[CONTRIBUTION FROM THE NOYES CHEMICAL LABORATORY, UNIVERSITY OF ILLINOIS]

Reactions of 2*H*,3*H*-Thieno[3,2-b]pyrrol-3-one. III.[1,2] Arylidene Derivatives and a New Polynuclear Heterocycle

BY R. J. TUITE[3] AND H. R. SNYDER

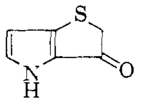
RECEIVED JANUARY 30, 1960

The *o*-aminobenzylidene derivative (IIc) of 2*H*,3*H*-thieno[3,2-b]pyrrol-3-one (I) undergoes cyclization to the novel heterocyclic compound III composed of linearly fused pyrrole, thiophene, pyridine and benzene rings. By the action of acetic anhydride the *o*-aminobenzylidene derivative IIc is converted into a triacetyl derivative V, which is hydrolyzed to a monoacetyl derivative VI, and the polynuclear heterocyclic compound III is acylated on the pyrrole nitrogen atom (yielding IV). Reduction of the unsubstituted benzylidene derivative IIa with lithium aluminum hydride occurs in the conjugate manner, leading to 2-benzyl-2*H*,3*H*-thieno[3,2-b]pyrrol-3-one.

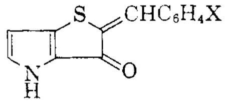
Although the carbonyl group of 2*H*,3*H*-thieno-[3,2-b]pyrrol-3-one (I) is readily reduced by sodium borohydride.[4] it is extremely resistant to other typical carbonyl reagents, including liquid hydrogen cyanide[5a] and Grignard reagents, with which it has been tested.[5b] It was of interest, therefore, to synthesize a molecule like IIc, containing a primary amino group situated so that its position is favorable to reaction with the carbonyl group and so that condensation would result in the formation of a new aromatic ring; such a molecule in the *cis* form would provide an extremely favorable opportunity for a normal addition to the carbonyl group.

The condensation of I with aromatic aldehydes affords excellent yields of the expected derivatives (II). The infrared spectrum[6] of each of these derivatives contains a doublet in the 1650–1600 cm.$^{-1}$ region, characteristic of a carbonyl group attached to an ethylenic system,[7] and that of IIc the expected three NH peaks. Each of the ultraviolet spectra (CH_3CN or abs. EtOH) has a band in the 320–350 mμ range (log ϵ *ca.* 4.4). In the ultraviolet spectra of 2-benzylidene-1-tetralone and 2-benzylidene-1-indanone the bands are at 305 mμ (log ϵ 4.24) and 318 mμ (log ϵ 4.35),[8] respectively, the bathochromic shift being attributed to the greater coplanarity and hence the greater orbital overlap in the latter compound. It is probable that coplanarity is even more rigidly enforced in II, in which the five-membered ring including the carbonyl group is fused to another five-membered ring, accounting for the further bathochromic shift in the spectra of II.

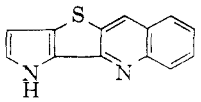
The *o*-aminobenzylidene compound IIc proved to be remarkably stable, although it was possible to effect its cyclization to the novel four-ring heterocycle, pyrrolo[3,2-b]thieno[3,2-b]quinoline (III), under drastic conditions. Its stability is in striking contrast to that of the corresponding product from *o*-aminobenzaldehyde and 2-acetylpyrrole, which was not obtained when these two reagents were refluxed in ethanol in the presence of potassium hydroxide, owing to the rapid formation of the quinoline.[9] Refluxing hydrochloric acid converted IIc only to its hydrochloride, which was formed quantitatively. When IIc was heated for six hours in diphenyl ether at temperatures above 180° with iodine as the catalyst, III was formed in 61% yield. In the absence of iodine somewhat lower yields were obtained, and unchanged IIc present in the product could be separated only by chromatography. Heating of IIc alone in a sublimation tube at 190–200° (0.05 mm.) effected very slow and incomplete conversion to III; after one week 60% of the cyclization product was obtained from the sublimate, and 35% of the unsaturated ketone IIc was recovered. It is to be noted that the sample of IIc so recovered was identical in melting point and infrared spectrum with the unsublimed sample.



I



IIa, X = H
b, X = *p*-NO_2
c, X = *o*-NH_2



III

Although attempts to find conditions or catalysts that would permit the conversion of IIc to III under mild conditions were unsuccessful, it was found accidentally that the cyclization occurs slowly at room temperature in very dilute absolute ethanol solution. Such a solution (5.9×10^{-5} *M*), prepared for spectroscopic study and set aside, lost the red color of IIc during a period of one week, and the infrared spectrum then measured on the residue obtained by concentrating the solution was that of III. Attempts to adapt this method to preparative purposes by continuous extraction of IIc into ethanol in a Soxhlet extractor, the solubility being very small, were not entirely successful; yields of III as high as 60% were obtained, but the color of IIc persisted even after two weeks.

It is obvious that the cyclization of IIc must proceed through the isomer in which the aminophenyl group is *cis* to the carbonyl function. It is probable that the resistance of IIc to cyclization is in part due to the formation of the isomer in which these groups are *trans* and hence the necessity for isomerization before cyclization. The data at hand are not sufficient for the determination of the configuration, but there was no evidence in the

---

(1) For the preceding paper, see R. J. Tuite, A. D. Josey and H. R. Snyder, THIS JOURNAL, **82**, 4360 (1960).

(2) This investigation was supported in part by a grant [3969(C1) Bio] from the National Cancer Institute, Public Health Service.

(3) National Science Foundation Fellow, 1958–1959.

(4) D. S. Matteson and H. R. Snyder, THIS JOURNAL, **79**, 3610 (1957); *J. Org. Chem.*, **22**, 1500 (1957).

(5) (a) Wayne Carpenter, Thesis, Doctor of Philosophy, University of Illinois, 1959; (b) R. J. Tuite, Thesis, Doctor of Philosophy, University of Illinois, 1960.

(6) All infrared spectra were determined as Nujol mulls with the exception of that of IX which was determined as a capillary smear.

(7) L. J. Bellamy, "The Infra-red Spectra of Complex Molecules," Ed. 2, John Wiley and Sons, Inc., New York, N. Y., 1958.

(8) A. Hassner and N. Cromwell, THIS JOURNAL, **80**, 893 (1958).

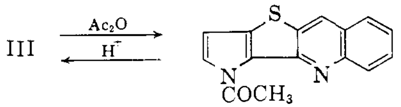
(9) A. P. Smirnoff, *Helv. Chim. Acta*, **4**, 808 (1921).

melting points and infrared spectra of any of the samples examined to indicate the presence of both isomers.

Compound III is nearly colorless, does not fluoresce, is high-melting (*ca.* 260°) and is very stable. Its ultraviolet spectrum (abs. EtOH) shows two sharp bands at 282 mμ (log ϵ 4.70) and at 256 mμ (log ϵ 4.48). (Thienopyrrole absorbs[4] at 260 mμ.) The infrared and nuclear magnetic resonance (n.m.r.) spectra of III are characteristic of a 2,3-disubstituted quinoline; the infrared spectrum shows a band at 890 cm.$^{-1}$, and the n.m.r. spectrum (Me_2SO)[10] a singlet at −3.80 p.p.m. (relative to water), both attributed to the presence of a lone hydrogen atom on the pyridine ring.

Like indole, III contains a pyrrole ring attached to an aromatic residue; however, III is resistant toward certain electrophilic reagents which readily attack indole. For example, attempted aminomethylation and formylation failed, and III was recovered. An attempted nitration afforded only a very high-melting material that could not be purified.

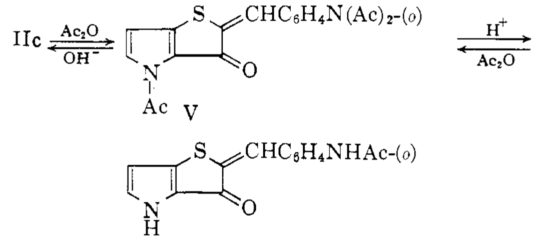
Acetylation of III in refluxing acetic anhydride gives 1-acetyl-pyrrolo[3,2-b]thieno[3,2-b]quinoline (IV). The structure of the product is proved by its infrared spectrum; the broad 3160 cm.$^{-1}$ N-H band of III is not present, and there is a carbonyl absorption at 1705 cm.$^{-1}$. The Raman spectrum of 1-acetylpyrrole[11] shows a carbonyl band at 1716 cm.$^{-1}$. Indole, under these conditions, or when heated in a sealed tube,[12] gives a mixture of 1-acetyl- and 1,3-diacetylindole. The acetyl group of IV is extremely susceptible to hydrolysis, as shown by the fact that recrystallization of the crude material from 95% ethanol is sufficient for deacetylation; a trace of acetic acid probably catalyzes the hydrolysis.



IV

In the presence of acids, III gives a yellow color, but in contrast to pyrroles in general its solution in refluxing hydrochloric acid undergoes no extensive discoloration; III forms a monohydrochloride salt and a picrate, but resists methylation. Treatment with methyl iodide in absolute ethanol for long periods of time led to the formation of the hydriodide salt. Possibly alcoholysis of methyl iodide occurred with III removing the hydrogen iodide generated in the reaction. Formation of the methiodide in another solvent was not attempted.

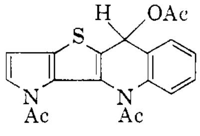
The ease with which the N-acetyl group of IV is removed by hydrolysis suggested the possibility of converting IIc to III with acetic anhydride. Treatment of IIc with acetic anhydride produced not III or IV but a triacetyl derivative (V), which was easily hydrolyzed by acid to a monoacetyl derivative (VI). Basic hydrolysis of V afforded the unacetylated IIc, and reacetylation of VI gave V. The following structures have been assigned to V and VI on the basis of spectral and chemical evidence.



V

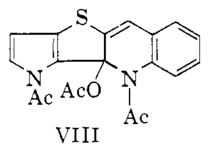
VI

The infrared spectrum of V contains three carbonyl peaks at 1715, 1702 and 1670 cm.$^{-1}$; in contrast, VI shows bands at 3280 and 3120 cm.$^{-1}$, and one carbonyl peak at 1657 cm.$^{-1}$. Evidently both carbonyl functions in VI absorb at the same frequency, a coincidence which is not unreasonable. The ultraviolet spectra (CH_3CN) of IIc, V and VI are nearly superimposable, all absorbing within a 10 mμ range. The n.m.r. spectrum of V ($CDCl_3$) shows no resonance between the aromatic region and the acetyl group protons. When considered as a whole, these data definitely exclude the alternative structures VII and VIII for the triacetyl derivative.



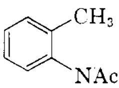
VII

or

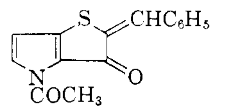


VIII

The formation of V is not surprising since, in general, primary aromatic amines with *ortho* substitution react with acetic anhydride to form the N,N-diacetyl derivative as the principal products.[13] Assignment of the carbonyl bands in the infrared spectrum of V was made by comparison with the spectra of model compounds. N,N-Diacetyl-*o*-toluidine (IX) absorbs at 1705 cm.$^{-1}$; N-acetyl-2-benzylidene-*2H,3H*-thieno[3,2-b]pyrrol-3-one (X),



IX



X

prepared by treatment of IIa with acetic anhydride, has a band at 1725 cm.$^{-1}$. The carbonyl group of IIc absorbs at 1645 cm.$^{-1}$. Thus, the 1715 cm.$^{-1}$ carbonyl band of V can be assigned with fair certainty to the pyrrole N-acetyl group, the 1702 cm.$^{-1}$ band to the N,N-diacetyl carbonyls and the 1670 cm.$^{-1}$ band to the 3-keto group.

Treatment of the benzylidene ketone IIa with excess lithium aluminum hydride gave 2-benzyl-*2H,3H*-thieno[3,2-b]pyrrol-3-one (XI) in low yield, thereby offering a potential route to 2-benzylthienopyrrole. The reaction evidently involves con-

---

(10) The nuclear magnetic resonance spectra were determined with a Varian Associates V-4300-B high resolution n.m.r. spectrophotometer on 20% solutions in the indicated solvents with methylene chloride as an external standard.

(11) E. Ghigi and P. Chiorboli, *Atti accad. nazl. Lincei, Rend. Classe Sci. fis., mat. e nat.*, **10**, 242 (1951); *C. A.*, **45**, 6930 (1951).

(12) W. C. Sumpter and F. M. Miller, "Heterocyclic Compounds with Indole and Carbazole Systems," Interscience Publishers, Inc., New York, N. Y., 1954, p. 44.

(13) W. J. Hickinbottom, "Reactions of Organic Compounds," 2nd ed., Longmans, Green, and Co., London, 1948, p. 297.

jugate addition of hydride ion to give the stabilized lithium enolate, which subsequently ketonizes upon hydrolysis; examples of such reductions have been recorded.[14]

The structure XI is proved by microanalysis and spectral analyses. The infrared spectrum has no absorption in the hydroxyl region, but has a band at 1620 cm.$^{-1}$, indicative of an acylpyrrole. The ultraviolet spectrum (abs. EtOH) is superimposable on the characteristic spectra of I and its many known 2-substituted derivatives.[15]

Experimental[16]

2-Benzylidene-2*H*,3*H*-thieno[3,2-b]pyrrol-3-one (IIa).—To a solution of 1.00 g. (7.20 millimoles) of I and 0.77 g. (7.25 millimoles) of freshly distilled benzaldehyde in 40 ml. of 95% ethanol was added 1.2 ml. of 1*N* sodium hydroxide. During 1-hour refluxing on the steam-bath, the product crystallized as brilliant orange needles. The yield was 1.54 g. (94.5%). An analytical sample, m.p. 255–256°, was prepared by recrystallization from methanol. A number of additional recrystallizations from methanol did not affect the melting point or infrared spectrum.

Anal. Calcd. for $C_{13}H_9NOS$: C, 68.70; H, 3.99; N, 6.16. Found: C, 68.46; H, 4.11; N, 6.30.

2-(*p*-Nitrobenzylidene)-2*H*,3*H*-thieno[3,2-b]pyrrol-3-one (IIb).[17]—A mixture of 0.14 g. (1 millimole) of I, 0.15 g. (1 millimole) of *p*-nitrobenzaldehyde, 5 ml. of 95% ethanol and 0.02 ml. of 1 *N* sodium hydroxide was heated on a steam-bath for 1.5 hr.; the bright red product crystallized in nearly quantitative yield, m.p. 297–300° dec. An analytical sample was recrystallized from acetic acid, m.p. 296–300°; the material contained 1 mole of acetic acid of crystallization, which was not removed by drying overnight at 100° (0.5 mm.).

Anal. Calcd. for $C_{15}H_{12}N_2O_5S$: C, 54.25; H, 3.64; N, 8.44. Found: C, 54.90; H, 3.47; N, 8.63, 8.67.

2-(*o*-Aminobenzylidene)-2*H*,3*H*-thieno[3,2-b]pyrrol-3-one (IIc).—To a solution of 4.88 g. (0.035 mole) of I in 100 ml. of 95% ethanol was added 4.24 g. (0.035 mole) of freshly prepared 2-aminobenzaldehyde[18] and 5.0 ml. of 1 *N* sodium hydroxide with swirling. The resulting red solution was refluxed on the steam-bath for 1.5 hours. The product crystallized as bright red prisms, m.p. 248–249° (with decomposition and ebullition). The yield was 4.79 g. (54.2%). After washing with 95% ethanol and drying overnight the material was suitable as an analytical sample without recrystallization.

Anal. Calcd. for $C_{13}H_{10}N_2OS$: C, 64.44; H, 4.16; N, 11.56. Found: C, 64.43; H, 4.32; N, 11.50.

The hydrochloride salt was prepared by boiling a suspension of IIc in 20% aqueous hydrochloric acid for 20 minutes. The product was washed with 95% ethanol and dried; m.p. (in a sealed capillary tube) 297–299° dec., darkens at 292°.

Anal. Calcd. for $C_{13}H_{11}N_2OSCl$: C, 56.01; H, 3.98; N, 10.05. Found: C, 55.80; H, 3.92; N, 10.06.

In an attempt to recover any of the unchanged ketone I, the filtrate was concentrated to dryness and the residue sublimed at 130° (0.01 mm.), giving 0.79 g. of I, which was identified by its infrared spectrum. The net yield of IIc was, therefore, 65.8% of the theoretical amount.

The black residue from the sublimation was treated with Darco and recrystallized from ethanol–water, affording 0.25 g. (3.72%) of slightly impure pyrrolo[3,2-b]thieno[3,2-b]quinoline (III), m.p. 254–258° (see next experimental procedure). The melting point was not depressed upon admixture with an authentic sample, and the infrared spectra were identical.

Pyrrolo[3,2-b]thieno[3,2-b]quinoline (III). (a) By Heating in Phenyl Ether with Iodine.—A mixture of 0.242 g. (1 millimole) of IIc, 10 ml. of phenyl ether (redistilled) and a small crystal of iodine was heated with stirring at 185–190° for 6 hours. After cooling to about 50°, 20 ml. of petroleum ether (30–60°) was added in one portion with the appearance of a dark brown flocculent precipitate. After standing for 3 minutes, the solution was filtered and the precipitate discarded. (Note: When the mixture was allowed to stand for a longer period of time, the product began to precipitate.) The phenyl ether was removed by passing a stream of dry air onto the surface of the heated filtrate until it was essentially dry. The dark residue was washed with two 10-ml. portions of petroleum ether (30–60°), leaving a gray-brown crystalline material. After treatment with Darco and recrystallization from 95% ethanol, the yield of straw-colored pyrrolo[3,2-b]thieno[3,2-b]quinoline (III) was 0.136 g. (60.8%). An analytical sample was prepared by four additional recrystallizations from 95% ethanol. The white needles thus obtained melted to a colorless liquid at 259.5–260° (k).

Anal. Calcd. for $C_{13}H_8N_2S$: C, 69.62; H, 3.60; N, 12.49. Found: C, 69.47; H, 3.39; N, 12.34.

(b) By Heating IIc Alone.—A small vial containing 0.952 g. (3.94 millimoles) of IIc was heated in a sublimation tube at 190–200° (0.05 mm.) for 7 days. The vial was removed, and the red and pink sublimate was suspended in 450 ml. of chloroform. After refluxing for 30 minutes (or until all the light colored material had dissolved), the mixture was filtered to give 0.332 g. (35.0%) of red crystalline material whose infrared spectrum was identical in every respect with that of IIc. The light orange filtrate was concentrated to *ca.* 200 ml., and while still hot it was passed through a column containing 2 g. of alumina. The red impurity IIc remained at the top of the column while the product passed through. The column was rinsed with two 25-ml. portions of hot 2:1 chloroform–ethyl acetate to remove the last traces of product. The eluate was concentrated to dryness, and the slightly yellow crystalline residue was dried *in vacuo* overnight. The crude III weighed 0.527 g., which represents a 59.8% conversion or a net yield of 92.3%. Recrystallization from 95% ethanol afforded white needles, m.p. 257–259°.

(c) By Heating IIc in Absolute Ethanol with *p*-Toluenesulfonic Acid.—A solution of IIc in absolute ethanol was prepared for an ultraviolet spectrum. After standing about a week on the shelf, the formerly red solution was colorless. The solution was concentrated to *ca.* 1 ml., a few drops of hot water were added, and the solution was allowed to cool. The white crystalline compound thus formed was filtered and dried, m.p. 263.5° (k). The infrared spectrum showed it to be identical with III.

An attempt was then made to adapt this method to a preparative procedure. The cup of a Soxhlet extractor was charged with 0.242 g. (1 millimole) of IIc and 75 ml. of ethanol was refluxed into it for 6 days without any apparent loss of color. A trace of *p*-toluene sulfonic acid was added and the refluxing continued for 8 additional days; the solution was still colored at the end of this period. The solvent was removed under reduced pressure and the residue dissolved in a mixture of 50 ml. of chloroform and 50 ml. of water. The chloroform layer was removed, and the aqueous layer was washed with 20-ml. portions of chloroform. The combined extracts were dried over potassium carbonate, filtered, and passed through a column containing alumina, as in procedure b. The solvents were removed and the crystalline residue dried *in vacuo* overnight. The yield of crude product was 0.132 g. (59.0%).

The picrate, prepared in a conventional way,[19] precipitated immediately from 95% ethanol. An analytical sample was prepared by recrystallization from ethanolic dimethylformamide; m.p. 278° (k), with decomposition beginning *ca.* 260–265°.

Anal. Calcd. for $C_{19}H_{11}N_5O_7S$: C, 50.33; H, 2.45; N, 15.45. Found: C, 50.46; H, 2.23; N, 15.55.

The hydrochloride was precipitated as yellow needles having metallic luster when dry hydrogen chloride gas was

---

(14) R. E. Lutz and J. S. Gillespie, THIS JOURNAL, **72**, 2002 (1950).

(15) Wayne Carpenter and H. R. Snyder, *ibid.*, **82**, 2739 (1960).

(16) Melting points are corrected. The notation (k) after a melting point indicates that the determination was made on a Kofler hot-stage melting point apparatus. The microanalyses were determined by Mr. Josef Nemeth, Mrs. Maria Stingl, Miss Claire Higham, Miss Jane Liu, and by the Clark Microanalytical Laboratory, Urbana, Ill.

(17) The authors are indebted to D. S. Matteson for this preparation.

(18) L. I. Smith and J. W. Opie in "Organic Syntheses," Coll. Vol. III, John Wiley and Sons, Inc., New York, N. Y., 1955, p. 56.

(19) R. Shriner, R. C. Fuson and D. Y. Curtin, "The Systematic Identification of Organic Compounds," 4th ed., John Wiley and Sons, Inc., New York, N. Y., 1956.

bubbled through a concentrated chloroform solution of III. After recrystallization from 95% ethanol to which a few drops of concentrated hydrochloric acid had been added, the compound melted at 295–298° dec., softening at 266°.

Anal. Calcd. for $C_{13}H_9N_2SCl$: C, 59.88; H, 3.48; N, 10.75. Found: C, 59.56; H, 3.32; N, 10.57.

The hydriodide was formed when a warm solution of III in 1:1 absolute ethanol–methyl iodide was allowed to stand in a stoppered flask for 9 days. After concentration of the solution, the salt precipitated as golden yellow needles. An analytical sample was prepared by treatment with Darco, followed by two recrystallizations from methanol; m.p. 254–257° dec.

Anal. Calcd. for $C_{13}H_9N_2SI$: C, 44.33; H, 2.58; N, 7.96. Found: C, 43.94; H, 2.31; N, 7.82.

The identity of the compound was further substantiated by treatment with aqueous sodium hydroxide to give III, which was identified by its infrared spectrum and melting point.

1-Acetylpyrrolo[3,2-b]thieno[3,2-b]quinoline (IV).—A solution of 0.20 g. (0.9 millimole) of III in 10 ml. of acetic anhydride was refluxed for 6 hours, and *ca.* 7 ml. of solvent was removed by distillation. Upon cooling, the product crystallized as long, white, cotton-like needles. The yield was 0.22 g. or over 90%. After treatment with Darco and two recrystallizations from benzene, an analytical sample melted at 168–169°.

Anal. Calcd. for $C_{15}H_{10}N_2OS$: C, 67.65; H, 3.78; N, 10.52. Found: C, 67.84; H, 3.79; N, 10.64.

4-Acetyl-2-(*o*-diacetylimidobenzylidene)-2*H*,3*H*-thieno-[3,2-b]pyrrol-3-one (V).—A suspension of 0.470 g. (1.94 millimoles) of IIc in 15 ml. of acetic anhydride was heated under reflux for 5 hours with the exclusion of moisture. After about 10 minutes, the solution had changed in color from red to yellow. About 10 ml. of solvent was distilled, and the red sirupy residue was allowed to cool in an ice–water-bath; 10 ml. of cold water was added in one portion, the mixture was refrigerated for 4 hours, and the resulting yellow solid was filtered and washed thoroughly with water. After drying *in vacuo* overnight, the product, m.p. 174–176°, weighed 0.689 g. (96.5%). An analytical sample was prepared by suspending a small amount of the compound in water, filtering, and washing again with water to free the sample from all traces of acid. After two recrystallizations from 95% ethanol the product melted at 173–174°.

Anal. Calcd. for $C_{19}H_{16}N_2O_4S$: C, 61.94; H, 4.38; N, 7.61. Found: C, 61.86; H, 4.13; N, 7.58.

2-(*o*-Acetamidobenzylidene)-2*H*,3*H*-thieno[3,2-b]pyrrol-3-one (VI).—A solution of 0.336 g. (1.19 millimoles) of V in 25 ml. of 10% aqueous acetic acid and 10 ml. of methanol was refluxed for 12 hours, during which time there appeared a beautiful orange crystalline precipitate. The material was filtered and washed thoroughly with water affording a nearly quantitative yield of VI, m.p. 280–281° dec. The highly insoluble product was suitable as an analytical sample after drying.

Anal. Calcd. for $C_{15}H_{12}N_2O_2S$: C, 63.36; H, 4.26; N, 9.85. Found: C, 63.64; H, 4.17; N, 9.91.

Reacetylation of VI.—A suspension of 0.251 g. (0.885 millimole) of VI in 10 ml. of acetic anhydride was heated under reflux for 4 hours. About one-half of the solvent was removed by distillation, the residue cooled, and 10 ml. of water added in one portion. After standing 2 hours, the product was filtered and washed thoroughly with water affording 0.301 g. (92.3%) of V, m.p. 175–176°.

Basic Hydrolysis of V.—To a warm solution of 1.00 g. of potassium hydroxide in 9 ml. of 95% ethanol was added 0.176 g. (0.479 millimole) of V. The resulting rose-colored solution was refluxed for 2 hours, 15 ml. of hot water was added, and the solution allowed to cool. The resulting orange precipitate was washed with water, and dried. The yield of IIc was 0.078 g. (74%). The identity of the product was verified by its melting point (258–260°), infrared spectrum and by microanalysis.

Anal. Calcd. for $C_{13}H_{10}N_2OS$: C, 64.44; H, 4.16; N, 11.56. Found: C, 64.07; H, 4.35; N, 10.95.

N,N-Diacetyl-*o*-toluidine (IX).—The procedure followed in the preparation of VIII was essentially that of Sudborough,[20] b.p. 105–105.5° (1.2 mm.), n^{26}_{D} 1.5270.

4-Acetyl-2-benzylidene-2*H*,3*H*-thieno[3,2-b]pyrrol-3-one (X).—A suspension of 0.250 g. of IIa in 10 ml. of acetic anhydride was refluxed for 5 hours, and *ca.* 7 ml. of solvent was distilled. The solution was allowed to cool, and the resulting precipitate was washed with water and dried. The yield of crude product was 0.264 g. (89.2%). An analytical sample, m.p. 147–148.5°, was prepared by treatment with Darco, followed by recrystallization from a large volume of methylcyclohexane.

Anal. Calcd. for $C_{15}H_{11}NO_2S$: C, 66.89; H, 4.12; N, 5.20. Found: C, 66.87; H, 4.17; N, 5.16.

2-Benzyl-2*H*,3*H*-thieno[3,2-b]pyrrol-3-one (XI).—Lithium aluminum hydride (0.50 g.) was added cautiously to an ice-cooled solution of 0.203 g. (0.894 millimole) of IIa in 15 ml. of tetrahydrofuran. The reaction mixture was allowed to stand overnight at room temperature in a loosely stoppered flask. The excess lithium aluminum hydride was hydrolyzed by the dropwise addition of water to the cold solution. The resulting mixture was diluted with 50 ml. of ether and filtered. The precipitate was suspended in ether and again filtered. The combined filtrates were dried over magnesium sulfate, and the ether was distilled. The yellow crystalline residue was washed with pentane and sublimed at 130° (0.1 mm.) to give a slightly oily substance. Two additional sublimations were required to purify the product. The yield of analytically pure X, m.p. 160–161°, was 0.028 g. (13.8%).

Anal. Calcd. for $C_{13}H_{11}NOS$: C, 68.09; H, 4.84; N, 6.11. Found: C, 68.17; H, 4.89; N, 5.88.

URBANA, ILL.

---

[20] J. J. Sudborough, *J. Chem. Soc.*, **79**, 533 (1901).

[CONTRIBUTION NO. 590 FROM THE CENTRAL RESEARCH DEPARTMENT, EXPERIMENTAL STATION, E. I. DU PONT DE NEMOURS AND CO.]

Cyanocarbon Chemistry. XV.[1] A New Synthesis of 3,4-Dicyano-2(1H)-pyridones

BY C. L. DICKINSON

RECEIVED JANUARY 28, 1960

A convenient new route to 3,4-dicyano-2(1H)-pyridones has been discovered. They are formed when $\beta,\beta,\gamma,\gamma$-tetracyanoketones, obtained by adding ketones to tetracyanoethylene, are heated in ethanol. In several cases, intermediate ethoxy dihydropyridones have been isolated.

We have found that the reaction of $\beta,\beta,\gamma,\gamma$-tetracyanoketones with ethanol provides a facile route to a variety of substituted 3,4-dicyano-2-(1H)-pyridones. The reaction is general and the only limitation appears to be that the carbon atom between the carbonyl and the dicyanomethylene group must possess a hydrogen. The ready availability of the $\beta,\beta,\gamma,\gamma$-tetracyanoketones from the addition of tetracyanoethylene (TCNE)[2] and

---

[1] See J. K. Williams, THIS JOURNAL, **81**, 4013 (1959), for paper XIV.

[2] W. J. Middleton, R. E. Heckert, E. L. Little and C. G. Krespan, *ibid.*, **80**, 2783 (1958).