water, and 11 ml. of ethanol. While the reaction mixture was still hot, about one-half of the solvent was removed under reduced pressure. Upon cooling, a pink solid (59 mg.) formed and was collected by filtration. This solid was taken up in ethanol, a few drops of 1:1 hydrochloric acid were added to dissolve the solid (a potassium salt), and the solution was cooled to give recovered diester VIII. The cooled filtrate was acidified to pH 5 with 85% phosphoric acid, whereupon a yellow solid precipitated. The solid was filtered, washed with water, and dried in a vacuum desiccator over Drierite. There was obtained 0.442 g. of a pink solid. The solid was taken up in 95% ethanol containing 10 drops of 1:1 hydrochloric acid, heated until most of the solid had dissolved, and filtered, and the volume was concentrated. Upon cooling, 0.386 g. of yellow crystals formed, m.p. 195–200°. The yield was 82% based on the diester VIII consumed. The use of a sixfold excess of base gave the same acid. An analytical sample was prepared by two recrystallizations from 95% ethanol, m.p. 197–199°.

Anal. Calcd. for $C_{17}H_{15}NO_5S$: C, 59.12; H, 4.38; N, 4.06. Found: C, 59.06; H, 4.22; N, 4.04.

Carbethoxylation of 6-Benzyl-3-oxo-2H,3H-thieno[2,3-*b*]pyrrole-4-carboxylic Acid (IX).—The keto acid IX (96 mg., 0.36 mmole) was heated under a nitrogen atmosphere in 12 ml. of diethyl carbonate. After 2 ml. of diethyl carbonate had been distilled, a solution of sodium ethoxide (1.06 mmoles) in 3 ml. of absolute ethanol was added. Eight milliliters of condensate was collected by slow distillation over a period of 1.5 hr. The reaction mixture was cooled under a stream of nitrogen. To the mixture was added 5 ml. of water and 5 ml. of methylene chloride. The aqueous phase was acidified with 1:1 hydrochloric acid and extracted with methylene chloride. The methylene chloride extract yielded some orange solid. The solid was recrystallized from 95% ethanol to give recovered keto acid IX, m.p. 177–180°. The infrared spectrum was superimposable upon that of an authentic sample of IX. The mother liquor yielded a few milligrams of the monoacid–monoester XII. The material was recrystallized twice from ethanol and once from chloroform, m.p. 192–197°. The identity of the material with XII was established by a mixture melting point and by comparison of the infrared spectra.

6-Benzylthieno[2,3-*b*]pyrrole-4-carboxylic Acid (X).—The keto acid IX (0.178 g., 0.65 mmole) was suspended in 10 ml. of absolute ethanol. The ethanolic suspension was flushed out with nitrogen. Sodium borohydride (78.5 mg., 2.1 mmoles) was added in portions to the suspension over a period of about 45 min. When the evolution of gas had ceased, the flask was filled with nitrogen, stoppered, and allowed to stand for 16 hr. The reaction mixture was gently warmed on a steam bath for 25 min., 10 mg. of sodium borohydride was added, and the mixture was warmed for 20 min. Upon cooling, the mixture was poured into a solution of 30 ml. of cold water and 0.38 ml. of glacial acetic acid. The aqueous phase was extracted with four portions of methylene chloride. The combined methylene chloride extracts were washed once with saturated sodium chloride solution and dried over magnesium sulfate. The drying agent was filtered and the solvent was removed under reduced pressure on a steam bath. An oil was obtained which slowly solidified upon cooling under a stream of nitrogen. There was obtained 0.162 g. of tan crystals. A n.m.r. spectrum of this material indicated that about 10% of unreduced keto acid IX was present. Two recrystallizations from methylene chloride–benzene gave 0.115 g. (75%) of tan crystals, m.p. 158–160°. Ultraviolet spectrum: $\lambda_{\max}$ 267 mμ (ϵ 14,500) and 232 mμ (ϵ 9900), $\lambda_{\min}$ 243 mμ (ϵ 7900) and 223 mμ (ϵ 9360). An analytical sample was prepared by two recrystallizations from methylene chloride, m.p. 161–162°.

Anal. Calcd. for $C_{14}H_{11}NO_2S$: C, 65.36; H, 4.31; N, 5.44. Found: C, 65.12; H, 4.19; N, 5.40.

6-Benzylthieno[2,3-*b*]pyrrole (IV).—The thienopyrrole acid X (82 mg., 0.32 mmole) was placed in a 30 mm. × 15 cm. tube whch had a break-seal side arm near the neck of the tube. The acid was dissolved in methylene chloride and the tube was rotated at an angle while the solvent was evaporated under a stream of nitrogen to cause the acid to be deposited as a thin layer on the lower inside surface of the tube. The tube was evacuated for 45 min. on a vacuum line at 10^{-4} mm. and sealed.[13] The portion of the tube which contained the solid was immersed in an oil bath heated at 200° and the temperature was raised to 220° over a period of 60 min. and held at this temperature for 30 min. Upon cooling, the tube contained some yellow oil in the bottom and some clear oil on the sides. The carbon dioxide formed was measured on the vacuum line and was determined to be 0.22 mmole (69%). The tube was rinsed with carbon disulfide. The carbon disulfide solution was evaporated on a steam bath to give a light yellow oil. The oil was heated at 80° (0.1 mm.) in a sublimation apparatus. A clear liquid (35 mg., 52%) collected on the cold finger. Analysis and n.m.r. measurements (described in the introduction) indicated the liquid to be pure 6-benzylthieno[2,3-*b*]pyrrole. Ultraviolet spectrum (95% EtOH): $\lambda_{\max}$ 250 mμ (ϵ 9800), shoulder, increasing absorption from 245 to 210 mμ. The isomer[5] II has $\lambda_{\max}$ 267 mμ (ϵ 12,000) and 334 mμ (ϵ 1320), $\lambda_{\min}$ 237 mμ (ϵ 5625).

Anal. Calcd. for $C_{13}H_{11}NS$: C, 73.19; H, 5.28; N, 6.56. Found: C, 73.12; H, 5.38; N, 6.76.

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[13] Appreciation is expressed to Professor R. F. Nystrom for assistance in carrying out this reaction.

The Formation of Methyl Thio Ethers in the Reaction of Thiocyanates with Methanol[1,2]

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Received August 10, 1964

The reaction of diethyl 1-benzyl-2-thiocyanopyrrole-3,4-dicarboxylate with aqueous methanolic potassium hydroxide in the presence of ethyl bromoacetate gives diethyl 1-benzyl-2-methylthiopyrrole-3,4-dicarboxylate instead of the expected product, ethyl (1-benzyl-3,4-dicarbethoxy-2-pyrrolylthio)acetate. The methyl thio ether was also the major product when the reaction was carried out in the absence of ethyl bromoacetate. The scope of this unusual alkylation reaction is investigated. Methyl 2-thiocyanobenzoate and methyl 4-thiocyanobenzoate each give the corresponding methyl thio ether in approximately 50% yield upon treatment with aqueous methanolic potassium hydroxide. Under the same reaction conditions, no thio ether is formed from either thiocyanomesitylene or *n*-butyl thiocyanate.

In the course of another investigation[4] the surprising observation was made that replacement of the cyano group by methyl occurred when the thiocyanopyrrole I was treated with aqueous methanolic potassium hydroxide and ethyl bromoacetate. The reaction was carried out in the anticipation that the thiocyano group of I would be hydrolyzed to the thiol, the anion

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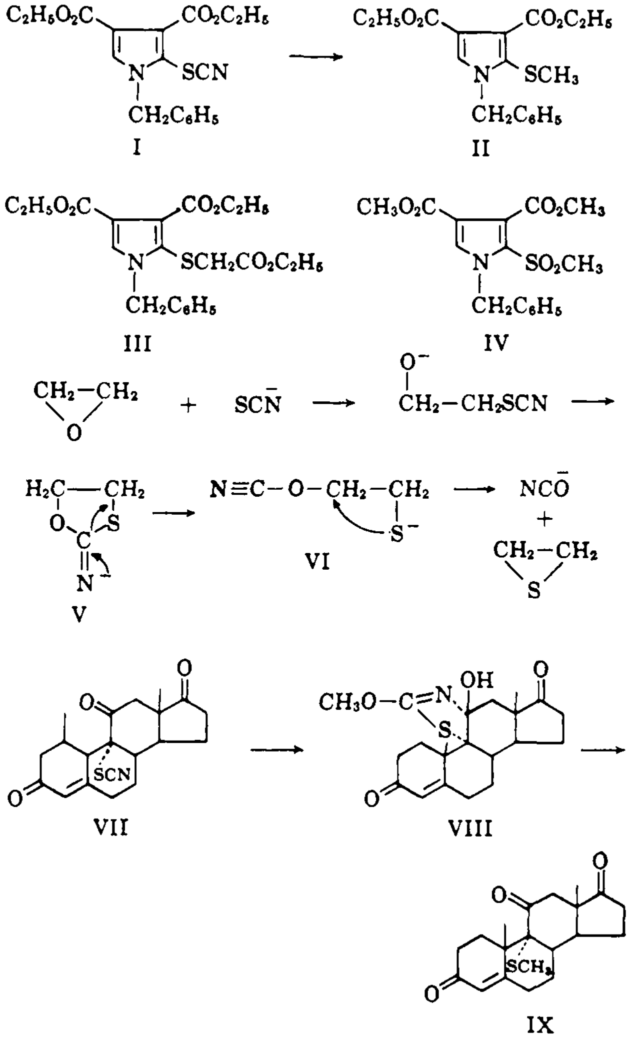
[1] Abstracted from a portion of the thesis submitted by R. K. Olsen to the Graduate College of the University of Illinois in partial fulfillment of the requirements for the degree of Doctor of Philosophy, Oct. 1964.

[2] Supported in part by a research grant (C 3969-Bio) from the National Cancer Institute, U. S. Public Health Service.

[3] National Science Foundation Predoctoral Fellow, 1962–1963; National Institutes of Health Predoctoral Fellow, 1963–1964.

[4] R. K. Olsen and H. R. Snyder, *J. Org. Chem.*, **29**, 184 (1964).

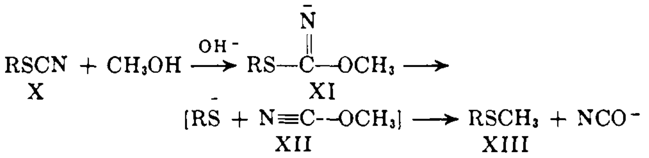
SCHEME I



of which would be alkylated by the bromoacetate to give the thio ether III, a sequence that is very satisfactory when applied to 2-thiocyanopyrrole.[5] That the ethyl bromoacetate did not participate in the process was shown by the isolation of the methyl thio ether II in 79% yield from a reaction mixture prepared from the thiocyano compound and aqueous methanolic potassium hydroxide only. When the reaction was carried out in ethanol, the ethyl thio ether was obtained, but in somewhat lower yield (52%). The structure of the methyl thio ether II follows from its composition, its n.m.r. spectrum (singlet at τ 7.88 assigned to the S–CH_3 protons), and its transformation by ester interchange and oxidation to the sulfone, dimethyl 1-benzyl-2-methanesulfonylpyrrole-3,4-dicarboxylate (IV). Hydrolysis of II occurred by attack at only one of the ester groups, presumably the less hindered one, yielding a half-ester. Although the originally desired S-alkylation product III was not isolated from any reaction carried out in aqueous methanol or ethanol, the mixture obtained from I in aqueous tetrahydrofuran with ethyl bromoacetate contained, according to n.m.r. analysis, about 50% of III and none of II.

The normal reaction of a thiocyanate in the presence of a strong base and ethanol leads to the symmetrical disulfide, sometimes in almost quantitative yield.[6-8] However, phenyl thiocyanate, which gave only phenyl disulfide on reaction with alcohol-free sodium ethoxide, did produce some ethyl phenyl sulfide (as well as some thiophenol) when the reaction was carried out in ethanol.[9] It has been reported[10] that treatment of 2-thiocyanoethanol with alkali results in its conversion to ethylene sulfide (which polymerizes under the conditions of the experiment), a transformation that is analogous to the alkylation of the sulfur atom by the alcohols in the experiments reported here. The formation of ethylene sulfide in this reaction is related to the preparation of episulfides from olefin oxides and potassium thiocyanate. The latter process has been examined in detail.[11,12] It has been shown to proceed by way of the anion of the cyclic imino thiocarbonate V which is considered to isomerize to the anion of the β-mercaptoalkyl cyanate VI, from which the episulfide arises by internal displacement of cyanate ion (see Scheme I).

An even closer analogy to the presently observed methylation of sulfur by methanol has been reported[13] in the two-step conversion of the thiocyano steroid VII to the S-methyl derivative IX. When the thiocyano compound VII was treated with aqueous methanolic potassium carbonate at room temperature it was converted to the thiazoline VIII; heating of the thiazoline with aqueous ethanolic potassium carbonate caused its decomposition to the S-methyl derivative IX. Although the mechanism of the second step of this process was not studied, a possible path by way of ring opening and hydrolytic displacement of nitrogen from the thiazoline was mentioned, the S-alkylation occurring as a result of attack of base on a monothiocarbonate. It seems to us that this reaction, as well as the sulfur alkylations we have observed, may instead occur by the same steps as the episulfide formation referred to above, the only essential difference being that the displacement of cyanate ion by mercaptide is intermolecular rather than intramolecular. The steps then would be as shown in the sequence X → XIII.



$$\underset{X}{RSCN} + CH_3OH \xrightarrow{OH^-} RS-\underset{XI}{\overset{\overset{\bar{N}}{\|}}{C}}-OCH_3 \longrightarrow$$

$$[\underset{XII}{\overset{-}{RS} + N\equiv C-OCH_3}] \longrightarrow \underset{XIII}{RSCH_3 + NCO^-}$$

No attempt to verify the mechanism has been made, but a few experiments were carried out in a limited investigation of the scope of the reaction. In the results obtained (Table I), an indication of the effect of electron-withdrawing groups is seen in the fact that I gives the methyl thio ether II in 52% yield under conditions by which 2-thiocyanopyrrole is converted only to the methanol addition product,[5] S-2-pyrrolyl O-methyl thioimidocarbonate, in 87% yield. According to the mechanism suggested above an electron-with-

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[5] (a) D. S. Matteson and H. R. Snyder, *J. Org. Chem.*, **22**, 1500 (1957); (b) R. K. Olsen and H. R. Snyder, *ibid.*, **28**, 3050 (1963).

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TABLE I

Thiocyanate	Methyl thio ether, %	Ethyl thio ether, %
Diethyl 1-benzyl-2-thiocyanopyrrole-3,4-dicarboxylate (I)	79	52
Diethyl 2-thiocyanopyrrole-3,4-dicarboxylate	44	. .
Methyl 2-thiocyanobenzoate	47	30
Methyl 4-thiocyanobenzoate	41	. .
Thiocyanomesitylene	. .	0
n-Butyl thiocyanate	0	. .

drawing group should facilitate the formation of the mercaptide anion in the cleavage step. That the hindrance around the thiocyano group of I is not important in determining the course of the reaction is indicated by the fact that the desbenzyl derivative, diethyl 2-thiocyanopyrrole-3,4-dicarboxylate, in which the thiocyano group should be less hindered than that in I, gives the methyl thio ether in 44% yield, whereas thiocyanomesitylene, in which the thiocyano group is at least as hindered as that in I but is not affected by electron-withdrawing substituents, gives none of the thio ether. That the electron-withdrawing group need not be so located that it can form a cyclic derivative of the intermediate thioimidocarbonate (as in VIII) is shown by the close similarity of the yields of methyl thio ethers from methyl *o*-thiocyanobenzoate and methyl *p*-thiocyanobenzoate.

The reaction appears to be limited to the simple alcohols methanol and ethanol, with higher yields being obtained from methanol. In reactions attempted in isopropyl alcohol and allyl alcohol, the thiocyano group was not affected. Methyl 2-thiocyanobenzoate was converted by ester hydrolysis in isopropyl alcohol to 2-thiocyanobenzoic acid, while in allyl alcohol it was recovered unchanged. The corresponding *para* isomer, which gives nearly the same yield of methyl thioether as the *ortho* isomer, was also recovered unchanged from the reaction in allyl alcohol. It is not clear why the thiocyanate group is not attacked in these alcohols, but it may be that the base-catalyzed addition of an alcohol is very slow under the conditions used. It appears that the attack of hydroxide ion on the thiocyano group is slow, as it would not be expected that the change in rate of hydroxide attack would be very large in changing the solvent from aqueous methanol to aqueous isopropyl alcohol.

Experimental[14]

Attempted Reaction of Diethyl 1-Benzyl-2-thiocyanopyrrole-3,4-dicarboxylate (I) with Ethyl Bromoacetate in Aqueous Methanolic Potassium Hydroxide.—The preparation of the thiocyanopyrrole I has been reported.[4] To a solution of I (2.0 g., 5.56 mmoles) in 30 ml. of methanol was added a solution of 85% potassium hydroxide (0.34 g., 5.16 mmoles) in 3 ml. of water and 3 ml. of methanol. The solution was stirred at room temperature for 25 min. A solution of ethyl bromoacetate (1.0 g., 6.1 mmoles) in 7 ml. of methanol was added over a period of 3 min. The reaction mixture was stirred for 2 hr. Most of the methanol was removed under reduced pressure on a steam bath, whereupon a yellow oil separated. Water and methylene chloride were added, the layers were separated, and the aqueous phase was extracted twice with methylene chloride. The combined extracts were dried over magnesium sulfate and yielded, after filtration of the drying agent and removal of the solvent, 2.4 g. (100%) of a yellow oil. The n.m.r. spectrum indicated this oil to be predominantly diethyl 1-benzyl-2-methylthiopyrrole-3,4-dicarboxylate (II): τ 2.70 (multiplet, aromatic), 4.71 (singlet, benzylic), 7.88 (singlet, methylthiol), 5.70 and 8.70 (multiplets, ethyl ester hydrogens). Essentially the same results were obtained when 2 equiv. of potassium hydroxide were used or when the alkali solution was added to a solution of the thiocyanopyrrole and ethyl chloroacetate. A sample, obtained when 0.345 g. of the crude oil was chromatographed on neutral alumina, was submitted for analysis. The sample was heated at 49° (0.1 mm.) for 14 hr. to free it of solvent.

Anal. Calcd. for $C_{18}H_{21}NO_4S$: C, 62.23; H, 6.09; N, 4.03. Found: C, 61.67; H, 6.04; N, 3.95.

Dimethyl 1-Benzyl-2-methylsulfonylpyrrole-3,4-dicarboxylate (IV).—Crude dimethyl 1-benzyl-2-methylthiopyrrole-3,4-dicarboxylate (0.92 g.), obtained by heating a solution of the crude diethyl ester obtained above at reflux in 25 ml. of methanol containing three drops of concentrated sulfuric acid, was dissolved in 5 ml. of acetic acid. To this solution was added 0.7 ml. of 30% hydrogen peroxide and the mixture was heated at reflux for 3.25 hr. The mixture was poured into 40 ml. of water and cooled overnight in a refrigerator. An orange, viscous oil separated and the solution was decanted from it. After standing for about 5 months the oil partially crystallized. Trituration with cold methanol caused the oil to dissolve leaving the crystals which were collected by filtration. One recrystallization from methanol gave material melting at 128.5–131.5°. An analytical sample was prepared by three more recrystallizations from methanol: m.p. 133–134°; $\nu_{\max}^{\text{KBr}}$ 1325, 1148 cm.$^{-1}$; τ 7.35 (singlet, methylsulfonyl hydrogens).

Anal. Calcd. for $C_{16}H_{17}NO_6S$: C, 54.68; H, 4.88; N, 3.99. Found: C, 54.58; H, 4.87; N, 4.23.

1-Benzyl-2-methylthiopyrrole-3,4-dicarboxylic Acid Monoethyl Ester.—About 250 mg. of crude diethyl 1-benzyl-2-methylthiopyrrole-3,4-dicarboxylate (II) was stirred at room temperature for 18 hr. in a solution of 5 ml. of methanol and 4 ml. of water containing 0.3 g. of 85% potassium hydroxide. The mixture was acidified with 1:1 hydrochloric acid and cooled in a refrigerator to give white crystals (185 mg.): τ 2.27 (singlet, hydroxylic), 2.70 (multiplet, aromatic), 4.65 (singlet, benzylic), 5.50 (quartet, ethyl group), 7.86 (singlet, methylthiol), 8.56 (triplet, ethyl group hydrogens). An analytical sample was prepared by three recrystallizations from methanol, m.p. 153–154°.

Anal. Calcd. for $C_{16}H_{17}NO_4S$: C, 60.16; H, 5.36; N, 4.39. Found: C, 60.09; H, 5.30; N, 4.68.

The Reaction of Thiocyanates with Alcohols under Basic Conditions.—The general experimental conditions are as follows. The thiocyanate (100–200 mg.) was dissolved in 5 ml. of the alcohol. To this solution, stirred at room temperature, was added dropwise an equivalent of potassium hydroxide in 2–3 ml. of water. The reaction mixture was stirred for 4 to 5 hr., following which most of the solvent was removed under reduced pressure on a steam bath. A few milliliters of water and either methylene chloride or ether were added. The aqueous phase was acidified with 1:1 hydrochloric acid and the phases were shaken and separated. The aqueous phase was extracted three times with the solvent used and the combined extracts were dried over magnesium sulfate. Filtration and evaporation of the solvent furnished the crude product mixture. The amount of alkyl thio ether present was determined from the n.m.r. spectrum of the mixture by an adaptation of the method described by Barza.[15] The weight of alkyl thio ether in a given sample was calculated using the following formula in which the terms are the same as defined previously.[15]

$$W = \frac{I\, n_s M\, W_s}{I_s n\, M_s}$$

For the methyl thio ethers, the intensity of the S-methyl peak was measured. This peak is a singlet and occurs in the range τ 7.5–8.0. For the ethyl thio ethers, the quartet due to the S-methylene hydrogens (τ 7.05–7.40) was measured. The standard most commonly used was acenaphthene, the area of the methylene hydrogens (τ 6.62) being measured. Of the thiocyanates used in this study, the preparation of diethyl 2-thiocyanopyrrole-3,4-dicarboxylate (IX),[5b] thiocyanomesitylene

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[14] All melting points are uncorrected. The spectra were determined by Mr. D. H. Johnson and his associates. The infrared spectra were determined with either a Perkin-Elmer Model 21 or a Perkin-Elmer Model 521 spectrometer. All n.m.r. spectra were measured with a Varian A-60 high-resolution spectrometer. The chemical shifts are expressed in τ-units relative to tetramethylsilane as an internal standard. The microanalyses were performed by Mr. Josef Nemeth and his associates.

[15] S. Barza, *J. Org. Chem.*, **28**, 1914 (1963).

(XII),[16] and *n*-butyl thiocyanate (XIII)[17] has been reported. The preparation of the other compounds used is described below.

Methyl 2-Thiocyanobenzoate.—Freshly distilled methyl anthranilate (10.0 g., 0.066 mole) in 100 ml. of water, to which 17 ml. of concentrated hydrochloric acid had been added, was diazotized by the addition of 5.24 g. (0.076 mole) of sodium nitrite in 20 ml. of water. The reaction flask was cooled in an ice bath during the diazotization. A suspension of cuprous thiocyanate was prepared by adding 8.75 g. of potassium thiocyanate to a solution of 20 g. of cupric sulfate pentahydrate and 37.5 g. of hydrous ferrous sulfate in 300 ml. of water. The grey precipitate of cuprous thiocyanate was filtered, washed with water, and suspended in 30 ml. of water containing 45 g. of potassium thiocyanate. The diazotized solution was added slowly to this suspension. Nitrogen evolution occurred and the reaction mixture turned dark brown. After standing at room temperature 1.5 hr., the mixture was heated on the steam bath for 15 min. and cooled. The solid was filtered and washed with water. Suspension of the solid in water and steam distillation gave 2.0 g. (16%) of a white solid. Two recrystallizations of the solid from methanol–water gave white needles: m.p. 75–76.5°, lit.[18] m.p. 76–77°; $\nu_{\max}^{\text{KBr}}$ 2160, 1710 cm.$^{-1}$.

Methyl 4-Thiocyanobenzoate.—A solution of diazomethane was prepared[19] by adding in portions N-methyl-N-nitrosourea (1.0 g.) to a stirred suspension of 7 ml. of 40% potassium hydroxide in 15 ml. of ether at 0°. The mixture was stirred at 0° for 20 min. and then the yellow ether solution of diazomethane was decanted. The aqueous phase was rinsed once with 10 ml. of ether and again with 5 ml. of ether, and the ether washings were combined with the original ether solution. To the ether solution of diazomethane was added in portions 4-thiocyanobenzoic acid[20] (0.60 g., 3.33 mmoles) over a period of 5 min. The flask was loosely stoppered and allowed to stand for 42 hr. The ether solution was washed once with 10% sodium bicarbonate and once with water, and dried over magnesium sulfate. Filtration and removal of the solvent gave 0.55 g. of a yellow oil which slowly crystallized. An analytical sample was prepared by four recrystallizations from ether–petroleum ether (b.p. 30–60°), m.p. 61–63°.

Anal. Calcd. for $C_9H_7NO_2S$: C, 55.95; H, 3.65; N, 7.25. Found: C, 55.94; H, 3.62; N, 7.42.

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Reactions of Benzyne with Pyrroles

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Received July 13, 1964

In contrast to furans, which react with benzyne to give 1,4-epoxy-1,4-dihydronaphthalenes, N-substituted pyrroles with alkyl or aryl groups in the 2- and 5-positions were found to give N-substituted 2-naphthylamines, not the expected 1,4-imines. Apparently the Diels–Alder reaction occurs to form the imine, but the latter immediately rearranges to the amine. The Grignard reagent, which is intermediate in the preparation of the benzyne, also seems to cause other reactions, such as the cleavage of the C–N bond in 1,4-dimethyl-N-benzyl-2-naphthylamine to give 1,4-dimethyl-2-naphthylamine.

N-Methylpyrrole has been reported[1] to condense with benzyne to give a small amount of imine (called endamine by these authors) isolated in the form of its quaternary iodide, but chiefly 1-methyl-10,11-dihydro-1,2-benzocarbazole. It was postulated that the basic imine nitrogen atom reacted with more benzyne to give the benzocarbazole. This observation has been supported recently by condensation of benzyne with N-phenyl and N-benzylpyrroles.[2] In both cases the reaction products were chiefly benzocarbazoles, especially when an excess of benzyne was used, but these investigators also reported the formation of N-phenyl and N-benzyl-1-naphthylamines. Supposedly these compounds were formed by rearrangement of the imines, although the latter were not isolated and characterized as such. It should be noted that the formation of the N-substituted 1-naphthylamines is entirely analogous to the conversion of the epoxides to 1-naphthols.[3]

Our previous work[4] has shown that, when the 1- and 4-positions in the 1,4-epoxides are blocked by alkyl groups, the epoxides are converted to substituted 2-naphthols or their ethers. Therefore, one of the objects of the present work was to see whether 1,4-naphthalene imines, substituted by alkyl or aryl groups in the 1- and 4-positions, would rearrange to substituted 2-naphthylamines. A further objective was to isolate if possible, and to characterize the imines, perhaps by reducing the basicity of the pyrrole nitrogen atom by proper substitution.

Two pyrroles were chosen such that the unshared nitrogen electron pair would be less available for secondary reaction with benzyne, making the isolation of the imine more likely. 2,5-Dimethyl-1-phenylpyrrole (**1**) possesses the N-phenyl group which obviously shares in the charge on the nitrogen atom, and 1-methyl-2,5-diphenylpyrrole (**2**) has an extensively conjugated system involving the phenyl and pyrrole groups and the nitrogen electron pair. One other compound, 1-benzyl-2,5-dimethylpyrrole (**3**), was also used for comparison with **1**.

These pyrroles were prepared by the usual method of condensing the appropriate 1,4-diketones with amines, with or without a solvent. A modification of the normal procedure was tried in the preparation of **3** and found to be a distinct improvement with respect to both yield and quality of product obtained. This method involves the azeotropic removal of the water formed, and is similar to that reported,[5] except that ligroin was substituted for benzene, thereby making isolation of the product easier owing to its lower solubility in ligroin.

The ultraviolet spectra of the pyrroles which were used have not been reported previously and provide an interesting comparison as shown in Figure 1. It has

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