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SYNTHESIS OF 9-AZAAZULENO[2,1-b]THIOPHENES

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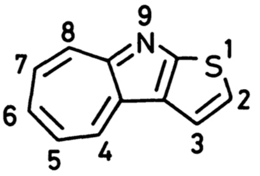
9-Azaazuleno[2,1-b]thiophene and its derivatives were synthesized from 2-chloro-3-ethoxycarbonyl- or 2-chloro-3-formyl-1-azaazulene in a few steps.

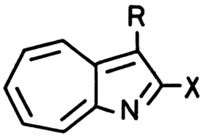
The polycyclic aromatic compounds which consist of the 1-azaazulene(cyclohepta[b]pyrrole) ring condensed with heterocyclic aromatics are of interest in their physical properties and the chemical behaviors.1) This communication describes the synthesis of 9-azaazuleno[2,1-b]thiophene(cyclohepta[b]thieno[3,2-d]pyrrole) (2a) and its derivatives.



2a

The Synthesis of 9-Azaazuleno[2,1-b]thiophenes from 2-Chloro-3-ethoxycarbonyl-1-azaazulene (1a) The reaction of 2-Chloro-3-ethoxycarbonyl-1-azaazulene (1a)2) with ethyl thioglycolate in pyridine gave 1c[orange yellow needles, mp 113-114° C] in 90% yield. The esterification of 1b[yellowish green needles, mp 165°C(decomp.), 68% yield], which was obtained by the reaction of 1a with thioglycolic acid, also yields 1c. Dieckmann reaction to 1c gave 2-ethoxycarbonyl-3-hydroxy-9-azaazuleno[2,1-b]-thiophene (2b) in 75% yield. The product gave a dull green coloration with ferric chloride and methyl ether (2c) by the treatment with diazomethane. The compound 2c was heated in alcoholic KOH followed by heating at 150°C under reduced pressure (2 mmHg) or in pyridine at 140°C to give 3-methoxy-9-azaazuleno[2,1-b]thiophene (2d).

On the other hand, 3-oxo-2,3-dihydro-9-azaazuleno[2,1-b]thiophene (3) was obtained by the treatment of 2b with 100% phosphoric acid. The spectral data show that 3 exists as a keto form. By the condensation of 3 with benzaldehyde, the benzylidene derivative (4)[yellow needles, mp 248.5-249.5°C, 79% yield] was obtained. But the ketone (3) did not give phenylhydrazone. On treatment with phosphoryl chloride, 3 gave 3-chloro-9-azaazuleno[2,1-b]thiophene (2e)[79% yield]. The reduction product was not obtained by the treatment of 3 with sodium borohydride in methanol.



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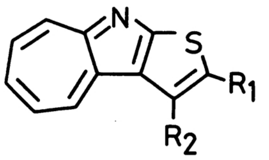

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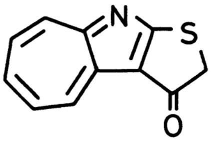
1a: R = COOEt, X = Cl
1b: R = COOEt, X = SCH_2COOH
1c: R = COOEt, X = SCH_2COOEt
1d: R = CHO, X = Cl
1e: R = CHO, X = SCH_2COOH
1f: R = CHO, X = SCH_2COOEt

2b: R_1 = COOEt, R_2 = OH
2c: R_1 = COOEt, R_2 = OCH_3
2d: R_1 = H, R_2 = OCH_3
2e: R_1 = H, R_2 = Cl
2f: R_1 = COOEt, R_2 = H



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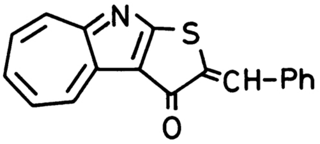

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The Synthesis of 9-Azaazuleno[2,1-b]thiophene (2) from 2-Chloro-3-formyl-1-azaazulene (1d) 2-Chloro-3-formyl-1-azaazulene (1d),2) on reaction with ethyl thioglycolate in pyridine, gave ethyl 3-formyl-1-azaazulen-2-ylthioglycolate (1f) [orange needles, mp 121-122°C, 83% yield]. The compound was also prepared by the esterification of 1e[yellow crystals, mp 181-184°C(decomp.)], which was obtained by the reaction of 1d with thioglycolic acid. When the ester (1f) was cyclized by the action of piperidine in ethanol, 2-ethoxycarbonyl-9-azaazuleno[2,1-b]thiphene (2f) was obtained in 93% yield. On heating with 100% phosphoric acid at 130°C, 2f resulted in deethoxycarbonylation to give 9-azaazuleno[2,1-b]thiophene (2a) in 68% yield.

The physical properties and spectral data of 2a-f were shown in Table 1.

Table 1. Physical Properties and Spectral Data of 9-Azaazuleno[2,1-b]thiophenes
IR(KBr) cm^{-1}; ES λmax nm(log ε); ^1H NMR($CDCl_3$) δppm; ^{13}C NMR($CDCl_3$) δppm

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2a: reddish purple needles; mp 94-95°C

IR 1581, 1485, 1389, 712

ES 223(4.28), 270(4.35), 278(4.39), 298(4.58), 304(4.69), 310(4.77), 330(4.37), 359(3.91), 362(3.81), 391(3.65), 554(2.49)(in cyclohexane)

^1H NMR 7.28(1H, d, J=5.6Hz, H-3), 7.51(1H, d, J=5.6Hz, H-2), 7.6-7.9(3H, m, H-5,6,7), 8.5-8.8(2H, m, H-4,8)

^{13}C NMR 116.49, 125.14, 127.80, 128.66, 131.06, 131.52, 134.93, 136.19, 136.78, 161.28, 171.52

2b: dark red needles; mp 166-167°C

IR 2990, 1650, 1329, 767

ES 243(4.23), 301(4.69), 330(4.57), 349(4.51), 429(3.63), 496(2.64)(in cyclohexane)

^1H NMR 1.42(3H, t, J=7.0Hz, $COOCH_2C\underline{H}_3$), 4.42(2H, q, J=7.0Hz, $COOC\underline{H}_2CH_3$), 7.6 - 8.0 (3H, m, H-5,6,7), 8.5-9.0(2H, m, H-4,8), 10.72(1H, s, OH)

2c: reddish brown needles; mp 129-130°C

IR 1694

ES 243(4.15), 303(4.64), 324(4.65), 343(4.46), 372(3.82), 410(3.60), 498(2.55) (in cyclohexane)

^1H NMR 1.42(3H, t, J=7.0Hz, $COOCH_2C\underline{H}_3$), 4.29(3H, s, $OC\underline{H}_3$), 4.38(2H, q, $COOC\underline{H}_2CH_3$), 7.5-7.9(3H, m, H-5,6,7), 8.5-8.6(1H, m, H-8), 8.81(1H, d, J=8.8Hz, H-4)

2d: brown needles; mp 126.5-127.5°C

ES 227(4.23), 272(4.48), 277(4.47), 289(4.43), 322(4.46), 347(4.29), 375(3.75), 410(3.23), 551(2.54)(in cyclohexane)

^1H NMR 4.01(3H, s, $OC\underline{H}_3$), 6.13(1H, s, H-2), 7.0-7.9(3H, m, H-5,6,7), 8.5-8.8(1H, m, H-8), 8.86(1H, d, J=8.8Hz, H-4)

2e: brown needles; mp 140-141°C

ES 227(4.26), 275(4.44), 283(4.44), 311(4.71), 331(4.32), 359(3.96), 369(3.73), 389(3.62), 538(2.52), 585(2.38)(in cyclohexane)

^1H NMR 7.00(1H, s, H-2), 7.4-7.8(3H, m, H-5,6,7), 8.4-8.6(1H, m, H-8), 8.78(1H, d, J=8.8Hz, H-4)

2f: dark red needles; mp 140-141°C

IR 1715

ES 230(4.15), 313(4.76), 320(4.85), 337(4.47), 368(3.94), 405(3.84), 543(2.56) (in cyclohexane)

^{1}H NMR 1.45(3H, t, J=7.0Hz, $COOCH_2C\underline{H}_3$), 4.43(2H, q, J=7.0Hz, $COOC\underline{H}_2CH_3$), 7.6-8.1(3H, m, H-5,6,7), 8.38(1H, s, H-3), 8.6-8.8(2H, m, H-4,8)

^{13}C NMR 14.41, 61.25, 123.49, 129.44, 130.38, 130.53, 131.89, 132.32, 135.66, 137.32, 138.76, 162.70, 162.64, 172.70

3: yellowish green plates; mp 216°C(decomp.)

IR 1668

ES 259(4.23), 268(4.20), 307(4.63), 373(3.90), 446(3.48)(in MeOH)

^{1}H NMR 4.21(2H, s, $C\underline{H}_2$), 7.7-8.0(3H, m, H-5,6,7), 8.4-8.7(1H, m, H-8), 8.8-9.0(1H, m, H-4)

REFERENCES

1) There is a survey of azaazulenes: T. Nishiwaki and N. Abe, Heterocycles, 15, 547(1981).

2) T. Toda, Bull. Chem. Soc. Jpn., 40, 590(1967).

3) All new compounds described in this paper gave satisfactory elemental analytical data.

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