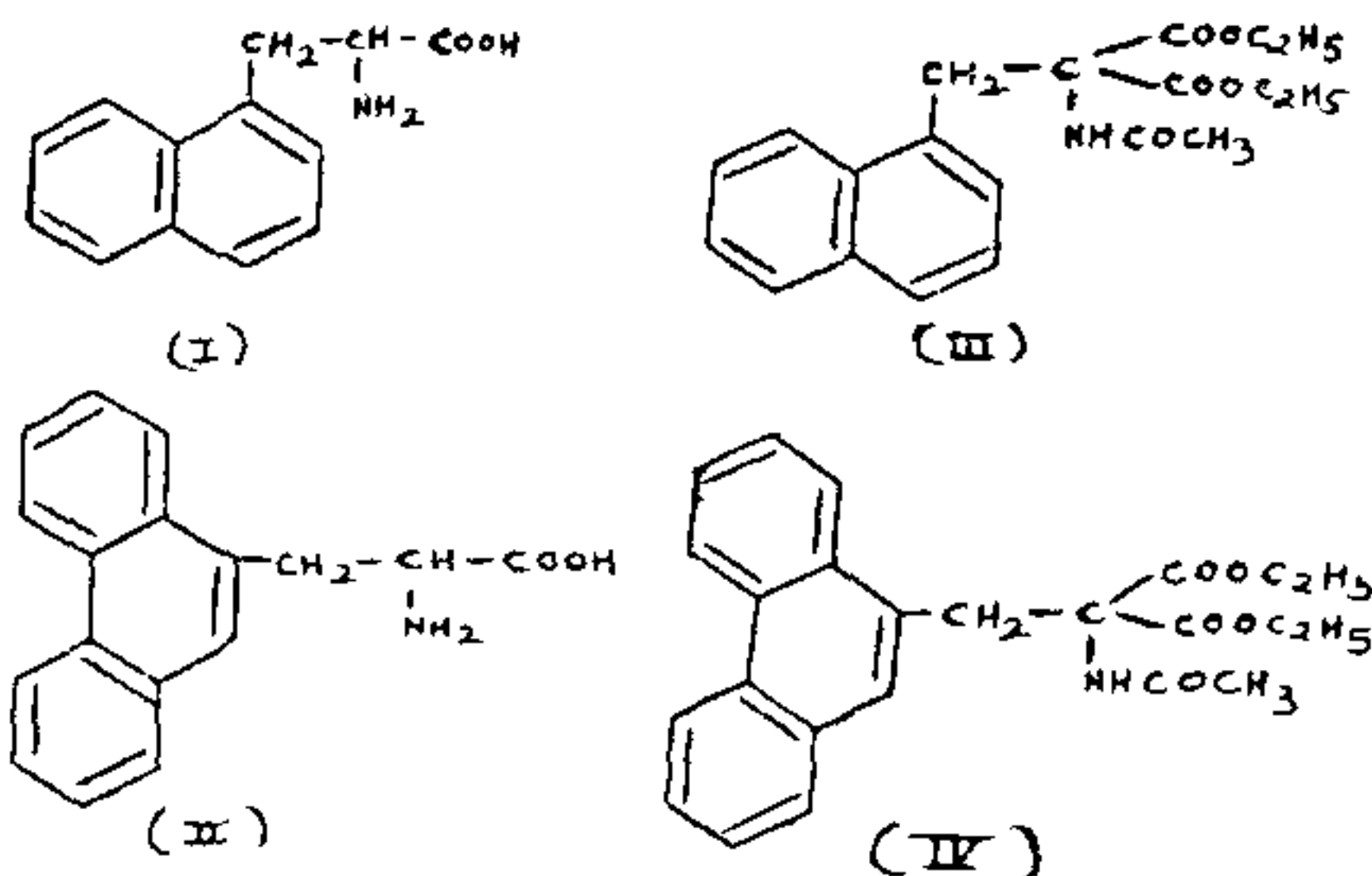


Carbonyl absorption in IR region 1750 cm^{-1} (ester $>C=O$ group) and 1685 cm^{-1} (Amido $>C=O$ group).

The above diester (III) (5 g) was refluxed with hydrobromic acid (48% ; 30 ml) for 8 hours. Hydrobromide separated on cooling and crystallised from water, m.p. 263° (decomp.). Free amino-acid was precipitated by treating the above hydrobromide with ammonia. β -1-Naphthylalanine² crystallised from water. M.P. 240° . Yield 2.8 g.



Similar condensation of 9-chloromethylphenanthrene with diethyl sodio acetamido malonate gave the diester (IV). It crystallised from benzene-petroleum ether mixture. M.P. 142° . Yield 40%. This diester (IV) on hydrolysis with 48% hydrobromic acid followed by treatment with ammonia afforded β -(9-phenanthryl) alanine. M.P. 210° .

All compounds described above gave satisfactory analytical results.

Thanks are due to Professor E. Gellert, Wollongong University College, Wollongong, Australia, for the IR Spectra, Professor S. Sethna for his interest in the work and Dr. S. S. Lele for microanalysis of the samples.

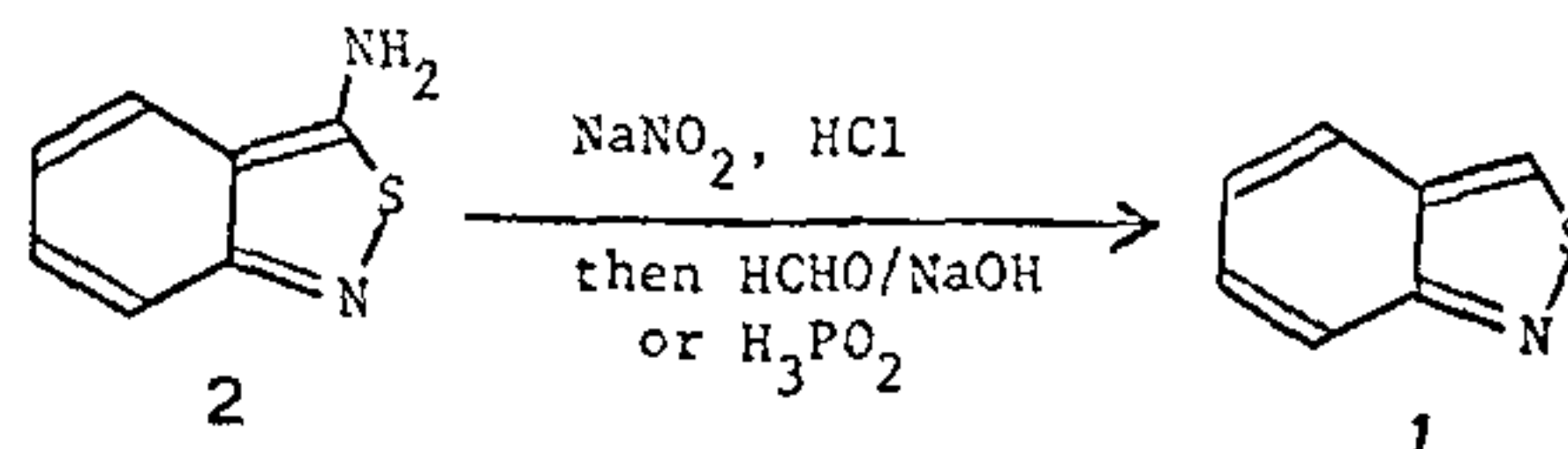
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Faculty of Science, K. N. TRIVEDI,
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A NOVEL SYNTHESIS OF 2, 1-BENZISOTHIAZOLE (THIOANTHRANIL)

ONLY three methods of preparation of 2,1-benzisothiazole (thioanthranil) (1) have so far been described in the chemical literature. The first two involve the reduction of *o*-nitro-

toluene-*a*-thiol¹ or the oxidation of *o*-aminotoluene-*a*-thiol;² the third and most recent method utilises the reaction between *o*-toluidine and thionyl chloride in boiling xylene solution.³



We now wish to report a fourth synthesis. 3-Amino-2,1-benzisothiazole (2), which is readily prepared⁴ by a two-step reaction from the commercially available *o*-aminobenzonitrile,⁵ is diazotised with hydrochloric acid and sodium nitrite. Treatment of the resulting diazonium chloride solution with alkaline formaldehyde solution, or with hypophosphorous acid, affords thioanthranil in moderate yield.

Since a considerable number of substituted 3-amino-2,1-benzisothiazoles is known,^{4,6,7} and since certain 2,1-benzisothiazoles possess potent biological activity, especially gastric antisecretory activity,^{4,8} this reductive deamination procedure may prove of some value in preparing not only thioanthranil itself but also substituted thioanthranils not readily accessible by the earlier methods.

EXPERIMENTAL

3-Amino-2,1-benzisothiazole (2)⁴ (1.0 g) was dissolved in warm hydrochloric acid (1.3 M; 32 ml). This solution was cooled in an ice-bath, when the amine hydrochloride separated. Aqueous sodium nitrite solution (10% ; 4 ml) was added portionwise with shaking; the final mixture was allowed to stand for about 10 minutes to complete diazotisation, and was then added slowly to a stirred mixture of formalin (37% HCHO; 5 ml), water (13 ml) and sodium hydroxide (2.0 g). The rapid decomposition of the diazonium salt, and consequent evolution of nitrogen, caused some frothing during this addition. The mixture was then steam-distilled, and the distillate extracted with diethyl ether. Evaporation of the dried extract afforded thioanthranil (2,1-benzisothiazole) (1) (0.35 g, 40%), which was identified by comparison of its n.m.r. and infrared spectra with those of an authentic sample, and by observation of the m.p. of the picrate derivative. The latter m.p. and mixed m.p. was $123\text{--}125^\circ$ (lit.⁹ $123\text{--}124^\circ$).

Hypophosphorous acid was equally effective as the alkaline formaldehyde in the second step of this procedure.

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2-(2-QUINOLYLAZO)-4-PHENANTHROL AND ITS METAL CHELATES

2-HYDRAZINOQUINOLINE was prepared by the method of Perkin and Robinson¹ and 9,10-phenanthrenequinone was prepared by the method of Schultz.

chromatography in which only one spot was obtained. Analysis of the compound corresponded with the molecular formula $C_{23}H_{15}N_3O$.

QAP is a dark brown solid. It is insoluble in water, dilute acids and alkalis. However, it is soluble in acids ($pH < 2$) to give a cation, yellow in colour which is due to the protonation of the nitrogen in the quinoline ring. In strong alkalis ($pH > 10$) it is slightly soluble to give an anion, pink in colour on account of the loss of a proton from the hydroxy group. It is soluble in methyl alcohol, ethyl alcohol, 1,4-dioxane, carbon tetrachloride, chloroform, isopropyl alcohol and benzene.

In addition to metal ions listed in Table I, QAP has been found to form coloured chelates with Co(II), Ni(II), Ag(I), Au(III), Sb(III), Ca(II), Ba(II), Sr(II), Bi(III), Os(VIII) and U(VI). The colour reactions are particularly sensitive for zinc, cadmium, mercury, copper, nickel, iron, cobalt and palladium.

The pH of the solution is of great importance for the formation of the chelates and minimum pH for chelation varies from metal to metal. All these chelates are insoluble in water. However, some of the chelates are soluble in common organic solvents. The colours of these chelates are recorded in Table I.

TABLE I
Colour of metal chelates of QAP (Solids and in organic solvents)

Metal ion	Solid	CCl_4	$CHCl_3$	C_6H_6	CH_2Cl_2
Zn (II)	.. Red	Red	Red	Red	Red
Cd (II)	.. Violet	"	"	"	"
Cu (II)	.. Blue	Blue	Blue	Blue	Blue
Fe (II)	.. Red	Red	Red	Red	Red
V (V)	.. Green	Green	Green	Green	Green
Pd (II)	.. "	"	"	"	"
Hg (II)	.. Pink	Pink	Pink	Pink	Pink
Pb (II)	.. "	"	"	"	"
Mn (II)	.. Red	Red	Red	Red	Red
Nb (V)	.. Yellow	Yellow	Yellow	Yellow	Yellow
Ta (V)	.. "	"	"	"	"

2.4 g of 9,10-phenanthrenequinone was dissolved in one litre of aqueous methanol (80%) and a solution of 2.0 g of 2-hydrazinoquinoline in 50 ml of 6 M HCl was added with constant stirring. The resulting solution was neutralized with ammonia solution when a dark brown precipitate of 2-(2-quinolylazo)-1-phenanthrol (abbreviated as QAP) separated out, the yield being 90%. The product was recrystallised from ethyl alcohol and its melting point was found to be 234-36° C. The purity of the sample was checked by thin layer

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