcd. for $C_{22}H_{35}NO_3$: C, 73.09; H, 9.76; N, 3.87. Found: C, 73.11; H, 9.82; H, 3.90.

3β-Acetoxy-5α,13α-17-oxaandrostan-16-one (12) from 7a.—To a solution of 200 mg. of benzamido acid (**7a**) in 10 ml. of glacial acetic acid was added 2.2 ml. of concentrated hydrochloric acid, and the mixture was refluxed under nitrogen for 20 hr. The acids were removed *in vacuo*, water was added, and the residue was extracted with dichloromethane. The extract was washed with a 2 *N* sodium carbonate solution and water and dried over sodium sulfate. Removal of solvent yielded 130 mg. of neutral material which was chromatographed on a column of 15 g. of silica gel. Elution with 5% ethyl acetate in benzene yielded 110 mg. of the lactone **12**, m.p. 140–143°. A portion of it was recrystallized from ether for analysis and had m.p. 145–146°; $[\alpha]^{22}D$ −23° (*c* 1.00 in dioxane); ν_{max} 1754 (γ-lactone), 1725 (3-acetate), and 1235 (3-acetate) cm.$^{-1}$; τ 7.17 (15α-H, $J_{15\alpha,15\beta}$ = 17 c.p.s. and $J_{15\alpha,14\alpha}$ = 6 c.p.s.), 7.79 (15β-H, $J_{15\beta,25\alpha}$ = 17 c.p.s. and $J_{15\beta,14\alpha}$ = 0 c.p.s.), 8.68 (18-CH_3), and 9.27 (19-CH_3).

Anal. Calcd. for $C_{20}H_{30}O_4$: C, 71.82; H, 9.04. Found: C, 71.58; H, 9.04.

Acknowledgment.—Thanks are due to Mr. Thomas A. Wittstruck for the recording, calculation, and interpretation of the n.m.r. data.

The Ionization Constants of Some Imidazoles

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The basic and the acidic ionization constants of some imidazole derivatives have been determined spectrophotometrically or potentiometrically. For the nitroimidazoles, the spectrophotometric method has been used in concentrated sulfuric acid solutions for which the Hammett acidity function, H_0, has been adopted. Tautomeric equilibrium constants of the imidazoles containing an imino hydrogen have been calculated. The ionization constants have been correlated to the substituents and their position in the imidazole ring. The usefulness of pK_a measurements in assigning structures of these compounds is pointed out.

The chemistry of imidazoles has been studied[1] extensively and attention has been paid to their ionization constants. The pK_a values of some imidazoles have been determined[1,2] and useful observations have been made recently for some nitro derivatives, whose basicity is diminished strongly by the electronegative nitro group.[3] We then have considered of interest a further study of the basicity of the imidazole derivatives of this type. The potentiometric method was used for the derivatives whose basic dissociation constants were still measurable in this way. For the nitro derivatives we adopted the spectrophotometric method in concentrated acid solutions, which provides a suitable way for obtaining correct values. The acidic ionization constants also were determined potentiometrically. All the results obtained, together with data referred to in literature, have been correlated and evaluations useful for structure determination have been found.

Results and Discussion

The absorption spectra of the nitroimidazoles studied are reported in Table I. The introduction of a nitro group in the imidazole ring markedly changes the ultraviolet spectrum: the imidazole band at 207–208 mμ (ϵ_{mol} 5010)[4] is shifted to about 300 mμ in the nitro derivatives. This latter band is affected by the pH of the medium, and it shifts to longer wave lengths by acidic ionization and to shorter ones by protonation (see Table I). The ultraviolet absorption then allowed us to calculate the basic pK_a values of nitroimidazoles. The electron withdrawing effect of the nitro group strongly diminishes the basicity of the nitroimidazoles, and those containing an imino hydrogen behave as acids in water solution. The protonation takes place only in solutions of concentrated acids, and the pK_{BH^+} values become very low or even negative. The acidity of the solutions used was expressed with the Hammett function, H_0.[5] A number of solutions of sulfuric acid in water were prepared, and, from the tables reported by Paul and Long,[6] the corresponding H_0 values were derived, some of them having been confirmed using *p*-nitroaniline, *o*-nitroaniline, and 2,4-dinitroaniline as indicators.[7] The H_0 function already has been adopted for substituted imidazoles[3] even though these compounds are very different in structure from the aniline derivatives used in establishing the H_0 scale. The similarity in slopes found for the nitroimidazoles and the indicators indicates that the H_0 values of sulfuric acid solutions may be used for

(1) K. Hofmann, "Imidazole and Its Derivatives," Part I, Interscience Publishers, Inc., New York, N. Y., 1953.

(2) A. Albert, "Physical Methods in Heterocyclic Chemistry," A. R. Katritzky, Ed., Academic Press, New York, N. Y., 1963, p. 97.

(3) A. Grimison, J. H. Ridd, and B. V. Smith, *J. Chem. Soc.*, 1352 (1960).

(4) G. Leandri, A. Mangini, F. Montanari, and R. Passerini, *Gazz. chim. ital.*, **85**, 769 (1955).

(5) L. P. Hammett, "Physical Organic Chemistry," McGraw-Hill Book Co., Inc., New York, N. Y., 1940, p. 267.

(6) M. A. Paul and F. A. Long, *Chem. Rev.*, **57**, 1 (1957).

(7) K. N. Bascombe and R. P. Bell, *J. Chem. Soc.*, 1096 (1959).

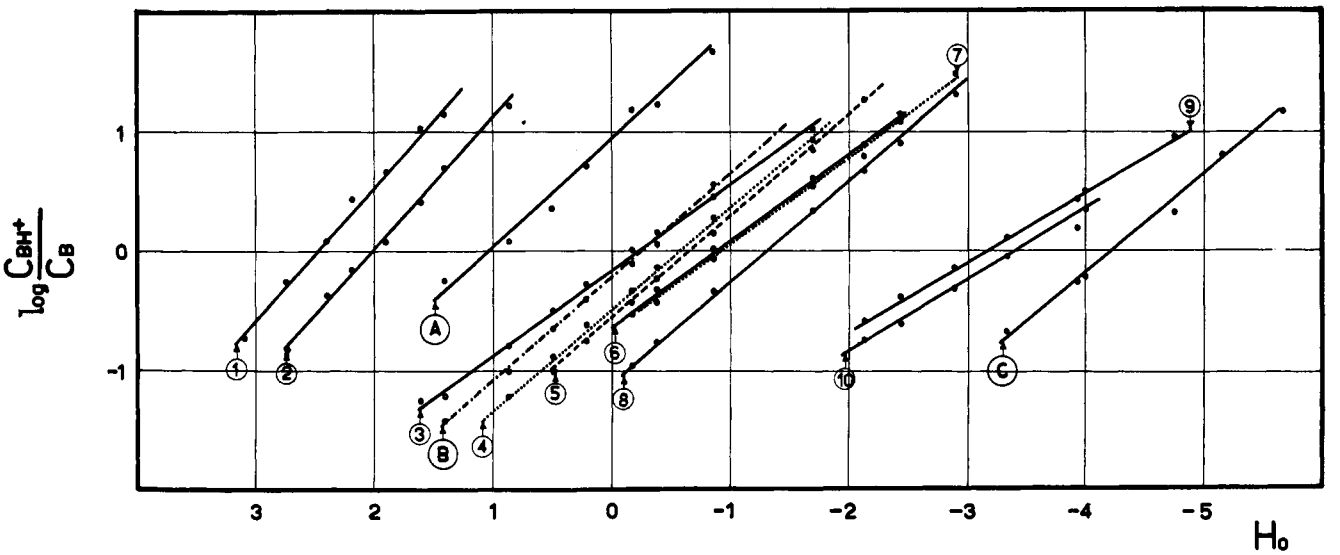


Fig. 1.—Plot of the logarithm of ionization ratios of indicators and imidazole derivatives against H_0. Indicators are A, *p*-nitroaniline; B, *o*-nitroaniline; and C, 2,4-dinitroaniline. Imidazole derivatives are 1, 1-(β-hydroxyethyl)-2-methyl-5-nitro; 2, 1-methyl-5-nitro; 3, 4(5)-nitro; 4, 1-methyl-2-nitro; 5, 1-methyl-4-nitro; 6, 2-nitro; 7, 1-(β-hydroxyethyl)-2-nitro; 8, 1-methyl-4-chloro-5-nitro; 9, 1-methyl-4-nitro-5-chloro; and 10, 4(5)-nitro-5(4)-chloro.

TABLE I

THE MAIN ABSORPTION BAND OF NITROIMIDAZOLES

Imidazole derivatives	Medium	Form[a]	λ_{max}, mμ	log ε
2-Nitro-	0.1 *M* NaOH	CB	372	4.13
	5×10^{-1} *M* H_2SO_4	N	325	3.95
	8.25 *M* H_2SO_4	CA	298	3.91
4(5)-Nitro	0.1 *M* NaOH	CB	350	4.01
	pH 7.38	N	298	3.86
	8.25 *M* H_2SO_4	CA	264	3.90
1-Methyl-2-nitro-	pH 4.63	N	325	3.93
	5 *M* H_2SO_4	CA	300	3.89
1-Methyl-4-nitro-	pH 4.63	N	300	3.90
	8.25 *M* H_2SO_4	CA	266	3.87
1-Methyl-5-nitro-	pH 7.38	N	305	3.81
	2 *M* H_2SO_4	CA	266	3.70
1-(β-Hydroxyethyl)-2-nitro-	5×10^{-3} *M* H_2SO_4	N	326	3.93
	8.25 *M* H_2SO_4	CA	300	3.90
4(5)-Nitro-5(4)-chloro-	0.1 *M* NaOH	CB	356	4.01
	10^{-4} *M* H_2SO_4	N	304	3.82
	17 *M* H_2SO_4	CA	267	3.86
1-Methyl-4-nitro-5-chloro-	*M* H_2SO_4	N	308	3.85
	14 *M* H_2SO_4	CA	272	3.88
1-Methyl-4-chloro-5-nitro-	5×10^{-3} *M* H_2SO_4	N	312	3.93
	14 *M* H_2SO_4	CA	272	3.82
1-(β-Hydroxyethyl)-2-methyl-5-nitro	pH 6.24	N	319	3.97
	2 *M* H_2SO_4	CA	277	3.81
2-4(5)-Dinitro	0.1 *M* NaOH	CB	354	4.09
	5×10^{-3} *M* H_2SO_4	N	304	4.05
1-Methyl-2,4-dinitro-	5 *M* H_2SO_4	N	305	4.06

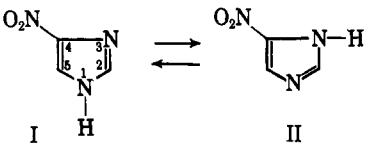
[a] CB, conjugate base; N, the neutral molecule; CA, conjugate acid.

these compounds. All the nitro derivatives were dissolved in the appropriate acidic solutions and, from the spectra recorded, the pK_{BH^+} values were calculated by the following equation.[6,7]

$$pK_{BH^+} = H_0 + \log \frac{\epsilon_B - \epsilon}{\epsilon - \epsilon_{BH^+}}$$

In the strongest acid solutions we have found also the absence of isosbestic points, attributed to the change of medium over the range of sulfuric acid concentrations used.[6,8] In these cases we obtained accurate pK_{BH^+} values by adopting two methods: (a) assuming that medium effects involve mainly lateral spectral shifts, we shifted the curves laterally until they intersected at a common isosbestic point[6]; (b) following the proposal by Davis and Geissman,[8] we plotted the differences of extinctions at two suitable wave lengths against H_0, minimizing in this way the effect of medium on the absorption. For the weakest bases investigated, *e.g.*, dinitroimidazoles, the protonation was still incomplete in the strongest sulfuric acid solution used. In these cases we adopted the method of least squares.[9] In the chloroimidazoles studied, the position of the absorption band is not suitable for a spectrophotometric determination, but their basicity allowed potentiometric measurements of the ionization constant. All the data obtained with the spectrophotometric or the potentiometric methods and also the pK_a values of interest for the present study reported by other authors are summarized in Table II.

Imidazoles containing an imino hydrogen can exist in two tautomeric forms which, for 4(5)-nitroimidazole, are I and II. We calculated the tautomer ratio of the



compounds studied of this type in the manner proposed by Mason[10] for N-heteroaromatic hydroxy compounds. The K_t values reported in the seventh column of Table II were derived from the pK_{BH^+} values of the two N-methyl isomers by the equation that follows.

(8) C. T. Davis and T. A. Geissman, *J. Am. Chem. Soc.*, **76**, 3507 (1954).
(9) J. C. D. Brand, W. C. Horning, and M. B. Thornley, *J. Chem. Soc.*, 1374 (1952).
(10) S. F. Mason, *ibid.*, 674 (1958).

TABLE II

THE ACIDIC AND BASIC IONIZATION CONSTANTS, THE TAUTOMERIC [K_t = (4-SUBST.)/(5-SUBST.)] CONSTANTS, AND THE CALCULATED pK_{BH^+} OF IMIDAZOLE DERIVATIVES

Imidazole derivative	Proton lost, potentiometry	Proton gained, potentiometry	Proton gained, spectrophotometry, literature	Proton gained, spectrophotometry, difference at two wave lengths[a]	Proton gained, spectrophotometry, $pK = H_0 + \log \frac{\epsilon_B - \epsilon}{\epsilon - \epsilon_{BH^+}}$	log K_t	Calcd. pK_{BH^+}
None		6.95[b]					
1-Methyl-		7.25[c]					
2-Methyl-		7.86[b, c]					
2-Nitro-	7.15[d]			−0.80	−0.81		
4(5)-Nitro-	9.20[e]		−0.05[b]	−0.23	−0.16	2.70	
1-Methyl-2-nitro-				−0.40	−0.48		
1-Methyl-4-nitro-			−0.53[b]	−0.61	−0.58		
1-Methyl-5-nitro-			2.13[b]	2.03	2.12		
4(5)-Chloro-[f]						1.65	
1-Methyl-4-chloro-		3.10[g, h]					
1-Methyl-5-chloro-		4.75[h, i]					
1-(β-Hydroxyethyl)-2-nitro-				−1.15	−0.86		
4(5)-Nitro-5(4)-chloro-	5.85[d]				−3.62	2.27[j]	
1-Methyl-4-nitro-5-chloro					−3.49		−3.08
1-Methyl-4-chloro-5-nitro-					−1.42		−2.03
1-(β-Hydroxyethyl)-2-methyl-5-nitro				2.40	2.55		2.68
2,4(5)-Dinitro-	2.85[d]				−7.33	Not calculated	−7.92
1-Methyl-2,4-dinitro-					−7.47		−8.34

[a] Ref. 8. [b] Ref. 2. [c] Ref. 1. [d] In CH_3OH–H_2O, 1:1 with 0.1 N NaOH. [e] In DMF–H_2O, 1:2 with 0.1 N NaOH. [f] Unknown. [g] As hydrochloride in water with 0.1 N NaOH. [h] A value of 6.23 for 1-methyl-4-chloroimidazole is reported[b] for the product synthesized by G. Dedichen [*Ber. deut. chem. Ges.*, **39**, 1831 (1906)] and later demonstrated by Sarasin[21] to be 1-methyl-5-chloroimidazole. It differs from our value possibly because of the different method used. [i] In CH_3OH–H_2O, 1:3 with 0.1 N HCl. [j] (4-nitro-5-chloro)/(4-chloro-5-nitro).

$$K_t = \frac{K_{N(1)-Me}}{K_{N(3)-Me}}$$

The K_t of 2,4(5)-dinitroimidazole, of which one methyl derivative is known, could be calculated by equation[11]

$$K_t = \frac{K_1}{K_{N(1)-Me}} - 1$$

but it gives a negative value, as the parent compound is a stronger base than its N(1)-methyl derivative.[10] From the K_t values it can be deduced that the less acidic tautomer is preponderant over the other. This behavior can be interpreted by considering the strength of the N–H bond in the two tautomeric forms. It appears evident that, as the hydrogen atom can migrate from one nitrogen to the other, the tautomeric system will predominantly assume the form in which the N–H bond is stronger.

It seems pertinent to emphasize some features of imidazole derivatives that can be deduced from an inspection of the data reported in Table II. We obtained the effect of each substituent on the basic ionization constant, calculating it as the difference between the pK_{BH^+} of the substituted imidazole and that of the parent compound. The calculated effects are reported in Table III as a function of the position in the imidazole ring, and the following considerations can be derived. The introduction of a methyl group increases the basic strength,[12a] while the hydroxyethyl group produces

TABLE III

EFFECT OF SUBSTITUENTS ON THE pK_{BH^+} OF THE IMIDAZOLE

Position	1	2	4	5	4(5)
CH_3—	+0.30	+0.91			
NO_2—		−7.76	−7.83	−5.13	−7.11
Cl—			−4.15	−2.50	
CH_2—OH | CH_2—	−0.05				

an opposite effect, even if very small, due to the presence of the electronegative hydroxyl.[12b] Concerning electronegative substituents, chlorine appears to affect the basicity much less than the nitro group. The influence of these substituents is stronger when they are in close proximity to the basic nitrogen, and the 2- and 4-positions are equivalent in this respect. It is noteworthy that, for the polysubstituted imidazoles, the effect of each substituent is in a fair approximation additive. In fact the values calculated in this way are in satisfactory accordance with the experimental ones, as can be observed in the eighth column of Table II. From these results it follows that the ionization constant of an imidazole derivative of uncertain molecular structure assists in establishing the position of the substituents. The structure of 1-(β-hydroxyethyl)-2-methyl-5-nitroimidazole,[13a] whose demonstration has not been published, can be confirmed by the fact that the experimental pK_{BH^+} is in agreement with the calculated one. Similarly, the structure of the methyldinitroimidazole, obtained from 2,4(5)-dinitroimidazole and diazomethane, could be established as 1-methyl-

(11) The two equations (4 and 5) reported by Mason[10] are misprinted and should be corrected as follows.

$$K_t = \frac{K_1}{K_{O-Me}} - 1 \quad (4)$$

$$K_t = \frac{1}{\frac{K_1}{K_{N-Me}} - 1} \quad (5)$$

(12) H. C. Brown, B. H. McDaniel and O. Häfliger, "Determination of Organic Structures by Physical Methods," Vol. I, E. A. Braude and F. C. Nachod, Ed., Academic Press, New York, N. Y., 1955, (a) p. 573, (b) p. 578.

(13)(a) C. Cosar and L. Joulou, *Ann. Inst. Pasteur*, **96**, 238 (1959); (b) British Patent, 836,854 (1960).

2,4-dinitroimidazole. This structure was confirmed by its transformation into 1-methyl-4-nitro-5-chloroimidazole with 2-chloroethanol.[14]

Experimental

Apparatus.—The potentiometric titrations were carried out with a Jonosis Q3 potentiometer. The spectrometric measurements were carried out on a Beckman DK2 spectrometer.

Materials.—The following imidazole derivatives had the melting points and properties reported in the literature and were prepared according to the cited references: **2-Nitro**, m.p. 284° dec.[14]; **4(5)-nitro**, m.p. 308°[3,15]; **1-methyl-4-nitro**, m.p. 133°[16]; **1-methyl-5-nitro**, m.p. 55°[17]; **1-methyl-4-chloro**, b.p. 252°,[18] purified by gas chromatography; **1-methyl-5-chloro**, b.p. 205°[19]; **4(5)-nitro-5(4)-chloro**, m.p. 216°[14]; **1-methyl-4-nitro-5-chloro**, m.p. 148°[14]; **1-methyl-4-chloro-5-nitro**, m.p. 78°[14]; **1-(β-hydroxyethyl)-2-methyl-5-nitro**, m.p. 160°[13b]; and **2,4(5)-dinitro**, m.p. 268°.[14]

1-Methyl-2-nitroimidazole.—To a 4% solution of diazomethane in ethyl ether, 200 mg. of 2-nitroimidazole was added, and the mixture was allowed to react at room temperature overnight. Evaporation of the solvent yielded 130 mg. of a light yellow product, which, after recrystallization from ethanol, melted at 101–102°.

Anal. Calcd. for $C_4H_5N_3O_2$: C, 37.80; H, 3.97; N, 33.06. Found: C, 37.91; H, 4.08; N, 32.95.

1-(β-Hydroxyethyl)-2-nitroimidazole.—A mixture of 2 g. of 2-nitroimidazole silver salt[20] and 8 ml. of 2-bromoethanol in 85 ml. of toluene was refluxed for 14 hr. then evaporated to dryness under reduced pressure. The residue was extracted three times with 50 ml. of boiling water each time, and the collected extracts were evaporated to dryness. The residue, recrystallized from ethyl acetate, yielded 800 mg. of light yellow crystals melting at 157°.

Anal. Calcd. for $C_5H_7N_3O_3$: C, 38.22; H, 4.49; N, 26.74. Found: C, 38.13; H, 4.63; N, 26.95.

1-Methyl-2,4-dinitroimidazole.—2,4(5)-Dinitroimidazole (200 mg.) was treated with diazomethane as described above for the mononitro derivative. By concentration of the solvent, 140 mg. of crystals was obtained, which, after two crystallizations from ethanol, melted at 172°.

Anal. Calcd. for $C_4H_4N_4O_4$: C, 27.92; H, 2.34; N, 32.56. Found: C, 27.87; H, 2.47; N, 32.64.

No traces of the isomeric 1-methyl-2,5-dinitroimidazole could be found in the mother liquor of the crystallization.

1-Methyl-4-nitro-5-chloroimidazole.—A mixture of 680 mg. of 1-methyl-2,4-dinitroimidazole and 10 ml. of 2-chloroethanol was refluxed for 2 hr. The resulting solution was evaporated to dryness under reduced pressure, and the residue was recrystallized from ethanol, yielding 400 mg. of product with m.p. 148° and infrared spectrum identical with that of 1-methyl-4-nitro-5-chloroimidazole obtained as described by Sarasin.[21] No traces of the isomeric 1-methyl-4-chloro-5-nitroimidazole could be detected in the mother liquor of the crystallization.

(14) G. C. Lancini, N. Maggi, and P. Sensi, *Farmaco* (Pavia) *Ed. Sci.*, **18**, 390 (1963).
(15) R. G. Fargher and F. L. Pyman, *J. Chem. Soc.*, **115**, 217 (1919).
(16) W. G. Forsyth and F. L. Pyman, *ibid.*, **127**, 573 (1925).
(17) C. E. Hazeldine, F. L. Pyman, and J. Winchester, *ibid.*, **125**, 1431 (1924).
(18) J. Sarasin, *Helv. Chim. Acta*, **6**, 370 (1923).
(19) F. F. Blicke and H. G. Godt, *J. Am. Chem. Soc.*, **76**, 3654 (1954).
(20) S. Nakamura, *Pharm. Bull.* (Tokyo), **3**, 379 (1955).
(21) J. Sarasin and E. Wegmann, *Helv. Chim. Acta*, **7**, 713 (1924).

Derivatives of 3-Methylthiazolo[3,2-*a*]benzimidazole[1,2]

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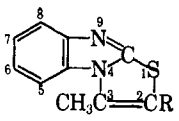
Depending upon reaction conditions, 3-(2-benzimidazolylthio)-2,4-pentanedione (I) or ethyl 2-(2-benzimidazolylthio)acetoacetate (II) when treated with acetic anhydride in pyridine either undergo cyclization or form enol acetates; however, 1-(2-benzimidazolylthio)-2-propanone (III) gives only the enol acetate. A possible mechanism and supporting infrared data are discussed.

As thiazolethiols and 2-mercaptobenzimidazole are known accelerators for the vulcanization of rubber with sulfur and antidegradants for rubber, respectively, it was desirable to prepare a novel heterocyclic compound containing both the thiazolyl and benzimidazolyl moieties. Thiazolo[3,2-*a*]benzimidazol-3(2*H*)-one has been prepared by the dehydration of 2-benzimidazolylthioacetic acid[3,4]; the purpose of this investigation was to prepare compounds having the following structure.



R = H, $COCH_3$, $COOC_2H_5$, COOH, $CHOHCH_3$, $CONHC_6H_5$, CCH_3 (‖ NOH)

The preparation of these new compounds was realized as illustrated in Fig. 1.

The key intermediates, 3-(2-benzimidazolylthio)-2,4-pentanedione (I), ethyl 2-(2-benzimidazolylthio)-acetoacetate (II), and 1-(2-benzimidazolylthio)-2-propanone (III), required for the synthesis of the new compounds, were prepared by the reaction of the potassium salt of 2-mercaptobenzimidazole with 3-chloro-2,4-pentanedione, ethyl α-chloroacetoacetate, and chloroacetone, respectively. The data are summarized in Table I.

When the mixture containing I, acetic anhydride, and pyridine was heated for only 10 min. at 90–100°, the product isolated in 96% yield was 3-(2-benzimidazolylthio)-4-hydroxy-3-penten-2-one acetate (IV). We had anticipated that acetylation would have occurred on the amino group. However, our postulate was not substantiated since the infrared spectrum revealed that the hydroxyl group was acetylated. However, when this mixture was heated at 90–100° for 3 hr., methyl 3-methylthiazolo[3,2-*a*]benzimidazolyl ketone (V) which contained no ester bonds in the infrared spectrum was obtained in 99% yield. When the mixture was heated at 90–100° for 1 hr., IV and V were ob-

(1) The *Chemical Abstracts'* preferred name for all compounds was kindly furnished by Dr. L. T. Capell of the *Chemical Abstracts'* service.
(2) Presented at the 146th National Meeting of the American Chemical Society, Denver, Colo., January, 1964.
(3) G. F. Buffin and J. D. Kendall, *J. Chem. Soc.*, 361 (1956).
(4) J. A. Van Allan, *J. Org. Chem.*, **21**, 24 (1956).