ester at the β-position with loss of one and two $CH_2CO_2CH_3$ units to give peaks at M − 73 and M − 146, respectively. These peaks amount to about 25% each of the base peak. These data may be compared with spectra obtained for similarly substituted pyrroles[8] (obtained by pyrolysis of mesoporphyrin dimethyl ester) where the M − 73 peak is the base peak and the molecular ion is only 20–30% as intense.

The molecular ion is the base peak in the mass spectrum of mesoporphyrin IX. The most intense fragment peaks are those at M − 18 and M − 59 corresponding to loss of water and $-CH_2COOH$, respectively. Doubly charged ion peaks are also observed, but no prominent peaks attributable to fragmentation of the porphyrin ring into pyrrole subunits have been detected.

The results of this work emphasize the utility of controlled pyrolysis as an adjunct to direct mass spectrometry. The molecular formula for a complex organic compound can often be obtained simply from a careful analysis of its high-resolution mass spectrum. The high-resolution mass spectrum of mesoporphyrin gives molecular weight and molecular formula; the fragmentation pattern indicates the high stability of the compound. Controlled pyrolysis selectively degrades the porphyrin into pyrrole subunits which can be readily identified and used in determining the structure of the parent porphyrin. Whereas oxidative and reductive degradation procedures require 50–250 mg. of material,[9] complete analysis by pyrolysis and mass spectrometry can be accomplished with as little as 1–2 mg. of porphyrin. Techniques developed with mesoporphyrin are being extended to other porphyrins and their metal complexes. Preliminary results indicate that selective cleavage to pyrroles occurs over the same temperature range for a wide variety of metal-free porphyrins and chlorins.

Experimental Section

Materials.—Mesoporphyrin was prepared from commercial ferric protoporphyrin IX chloride by alkaline hydrogenation.[10] Mesoporphyrin dimethyl ester and its ferric complex were prepared by the procedure of Erdman and Corwin.[11] Porphyrin compounds were analyzed by electronic absorption and mass spectrometric methods. The identity and purity of pyrrole standards were checked by n.m.r. and gas chromatographic analysis.

Pyrolysis–Gas Chromatography.—The sample to be pyrolyzed was weighed into a thin-walled, quartz capillary tube (*ca.* 1 in. in length). The sample tube was placed in a stainless steel U tube (1/8 × 6 in., 0.012-in. wall) with the open end of the quartz tube at the bottom of the U tube. The position of the sample tube was fixed by an open quartz tube, placed above it. The U tube containing the sample was connected to a Loenco heated sample valve and pyrolyzer assembly. The sample valve was connected directly to the injection port of a Loenco Model 70 Hi-Flex dual-column gas chromatograph. The heat-sink furnace of the assembly was placed over the U tube for 2 min. and the sample was pyrolyzed in a stream of helium flowing at 50 cc./min. Pyrolysis products were separated satisfactorily on columns of silicone gum XE-60 or Carbowax 20M on Chromosorb G support. Stainless steel and glass columns (6 ft. × 0.25 in.) were used interchangeably. Columns were operated isothermally at temperatures of 50–200°. No additional products were detected by continuing elution for several hours at 200°. A hot-wire thermal-conductivity detector was calibrated with standard pyrroles: 2,3-dimethylpyrrole, 2,4-dimethylpyrrole, and 2,4-dimethyl-3-ethylpyrrole. A plot of detector response *vs.* alkylpyrrole molecular weight was used to obtain quantitative values for the pyrolysis products detected. Separated products were trapped, according to their volatility, in liquid nitrogen cooled traps equipped with high-vacuum stopcocks or, in the case of most alkylpyrroles, in looped capillary tubes immersed in liquid nitrogen or Dry Ice–acetone.

Mass Spectra.—Mass spectra of chromatographic fractions were obtained with a Consolidated Electrodynamics Corp. mass spectrometer no. 21-103C. Fractions of high volatility were analyzed using a metal and glass inlet system. The less volatile alkylpyrroles, usually oils or solids, were introduced through an all-glass inlet system heated to 230°. The ionizing energy was 70 e.v. and the ionizing current 10–50 μa. Porphyrin mass spectra were obtained on an Associated Electrical Industries, Ltd., mass spectrometer, Model No. MS-9.[6]

(8) D. G. Whitten and K. E. Bentley, unpublished results.

(9) J. E. Falk, "Porphyrins and Metalloporphyrins," Elsevier Publishing Co., New York, N. Y., 1962, p. 152.

(10) E. W. Baker, M. Ruccia, and A. H. Corwin, *Anal. Biochem.*, **8**, 512 (1964).

(11) J. G. Erdman and A. H. Corwin, *J. Am. Chem. Soc.*, **69**, 750 (1947).

Perchloric Acid Catalyzed Acylations. Enol Lactonization and Enol Acetylation of Steroids[1]

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The use of perchloric acid as catalyst for enol acetylation was first described by Barton, *et al.*,[2] who used carbon tetrachloride as solvent and obtained good yields of 17(20)-enol acetates. Subsequently, other workers[3] employed this system for the enol acetylation of 3-keto steroids and related compounds. Perchloric acid catalyzed acetylation by acetic anhydride in ethyl acetate has been used by Schenk and Fritz[4] in a method for the quantitative determination of alcohols, phenols, thiols, and amines, and Whitman and Schwenk[5] used perchloric acid with acetic anhydride and acetic acid for the acetylation of hydroxy steroids.

The enol lactonization of steroidal 4-nor-3,5-seco-5-oxo-3-oic acids (**1**) is an essential step in the synthesis of 3- or 4-^{14}C-labeled steroids[6] as well as of 4-hetero steroids.[7] The conversion of δ-keto acid **3** to enol lactone **4** is an essential step in a recent total synthesis of steroids.[8] Other workers have employed refluxing acetyl chloride–acetic anhydride or acetic anhydride–sodium acetate for this conversion with varying degrees of success.[9]

(1) Presented in part as Paper No. E-10-50, I.U.P.A.C. Symposium on the Chemistry of Natural Products, April 1964, Kyoto, Japan.

(2) D. H. R. Barton, R. M. Evans, J. C. Hamlet, P. G. Jones, and T. Walker, *J. Chem. Soc.*, 747 (1954).

(3) M. P. Hartshorn and E. R. H. Jones, *ibid.*, 1312 (1962); B. Berkoz, E. P. Chavez, and C. Djerassi, *ibid.*, 1323 (1962).

(4) G. H. Schenk and J. S. Fritz, *Anal. Chem.*, **32**, 987 (1960).

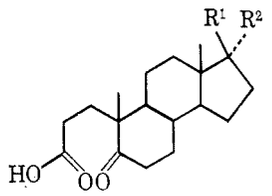
(5) B. Whitman and E. Schwenk, *J. Am. Chem. Soc.*, **68**, 1865 (1946).

(6) A. Murray and D. L. Williams, "Organic Syntheses with Isotopes," part I, Interscience Publishers, Inc., New York, N. Y., 1958, p. 1051.

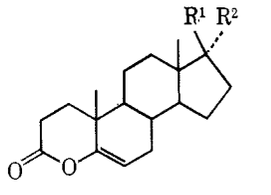
(7) M. Gut and M. Uskokovic, *J. Org. Chem.*, **26**, 1943 (1961).

(8) L. Velluz, G. Nomine, G. Amiard, V. Torelli, and J. Cerede, *Compt. rend.*, **257**, 3086 (1963).

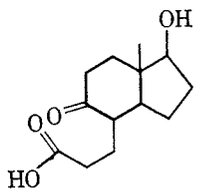
(9) (a) R. B. Turner, *J. Am. Chem. Soc.*, **72**, 579 (1950); (b) R. B. Woodward, F. Sondheimer, D. Taub, K. Heusler, and W. M. McLamore, *ibid.*, **74**, 4223 (1952); (c) M. Gut, *Helv. Chim. Acta*, **36**, 906 (1953).



1a, R^1 = OH; R^2 = H
b, R^1, R^2 = =O
c, R^1 = C_8H_{17}; R^2 = H
d, R^1 = CH_3CO; R^2 = H
e, R^1 = CH_3CO; R^2 = OAc



2a, R^1 = OAc; R^2 = H
b, R^1, R^2 = =O
c, R^1 = C_8H_{17}; R^2 = H
d, R^1 = CH_3CO; R^2 = H
e, R^1 = CH_3CO; R^2 = OAc



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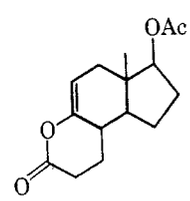

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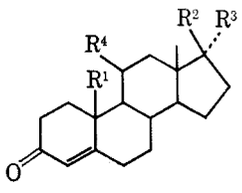
In connection with the synthesis by one of us of 19-C^{14}-testosterone,[10] it was found that 17β-hydroxy-4-nor-5-oxo-3,5-seco-3-androstanoic acid (**1a**) is converted to the corresponding 17β-acetoxy-3,5-enol lactone (**2a**) by acetic anhydride in ethyl acetate containing a trace of perchloric acid in yields of 85% or better in 2 min. at room temperature. Further experimentation established an optimum reagent composition of 1 *M* acetic anhydride and 10^{-3} *M* perchloric acid in ethyl acetate. Ethyl acetate seems to be an ideal solvent for these reactions as most of the keto acids are reasonably soluble in it. Addition of even traces of ether quenches the reaction, perhaps by complexing with the intermediate acetylium ion.[2]

In the course of work on the preparation of 4-^{14}C-pregnenolone,[11] we found that acetic anhydride and perchloric acid in ethyl acetate gave very rapid and complete enol acetylation of Δ^4-3-keto (**5**) and 3-keto steroids (**7**, **9**) at room temperature. Progesterone (**5c**) is quantitatively converted to 3-acetoxy-3,5-pregnadien-20-one (**6c**) in 5 min. with a reagent containing 1 *M* acetic anhydride and 10^{-3} *M* perchloric acid in ethyl acetate (reagent A). Saturated 3-keto steroids are best treated with a reagent containing



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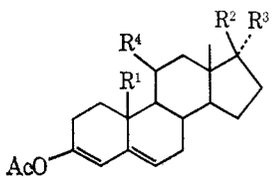


6

a, R^1 = CH_3; R^2 = C_8H_{17}; R^3, R^4 = H
b, R^1 = CH_3; R^2, R^3 = =O; R^4 = H
c, R^1 = CH_3; R^2 = CH_3CO; R^3, R^4 = H
d, R^1 = CH_3; R^2 = CH_3CO; R^3 = OH(Ac); R^4 = H
e, R^1 = CH_3; R^2, R^3 = =O; R^4 = OH(Ac)
f, R^1 = CH_3; R^2 = OH(Ac); R^3, R^4 = H
g, R^1 = H; R^2 = OH(Ac); R^3, R^4 = H

10^{-2} *M* perchloric acid (reagent B), as at the lower perchloric acid concentration, the reaction is not complete in 5 min. The reagent acetylates all free hydroxyl groups of the steroids, including those at the hindered

(10) (a) P. N. Rao and L. R. Axelrod, *Chem. Ind.* (London), 1838 (1963); (b) *J. Chem. Soc.*, 1356 (1965).
(11) P. N. Rao and L. R. Axelrod, *J. Org. Chem.*, **26**, 1607 (1961).

TABLE I
KETO ACID AND THEIR ENOL LACTONES

Keto acid	M.p., °C.	[α]D, deg.[a]	Formula	Calcd., % C	Calcd., % H	Found, % C	Found, % H	Enol lactone	M.p., °C.	[α]D (CHCl3), deg.	Yield, %	Formula	Calcd., % C	Calcd., % H	Found, % C	Found, % H	Ref.
1a	204–206	+37.4 (E)	$C_{18}H_{28}O_4$	70.09	9.15	69.97	9.39	**2a**	129–130.5	−10.6	85	$C_{20}H_{28}O_4$	72.26	8.49	72.51	8.44	10
b	108–110	+123 (M)	$C_{18}H_{28}O_4$	70.56	8.55	70.14	8.27	**b**	143.5–144.5	−31.2	93	$C_{18}H_{24}O_3$	74.97	8.39	75.26	8.45	...
c	153–154	+34 (C)[b]	...	...	...	...	*c*	**c**	92–93	−55.3	97	$C_{26}H_{42}O_2$	80.77	10.95	80.67	11.13	9a
d	171–172	+10.8 (A)[d]	...	...	...	...	*c*	**d**	153–155	+4	98	$C_{20}H_{28}O_3$	75.92	8.91	76.27	8.81	9c
e	177–178	+22 (M)	$C_{22}H_{32}O_6$	67.32	8.21	67.29	8.11	**e**	288–298	−97.8	99	$C_{22}H_{30}O_5$	70.56	8.07	70.74	8.01	...
3	153[e]	+12 (E)[e]	...	...	...	...	*f*	**4**	115–116	−75	70[f]	$C_{15}H_{20}O_4$	68.16	7.63	68.09	7.75	8

[a] E = ethanol, M = methanol, C = chloroform, A = acetone. [b] Taken from ref. 9a. [c] Identified by comparison with an authentic sample. [d] Taken from ref. 9c. [e] Taken from ref. 8. [f] The keto acid was obtained by ozonolysis and was not highly purified. The yield of lactone is based on impure starting acid.

TABLE II

ENOL ACETATES PREPARED BY PERCHLORIC ACID CATALYZED ACETYLATION

Reagent	Enol Acetate	M.p., °C.	Yield, %	Formula	Calcd., % C	Calcd., % H	Found, % C	Found, % H
A	6a[a]	75–77	72[b]	$C_{29}H_{46}O_2$	81.63	10.86	81.69	10.69
A	b	123–125	81[b]	$C_{21}H_{48}O_3$	76.79	8.59	76.66	8.47
A	c[c]	130–131	88[b]	Compared with authentic sample				
A	d[d]	178–188	100	$C_{25}H_{34}O_5$	72.43	8.27	72.00	8.41
A	e[d]	140–158	100	$C_{23}H_{30}O_5$	71.48	7.83	71.84	8.01
A	f	152–156	98	$C_{23}H_{32}O_4$	74.16	8.66	73.88	8.64
A	g	156–168	93	$C_{22}H_{30}O_4$	73.71	8.44	73.41	8.43
B	8a[e]	92–98	86[b]	$C_{29}H_{48}O_2$	81.24	11.29	81.16	11.52
B	b[f]	172–174	96	$C_{23}H_{34}O_4$	73.76	9.15	73.64	9.20
B	10	94–98	100	$C_{23}H_{34}O_4$	73.76	9.15	73.53	9.09

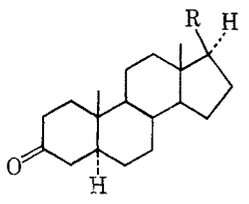
[a] W. G. Dauben and J. F. Eastham, *J. Am. Chem. Soc.*, **73**, 3260 (1951). [b] Yield of once-recrystallized material. [c] Reference 11. [d] Run for 15 min. [e] C. Djerassi, N. Finch, R. C. Cookson, and C. W. Bird, *J. Am. Chem. Soc.*, **82**, 5488 (1960). [f] R. Villotti, H. J. Ringold, and C. Djerassi, *ibid.*, **82**, 5693 (1960).

TABLE III

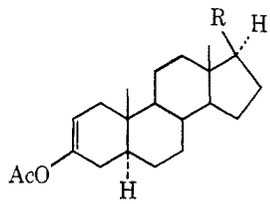
N.M.R. SPECTRA[a] OF COMPOUNDS 8a AND 10

Compd.	C.p.s. (p.p.m.) 18-H	19-H	Acetate-H	17α-H (triplet)	O H \ / C=C	Width at half-height, c.p.s.
8a	47 (0.783)	50 (0.833)	121 (2.02) 125 (2.08)	274 (4.57)	313 (5.21)	9
10	46 (0.766)	58 (0.966)	120 (2.00) 124 (2.06)	274 (4.57)	300 (5.00)	4

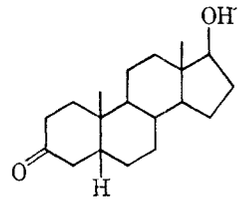
[a] Reference 13.



7a, R = C_8H_{17}
b, R = OH



8a, R = C_8H_{17}
b, R = OAc



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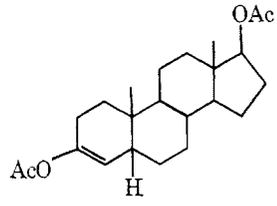


10

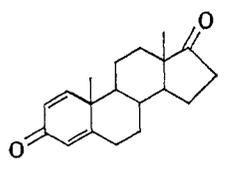
11β and 17α positions which are resistant to the usual acetylation techniques. To ensure complete acetylation of hindered hydroxyls, these compounds were treated for 15 min. Keto functions at other sites, such as 6, 11, 17, and 20, are not affected under the conditions of the reaction.

Table I lists the enol lactones and Table II lists the enol acetates which were prepared by treatment with the reagent. Some representative compounds which were recovered unchanged after treatment with reagent A are 5α-androst-1-ene-3,17-dione, 17β-hydroxy-5α-androst-1-en-3-one, 3β-hydroxy-5-pregnen-20-one (pregnenolone), 3β-hydroxy-5,16-pregnadien-20-one, and 3β-hydroxy-cholest-5-en-7-one.

That the enol acetates derived from the saturated 3-ketones **7** and **9** were actually those expected on the basis of analogous reactions[12] and shown in structures **8** and **10** was supported by comparison of the n.m.r. spectra[13] of **8a** and **10**. Table III lists the major features of the spectra, which are in good agreement with values compiled by Bhacca and Williams.[14]

The vinyl proton of **8a** is observed as an unresolved multiplet with a width at half-height of 9 c.p.s. Using dihedral angles measured from a Dreiding model of **8a**, $J_{1\alpha,2} + J_{1\beta,2}$ is estimated[14] to be 6 c.p.s. The expected ABX triplet pattern is apparently obscured by long-range coupling effects. In **10** the vinyl proton appears as a much narrower band (width at half-height, 4 c.p.s.). Examination of a Dreiding model of **10** reveals two reasonable conformations for the A ring which yield values for $J_{4,5}$ of 0.5 or 2 c.p.s. Again, no splitting is observed, presumably because of long-range coupling effects.

Treatment of 1,4-androstadiene-3,17-dione (**11**) with reagent B brought about a dienone–phenol rearrangement to give, after saponification, 1-hydroxy-4-methyl-1,3,5(10)-estratrien-17-one (**12**), identical with



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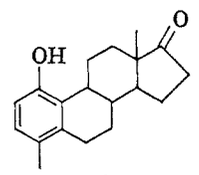

12

(12) L. F. Fieser and M. Fieser, "Steroids," Reinhold Publishing Corp., New York, N. Y., 1959, p. 310.

(13) The n.m.r. spectra were determined in deuteriochloroform solution on a Varian Associates A-60 spectrometer through the courtesy of Mr. Bill Storey of the Southwest Research Institute.

(14) N. S. Bhacca and D. H. Williams, "Application of NMR Spectroscopy in Organic Chemistry," Holden-Day, Inc., San Francisco, Calif., 1964, pp. 19–24, 33, 50, 77–18.

that obtained by the method of Dreiding and Voltman.[15] The perchloric acid catalyzed reaction was complete in 45 min. as contrasted to the 24 hr. required by the Dreiding and Voltman procedure.

Experimental Section[16]

Reagent A (10^{-3} *M* $HClO_4$).—To 50 ml. of absolute ethyl acetate was added 0.05 ml. of 72% perchloric acid (0.575 mmole). Ten milliliters of this solution was then added to 30 ml. of absolute ethyl acetate and 4.8 ml. (51 mmoles) of acetic anhydride, and the solution was made up to 50 ml. with ethyl acetate to give a reagent 1 *M* in acetic anhydride and 10^{-3} *M* in perchloric acid.

Reagent B (10^{-2} *M* $HClO_4$).—To 40 ml. of absolute ethyl acetate was added 0.05 ml. (0.58 mmole) of 72% perchloric acid and 4.8 ml. (5.1 mmoles) of acetic anhydride, and the solution was made up to 50 ml. with ethyl acetate.

General Procedure.—The keto acid or ketone was dissolved using 1 ml. of reagent for each 10 mg. of compound (reagent A for keto acids and Δ^4-3-ketones and reagent B for saturated 3-ketones), and the solution was let stand for 5 min. at room temperature. Compounds bearing hindered hydroxyl groups (11β or 17α) were allowed 15 min. to ensure complete acetylation. The solution was then washed with saturated sodium bicarbonate solution, dried over anhydrous sodium sulfate, and evaporated to dryness. Residual acetic anhydride, if any, could be removed by adding a few milliliters of methanol containing a trace of pyridine and again evaporating to dryness. Analytical samples were prepared by recrystallization from methanol containing a trace of pyridine, hexane–ether or acetone, or aqueous acetone. The melting points, yields, and analyses of the products are shown in Tables I and II. For large-scale reactions it was found best to prepare a double-strength reagent which was added to an equal volume of ethyl acetate in which the starting material was previously dissolved.

The reagent can be stored in the refrigerator for several weeks without any noticeable loss of activity, though it slowly acquires a yellow to brown color. It tends to darken more rapidly as the acid concentration is increased and the darkening becomes more pronounced in the reaction mixture. Although good yields may still be obtained at acid concentration up to 0.15 *M* and as low as 10^{-4} *M*, the concentration for optimum yield of lactones and enol acetates of α,β-unsaturated ketones with minimum coloration of the product is 10^{-3} *M* (reagent A).

Dienone–Phenol Rearrangement.—1,4-Androstadiene-3,17-dione (55 mg.) was dissolved in 5 ml. of reagent B. Small samples were removed after 5, 30, and 45 min. and spotted on silica gel t.l.c. microplates, and the plates were developed with benzene–ethyl acetate 19:1. The spot corresponding to the product increased in intensity, and at 45 min. the starting material spot was no longer detected. The reaction mixture was washed with saturated sodium carbonate solution, dried over anhydrous sodium sulfate, and evaporated to dryness under nitrogen. The residue (51 mg., 92%) was saponified by refluxing in aqueous methanolic potassium hydroxide for 1 hr. The solution was acidified with dilute hydrochloric acid, and the resulting solid was collected, washed with water, and crystallized from methanol to give 1-hydroxy-3-methyl-1,3,5(10)-estratrien-17-one. The melting point and mixture melting point of a sample prepared by the method of Dreiding and Voltman[15] was 246–249°. The reaction carried out by the method of Dreiding and Voltman (zinc chloride in acetic anhydride) was also monitored by t.l.c. No appreciable reaction had occurred at 45 min., but the reaction appeared to be essentially complete at 20 hr.

Acknowledgments.—The authors are grateful to Dr. Leonard R. Axelrod for his interest and encouragement during the course of this investigation. This work was supported by Grant AM 03270-06 from the National Institute of Arthritis and Metabolic Diseases, National Institutes of Health, Bethesda, Maryland.

(15) A. S. Dreiding and A. Voltman, *J. Am. Chem. Soc.*, **76**, 537 (1954).

(16) Melting points were taken in a Thomas–Hoover melting point apparatus and are uncorrected. Optical rotations were determined using a Zeiss-Winkel optical polarimeter. Elemental analyses were performed by Micro-Tech Laboratories, Skokie, Ill.

Reactions of Phenyl Isocyanate with Some Metal Derivatives of Pyrrole

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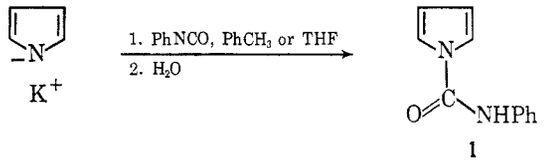
The reactions of phenyl isocyanate with Grignard reagents,[2a] 1,3-dicarbonyl compounds,[2b] and aromatic compounds under Friedel–Crafts conditions[3] to give the corresponding anilides are well known. Among heterocyclic compounds, pyrroles and Grignard reagents of substituted pyrroles react with phenyl isocyanate to form 2-pyrrolecarboxanilides.[4,5] Imidazole yields 1-imidazolecarboxanilide,[6,7] whereas 4,5-diphenylimidazole forms the 1-carboxanilide, the 2-carboxanilide, or a mixture of the latter compound and 2,5,6-triphenylimidazo[1,2-*c*]hydantoin, depending on the experimental conditions.[8]

In the course of a study on acyl derivatives of pyrrole, we found that the reaction of pyrrolylpotassium with phenyl isocyanate in toluene or tetrahydrofuran gives 1-pyrrolecarboxanilide (**1**) in very good yield. The product of this reaction is formulated as **1** because it contains only one active hydrogen atom, and its infrared spectrum shows a carbonyl absorption at 1720 cm.$^{-1}$ [9] but no characteristic absorption in the 3400–3500-cm.$^{-1}$ region (pyrrole N–H stretching[10]). In contrast, the spectrum of the known 2-pyrrolecarboxanilide (**2**)[4] has bands at 1660[9] and 3450 cm.$^{-1}$



1

Like 1-imidazolecarboxanilide,[7] the pyrrole derivative **1** undergoes transamination. As expected,[11] however, 1-pyrrolecarboxanilide is more sluggish than its imidazole analog. Thus, reaction of **1** with aniline or piperidine in refluxing tetrahydrofuran proceeded very slowly, and the substitution products, N,N′-diphenylurea (**3**) and N-phenyl-N′,N′-pentamethyleneurea (**4**), could be obtained in satisfactory yields only at higher temperatures in the absence of the solvent.

Refluxing with ethanolic potassium hydroxide for 4 hr. hydrolyzed **1** to pyrrole and aniline. This behavior

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