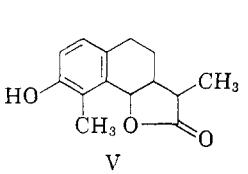
2-naphthol,[8] m.p. 93–94°. The reation in ethylene glycol gave the 9//10 seco compound (VI) as a solvated crystal, m.p. 100–108°, λ_{max}^{Nujol} 815 cm.$^{-1}$ NMR[7] τ, 7.69, 7.75 ppm. (two benzenoid methyl), 9.13 ppm. triplet (methyl of ethyl group). The substance after the crystal solvent is removed is an oil, $[\alpha]_D^{20}$ −25° (chloroform), $\lambda_{max}^{CH_3OH}$ 288 mμ (ε 3,000), (*Anal.* Calcd. for $C_{15}H_{20}O_3$: C, 72.55; H, 8.12. Found: C, 72.26; H, 8.12), acetate, m.p. 145–150° (*Anal.* Calcd. for $C_{17}H_{22}O_4$: C, 70.32; H, 7.64. Found: C, 70.58; H, 7.61).



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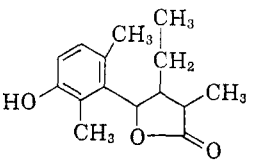

VI

Methane generated from all the reactions involving the loss of the angular methyl group, was detected by gas chromatography. As only starting material was recovered from the reaction in anhydrous pyridine, ethylene glycol or water in pyridine may be a hydrogen donor in the reaction. The treatment of the above dienone (Ie) or trienone (Ia or Id) in acetic acid with zinc[9] does not give an aromatic A-ring steroid, but a substance assumed to be a bis compound showing polyene absorption. The detailed presentation of these reactions will be published in a forthcoming report.

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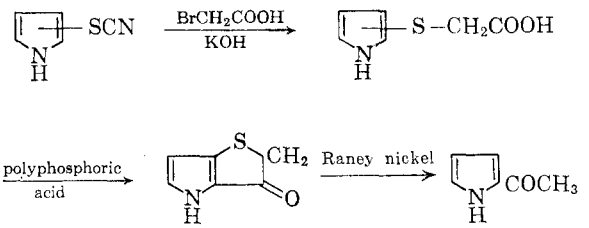
On the Thiocyanation of Pyrrole

Sir:

Matteson and Snyder[1] have recently claimed that thiocyanation of pyrrole with methanolic thiocyanogen at −70° or with cupric thiocyanate at 0° yields 3-thiocyanopyrrole (I) (m.p. 41.5–43°). This is rather unexpected since most reagents attack pyrroles at an unsubstituted α-position in preference to an unsubstituted β-position. They proved the structure of the thiocyanopyrrole by converting it to the (pyrrolylthio)acetic acid (II) which was ring closed to 2*H*,3*H*-thieno[3,2-*b*]pyrrole-3-one (III) and desulfurized to authentic 2-acetylpyrrole (IV)



In connection with our work on the NMR spectra of heteroaromatic compounds,[2–5] we have studied the NMR spectrum of thiocyanopyrrole and some of its derivatives. The three bands in the aromatic region of thiocyanopyrrole display the shifts[6] τ_A = 3.10, τ_B = 3.47, τ_C = 3.85 p.p.m. and the coupling constants J_{AB} = 1.5, J_{AC} = 2.9, and J_{BC} = 3.6 c/s, which prove that the compound formed is the 2- isomer. This conclusion is based on comparison of the above NMR parameters with those observed in other pyrroles[5] and in 2- and 3-thiocyanothiophenes.[2] Furthermore, the NMR spectrum of the methylthiopyrrole obtained through the reaction of the thiocyanopyrrole with alkali and methyl iodide[1] is in agreement only with that expected for the 2- isomer (τ_A = 3.28, τ_B = 3.77, τ_C = 3.90 p.p.m., J_{AB} = 1.5, J_{AC} = 2.8, and J_{BC} = 3.4 c/s). The same methylthiopyrrole (b.p. 87–90°/17 mm., n_D^{20} 1.5730. *Anal.* Calcd. for C_5H_7NS: C, 53.06; H, 6.23; N, 12.38; S, 28.33: Found: C, 53.17; H, 6.42; N, 12.35; S, 28.25) is obtained by treating pyrrolemagnesium iodide with dimethyl disulfide and also by treating pyrrole with methylsulfenyl chloride. These results provide independent evidence that the methylthiopyrrole is the 2-isomer, as it is known that these types of reactions lead to α-substitution.[7,8]

The NMR spectrum of the aldehyde obtained through Vilsmeier formylation of the methylthiopyrrole shows that the compound formed is 2-

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(2) S. Gronowitz, and R. A. Hoffman, *Arkiv Kemi*, **16**, 539 (1960).

(3) R. A. Hoffman and S. Gronowitz, *Arkiv Kemi*, **16**, 563 (1960).

(4) S. Gronowitz and R. A. Hoffman, *Arkiv Kemi*, **16**, 459 (1960).

(5) S. Gronowitz, A-B. Hörnfeldt, B. Gestblom, and R. A. Hoffman, *Arkiv Kemi, in press.*

(6) The NMR spectra were obtained with a Varian Associates Model V-4300b spectrometer operating at 40 Mc/s. The chemical shifts [τ-values, *cf.* G. V. D. Tiers, *J. Phys. Chem.*, **62**, 1151 (1958)] were obtained from dioxane solutions to which were added traces of piperidine in order to eliminate the complicating effects of the couplings with the *N*-hydrogens.

(7) M. S. Kharasch and O. Reinmuth, *Grignard Reaction of Nonmetallic Substances*, Prentice-Hall, Inc., New York, N. Y., 1954 pp. 75 ff.

(8) A. H. Corwin in R. C. Elderfield, ed., *Heterocyclic Compounds*, Vol. I, John Wiley & Sons, Inc., New York, N. Y., 1950, Chapter VI.

methylthio-5-pyrrolealdehyde (m.p. 105–106°, τ_{CHO} = 0.69, τ_3 = 3.78, τ_4 = 3.12, τ_{SCH} = 7.59 p.p.m., J_{34} = 3.8 c/s. *Anal.* Calcd. for C_6H_7NOS C, 51.04; H, 4.99; N, 9.92; S, 22.71: Found: C, 51.41; H, 5.15; N, 10.08; S, 22.56), thus giving further evidence that the original methylthiopyrrole is the 2- isomer. Additional evidence against preferential β-thiocyanation in pyrroles is obtained from the fact that 2-methylpyrrole yields 5-thiocyano-2-methylpyrrole (m.p. 65.5–66°, τ_3 = 4.13, τ_4 = 3.56 p.p.m., $J_{CH_3\text{-}3}$ = 0.80, $J_{CH_3\text{-}4}$ = 0.35, J_{34} = 3.55 c/s. *Anal.* Calcd. for $C_6H_6N_2S$: C, 52.15; H, 4.38; N, 20.28; S, 23.19: Found: C, 52.22; H, 4.39; N, 20.21; S, 22.86:) upon thiocyanation with cupric thiocyanate, the NMR evidence for its structure being based on the values of the chemical shifts and ring-coupling constants, in addition to the side-chain couplings.[3]

Since the structure of III is proved beyond any doubt by Snyder *et al.*[1,9] and since it is very improbable that any rearrangement occurred in the transformation of the thiocyanopyrrole to methylthiopyrrole or (pyrrolylthio)acetic acid, the discrepancy between our results and those of Matteson and Snyder regarding the structure of the thiocyanopyrrole must be ascribed to a rearrangement during the cyclization of (2-pyrrolylthio)acetic acid with polyphosphoric acid to III. Rearrangements during treatment with polyphosphoric acid, although not analogous to that found here, have been observed by others.[10,11]

A detailed account of the observations reported here will be published in *Arkiv Kemi*.

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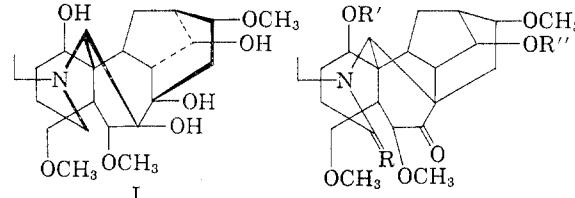
On Anhydrodiacetyllucaconine (Diacetyldelcosine,[1] M.P. 159–161°) and Its Derivatives

Sir:

Previously, it was shown that an aconite alkaloid, lucaconine (I) ($C_{24}H_{39}O_7N$), gave anhydrodiacetyllucaconine (II) ($C_{28}H_{41}O_8N$) on treatment with acetyl chloride.[4] Compound II has been found to have a ketone carbonyl group formed with elimination of one mole of water, and to absorb one mole of hydrogen without reduction of the carbonyl group.[5] Moreover, it has been shown that this dehydration takes place between two tertiary hydroxyl groups of compound I.[5]

On the other hand, on the basis of the biogenetical viewpoint as well as experimental results, Marion and his co-workers[6–8] have pointed out that delcosine[1] (lucaconine) (I) probably possesses the same carbon-nitrogen nucleus as lycoctonine, and also that this base is represented by the structure I shown below. In the belief that their conclusions



I

II. R = H_2, R′ = R″ = Ac
III. R = O, R′ = R″ = H

are quite reasonable, the present authors now would like to propose structures II and III for anhydrodiacetyllucaconine[4] and anhydrooxolucaconine (III),[4] respectively. Compound III has previously been obtained from both compound II and oxolucaconine through two steps.[4] The mechanism of the above dehydration is considered to be analogous to that of the dehydration of oxolycoctonine or demethyleneoxodelpheline.[9]

The ultraviolet absorption spectrum of compound III in methanol shows a maximum at 301 mμ (log ϵ 2.01) while compound II manifests a maximum at 237 mμ (log ϵ 3.20). The limiting structure IIa of compound II seems to give a good explanation of the marked difference between these two absorption bands. A similar phenomenon was observed and interpreted in the case of some delphinine and neoline derivatives.[10]

(1) It has been shown that lucaconine is identical with delcosine,[2] and therefore anhydrodiacetyllucaconine is identical with diacetyldelcosine (m.p. 159–161°) obtained by Marion *et al.*.[3] The name "lucaconine" should be revised to "delcosine."

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(8) R. Anet and L. Marion, *Can. J. Chem.*, 36, 766 (1958).

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