major portion of the hydrogenated material boiled at 57–58° (2 mm.) or 208–209° (760 mm.); n^{20}D 1.4668. Its melting point was about −22° as determined with a thermometer immersed in the mixture of liquid and crystals.

Anal. Calcd. for $C_{12}H_{22}$: C, 86.65; H, 13.35. Found: C, 86.79; H, 13.11.

RIVERSIDE, ILLINOIS

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF WYOMING]

Further Studies of Anomalous Alkylations with β-Dialkylaminoethyl Chlorides

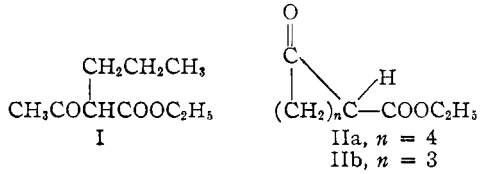
BY SARA JANE RHOADS, ROSALIE D. REYNOLDS AND REBECCA RAULINS

RECEIVED OCTOBER 31, 1951

The alkylations of the cyclic β-ketoesters, 2-carbethoxycyclohexanone and 2-carbethoxycyclopentanone with β-dimethylaminoethyl chloride and β-diethylaminoethyl chloride give rise to mixtures of C- and O-alkylated products under a variety of conditions. The open chain analog, ethyl α-acetylvalerate, undergoes C-alkylation exclusively with β-dimethylaminoethyl chloride.

The appearance in the recent literature[1a,b,c] of several examples of anomalous O-alkylation of active carbonyl compounds by β-dialkylaminoethyl halides and structurally similar compounds[2] has prompted an investigation of the extent of the abnormal reaction as influenced by the following factors: structure of the carbonyl compound[3] (*i.e.*, degree of substitution at the α-carbon, ring *vs.* open chain structure), solvent and temperature. The influence of solvent has been demonstrated in one case[1a]; the use of a non-polar solvent appears to favor C-alkylation. A temperature dependence in situations of this general type which involve competitive reactions of a mesomeric anion has been predicted by Dewar.[4]

In this investigation, three β-ketoesters, ethyl α-acetylvalerate (I), 2-carbethoxycyclohexanone (IIa) and 2-carbethoxycyclopentanone (IIb) have been studied under a variety of conditions. The results are summarized in Table I.



I

IIa, n = 4
IIb, n = 3

With β-dimethylaminoethyl chloride (IIIa) the potassio-derivative of I in refluxing *t*-butyl alcohol reacts to give only the normal C-alkylated product, IV (Expt. 1). Acid hydrolysis and decarboxylation of the alkylated product proceed without loss of basicity to yield 1-dimethylamino-3-propylpentanone-4 (V) in good yield. Under these same conditions the cyclic anlog IIa has been observed to give mainly the O-alkylated product VIa (Expt. 2).

TABLE I

Expt. no.	β-Keto-ester	Alkylating reagent	Conditions: base, solvent temp. and time	Alkylated Total yield, %	Products Composition C, %	O, %
1	I	IIIa	Potassium *t*-butoxide, *t*-butyl alcohol, reflux, 3 hours	49	100[a]	0
2[b]	IIa	IIIa	Potassium *t*-butoxide, *t*-butyl alcohol, reflux, 6 hours	60	19	72
3	IIa	IIIa	Potassium *t*-butoxide, *t*-butyl alcohol, room temp., 67 hours	40	26	66
4[b]	IIa	IIIa	Sodium sand, toluene, reflux, 6 hours	42[c]	42	42
5	IIa	IIIa	Sodium *t*-butoxide, *t*-butyl alcohol, reflux, 6 hours	70	22	68
6	IIa	IIIb	Sodium sand, toluene, reflux, 6 hours	71	34[d]	51[d]
7	IIb	IIIb	Sodium hydride, benzene, reflux, 6 hours	50	24	61
8	IIb	IIIb	Potassium *t*-butoxide, *t*-butyl alcohol, reflux, 3 hours	63	22	62
9	IIb	IIIb	Potassium *t*-butoxide, *t*-butyl alcohol, room temp., 4 hours	71	22	56

[a] Percentage is based on the fact that no O-derivative could be detected. [b] Data taken from ref. 1a. [c] On repetition, this yield has been materially improved (63%); the composition of the product remains the same, however: 42% O-; 42% C-. [d] Duplicate determinations gave results in agreement within 1.5% and provide a reasonable indication of the probable error in the other percentages reported.

Barltrop[5] reported the sodio-derivative of IIa to give the normal C-alkylated product when treated with β-diethylaminoethyl chloride in refluxing toluene. Repetition of this work has shown that the alkylation product is actually a mixture of C- (VIIb) and O-alkylated (VIb) derivatives, the abnormal product predominating (Expt. 6).

With β-diethylaminoethyl chloride (IIIb), the sodio- or potassio-enolate of 2-carbethoxycyclopentanone (IIb), is alkylated rapidly in benzene or

(1) (a) W. von E. Doering and S. J. Rhoads, THIS JOURNAL, **73**, 3082 (1951); (b) J. C. Sheehan and C. E. Mumaw, *ibid.*, **72**, 2127 (1950); (c) N. Sperber, R. Fricano and D. Papa, *ibid.*, **72**, 3068 (1950).

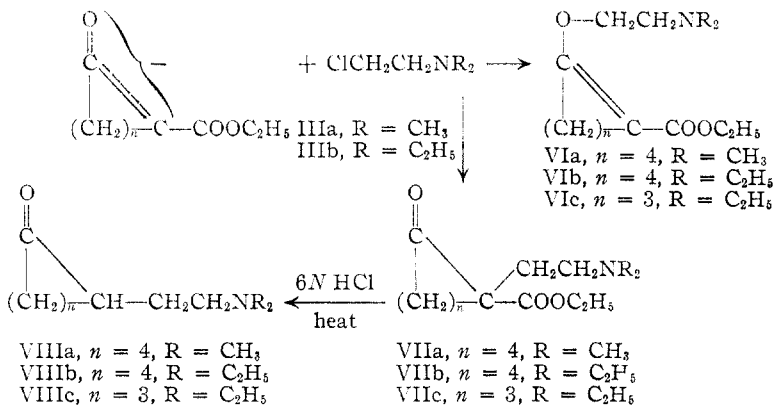
(2) See the sources cited and references there for other examples.

(3) Although the anomalous alkylation has been observed most frequently with halides of unusual reactivity, evidence that the nature of the alkylating agent is not the sole cause of the anomaly is derived from the fact that certain cyclic compounds such as 2-cyanocyclohexanone [K. von Auwers, *Ber.*, **61**, 408 (1928)] and 2-carbethoxy-5-cyanocyclopentanone [S. R. Best and J. F. Thorpe, *J. Chem. Soc.*, **95**, 685 (1909)] have been reported to undergo both C- and O-alkylation under normal alkylating conditions even with the relatively unreactive alkyl halides. *Cf.*, also, the exclusive C-alkylation experienced with the open chain acetoacetic ester (ref. 1a and footnote 8 of that reference) and β-dialkylaminoethyl chlorides.

(4) M. J. S. Dewar, "The Electronic Theory of Organic Chemistry," Oxford at the Clarendon Press, 1949, p. 104.

(5) J. A. Barltrop, *J. Chem. Soc.*, 399 (1947).

in *t*-butyl alcohol to give a mixture which is 60–62% O-alkylated and 22–24% C-alkylated (Expt. 7 and 8). In this case, a change of solvent causes no marked difference in the proportions of isomers in contrast to the findings for the six-membered homolog (*cf.* Expt. 2, 4 and 5).



The possibility of a detectable temperature dependence in the course of the alkylation reactions has been examined within the experimentally feasible range. Lower reaction temperatures appear to favor C-alkylation slightly (*cf.* Expt. 2 and 3), but because of the error inherent in the method of determining the proportions of isomers no real significance can be attributed to these small differences. Certainly they have little practical value.

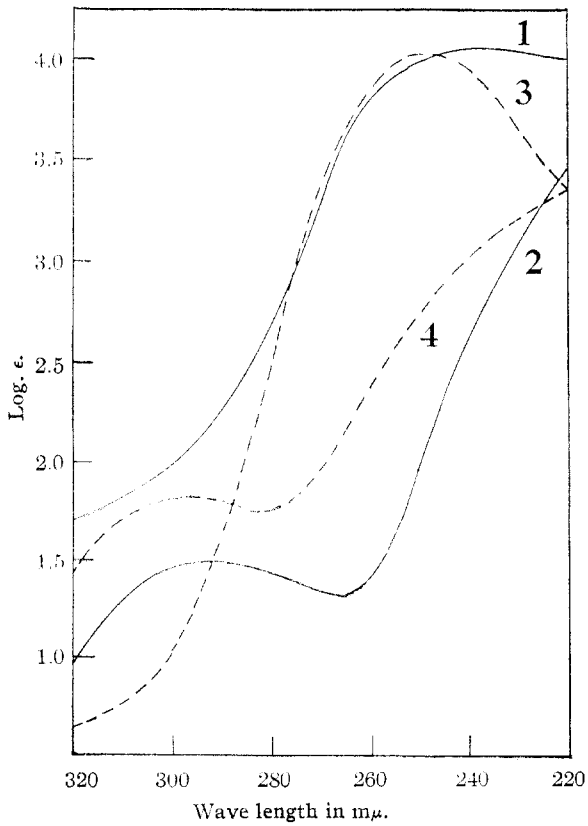


Fig. 1.—Absorption spectra: curves 1 and 2 (——), isomeric bases VIa and VIIa, respectively; curves 3 and 4, (– – –), isomeric bases VIc and VIIc, respectively.

The structures of the isomeric alkylated products have been established and the proportions of isomers determined by methods previously described.[1a] The facile cleavage of the enol–ether linkage by dilute acid to regenerate the orginal β-ketoester provides a means of estimating the extent of O-alkylation; the C-alkylated product, stable toward mild acid treatment, may then be purified and subjected to hydrolysis and decarboxylation under more vigorous conditions. In this manner, two new aminoketones, VIIIb and VIIIc, have been prepared.

It has been possible to separate the isomeric alkylated products, VIa and VIIa and VIc and VIIc, into relatively pure end fractions by fractional distillation under reduced pressure. The ultraviolet absorption spectra of the C- and O-derivatives, purified in this manner, confirm their structural assignments (Fig. 1).[6] The interesting bathochromic shift of the maximum observed in the case of the O-derivative of the cyclopentene compound[7] can possibly be ascribed to the greater strain in the five-membered ring.

The results of this investigation indicate that an appreciable degree of abnormal alkylation can be anticipated when cyclic β-ketoesters are treated with halides of unusual reactivity. The use of non-polar solvents and low reaction temperatures may help to minimize the abnormal reaction in some cases.

Acknowledgments.—This work was assisted by grants from the American Academy of Arts and Sciences, Boston, Mass., and from the Graduate Research Council of the University of Wyoming. This help is gratefully acknowledged.

Experimental[8]

Procedure for Alkylations.—All alkylations were carried out in the conventional three-necked flask, equipped with a mechanical stirrer, condenser and dropping funnel and protected against atmospheric moisture. The purified β-ketoester was added dropwise to the base of choice (*cf.* conditions Table I) which was dissolved or suspended in the dry solvent. When sodium sand and sodium hydride were employed (Expt. 4, 6 and 7) the reactions were conducted under an atmosphere of dry nitrogen and the addition of a few ml. of absolute ethanol and gentle heating were required to complete the conversion of the esters to their sodium salts. To the sodio- or potassio-enolate thus prepared was added dropwise and with stirring a solution of the dialkylaminoethyl chloride in the appropriate solvent. Stirring was continued for the time and at the temperature indicated in Table I. The reaction mixtures were worked up in the manner previously described[1b,9] and the alkylated products were purified by distillation.

(6) *Cf.* ref. 1b; A. Hantzsch, *Ber.*, **43**, 3058 (1910); L. N. Owen, *J. Chem. Soc.*, 385 (1945).

(7) A similar shift is noted with the analogous 1-cyclopentene-1-carboxaldehyde, λ_{max} 237–238 mμ, log ϵ_{max} 4.13 in ethanol, reported by J. B. Brown, H. B. Henbest, and E. R. H. Jones, *J. Chem. Soc.*, 3639 (1950), and 1-cyclohexene-1-carboxaldehyde, λ_{max} 229 mμ, log ϵ_{max} 4.08 in ethanol, reported by I. Heilbron, E. R. H. Jones, R. W. Richardson and F. Sondheimer, *ibid.*, 737 (1949).

(8) Microanalyses were performed by the Clark Microanalytical Laboratory, Urbana, Illinois. Melting points are corrected.

(9) Special precaution must be observed in the isolation of the alkylated products in order to avoid cleavage and loss of the O-derivative. Rapid extraction with ice-cold 2 *N* hydrochloric acid, followed by immediate neutralization of the acid extracts minimizes losses from this source.

Ethyl α-(β-Dimethylaminoethyl)-α-acetylvalerate (IV).—Alkylation of 17.2 g. (0.10 mole) of I[10] (b.p. 104.5–106° at 19 mm.) with IIIa[11] (11.9 g., 0.11 mole) was accomplished according to the general alkylation procedure using 0.10 mole of potassium *t*-butoxide in 200 ml. of *t*-butyl alcohol. After a three-hour reflux period, the yellow reaction mixture was filtered to remove solid salts and concentrated *in vacuo* on the steam-bath. The basic fraction isolated from the concentrate distilled as a colorless oil, b.p. 107–114° at 3.4 mm. and weighed 11.9 g. (49%). This material gave no evidence of the presence of an O-alkylated product when treated with dry hydrogen chloride in ethanol or when warmed with 2 *N* hydrochloric acid.

The methiodide of IV, which formed spontaneously when IV and methyl iodide were combined, was recrystallized from dry acetone, m.p. 151.5–152°.

Anal. Calcd. for $C_{14}H_{28}O_3NI$: C, 43.6; H, 7.3; N, 3.6. Found: C, 43.9; H, 7.1; N, 3.5.

1-Dimethylamino-3-propylpentanone-4 (V).—Refluxing a solution of 5.4 g. (0.022 mole) of IV in 100 ml. of 6 *N* hydrochloric acid for 12 hours assured complete decarboxylation. The acid solution was evaporated to dryness under reduced pressure and the crude hydrochloride converted to the free base with aqueous potassium carbonate. After drying over anhydrous magnesium sulfate, the ethereal solution of the free base was distilled to give 2.7 g. (71% from IV) of V, b.p. 82–86° at 11 mm.

The methiodide of V separated as shiny, white plates when methyl iodide and V were combined in ethyl acetate–ethanol, m.p. 111.5–112.5°, unchanged by further recrystallization.

Anal. Calcd. for $C_{11}H_{24}ONI$: C, 42.2; H, 7.7; N, 4.5. Found: C, 42.5; H, 8.1; N, 4.1.

The picrate of V was prepared by combining equivalent amounts of V and picric acid in hot benzene. On cooling, fine yellow crystals formed, m.p. 68–70°. Recrystallization from benzene raised this m.p. to 71–71.5°.

Anal. Calcd. for $C_{16}H_{24}O_8N_4$: C, 48.0; H, 6.0; N, 14.0. Found: C, 48.2; H, 5.8; N, 14.1.

Alkylation of 2-Carbethoxycyclohexanone (IIa) with β-Diethylaminoethyl Chloride (IIIb); Barltrop's Alkylation.[12]—The alkylation of IIa[13] with IIIb[14] was carried out according to Barltrop.[5] From 10.0 g. (0.06 mole) of IIa (b.p. 135–137° at 41 mm.) and excess IIIb (0.09 mole) was obtained 11.1 g. (71%) of basic alkylated products distilling at 128–131° at 0.7 mm. This material gave a negative ferric chloride test and failed to yield any solid derivatives.

Anal. Calcd. for $C_{15}H_{27}O_3N$: C, 66.9; H, 10.0; N, 5.2. Found: C, 66.8; H, 10.0; N, 5.5.

A solution of 5.59 g. of the alkylated products in 25 ml. of 2 *N* hydrochloric acid was warmed in a hot water-bath until the development of turbidity and the separation of a heavy oil indicated that cleavage of the alkylated product had occurred (*ca.* three minutes). The cooled solution was thoroughly extracted with ether. Concentration of the ether extracts afforded 1.80 g. of IIa, identified by its 2,4-dinitrophenylhydrazone, m.p. 154–155°. This amount of IIa corresponds to 51.0% O-alkylation in the original mixture.

The acid solution remaining after cleavage and removal of the neutral material was saturated with solid potassium carbonate. The basic oil which separated was taken up with ether, dried, and distilled to give the following fractions: I, 0.85 g., b.p. 55–60° at 30 mm.; II, 1.90 g. (corresponding to 34.0% C-alkylation in the original mixture), b.p. 130–135° at 1.6 mm. Treatment of fraction I with picric acid produced the picrate of β-diethylaminoethyl alcohol, m.p. 79–79.5° from absolute ethanol, undepressed when mixed with an authentic sample. Jones, *et al.*, report m.p. 79°.[15]

Fraction II, 2-(β-diethylaminoethyl)-2-carbethoxycyclohexanone (VIIb), was characterized by its crystalline **picrate**, m.p. 108.5–110° from absolute ethanol.

Anal. Calcd. for $C_{21}H_{30}O_{10}N_4$: C, 50.6; H, 6.1; N, 11.2. Found: C, 50.7; H, 6.0; N, 11.3.

A duplicate run made on a second portion of the original mixture of alkylated products gave results in agreement with these findings, *i.e.*, O-alkylated product, 49.5%, C-alkylated product, 33.6%.

2-β-Diethylaminoethylcyclohexanone (VIIIb).—A solution of 3.2 g. of VIIb in 20 ml. of 6 *N* hydrochloric acid was boiled under reflux for eight hours. The crude basic oil, liberated by treatment of the acid solution with 20% sodium hydroxide solution, weighed 1.9 g. Distillation produced 1.5 g. (63%) of colorless oil, b.p. 60–65° at 0.1 mm.

The semicarbazone of VIIIb, prepared by the method of Wohlgemuth,[16] could be crystallized from ethyl acetate, m.p. 141–142°.

Anal. Calcd. for $C_{13}H_{26}ON_4$: C, 61.4; H, 10.3; N, 22.0. Found: C, 61.4; H, 10.1; N, 21.9.

The oxalate of VIIIb, prepared by treatment of VIIIb with a saturated solution of oxalic acid in acetone, separated as rosettes of fine, colorless needles on standing, m.p. 116–118°. Recrystallized from dry acetone, it melted at 118.5–119.5°.

Anal. Calcd. for $C_{14}H_{25}O_5N$: C, 58.5; H, 8.8; N, 4.9. Found: C, 58.5; H, 8.5; N, 4.8.

Alkylation of IIa with IIIa.—The results of the alkylation of IIa with IIIa under different conditions of solvent, base, reaction time and temperature are summarized in Table I (Expt. 2, 3, 4 and 5). The proportions of isomers were determined in the usual manner. Derivatives of the alkylated products are reported elsewhere.[1a]

Alkylation of 2-Carbethoxycyclopentanone (IIb) with β-Diethylaminoethyl Chloride (IIIb).—Data for this alkylation under varying conditions are given in Expt. 7, 8 and 9 of Table I. Best results were obtained by employing mild reaction conditions. Because of the very reactive nature of IIb it was found advisable to modify the general alkylation procedure slightly in order to minimize the side reactions of ring opening and self-condensation. Details of Expt. 9 are given.

To a solution of 0.113 mole of potassium *t*-butoxide in 150 ml. of anhydrous *t*-butyl alcohol was added dropwise and *with cooling* (ice–salt-bath) 17.6 g. (0.113 mole) of IIb[17] (b.p. 116–117° at 21 mm., $n^{20}D$ 1.4517) dissolved in 50 ml. of the same solvent. The potassium salt of the ester separated immediately as a white solid. One mole equivalent of IIIb in 25 ml. of toluene was added to the cold suspension of the salt in *one* portion. Stirring was started and the reaction mixture allowed to warm to room temperature. Stirring at room temperature was continued for four hours, at which time absence of a ferric chloride test indicated that the reaction had gone to completion. The basic fraction, isolated in the usual manner, weighed 20.6 g. (71%), b.p. 131–140° at 1.5 mm. When 5.0 g. of the basic fraction was subjected to the acid-catalyzed cleavage 1.7 g. of IIb was recovered. This amount corresponds to 56% O-alkylation in the original mixture.

2-(β-Diethylaminoethyl)-2-carbethoxycyclopentanone (VIIc).—When the ether-extracted acid solution from the above cleavage was saturated with solid potassium carbonate a basic oil separated and was taken up in ether, dried, and distilled. After a forerun of IIIb, VIIc distilled as a colorless oil weighing 1.1 g. (corresponding to 22% C-alkylation), b.p. 123–125° at 1.5 mm.

The picrate of VIIc was prepared and recrystallized from absolute ethanol, m.p. 89.5–90°.

Anal. Calcd. for $C_{20}H_{28}O_{10}N_4$: C, 49.6; H, 5.8; N, 11.6. Found: C, 49.9; H, 5.8; N, 11.5.

2-β-Diethylaminoethylcyclopentanone (VIIIc).—Hydrolysis and decarboxylation of 2.0 g. of VIIc with 6 *N* hydrochloric acid afforded the aminoketone VIIIc in 71% yield, b.p. 112–115° at 22 mm.

The picrate of VIIIc, prepared in absolute ethanol, melted at 98.5–99°.

Anal. Calcd. for $C_{17}H_{24}O_8N_4$: C, 49.5; H, 5.9; N, 13.6. Found: C, 49.2; H, 5.5; N, 13.7.

(10) Prepared according to the general method described in "Organic Syntheses," Coll. Vol. I, John Wiley and Sons, Inc., New York, N. Y., 1941, p. 248.

(11) See ref. 1a for preparation and use.

(12) *Cf.* the alkylation with β-dimethylaminoethyl chloride, ref. 1a and Expt. 4 of Table I.

(13) "Organic Syntheses," Coll. Vol. II, John Wiley and Sons, Inc., New York, N. Y., 1943, p. 531.

(14) G. A. C. Gough and H. King, *J. Chem. Soc.*, 2436 (1928).

(15) E. R. H. Jones, F. A. Robinson and M. N. Strachan, *ibid.*, 89 (1946).

(16) H. Wohlgemuth, *Ann. chim.*, [9] **3**, 164 (1915).

(17) Prepared and purified according to "Organic Syntheses," Coll. Vol. II, John Wiley and Sons, Inc., New York, N. Y., 1943, p. 116.

Purification of the Isomeric Bases VIa and VIIa and VIc and VIIc.—Ten grams of the redistilled, uncleaved alkylated products obtained in Expt. 5 was fractionally distilled through a Podbielniak-type column (8 × 860 mm.) fitted with a tantalum wire packing and a partial reflux head.[18] Eight fractions were cut, the last two of which proved to be essentially pure O-alkylated product, **1-carbethoxy-2-(β-dimethylaminoethoxy)-cyclohexene (VIa)**, 4.0 g., b.p. 138–139° at 3.2 mm., $n^{20}D$ 1.4849. When a sample of this material was cleaved with 2 *N* hydrochloric acid, IIa was recovered in an amount corresponding to 90% O-alkylation. Purification of the C-alkylated product (VIIa) was accomplished in the same column by distillation of a sample of alkylated product from which the abnormal O-derivative had been removed by cleavage. After a small, low boiling forerun, pure VIIa distilled at 121° at 1.7 mm., $n^{20}D$ 1.4654.

In the same manner, the isomeric bases VIc and VIIc were purified. When 14 g. of the mixed alkylated products obtained in Expt. 9 was fractionated, the higher boiling O-alkylated product, **1-carbethoxy-2-(β-diethylaminoethoxy)-cyclopentene (VIc)** was found in relatively pure form in the end fractions, 4.9 g., b.p. 142–143° at 1 mm., $n^{20}D$ 1.4862. Cleavage of a sample of this material regenerated IIb in an amount corresponding to 80% O-alkylation. The purified C-alkylated product (VIIc) had the following properties: b.p. 132–133° at 1.4 mm., $n^{20}D$ 1.4639.

Absorption Spectra.—The ultraviolet absorption spectra of the purified alkylated products VIa, VIIa, VIc and VIIc were taken in purified cyclohexane with a model DU Beckman spectrophotometer.

LARAMIE, WYOMING

(18) For details of construction see J. Cason and H. Rapoport, "Laboratory Text in Organic Chemistry," Prentice-Hall, Inc., New York, N. Y., 1950, pp. 237–243.

[CONTRIBUTION FROM THE DEPARTMENT OF PHYSIOLOGICAL CHEMISTRY, SCHOOL OF MEDICINE, UNIVERSITY OF PENNSYLVANIA]

Substituted Imidazoles as Precursors of the Purines[1]

BY CHARLES S. MILLER,[2] SAMUEL GURIN AND D. WRIGHT WILSON

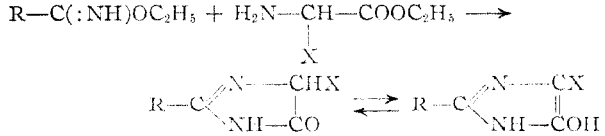
RECEIVED DECEMBER 26, 1951

Syntheses are reported for several new 5(4)-imidazole carboxamide or carbethoxy derivatives containing either hydroxy or amino groups in the 4(5)-position. C^{14}-Labeled 4(5)-hydroxy-5(4)-imidazolecarboxamide is not a biological precursor of the purines. The 4(5)-carbon of C^{14}-labeled 4(5)-amino-5(4)-imidazolecarboxamide is incorporated biologically into carbon 4 of "nucleic acid" guanine.

In an earlier report from this Laboratory,[3] a new and convenient synthesis of C^{14}-labeled 4(5)-amino-5(4)-imidazolecarboxamide was described. It was also demonstrated that this substance is utilized by the rat not only for the biosynthesis of adenine and guanine derived from nucleic acids, but also for nucleotide adenine and urinary allantoin.

As an extension of this work, syntheses have been developed for a number of imidazoles of related structure. One of these 4(5)-hydroxy-5(4)-imidazolecarboxamide was labeled with C^{14}, and its possible role as a precursor of the purines was investigated.

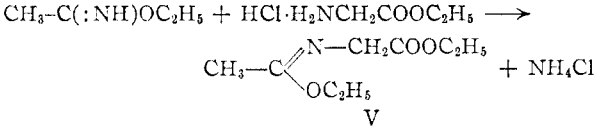
4(5)-Hydroxyimidazoles.—The method reported by Finger[4] for the preparation of 2-methyl-4(5)-hydroxyimidazole (1) was used for the synthesis of (II) and (III) by condensation of the appropriate



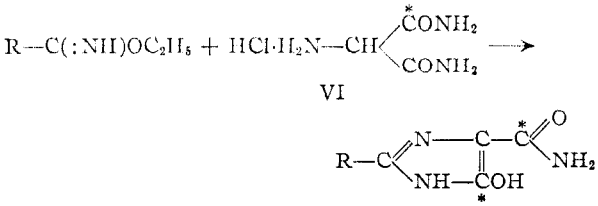
I, R = $-CH_3$, X = $-H$
II, R = $-H$, X = $-COOC_2H_5$
III, R = $-CH_3$, X = $-COOC_2H_5$
IV, R = $-H$, X = $-H$

iminoesters and amino acid esters. The preparation of (IV) was not accomplished. Attempts to convert the carbethoxy compounds to their corresponding amides by means of NH_3 were unsuccessful.

Schmidt[5] described the preparation of ethyl acetiminoester-N-ethylacetate (V) by a condensation of ethyl acetaminoester and glycine ethylester hydrochloride. When this reaction was applied



to iminoesters and aminomalonamide hydrochloride (VI), a similar condensation resulted which was followed by rapid ring closure to yield the corresponding 4(5)-hydroxy-5(4)-imidazolecarboxamides (VII, VIII).



VII, R = $-H$
VIII, R = $-CH_3$

C^{14}-Labeled 4(5)-hydroxy-5(4)-imidazolecarboxamide (VII) was prepared in 30% yield from carbonyl-labeled aminomalonamide and ethyl formiminoester. (VIII) was similarly prepared (nonlabeled) from ethyl acetaminoester in 70% yield. For these reactions the free iminoesters were pre-

(1) Aided by a grant from the American Cancer Society administered by the Committee on Growth of the National Research Council. One of us (C. S. M.) wishes to express his thanks to Sharp and Dohme, Inc., for financial aid. The C^{14} was received on allocation from the Atomic Energy Commission.

(2) This report as well as an earlier communication[3] are taken from a thesis submitted by Charles S. Miller in partial fulfillment of the requirements for the degree of Doctor of Philosophy in the Graduate School of the University of Pennsylvania.

(3) C. S. Miller, S. Gurin and D. W. Wilson, *Science*, **112**, 654 (1950).

(4) H. Finger, *J. prakt. Chem.*, **76**, 93 (1907).

(5) E. Schmidt, *Ber.*, **47**, 2545 (1914).