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2-Benzo[*b*]thien-2-yl-1,3,3-trimethyl-2-indolinecarbonitrile

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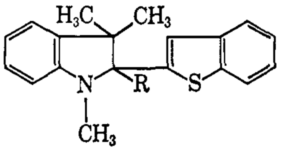
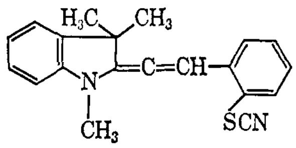
1,3,3-Trimethyl-2-methyleneindoline and 2-thiocyanatobenzaldehyde combine to give a material which herein is shown to be the title compound (Ia); thus the reaction involves the formation of a thianaphthene ring under unusually mild conditions.



Ia, R = CN
b, R = OH



II

The infrared spectrum of Ia shows no absorption attributable to NH, SH, C=C=C, C≡C, C≡N, SC≡N, $N\rightleftarrows C$, or C=N=S groups. This eliminates from further consideration the allenic[1] structure II.

The n.m.r. spectrum of Ia shows three N–Me protons as a singlet at 2.93 p.p.m. (indicating that the nitrogen atom bears little or no formal positive charge),[3] six CMe$_2$ protons as two singlets at 1.03 and 1.68 p.p.m. (suggesting that the adjacent atom bears two different substituents),[3] a multiplet of eight aromatic protons at 6.5–8.0 p.p.m., and one proton as a singlet at 7.65 p.p.m.

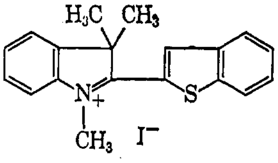
Structures containing the cyano group remained under consideration, for the lack of CN absorption in the infrared might possibly be attributed to the presence of the sulfur atom. Cyano absorptions are sometimes strongly attenuated by a nearby oxygen atom.[4] We therefore sought chemical evidence regarding the presence of a cyano group. The hydroxamic acid test for nitriles[5] was indeterminate. A solution of Ia in methanol saturated with hydrogen chloride slowly deposited ammonium chloride and gave after neutralization a material (Ib) with the empirical formula $C_{19}H_{19}NOS$ rather than the C_{21} products corresponding to the anticipated changes CN → CO_2Me or C(=NH)OMe. When the reaction was repeated using ethanol, the same C_{19} product was obtained. The hydroxamic acid test for esters[5] was negative when applied to Ib. That Ib was not an ordinary or imino ester was further shown by its infrared spectrum, which exhibits no C=O, C=NH, or N—H absorption, but does exhibit O—H absorption.

The n.m.r. spectrum of Ib is similar to that of Ia, but shows, in addition, a one-proton singlet at 2.60 p.p.m. attributable to an OH group. The ultraviolet spectrum of Ib in neutral ethanol is very similar to that of Ia; in acidic ethanol the absorptions change markedly, and both Ib and Ia have identical spectra.

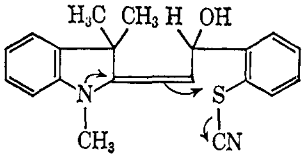
An alcoholic solution of either Ib or Ia gave red crystals (III) upon treatment with hydriodic acid. The n.m.r. spectrum of III shows N–Me at 4.66 p.p.m. (suggesting that the nitrogen atom bears a formal positive charge)[3] and a single (6H) C–Me absorption at 1.89 p.p.m.

The only reasonable structures for Ia, Ib, and III that accommodate the data are those shown, which incorporate a thianaphthene nucleus. These structures were confirmed by synthesis. The reaction between 2-thianaphthenyllithium and 1,3,3-trimethyloxindole gave Ib, which was converted to III. A solution of III when treated with potassium cyanide gave Ia.

A possible route for the formation of Ia may involve the cyclization and dehydration of IV to the ion III (as the cyanide), which reverts to the covalent form Ia, as in the synthesis above.



III



IV

An example of the formation of a thianaphthene ring by intramolecular displacement of cyanide from a thiocyanate is known,[6] but it requires strongly basic conditions.

Experimental[7]

2-Benzo[*b*]thien-2-yl-1,3,3-trimethyl-2-indolinecarbonitrile (Ia).—A solution of 3.26 g. (0.02 mole) of *o*-thiocyanatobenzaldehyde[8] and 3.46 g. (0.02 mole) of 1,3,3-trimethyl-2-methyleneindoline in 200 ml. of ethanol was refluxed 1 hr., concentrated *in vacuo*, and chilled to give 4.92 g. (77%) of crude Ia, m.p. 154–169°. Recrystallization from ethanol with Norit treatment gave material of m.p. 161.0–164.0° (further recrystallizations from ethanol or benzene did not narrow this range): ultraviolet, $\lambda\lambda_{\max}^{\mathrm{EtOH}}$ mμ (ϵ) 229 (35,000), 258 (17,000), 266 (14,900), 291 (6350), 301 (4800); $\lambda\lambda_{\max}$ (EtOH saturated with dry HCl) mμ (ϵ) 248 (11,500) 378 (26,800); n.m.r., see discussion; infrared, 1610 (s), 1485 (s),

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[1] Allenes are reported[2] to be formed by the condensation of heterocyclic methylene bases with aromatic aldehydes. They were unstable and reactive, and their structures have not been confirmed by spectral evidence.

[2] W. H. Mills and R. Raper, *J. Chem. Soc.*, **127**, 2466 (1925).

[3] See Experimental.

[4] L. J. Bellamy, "The Infrared Spectra of Complex Molecules," 2nd Ed., John Wiley and Sons, Inc., New York, N. Y., 1958, p. 266.

[5] R. L. 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, p. 123.

[6] F. Arndt, A. Kirsch, and P. Nachtwey, *Ber.*, **59**, 1074 (1926).

[7] Analyses are by Galbraith Laboratories, Knoxville, Tenn.; melting points are corrected, taken on a Thomas–Hoover apparatus; infrared spectra were measured on a Perkin-Elmer Infracord 137 in CHCl$_3$ solvent, positions of sharp absorption maxima given in reciprocal centimeters followed by relative intensities: s = strong, m = medium, w = weak; ultraviolet spectra were run on a Beckman DK-1; n.m.r. spectra were measured on a Varian A-60 in DCCl$_3$ solvent, with TMS reference, shifts are given in parts per million followed in parentheses by the relative integrated intensity and the multiplicity: s = singlet, m = multiplet. We thank Dr. D. P. Hollis of Varian Associates and Mr. F. E. Dickson of NMR Specialties, Inc., for obtaining and interpreting the n.m.r. spectra.

[8] P. Friedlaender and E. Lenk, *Ber.*, **45**, 2083 (1912).

1460 (m), 1390 (m), 1295 (s), 1285 (m), 1160 (m), 1125 (m), 1115 (s), 1030 (s) cm.$^{-1}$.

Anal. Calcd. for $C_{20}H_{18}N_2S$: C, 75.43; H, 5.69; N, 8.79; S, 10.07; mol. wt., 318. Found: C, 75.46; H, 5.89; N, 8.60; S, 10.25; mol. wt., 320.

2-Benzo[*b*]thien-2-yl-1,3,3-trimethyl-2-indolinol (Ib).—To 20 ml. of anhydrous methanol saturated with dry hydrogen chloride was added 1.00 g. of Ia. The mixture was warmed until the solid dissolved and the yellow solution was allowed to stand at room temperature 4 days, slowly precipitating 0.15 g. (89%) of ammonium chloride, identified by its infrared spectrum and complete solubility in water and qualitative tests for the ions. The filtrate was neutralized by dropwise addition of dilute sodium hydroxide solution; the precipitate was removed by filtration, washed with water, and air dried to give 0.97 g. (88%) of crude Ib. Attempted crystallizations from benzene, benzene–pentane, methanol, or aqueous ethanol gave only dark gums. Finally it was taken up in warm (80°) isooctane and the stoppered solution was allowed to stand at room temperature 4 weeks, during which time hemispherical nodules slowly formed. These showed m.p. 115–123°, and neither two recrystallizations nor two "Hooker dry crystallizations" changed this value; ultraviolet, $\lambda\lambda_{max}^{EtOH}$ mμ (ϵ) 232 (32,500), 240 (28,000), 258 (13,500), 266 (11,200), 291 (6100), 300 (5600); $\lambda\lambda_{max}^{EtOH-HCl}$ mμ (ϵ) 248 (10,600), 378 (27,300); n.m.r., 0.93 (3, s), 1.43 (3, s), 2.60 (1, s), 2.80 (3, s), 7.08 (1, s), 6.5–8.0 (8, m) p.p.m.; infrared, 3600 (m) cm.$^{-1}$, rest of spectrum identical with that of Ia except 1285 (m) becomes 1280 (w) cm.$^{-1}$.

Anal. Calcd. for $C_{19}H_{19}NOS$: C, 73.75; H, 6.19; N, 4.53; S, 10.36. Found: C, 73.60; H, 6.18; N, 4.34; S, 10.35.

2-Benzo[*b*]thien-2-yl-1,3,3-trimethyl-3H-indolium Iodide (III).—A solution containing 0.10 g. of Ib in 5 ml. of methanol and 5 drops of 57% hydriodic acid was concentrated to about 1 ml. by boiling and then chilled to give 0.11 g. (81%) of red needles: m.p. 209–210° dec. (MeOH); ultraviolet, $\lambda\lambda_{max}^{EtOH}$ mμ (ϵ) 248 (11,500), 378 (16,400); $\lambda\lambda_{max}^{EtOH-HCl}$ mμ (ϵ) 248 (9900), 378 (28,400); n.m.r., 1.89 (6, s), 4.66 (3, s), 7.32 (1, s), 7.5–7.9 (8, m) p.p.m.; infrared (KBr), 1540 (s), 1485 (s), 1460 (m), 1400 (s), 1190 (s), 1135 (s), 965 (m), 945 (m), 770 (vs), 735 (s) cm.$^{-1}$. Similarly, Ia also gave III.

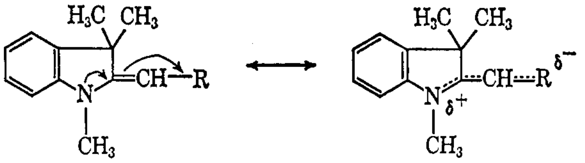
Anal. Calcd. for $C_{19}H_{18}INS$: C, 54.42; H, 4.33; I, 30.26; N, 3.34; S, 7.65. Found: C, 54.51; H, 4.35; I, 30.43; N, 3.30; S, 7.61.

Syntheses of Ib and III.—To a solution of 2.15 g. (0.016 mole) of thianaphthene in 100 ml. of dry ether was added under nitrogen 10 ml. of a 1.6 *M* hexane solution of butyllithium (Foote Mineral Co.), and the mixture was stirred and refluxed 45 min. A solution of 1.96 g. (0.0112 mole) of 1,3,3-trimethyloxindole[9] in 50 ml. of ether was added dropwise, and the mixture was stirred and refluxed an additional 2 hr. Water (50 ml.) was cautiously added to the cooled solution and, after stirring vigorously for 5 min., the layers were separated. The ether layer was dried and evaporated, and the residue was recrystallized from isooctane as before to give 1.92 g. (55%) of material having m.p. 112–121°, identical with Ib by mixture melting point and infrared spectra comparisons.

Treatment with hydriodic acid as before gave material of m.p. 209–210° dec., identical with III by mixture melting point and infrared spectra comparisons.

Synthesis of Ia.—To a boiling solution of 0.84 g. (0.002 mole) of III in 20 ml. of 75% aqueous ethanol was added 0.5 g. of potassium cyanide. The orange color of the solution rapidly disappeared. The solution was concentrated and chilled, and the precipitate was removed by filtration, washed, and air dried to give 0.55 g. (86%) of material of m.p. 160–163°, identical with Ia by mixture melting point and infrared spectra comparisons.

N.m.r. Spectra of Indoline Derivatives.—In connection with this and other work the n.m.r. spectra of a variety of 1,3,3-trimethylindoline derivatives have been determined. The shift of the protons of the N–Me group is 2.70 p.p.m. in 1,2,3,3-tetramethylindoline and 4.10 p.p.m. in 1,2,3,3-tetramethylindolenium iodide. The shifts for methylene indolines of formula i vary between these values roughly as the electron-attracting ability of the R group, suggesting a greater contribution from the polarized form ii. Thus, for example, δ is given for the following R groups: H, 3.00; CO_2Et, 3.15; $CONHC_6H_5$, 3.15; $COCH_3$, 3.20; $CONHC_6H_4NO_2$-4, 3.20; CHO, 3.25; $N{=}NC_6H_5$, 3.26; $SC_6H_3(NO_2)_2$-2,4, 3.26; $CH{=}C(CN)C_6H_5$, 3.28; $CH{=}CHNO_2$, 3.30; COC_6H_5, 3.35; $COC_6H_4NO_2$-4, 3.40; $CH{=}(CN)CO_2Et$, 3.40; $CH{=}C(CN)COC_6H_5$, 3.45; $CH{=}C(CN)_2$, 3.45; $C(CN){=}C(CN)_2$, 3.60; $CSNHC_6H_5$, 3.60; $CH{=}C(CHO)NO_2$, 3.62; and $N{=}NHC_6H_5{}^+I^-$, 3.96.



i ii

When carbon atom 2 of a 1,3,3-trimethylindoline bears a double bond, the protons of the methyl groups on carbon 3 appear as a single (6H) peak. When it bears two different substituents, however, the protons appear as two peaks (3H each) in the n.m.r. spectrum.[10]

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[9] P. L. Julian, J. Pikl, and D. Boggess, *J. Am. Chem. Soc.*, **56**, 1797 (1934).

[10] For example, compare Spectra 610 and 677 in N. S. Bhacca, D. P. Hollis, L. F. Johnson, and E. A. Pier, "NMR Spectra Catalog," Vol. 2, Varian Associates, Palo Alto, Calif., 1963. The formula of compound 677 should show the nitro group *para* to the oxygen atom rather than *meta*.