



was filtered through a sintered glass crucible No. 4. There was no need of digesting the precipitates on water-bath. The precipitates on the crucible were washed twice with 20% ethanol and dried at 110-15° C. in an oven. The results obtained are in conformity with those obtained by precipitation of the complex with PPAO.

The authors express their thanks to Prof. T. R. Seshadri, F.R.S., for his helpful discussions. One of them (M. K.) is also thankful to the Council of Scientific and Industrial Research for financial assistance.

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#### ON THE USE OF ACYL SEMICARBAZIDE FOR THE SYNTHESIS OF ALDEHYDE

IN connection with a need for an aldehyde in the syntheses of iso-quinoline derivative that are being followed in this Institute, an attempt was made to utilise the reaction as developed by McFadyen and Stevens,<sup>1</sup> but by using N<sub>1</sub>-acyl semicarbazide in place of benzene sulphonyl acyl-hydrazine. A mixture of benzoyl hydrazine and urea in molecular proportions was heated under reflux for 10 hours in aqueous solution to give N<sub>1</sub>-benzoyl semicarbazide, m.p. 226° (decomp.) on crystallisation from water (Found: N, 23.1%; C<sub>8</sub>H<sub>9</sub>O<sub>2</sub>N<sub>3</sub> requires, N, 23.4%). In a similar way several other acyl semicarbazides have been prepared (cf. Guha<sup>2</sup>) from p-chloro-benzoyl, anisoyl-, iso-nicotinoyl- and 1:3-dimethyl 3:4-dihydro-iso-quinoline-3-carboxy hydrazines and the respective melting points of the corresponding semicarbazides are 225-26°, 226-27°, 244-45° (decomp.) and 193-94°.

The benzoyl-semicarbazide (9 gm.) when heated with sodium carbonate (11 gm.) gave an oil, b.p. 178-79°, whose 2:4-dinitrophenyl hydrazone crystallises from ethyl acetate in orange yellow needles, m.p. 235-36°, not depressed when admixed with an authentic sample of 2:4-dinitrophenyl hydrazone of benzaldehyde. (Found: N, 19.05%; C<sub>13</sub>H<sub>11</sub>O<sub>4</sub>N<sub>4</sub> requires N, 19.5%).

In using urethane in place of urea a different type of reaction was noticed. Thus, for example, when iso-nicotinoyl hydrazine was heated with urethane on a wiregauze furnished 2-(4'-pyridyl)-1,3,4-oxadiazole-5-one, m.p. 266-68° (decomp.) (Found: N, 25.51; C<sub>7</sub>H<sub>5</sub>N<sub>3</sub>O<sub>2</sub> requires N, 25.77%). The properties of the compound agree in all respects with those of the similar product from iso-nicotinoyl hydrazine and carbonyl chloride (cf. Smith<sup>3</sup>). The work is in progress.

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#### 2', 3', 4'-TRIHOROXYCHALCONE AS AN ANALYTICAL REAGENT

LENSE *et al.*<sup>1</sup> examined the reactions of metallic ions with chalcones and reported that they are more sensitive than the aldehydes and ketones from which they are prepared. Tokuichi Tsumaki *et al.*<sup>2</sup> investigated the reactions of 4-chloro-2'-hydroxychalcone and 2, 2'-dihydroxychalcone with copper acetate in alcohol medium and obtained dark yellowish orange needles and dark yellow needles respectively. These complexes are shown to be of definite chemical composition. Gy Almasy *et al.*<sup>3</sup> reported on the use of 2'-hydroxy-4-nitrochalcone in microanalysis for the direct determination of alkaline earth metals. These authors reported that this reagent yielded precipitates exclusively with divalent metals and that the three functional groups present in it were involved in complex formation. Saiyad *et al.*<sup>4</sup> reported that 2', 4'-dihydroxychalcone yielded an intense reddish brown color with ferric iron. The present author<sup>5</sup> carried out spectrophotometric investigation on the color reaction and estab-

lished that the composition of the complex formed with Fe(III) was 1 : 3.

Among the chalcones under investigation by the present author it was found that 2', 3', 4'-trihydroxychalcone gave a brown precipitate with 0.125 $\gamma$  of Cu(II) at a dilution of 1 in  $4 \times 10^5$ . An amperometric method of estimation carried out by the author<sup>6</sup> with this reagent yielded good results for 1.0–6.0 mg. of copper. Further investigations showed that this reagent was highly sensitive, though not equally specific, to several other di-, tri- and tetravalent metallic ions. Among the ions examined only uranyl (0.308 $\gamma$ ) gave an orange color at pH 3.9–5.5 and at a dilution of 1 in  $1.6 \times 10^5$ . At a higher pH (5.7–8.4), however, an orange precipitate was obtained. In all other cases precipitates were obtained within the pH range given in Table I.

TABLE I

| Metal ion          | Colour          | pH      | Limit of Identification $\gamma$ | Limit of dilution |
|--------------------|-----------------|---------|----------------------------------|-------------------|
| Cu <sup>++</sup>   | Brown           | 3.8–4.5 | 0.125                            | 4,00,000          |
| Cd <sup>++</sup>   | Dark brown      | 6.8–8.2 | 0.320                            | 1,56,000          |
| Pb <sup>++</sup>   | Orange brown    | 3.9–5.9 | 1.250                            | 40,000            |
| Zn <sup>++</sup>   | Orange          | 6.1–8.2 | 2.500                            | 40,000            |
| Ni <sup>++</sup>   | Orange brown    | 5.8–6.4 | 0.154                            | 1,62,000          |
| Co <sup>++</sup>   | Dark brown      | 6.3–8.0 | 2.500                            | 20,000            |
| Be <sup>++</sup>   | Orange brown    | 5.0–6.7 | 0.256                            | 3,89,700          |
| Al <sup>+++</sup>  |                 | 4.7–5.0 | 0.320                            | 1,56,000          |
| Fe <sup>+++</sup>  | Grey            | 2.6–5.3 | 0.200                            | 2,50,000          |
| La <sup>+++</sup>  | Dark brown      | 5.4–7.5 | 1.000                            | 50,000            |
| Y <sup>+++</sup>   | Orange red      | 4.7–6.6 | 0.800                            | 1,62,400          |
| In <sup>+++</sup>  | Orange brown    | 3.1–4.0 | 0.312                            | 1,60,300          |
| Ti <sup>++++</sup> | Chocolate brown | 1.5–2.5 | 0.0625                           | 8,00,000          |
| Th <sup>++++</sup> | Orange          | 3.7–4.4 | 3.000                            | 16,600            |
| Ge <sup>++++</sup> | Yellow          | 4.1–6.4 | 0.625                            | 80,000            |

It is obvious that by controlling the pH range the selectivity of the reagent could be enhanced. The analytical applications of this reagent with the metallic ions are under investigation.

The author wishes to express his grateful thanks to Prof. K. Neelakantam for the kind interest in this work and to the C.S.I.R., New Delhi, for the award of a Junior Research Fellowship.

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## OCCURRENCE OF RAPAKIVI GRANITE IN SOUTH INDIA

FOR the first time, in South India is recorded an occurrence of rapakivi granite and granodiorite at Manapparai (10° 36' : 78° 26'), Tiruchirapalli, Madras State. The outcrop covers an area of about five square miles. The rocks could be traced up to the village of Kudirai-kuttippatti, two and a half miles N. 30 W. of Manapparai and in the hill 950 west of the village. Outcrops are also noted round about Andavarkovil, a mile and a half north-east of Manapparai.

The rock mass is traversed by horizontal and vertical joints. The quarries that were opened in 950 hill have been abandoned, as the rocks easily crumble—a characteristic of the rapakivi granite which has earned for it the name rotten stone.

The rapakivi structures are conspicuously absent in the geologically associated rocks, outside the area referred to. The rapakivi granites are traversed by pegmatites and aplites parallel to and across the foliation.

Within the area the ovoids make their appearance at the contact with the granodiorites, which have developed a foliation. The rapakivi structure is typical. The ovoids of orthoclase microcline and perthite—varying in size from about one-fourth to a maximum of two inches—are surrounded by mantles of plagioclase (Ab<sub>70</sub> An<sub>30</sub>), wart-like intergrowths of vermicular quartz and plagioclase and hornblende. This ferromagnesian is observed in the micro-sections in parallel, subparallel and tangential positions to the potash felspar. The matrix also shows potash feldspars and plagioclase besides hornblende and biotite. The feldspars therefore occur in two generations.

Various views have been given for the genesis of the ovoids, which have been summarised by Read.

The magmatists hold that they are due to (i) crystallisation of drops of magma shed from the feldspars (Holmquist); (ii) eutectic crystallisation of orthoclase and oligoclase (Vogt); (iii) refusion of the early formed orthoclase under conditions of reduction of gas pressure (Wahl.); (iv) a disturbed phase equilibrium in the crystallisation of the magma (Eckermann); (v) supersaturation of orthoclase and oligoclase alternatively (Harker); (vi) depletion of potash of the orthoclase—giving rise to oligoclase due to the potash being fixed up in biotite (Thomas and Cambell Smith); (vii) progressive con-