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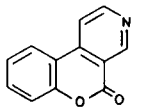
Received April 13, 1977

3-Aminocoumarin undergoes the Skraup reaction to give a new ring system, 5*H*[1]benzopyrano[3,4-*b*]pyridin-5-one (IVa). When 3-aminocoumarin was condensed with the ethoxymethylene derivatives of active methylene compounds, ethyl acetoacetate, and dimethyl acetylenedicarboxylate, the intermediates VIa-VIf were formed which on thermal cyclizations afforded other derivatives of 5*H*[1]benzopyrano[3,4-*b*]pyridin-5-one (IVb-IVf). The nitration of IVa gave IVg.

J. Heterocyclic Chem., **14**, 1009 (1977)

The fusion of a pyridine ring to the 3,4 bond of the coumarin ring can lead to four isomeric 5*H*[1]benzopyranopyridin-5-ones. While the derivatives of the ring systems 5*H*[1]benzopyrano[3,4-*c*]pyridin-5-one (1) (2), 5*H*[1]benzopyrano[4,3-*c*]pyridin-5-one (II) (3), and 5*H*[1]benzopyrano[4,3-*b*]pyridin-5-one (III) (4) have been described, there is no mention in the literature of the ring system 5*H*[1]benzopyrano[3,4-*b*]pyridin-5-one (IVa).



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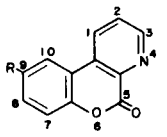
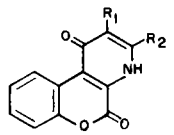
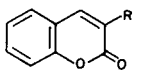


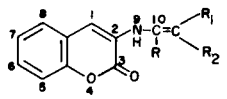
IVa R = H
IVg R = NO_2



IVb $R_1 = CO_2Et$, $R_2 = H$
IVc $R_1 = CN$, $R_2 = H$
IVd $R_1 = COMe$, $R_2 = H$
IVe $R_1 = H$, $R_2 = Me$
IVf $R_1 = H$, $R_2 = CO_2Me$



Va R = NH_2
Vb R = NHAc



VIa R = H, $R_1 = R_2 = CO_2Et$
VIb R = H, $R_1 = CN$, $R_2 = CO_2Et$
VIc R = H, $R_1 = COMe$, $R_2 = CO_2Et$
VId R = H, $R_1 = R_2 = COMe$
VIe R = Me, $R_1 = H$, $R_2 = CO_2Et$
VIf R = CO_2Me, $R_1 = H$, $R_2 = CO_2Me$

Derivatives of 3-aminocoumarin have previously been reported (5) and to us it seemed to be a reasonable starting material for the synthesis of IVa and its derivatives. However, to our knowledge, no attempt was made in the past to use it as a buliding block for other heterocyclic systems. 3-Aminocoumarin (Va) was formed in the hydrolysis of Vb which in turn was easily obtained from salicylaldehyde and glycine (6). In virtue of its "enamine" structure, on prolonged heating in acids, Va was easily hydrolysed to the corresponding 3-hydroxy compound (6).

In our attempts to construct a pyridine ring on the coumarin ring, using Va as the starting material, we initially chose thermal cyclization methods such as the Gould-Jacobs (7), the Conrad-Limpach (8), and the acetylenedicarboxylic ester method (9). These methods have been successfully used in the synthesis of quinolines and besides providing quinolines with different substituents in the pyridine part of the molecule such as an ester group in the 2 or the 3 position, a methyl group in the 2 position, and a hydroxy group in the 4 position of a quinoline, they have the further advantage of not requiring acid catalysis a reaction condition which may have deterimental effect on the starting material.

Our first attempt, to use Vb in a condensation reaction with ethyl ethoxymethylenecyanoacetate, was not successful. It seems that Vb, as can be expected, is not basic enough to enter in condensation reaction. The 3-acetylaminocoumarin was recovered from this reaction. Next we were successful in the condensation of Va in ethanol under reflux with various ethoxymethylene compounds and the compounds VIa-VId were isolated from these condensations. While VIe and VIf were obtained from the condensation of Va with ethyl acetoacetate, and with dimethyl acetylenedicarboxylate, respectively. When heated under reflux all these condensation products, with the only exception of VId, cyclized to give the 5*H*[1]-benzopyrano[3,4-*b*]pyridin-5-ones (IVb-IVf).

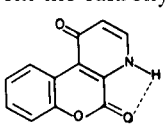
Once we were successful in obtaining IVb-IVf we turned our attention to the Skraup reaction of Va. We were, in our first attempt, able to isolate IVa in 59% yield. This proves that contrary to the assertion of Linch who had proposed an imino structure for Va, this amine, in fact, behaves like an aromatic amine. The amino structure is borne out from a study of the infrared absorption spectrum of Va. Strong absorption bands for the amino group were observed at 3428 and 3330 cm^{-1} together with an absorption band at 1708 cm^{-1} for the carbonyl group of the pyrone ring. The amino structure also gets its support from the pmr spectrum of Va in deutrochloroform where a sharp singlet for the four aromatic protons appeared at δ 7.4, one proton singlet at δ 6.68 for the proton at the 4 position, and a broad

signal at δ 3.72 (exchangeable hydrogens) for the two amino protons. There were no noticeable signals which could be ascribed to the imino form.

The study of the infrared absorption spectra of the compounds IVa-IVg revealed that the carbonyl group of the pyrone ring absorbs at higher wave numbers. The basic ring system IVa and its nitrated product IVg show this absorption at 1750 and 1740 cm^{-1}, respectively, while in the other compounds IVb-IVf this is generally shifted to the shorter wave numbers (1730-1720 cm^{-1}) possibly due to the formation of an intramolecular hydrogen bond with the NH of the pyridine ring. The NH absorption of the pyridine ring also appears as a broad band between 3360 and 2860 cm^{-1}. For comparison purposes the infrared absorption spectra of the reported ring systems I-III were searched. There seems to be very little information on the infrared absorption spectra of the derivatives of I-III and for the compounds whose infrared absorption spectra are reported we could make some comparison. The variations in the carbonyl absorption bands of the pyrone ring were also noted in their spectra. For example in the compounds 2-(coumarin-3-yl)-4-methyl-5*H*[1]benzopyrano[4,3-*b*]-pyridin-5-one (4a) and ethyl 7,9-dibromo-2,4-dimethyl-5-oxo-[1]benzopyrano[3,4-*c*]pyridine-1-carboxylate (2h) this absorption was observed at 1740, and 1750 cm^{-1}, respectively, but in the compounds where groups such as hydroxyl or amino in the proximity are available for the intramolecular hydrogen bond formation with the carbonyl of the pyrone ring the carbonyl absorption was seen to be at the shorter wave numbers, for example, 4-hydroxy-5*H*[1]benzopyrano[3,4-*c*]pyridin-5-one at 1700 cm^{-1} (2f) and 4-amino-2-phenyl-5*H*[1]benzopyrano[3,4-*c*]pyridin-5-one at 1695 cm^{-1} (2d).

Furthermore the carbonyl of the ester group in the compounds IVb and IVf and of the acetyl group in IVd do not seem to be hydrogen bonded, absorbing at 1749, 1745, and 1670 cm^{-1} respectively. The nitrile absorption was observed at 2255 cm^{-1} for IVc. In addition, for the compounds IVb-IVf, absorption bands were observed between 1630 and 1615 cm^{-1}. These absorptions at 1630-1615 cm^{-1} can be assigned to the carbonyl group of the pyridine ring. In addition, in the pmr spectra, broad signals due to NH were also observed between δ 8 and 9.5 for the compounds IVb-IVf.

In the light of these observations we are led to belive that the compounds IVb-IVf exist predominantly in the pyridone form rather than in the 1-hydroxy form and that the pyridone tautomeric form owes its stability to the tendency of the NH of the pyridone to form an intramolecular hydrogen bond with the carbonyl of the pyrone ring as shown in VII.



When IVa was nitrated with a mixture of nitric and sulfuric acid, the nitrated product IVg was obtained. The analysis of the pmr spectrum of IVg in deuterated dimethyl sulfoxide revealed two quartets at δ 7.92 (J = 8.5 and 4.5 Hz), and δ 8.35 (J = 8.5 and 1.5 Hz) due to the protons at 2 and 1 position respectively, a downfield complex multiplet between δ 8.8 and 9.2 due to the protons at the 3, 8, and 10 position and a doublet at δ 7.62 (J = 9 Hz) due to the proton at 7 position. The pmr spectrum of IVa in deuterochloroform showed signals at δ 7.73, 8.45, and 8.90 as quartets for the protons at the 2, 1, and 3 position respectively. There was another quartet at δ 8.0 probably due to the proton at the 10 position and a complex multiplet between δ 7.15 and 7.55 due to the three protons at the 7,8 and 9 position.

EXPERIMENTAL

All melting points are uncorrected. Pmr spectra were taken on a 60 MHz Hitachi Perkin-Elmer R-20B using tetramethylsilane as an internal standard. Ir absorption spectra were measured on Perkin-Elmer model 180 and the elemental analysis on Perkin-Elmer 240.

The following starting material were prepared according to the literature method: ethyl ethoxymethylenecyanoacetate b.p. 169°/17 mm (10); ethyl ethoxymethyleneacetoacetate b.p. 149-151°/16 mm (11); ethoxymethyleneacetylacetone b.p. 138-141°/16 mm (12); and 3-aminocoumarin (Va) m.p. 132-133° (6). Diethyl ethoxymethylenemalonate and other reagents were commerical products and were used without purification.

Condensation of 3-Aminocoumarin with Variuos Ethoxymethylene Compounds.

General Procedure.

To a stirring solution of 0.1 mole of Va in 200 ml. of ethanol, there was added 0.1 mole of the ethoxymethylene compound. The mixture was heated under reflux for 1-4 hours, allowed to cool to room temperature and then filtered. The filtered product was purified by crystallization. By this procedure compounds VIa-VId were prepared.

Ethyl α-Carbethoxy-β-(*N*-coumarin-3-yl)aminoacrylate (VIa).

Compound VIa was obtained from the condensation of Va and diethyl ethoxymethylenemalonate over a period of 2 hours, yellow needles m.p. 143.5-144° (ethanol), yield 90%; pmr δ (deuteriochloroform): 7.1-7.6 (m, H-4 and H-5 - H-8); 8.28 (d. H-10) $J_{9,10}$ = 14 Hz; 10.87 (d, H-9) $J_{9,10}$ = 14 Hz; and 1.30 (m, 6H), 4.20 (m, 4H) (*O*-Et); ir cm^{-1} (potassium bromide pellet): 3250 (br., NH); 1690, 1590 (ester C=O); 1710 (pyrone C=O).

Anal. Calcd. for $C_{17}H_{17}NO_6$: C, 61.62; H, 5.17; N, 4.23. Found: C, 61.25; H, 5.10; N, 4.30.

Ethyl α-Cyano-β-(*N*-coumarin-3-yl)aminoacrylate (VIb).

Compound VIb was obtained in 67% yield by the condensation of Va with ethyl ethoxymethylenecyanoacetate over a period of 1.5 hours, m.p. 238-238.5° (ethanol); pmr δ (DMSO-d6): 8.15 (s, H-4); 7.2-7.8 (m, H-5 - H-8); 8.58 (d, H-10) $J_{9,10}$ = 14 Hz; 11.79 (d, H-9) $J_{9,10}$ = 14 Hz; and 1.30 (t, 3H), 4.27 (q, 2H) (*O*-Et); ir cm^{-1} (potassium bromide pellet): 3220 (br., NH); 2219 (C≡N); 1690, 1620 (ester C=O); 1715 (pyrone C=O).

Anal. Calcd. for $C_{15}H_{12}N_2O_4$: C, 63.38; H, 4.26; N, 9.86. Found: C, 63.58; H, 4.50; N, 9.80.

Ethyl α-Acetyl-β-(*N*-coumarin-3-yl)aminoacrylate (VIc).

This compound was obtained from Va and ethyl ethoxymethyleneacetoacetate over a reaction period of 1 hour, m.p. 168.5-169.5° (ethanol), yield 88%; pmr δ (deuteriochloroform): 7.1-7.8 (m, H-4 and H-5 - H-8); 8.35 (d, H-10) $J_{9,10}$ = 13 Hz; 12.5 (d, H-9) $J_{9,10}$ = 13 Hz; and 1.37 (t, 3H), 4.25 (q, 2H) (*O*-Et) and 2.52 (s, $COCH_3$); ir cm^{-1} (potassium bromide pellet): 3160 (br., NH); 1695 (ester C=O); 1635 (acetyl C=O); 1720 (pyrone C=O).

Anal. Calcd. for $C_{16}H_{15}NO_5$: C, 63.78; H, 5.02; N, 4.65. Found: C, 63.45; H, 4.97; N, 4.67.

3-(*N*-Coumarin-3-yl)aminomethylenepentan-2,4-dione (VId).

Compound VId was obtained by the condensation of Va with ethoxymethyleneacetylacetone over a period of 3.5 hours, m.p. 218-219° (ethanol), yield 81%; pmr δ (DMSO-d6): 8.15 (s, H-4); 7.5-7.8 (m, H-5 - H-8); 8.41 (d, H-10) $J_{9,10}$ = 13 Hz; 11.38 (d, H-9) $J_{9,10}$ = 13 Hz; 2.44 (s, $COCH_3$); δ (deuteriochloroform): 2.45 (s, $COCH_3$) and 2.49 (s, $COCH_3$); ir cm^{-1} (potassium bromide pellet): 3400 (br., NH); 1630, 1575 (acetyl C=O); 1710 (pyrone C=O).

Anal. Calcd. for $C_{15}H_{13}NO_4$: C, 66.41; H, 4.83; N, 5.16. Found: C, 66.58; H, 5.05; N, 5.16.

Ethyl β-Methyl-β-(*N*-coumarin-3-yl)aminoacrylate (VIe).

A mixture of 1.6 g. (0.01 mole) of Va and 1.3 g. (0.01 mole) of ethyl acetoacetate and a few drops of concentrated hydrochloric acid was heated on a water bath over a period of 40 minutes and the reaction product was crystallized from ethanol giving VIe as pale yellow crystals, m.p. 158-159°, yield 2.3 g. (86%); pmr δ (DMSO-d_6): 7.78 (s, H-4); 7.30-7.75 (m, H-5 - H-8); 1.30 (t, 3H), 4.20 (q, 2H) (*O*-Et); 2.31 (s, CH_3) and 4.99 (s, H-α); δ (deuteriochloroform), 11.0 (s, H-9); ir cm^{-1} (potassium bromide pellet): 3440 (br., NH); 1610 (ester C=O); 1710 (pyrone C=O).

Anal. Calcd. for $C_{15}H_{15}NO_4$: C, 65.92; H, 5.53; N, 5.13. Found: C, 66.14; H, 5.39; N, 5.02.

Methyl β-Carbomethoxy-β-(N-coumarin-3-yl)aminoacrylate (VIf).

A mixture of 1.6 g. (0.01 mole) of Va and 1.4 g. (0.01 mole) of dimetyl acetylenedicarboxylate in 10 ml. of anhydrous methanol was heated under reflux for 5 hours. After cooling to room temperature the precipitate was filtered and crystallized from methanol giving 2.3 g. (76%) of VIf, m.p. 156-157°; pmr δ (deuteriochloroform): 6.81 (s, H-4); 7.3 (m, H-5 - H-8); 9.72 (s, H-9); 3.75 (s, *O*-CH_3); 3.81 (s, CH_3) and 5.64 (s, H-α); ir cm^{-1} (potassium bromide pellet): 3440 (br., NH); 1730,1610 (ester C=O); 1710 (pyrone C=O).

Anal. Calcd. for $C_{15}H_{13}NO_6$: C, 59.41; H, 4.32; N, 4.62. Found: C, 59.59; H, 4.27; N, 4.65.

Cyclizations.

General Procedure.

The acrylates VIa-VIc, VIe and VIf (0.003 mole) in 15 ml. of Dowtherm were heated under reflux for a period of 15 minutes to 2.5 hours. After the reaction mixture has cooled down to room temperature, petroleum ether (b.p. 40-60°) was added and the precipitated product was filtered off, washed with petroleum ether (b.p. 40-60°) till it was free of Dowtherm and then crystallized from an appropriate solvent. By this procedure compounds IVb-IVf were obtained.

Ethyl 1,4-Dihydro-1,5-dioxo-5*H*[1]benzopyrano[3,4-*b*]pyridine-2-carboxylate (IVb).

The compound IVb was obtained in 93% yield from the cyclization of VIa over a period of 1 hour, m.p. > 300° (*N,N*-dimethylformamide-water); pmr δ (DMSO-d_6): 8.28 (s, H-3); 7.2-7.7 (m, H-7 - H-10); 9.52 (NH); 1.40 (t, 3H), 4.31 (q, 2H) (*O*-Et); ir cm^{-1} (potassium bromide pellet): 3100-2860 (NH); 1749 (ester C=O); 1620 (pyridone C=O); 1720 (pyrone C=O).

Anal. Calcd. for $C_{15}H_{11}NO_5$: C, 63.16; H, 3.89; N, 4.91. Found: C, 62.78; H, 3.70; N, 5.03

1,4-Dihydro-2-cyano-5H[1]benzopyrano[3,4-*b*]pyridin-1,5-dione (IVc).

The cyclization of VIb over a period of 2.5 hours gave IVc in 84% yield, m.p. > 300° (*N,N*-dimethylformamide-water); pmr δ (DMSO-d_6; 155°): 8.38 (s, H-3); 7.1-7.8 (m, H-7 - H-10); 9.35 (br., NH); ir cm^{-1} (potassium bromide pellet): 3360-2980(NH); 2255 (C≡N); 1615 (pyridone C=O); 1728 (pyrone C=O).

Anal. Calcd. for $C_{13}H_6N_2O_3$: C, 65.55; H, 2.54; N, 11.76. Found: C, 65.62; H, 2.63; N, 11.46.

1,4-Dihydro-2-acetyl-5*H*[1]benzopyrano[3,4-*b*]pyridin-1,5-dione (IVd).

Compound VIc over a reaction period of 2.5 hours gave 66% of IVd, m.p. 287-288° (*N,N*-dimethylformamide-water); pmr δ (DMSO-d_6; 140°): 8.10 (s, H-3); 7.1-7.7 (m, H-7 - H-10); 9.40 (br., NH); 2.55 (s, $COCH_3$); ir cm^{-1} (potassium bromide pellet), 3230-3120 (NH); 1670 (acetyl C=O); 1620 (pyridone C=O); 1740 (pyrone C=O).

Anal. Calcd. for $C_{14}H_9NO_4$: C, 65.88; H, 3.56; N, 5.48. Found: C, 65.62; H, 3.67; N, 5.60.

1,4-Dihydro-3-methyl-5*H*[1]benzopyrano[3,4-*b*]pyridin-1,5-dione (IVe).

Compound IVe was obtained in 69% yield when VIe was heated under reflux in Dowtherm for 0.5 hour, m.p. > 300° (ethanol-petroleum ether (b.p. 40-60°)); pmr δ (deuteriochloroform): 8.61 (s, H-2); 7.1-7.7 (m, H-7 - H-10); 8.09 (NH); 2.22 (s, CH_3); ir cm^{-1} (potassium bromide pellet): 3340-2880 (NH); 1625 (pyridone C=O); 1730 (pyrone C=O).

Anal. Calcd. for $C_{13}H_9NO_3$: C, 68.72; H, 3.99; N, 6.16. Found: C, 68.94; H, 4.01; N, 6.39.

Methyl 1,4-Dihydro-1,5-dioxo-5*H*[1]benzopyrano[3,4-*b*]pyridine-3-carboxylate (IVf).

Compound VIf over a reaction period of 15 minutes gave IVf in 95% yield, m.p. 236-237° (methanol); pmr δ (deuteriochloroform): 7.1-7.77 (m, H-2 and H-7 - H-10); 9.50 (NH); 4.05 (s, *O*-CH_3); ir cm^{-1} (potassium bromide pellet): 3341 (br., NH); 1745 (ester C=O); 1630 (pyridone C=O); 1725 (pyrone C=O).

Anal. Calcd. for $C_{14}H_9NO_5$: C, 62.00; H, 3.34; N, 5.16. Found: C, 61.67; H, 3.38; N, 5.12.

Skraup Reaction of Va.

A mixture of 3.2 g. (0.02 mole) of Va, 3.5 g. of arsenic pentoxide, 8 g. of dry glycerol and 4 g. of concentrated sulfuric acid was heated carefully in an oil bath to 170° when the reaction occured. After the exothermic reaction subsided the reaction mixture was heated at 170-180° for a further period of 3 hours and after cooling poured onto 100 ml. of ice water, filtered and the residue further extracted with boiling water (3 x 30 ml). The combined extract and the filtrate was basified with 5% sodium hydroxide. The precipitate was filtered and crystallized from ethanol (activated charcoal) to give 5*H*[1]benzopyrano[3,4-*b*]-pyridin-5-one (IVa) m.p. 186-187° as cream colored needles, yield 2.3 g. (59%); pmr δ (deuteriochloroform): 8.90 (q, H-3) $J_{2,3}$ = 4.5 Hz and $J_{1,3}$ = 1.5 Hz; 8.45 (q, H-1) $J_{1,2}$ = 8.5 Hz and $J_{1,3}$ = 1.5 Hz; 7.73 (q, H-2) $J_{1,2}$ = 8.5 Hz and $J_{2,3}$ = 4.5 Hz; 8.00

(q, H-10) $J_{9,10}$ = 9 Hz and $J_{8,10}$ = 2.3 Hz; and 7.15-7.50 (m, H-7 - H-9): ir cm^{-1} (potassium bromide pellet): 1750 (pyrone C=O).

Anal. Calcd. for $C_{12}H_7NO_2$: C, 73.09; H, 3.58; N, 7.10. Found: C, 72.91; H, 3.52; N, 7.02.

Nitration of IVa.

To a solution of 1 g. of IVa in 2 ml. of Concentrated sulfuric acid at 0-5°, there was added with stirring a mixture of 2 ml. of nitric and 2 ml. of concentrated sulfuric acid. The temperature of the reaction mixture was maintained at 0-5° during this addition and then the reaction mixture was allowed to warm up to the room temperature, stirred for additional 10 minutes and then poured onto 100 g. of crushed ice, filtered, washed with water and dried. The crude product melted over a range of 240-264°. It was purified by sublimation at reduced pressure (220°/1 mm) to give 9-nitro-5*H*[1]benzopyrano[3,4-*b*]pyridin-5-one, m.p. 285°, yield 0.8 g. (67%); pmr δ (DMSO-d_6): 8.80-9.20 (m, H-3, H-8, and H-10); 8.35 (q, H-1) $J_{1,2}$ = 8.5 and $J_{1,3}$ = 1.5 Hz; 7.92 (q, H-2) $J_{1,2}$ = 8.5 and $J_{2,3}$ = 4.5 Hz; 7.62 (d, H-7) $J_{7,8}$ = 9 Hz; ir cm^{-1} (potassium bromide pellet), 1740 (pyrone C=O); 1525, 1338 (NO_2).

Anal. Calcd. for $C_{12}H_6N_2O_4$: C, 59.51; H, 2.50; N, 11.57. Found: C, 59.83; H, 2.50; N, 11.78.

ACKNOWLEDGMENTS.

We wish to thank Conselho Nacional de Desenvolvimento Cientifico e Tecnológico (CNPq) for the award of a scholarship to André Luis Gemal.

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