NOTES.

Diacetylethylene. By K. F. Armstrong and Robert Robinson.

This substance (I), which has not hitherto been described, is obtained in 15% yield (pure crystalline product) by the oxidation of acetonylacetone with selenious acid: Me•CO•CH_2•CH_2•COMe ⟶ Me•CO•CH:CH•COMe (I). The only isomeride so far isolated is faintly yellow and, by analogy with the dibenzoylethylenes, of which the *cis*-form is colourless and the *trans*- is yellow (Conant and Lutz, *J. Amer. Chem. Soc.*, 1923, **56**, 1303), it would appear to be the *trans*- modification. The oxidation of acetonylacetone takes a course analogous to that of ethyl succinate, which Astin, Riley, and Newman (J., 1933, 391) found to be oxidised by selenious acid with formation of ethyl fumarate (and ethyl hydrogen fumarate) in 40% yield.

Diacetylethylene.—Acetonylacetone was refluxed for 1 hour with selenious acid (15 g.) in water (500 c.c.), and the liquid then distilled in steam. A brown oil was isolated from the distillate, saturated with ammonium sulphate, by means of ether, and this partly crystallised. It was exhausted with boiling light petroleum (b. p. 40—60°) and, when the yellow extract was cooled to 0°, crystals (5 g.) were deposited (recrystallised, 3·75 g. or 15%). The faintly yellow, flat needles, m. p. 75·5—76·5°, are soluble in water and in organic solvents with the exception of light petroleum (Found: C, 64·5; H, 7·1. $C_6H_8O_2$ requires C, 64·3; H, 7·1%). The b. p. is about 90°/15 mm. The substance gave no ferric reaction, but a second product of the oxidation, not yet isolated, responds to this test.

Diacetylethylene rapidly decolorises alkaline permanganate and instantly absorbs bromine; it reduces Fehling's solution in the cold. The solution in concentrated sulphuric acid is orange-brown and, on treatment with aqueous caustic alkali, a characteristic cherry-red coloration (yellow on acidification) is produced.

The mother-liquors from the preparation afforded 6·5 g. of a colourless liquid, b. p. 87—91°/15 mm., the properties of which indicated that it consisted of an uncrystallisable mixture of the isomeric diacetylethylenes; it was certainly not unchanged acetonylacetone.

The *bis*-2 : 4-*dinitrophenylhydrazone* was prepared in methyl-alcoholic solution and separated at once. It crystallised from pyridine as bright red needles, m. p. 291—292° (Found: C, 46·0; H, 3·5; N, 23·4. $C_{18}H_{16}O_8N_8$ requires C, 45·8; H, 3·4; N, 23·7%).

Hydrogenation.—One mol. of hydrogen was rapidly absorbed in methyl-alcoholic solution in the presence of a silica-supported platinum catalyst and absorption then ceased. Diacetylethylene (112 mg.) and catalyst (20 mg.) absorbed 22·4 c.c. of hydrogen in 10 minutes. The 2 : 4-dinitrophenylhydrazone was prepared (280 mg.) and crystallised from pyridine, m. p. 257°, alone or mixed with an authentic specimen of the *bis*-2 : 4-*dinitrophenylhydrazone* of acetonylacetone (Found: N, 23·5. $C_{18}H_{18}O_8N_8$ requires N, 23·6%). Again, diacetylethylene (112 mg.), reduced in acetic acid solution in the presence of the catalyst, was then treated with phenylhydrazine (50% acetic acid solution, heated on the steam-bath for 30 minutes) and 1-anilino-2 : 5-dimethylpyrrole (75 mg.) was obtained. This derivative crystallised from aqueous alcohol in glistening plates, m. p. 90—91°, alone or mixed with an authentic specimen (Knorr, *Ber.*, 1889, **22**, 170). Diacetylethylene (56 mg.), with catalyst (100 mg.), in acetic acid solution absorbed 3 mols. of hydrogen corresponding to the production of a saturated glycol.

The reduction of diacetylethylene can also be accomplished by means of zinc dust and acetic acid or by weakly alkaline hydrosulphite and in both cases the product is acetonylacetone.—The Dyson Perrins Laboratory, Oxford University. [*Received, August 9th*, 1934.]

Observations in the Xanthene Group. By E. A. H. Roberts and Robert Robinson.

Chloroanil is useful as an oxidising agent for leuco-derivatives in the xanthylium-salt and similar series, especially when the aromatic nuclei are hydroxylated or when there are other reasons why halogens should not be employed.

1 : 3 : 6 : 8-*Tetrahydroxyxanthene.*—An aqueous solution of sodium hydrosulphite was gradually added to one of 1 : 3 : 6 : 8-tetrahydroxyxanthylium chloride (12 g.) (Pratt and Robinson, J., 1923, **123**, 739) in 2*N*-sodium hydroxide, vigorously stirred and heated on the steam-bath, under hydrogen for about 2 hours. The progress of the reduction could be followed by noting the decoloration and, on cooling, the *xanthene* separated in long white needles (10 g.). The substance was recrystallised from water (sulphur dioxide). It gradually decomposed above

100° and finally charred without melting (Found : C, 63·2; H, 4·2. $C_{13}H_{10}O_5$ requires C, 63·4; H, 4·0%). On bromination with 2 or 4 mols. of bromine in cold acetic acid solution, it afforded a tetrabromo-derivative, pale orange-brown crystals from 95% alcohol. This substance gave concordant results in C and H estimations but the content of bromine found was always 1—2% low (*e.g.*, Br, 55·8; calc., 56·9%). When the acetic acid solution was boiled *after* the bromination, an orange xanthylium bromide separated in deep red needles that could be recrystallised from a large volume of glacial acetic acid (Found : C, 27·9; H, 1·1. $C_{13}H_6O_5Br_4$ requires C, 27·8; H, 1·1%). This is probably *tribromotetrahydroxyxanthylium bromide*; its orange-yellow solution in 0·5% hydrochloric acid becomes deep pink on the addition of alkalis owing to fluorone formation.

The xanthene (2 g.), dissolved in acetic acid (10 c.c.), was oxidised at the boiling point of the solvent by means of chloroanil (2 g.) in the minimum of hot acetic acid. The xanthylium acetate crystallised, and was collected and freed from chloroanil by extraction with hot acetic acid. It was then dissolved in dilute hydrochloric acid and the chloride produced was crystallised from dilute hydrochloric acid. The yield was almost quantitative (Found : C, 52·4; H, 3·8. Calc. for $C_{13}H_9O_5Cl,H_2O$: C, 52·4; H, 3·7%). The identity of the salt with 1 : 3 : 6 : 8-tetrahydroxyxanthylium chloride was established by direct comparison, including spectrographic examination of an alkaline solution, which exhibits an absorption band in the green.

Other dihydro-derivatives of pyrylium salts, for example, anhydrotrimethylbrazilin (deoxytrimethylbrazilone) and dinaphthapyran, have been quantitatively oxidised by chloroanil in acetic acid solution.

Xanthylium salt glucosides were prepared by tetra-acetylglucosidation of this xanthene, followed by oxidation with chloroanil and hydrolysis. Homogeneous products could not, however, be obtained. The distribution number of the crude product (6·7 mg. in 25 c.c. each of equilibrated *iso*amyl alcohol and 0·5% hydrochloric acid) was 34·0 and diminished by extraction with amyl alcohol.

A monoglucoside of definite constitution was synthesised by condensation of 2-*O*-benzoyl-4-*O*-tetra-acetyl-β-glucosidylphloroglucinaldehyde (J., 1931, 2672) with phloroglucinol and hydrogen chloride in ethyl acetate solution. The product was precipitated by means of ether and hydrolysed in the usual manner and finally purified by crystallisation from 3·5% hydrochloric acid. The distribution number under the standard conditions was 43·7 (7·13 mg. in 50 c.c. of mixed solvents) and 48·3 (1·75 mg.). It thus shows a concentration effect but not a large enough one to indicate complete association to double molecules in the aqueous layer.—THE DYSON PERRINS LABORATORY, OXFORD UNIVERSITY. [*Received, August 9th*, 1934.]

An Attempted Flavonol Synthesis. By E. H. CHARLESWORTH and ROBERT ROBINSON.

IN view of the very facile condensation of *o*-vanillin with ω-hydroxyacetophenones and the analogy existing between the cyano- and the formyl group it was thought that *o-vanillonitrile* might condense with ω-hydroxyacetophenones with formation of flavonol derivatives. A favourable case was tested, but the reaction did not proceed in the suggested direction.

3 : 3′ : 4′-*Trihydroxy*-8-*methoxyflavylium Chloride*.—A solution of *o*-vanillin (3 g.) and ω : 3 : 4-triacetoxyacetophenone (6 g.) in ethyl acetate (80 c.c.) was saturated with hydrogen chloride in the cold and kept for a week. The dark red crystalline material (6 g.) that separated was dissolved in hot alcoholic hydrogen chloride (90 c.c. of 0·5%), and hot concentrated hydrochloric acid (35 c.c.) added. The long red needles obtained were dried in a vacuum over sulphuric acid (Found : C, 56·8; H, 4·6; Cl, 10·3; loss in a high vacuum over phosphoric oxide, 5·4. $C_{16}H_{13}O_5Cl,H_2O$ requires C, 56·7; H, 4·5; Cl, 10·5; H_2O, 5·3%).

The solution in hydrochloric acid is orange-red; that in alcoholic hydrochloric acid is bright red and feebly dichroic. Aqueous sodium carbonate develops a blue-violet coloration and sodium acetate gives a fading reddish-violet. The iron reaction in alcoholic solution is blue-violet.

o-Vanillaldoxime crystallises from water in long colourless prisms, m. p. 125° (lit., 121° and 123°); its alcoholic solution develops a blue coloration on the addition of ferric chloride. The action of boiling acetic anhydride on this oxime led to extensive decomposition; a small quantity of green rectangular prisms, m. p. 297° (decomp.), but no *o*-vanillonitrile, was isolated. At room temperature, or at 85°, the *monoacetyl* derivative was produced, colourless prisms, m. p. 101°, from benzene–light petroleum (Found : N, 7·1, 6·8. $C_{10}H_{11}O_4N$ requires N, 6·7%). The iron reaction was positive (blue) and hence the oximino-group was acetylated (compare Brady and

Dunn, J., 1914, **105**, 821; Brady, J., 1931, 105). Alkaline hydrolysis regenerated *o*-vanillaldoxime.

The *diacetyl* derivative was obtained when *o*-vanillaldoxime (20 g.) was refluxed with acetyl chloride (90 c.c.) for 2½ hours. The crude product (27·5 g.) crystallised from benzene–light petroleum in colourless prisms, m. p. 100° (Found : N, 5·4. $C_{12}H_{13}O_5N$ requires N, 5·6%) (ferric reaction, negative). The diacetyl derivative (27 g.) was refluxed for 2½ hours with acetic anhydride (50 c.c.) and the oily *O*-acetylvanillonitrile produced was hydrolysed below 40° with 10% aqueous potassium hydroxide. The cooled solution was acidified, and the *nitrile* isolated by means of ether. It crystallised from benzene–light petroleum in small colourless prisms, m. p. 61° (Found : C, 64·7; H, 4·7; N, 9·5. $C_8H_7O_2N$ requires C, 64·4; H, 4·7; N, 9·4%). The iron reaction in alcoholic solution is violet-blue, changing rapidly to a greenish coloration.

Under no conditions could a flavonol be obtained by condensation of *o*-vanillonitrile with ω : 4-dihydroxyacetophenone by using various solvents and hydrogen chloride, with or without zinc chloride. Moreover, acetylation of the hydroxyl groups, of this and other similar second components, was useless. The nitrile does not condense with acetylacetone to an isolable product. Salicylonitrile was equally inactive. In some of these experiments a hydrochloride, m. p. 100—112°, was isolated; this regenerated *o*-vanillonitrile on treatment with water.

Following the method of Nishikawa and Robinson (J., 1922, **121**, 839) for the condensation of salicylonitrile and phloroglucinol, the condensation of *o*-vanillonitrile and the trihydric phenol did not proceed as expected. A definite product was purified by solution in 2% aqueous sodium hydroxide and precipitation by acidification as colourless needles that appeared homogeneous under the microscope. The substance softened at 62° and was molten at 90° (Found : C, 61·0; H, 4·5; N, 6·5%). The low melting point, ready solubility in hot water, and high nitrogen content show that this substance is not the analogue of Nishikawa and Robinson's ketimine, m. p. above 300°, obtained from salicylonitrile and phloroglucinol.—THE DYSON PERRINS LABORATORY, OXFORD UNIVERSITY. [*Received, August 9th,* 1934.]

An Extraction Apparatus for Solids and Liquids. By ERIC L. MAYS and FRANK L. WARREN.

DURING continuous work on the extraction of different products it became desirable to construct an apparatus having a wider adaptability than those commonly used, *e.g.*, that of Soxhlet. The designs described below meet these requirements in that the apparatus can be fitted with the ordinary laboratory apparatus and used for extracting various quantities of material at any temperature above or below that of the room. Ordinary corks used in the apparatus do not come in contact with the liquid solvent, for air is trapped in the extraction flask when it is nearly full (hole *H*, see below). The construction is simple, strong, and permits of easy repair.

FIG. 1.

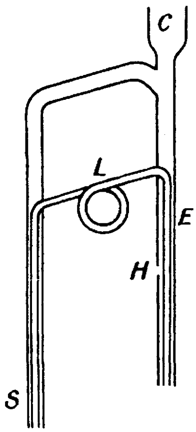
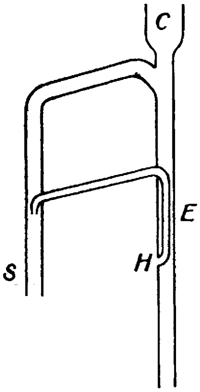


FIG. 2.



Extraction of Solids.—The apparatus (Fig. 1) is connected at *C* with a reflux condenser, at *S* with a flask containing the solvent, and at *E* with a wide-mouthed bottle containing the substance to be extracted held in a paper thimble or a cloth bag. The vapours of the solvent are condensed back to fill the extraction-bottle until the liquid covers the hole *H*, whereupon the tube *EC* begins to fill and the liquid runs back *via* the small tube. The introduction of the loop *L* is essential to promote syphoning in wide tubes.

Extraction of Liquids.—The apparatus (Fig. 2) of a similarly simple construction is for the continuous extraction of a solution with a solvent lighter than the extracted liquid. Besides the advantages referred to above, the apparatus does not become blocked by the separation, due to the removal of water by the extracting liquid, of the inorganic material with which the solution is usually saturated before extraction, for the solid separates over the bottom of the bottle and not in the tube.—EGYPTIAN UNIVERSITY, ABBASSIA, CAIRO. [*Received, August 15th,* 1934.]

Preparation of Arabinose from Gum Acacia (Gum Kordofan). By H. C. Carrington, W. N. Haworth, and E. L. Hirst.

Although it has long been known that *l*-arabinose is obtainable from gum acacia, we have devised a particularly useful procedure giving a considerably improved yield.

Arabic acid was prepared from gum acacia by a slight modification of Neubauer's method (*Annalen*, 1857, **102**, 105). The gum acacia used had $[\alpha]_D^{20^\circ}$ $-$ 30° in water. A solution of the gum (100 g.) in warm water (100 c.c.) was filtered through glass wool and acidified with dilute hydrochloric acid. The gum was then precipitated by adding slowly, with constant stirring, 1 l. of methylated spirit. The precipitate was filtered off, and the procedure of dissolution in water, acidification and precipitation with methylated spirit was repeated three times. A final precipitation was carried out without acidification of the aqueous solution, so that the product should contain no mineral acid. The arabic acid was a white powder which was dried in a vacuum oven at 50°. Yield, 80 g. Ash content, 0·2%.

A solution of arabic acid (100 g.) in 1 l. of 0·01*N*-sulphuric acid was heated on the water-bath at 95° for 14 hours; the rotation rose from $[\alpha]_D^{20^\circ}$ $-$ 24° to $+$ 32°, at which value it remained constant. The solution was neutralised by stirring with barium carbonate, and the liquid was filtered. The filtrate was added slowly, with stirring, to 2·5 l. of alcohol (P.B.S.). The precipitate was filtered off, and the filtrate evaporated to a syrup under reduced pressure at 40°. The syrup crystallised rapidly on nucleation with a crystal of arabinose. After a week it had crystallised almost completely. It was then kept under alcohol over-night, and was purified by trituration under alcohol. The product was a snow-white powder, which was washed with a little alcohol and dried in a vacuum. Yield, 18 g. Recrystallisation from aqueous alcohol gave pure *l*-arabinose, m. p. 157°. $[\alpha]_{5780}^{20^\circ}$ $+$ 185° in water (initial value) $\longrightarrow$ $+$ 108° (constant value). It was further characterised by preparation in quantitative yield of the benzylphenylhydrazone, m. p. 170°.—University of Birmingham, Edgbaston. [*Received, August* 17*th*, 1934.]