NOTES.

Dimorphism of Rotenone. By R. S. Cahn.

Rotenone is usually described as melting at 163°, but is, however, readily obtained with m. p. 164° by crystallisation. It separates from carbon tetrachloride with one molecule of solvent of crystallisation, from which it is freed by crystallisation from another solvent or by heating in a vacuum; the solvate resinifies when heated in an oven above about 80°, but is stable below about that temperature. Jones (*J. Amer. Chem. Soc.*, 1931, **53**, 2738) states that solvent-free rotenone, obtained from the solvate by the aid of heat, melts between 171° and 179°, and Butenandt and Hildebrandt (*Annalen*, 1930, **477**, 245) obtained a form, m. p. 176°, by grinding rotenone for a long time in an agate mortar.

I find that the material recovered by heating the solvate at 100° in a water-pump vacuum melts at 181—182° when freshly prepared. Further, when rotenone, m. p. 164°, is kept for a few minutes at 170—175° and scratched, it resolidifies and melts at 176—179°. On one occasion this occurred, without scratching, during an ordinary m. p. determination in a capillary tube, a double m. p., 164° and 183°, being observed.

Grinding in an agate mortar is unnecessary. After being pressed on a porous tile with a spatula, rotenone sinters at about 163° and then melts sometimes sharply at 183° and sometimes unsharply below 179°. The high-melting form is changed to the low-melting form by recrystallisation, as stated by Butenandt and Jones (*locc. cit.*); this change also occurs slowly on keeping, the m. p. falling and becoming very indefinite; the rate of change is very variable in different specimens, but appears not to be affected by heating at 100°. Attempts to crystallise rotenone in the high-melting form by (*a*) chilling a boiling solution in tetralin and (*b*) crystallisation at 100° of a xylene solution (30 g. in 50 c.c.) yielded the low-melting form.

Care is necessary in identifying rotenone by the mixed m. p. method, the m. p. 181—182° being now usually obtained in this laboratory. This difficulty was not met during several years before the laboratory became thoroughly seeded with the high-melting form.—The Cooper Technical Bureau, 47 Russell Square, London, W.C. 1. [*Received, May* 17*th*, 1934.]

Trimethylrhenium. By J. G. F. Druce.

Rhenium trichloride (Geilmann and Wrigge, *Z. anorg. Chem.*, 1933, **214**, 248) (2 g.) in ethereal solution reacted vigorously with methylmagnesium iodide (about 4 g.). The product was treated with an equal volume of 2*N*-hydrochloric acid (about 50 c.c.) and the yellow ethereal layer was separated, placed over calcium chloride for 24 hours, and distilled. Nearly a gram of a liquid came over at about 60°, and some previously distilled with the ether. On analysis by oxidation with fuming nitric acid under reflux and subsequent reduction with zinc foil and hydrochloric acid by the method of Briscoe, Robinson, and Stoddart (J., 1931, 666), 0·1235 g. of the liquid gave 0·1390 g. of $ReO_2,2H_2O$ (Re, 82·5%), and this, on oxidation by the method of Geilmann and Hurd (*Z. anorg. Chem.*, 1932, **210**, 350), gave 0·1352 g. of $HReO_4$ (Re, 81·2%) [$Re(CH_3)_3$ requires Re, 80·5%].

Trimethylrhenium thus obtained was an almost colourless oil, somewhat heavier than water, with which it did not appear to mix, although it imparted to this its not unpleasant, slightly ethereal odour. The oil was not very inflammable, but burned with an almost non-luminous flame, accompanied by a cloud of rhenium heptoxide. It reacted slowly with aqueous hydrogen peroxide, per-rhenic acid being among the products.

The reaction product of rhenium trichloride and methylmagnesium iodide had a sharp odour reminiscent of certain tin alkyl halides. When the acid aqueous layer was distilled, a few drops of a halogen-containing oil (heavier than water) separated; this might be a methylrhenium chloride.—[*Received, May* 12*th*, 1934.]

A Case of Hydrogenation in the Sterol Group by the Action of Selenium. By Charles Dorée and Vladimir A. Petrow.

In an attempt to obtain partially dehydrogenated derivatives of cholesterol, cholesterilene, $C_{27}H_{44}$, was heated in the usual way with selenium for 155 hours at 230—250°. Very little hydrogen selenide was evolved. The fluorescent oil obtained was distilled and from the fraction, b. p. 250°/1 mm., cholestane, $C_{27}H_{48}$, was isolated in a yield of 25%.

The hydrocarbon formed plates, m. p. 80·0°, $[\alpha]_D^{18^\circ}$ + 30·2° (Found : C, 87·0; H, 13·0. Calc.

for $C_{27}H_{48}$: C, 87·0; H, 13·0%). Values given for cholestane in the literature are m. p. 80°, $[\alpha]_D^{18°}$ varying from + 24° to + 43°. The hydrocarbon did not react with picric acid, bromine in ethereal solution, sodium in ethyl alcohol, sodium amyloxide, or with ozone (2% ozone for 3 hours in chloroform). It gave no colour with tetranitromethane in chloroform, and no melting point depression in admixture with authentic cholestane. Its identity seems satisfactorily proved.

Fractionation of the mother-liquors did not yield any ψ-cholestane, a result of interest in connexion with the observations of Windaus and Seng (*Z. physiol. Chem.*, 1921, **137**, 158) and also of Bose and Doran (J., 1929, 2244), who found that cholesterilene, on catalytic hydrogenation, gave cholestane together with ψ-cholestane in smaller amount.

A case in which hydrogenation apparently occurs under the action of selenium has recently been reported by Ruzicka, Hösli, and Ehmann (*Helv. Chim. Acta*, 1934, **17**, 442), who obtained from oleanolic acid, $C_{30}H_{48}O_3$, a small yield of a saturated hydrocarbon, oleanane, $C_{29}H_{50}$. They attributed the formation of this substance to the hydrogenation of the double bond in oleanolic acid together with the loss of carbon dioxide and water. The observation is of interest in that previous attempts to hydrogenate catalytically the double bond in oleanolic acid have been unsuccessful.

The formation of cholestane in comparatively high yield under the conditions cited above is a definite case of hydrogenation, and the action of selenium on other organic compounds is being examined.—CHELSEA POLYTECHNIC, LONDON, S.W. 3. [*Received, June* 16*th*, 1934.]

Preparation of iso*Stilbene.* By T. W. J. TAYLOR and CHARLES E. J. CRAWFORD.

THE methods which have been described for the preparation of *iso*(*cis*)stilbene either give a small yield or are extremely tedious, so that the compound has been scarcely available in quantity. The most important that have been used are the partial catalytic reduction of tolane (Kelber and Schwarz, *Ber.*, 1912, **45**, 1951); reduction of tolane by zinc dust, which involves 180 hours' boiling in the dark (Böeseken and Gloen, *Rec. trav. chim.*, 1928, **47**, 694); and the decarboxylation of α-phenylcinnamic acid by distillation from baryta, where a yield of less than 2 g. is obtained from 24 g. of the acid (Stoermer, *Annalen*, 1915, **409**, 41).

A satisfactory modification of the last method takes advantage of the high catalytic power of copper chromite for decarboxylation (Kinney and Langlois, *J. Amer. Chem. Soc.*, 1931, **53**, 2189; Reichstein, Grüssner, and Zschokke, *Helv. Chim. Acta*, 1932, **15**, 1067). α-Phenylcinnamic acid is an easily accessible substance and in quinoline solution at 210° it loses carbon dioxide rapidly in the presence of copper chromite; the yield of pure *iso*stilbene amounts to 60—65% of the theoretical value. The efficiency of the process seems partly to depend on the enhanced stability of *iso*stilbene in quinoline solution. The compound, if heated alone, is converted rapidly into (*trans*)stilbene at 180°, but in the presence of quinoline the change is very slow even at 230°.

12 G. of α-phenylcinnamic acid (Bakunin, *Gazzetta*, 1897, **27**, ii, 49; 1901, **31**, ii, 77) were dissolved in 120 c.c. of quinoline and 1 g. of copper chromite (Adkins and Connor, *J. Amer. Chem. Soc.*, 1931, **53**, 1092) was added. On heating, slow evolution of carbon dioxide began at 190° (thermometer in the flask); the mixture was kept at 210—220° for 50 minutes. The cooled solution was poured into sufficient dilute hydrochloric acid to dissolve the quinoline, the whole extracted with ether, and the extract washed with dilute aqueous sodium carbonate to remove unchanged acid and dried. The residue after removal of the ether was dissolved in light petroleum (b. p. 40—60°) at 0°, and the solution filtered. Removal of the petroleum left an oil, from which, by fractionation under reduced pressure, 6·25 g. of *iso*stilbene, b. p. 134°/10 mm., were obtained. The yield is not appreciably changed by small alterations in temperature of reaction or time of heating.—THE DYSON PERRINS LABORATORY, OXFORD. [*Received, June* 9*th*, 1934.]

Derivatives of Normeconin. By ROBERT ROBINSON and H. R. L. STREIGHT.

ATTEMPTS to demethylate meconin were unsuccessful owing to the formation of condensation products. However, the demethylation of bromomeconin by means of hydrobromic acid (but not hydriodic acid) proceeded smoothly.

Bromonormeconin.—A mixture of bromomeconin (15 g.), hydrobromic acid (120 c.c., *d* 1·5), acetic acid (75 c.c.), and acetic anhydride (25 c.c.) was heated, in a bath at 90° and later at 110—115°, in an atmosphere of carbon dioxide for 7 hours. The product was added to water (2000 c.c.) and after 2 days the precipitate was collected, dried (11·5 g.), and crystallised from 45% aqueous alcohol, forming colourless plates, m. p. 203—209° (8 g., recrystallised) (Found: C, 39·3; H, 2·1; MeO, 0·0. $C_8H_5O_4Br$ requires C, 39·2; H, 2·0%). *Bromonormeconin* is easily soluble in ether or chloroform and sparingly soluble in benzene; it crystallises from tetrachloroethane in small rectangular prisms and from xylene in feathery needles. The catechol-type iron reaction and subsequent change from green to dull red on the addition of sodium carbonate are bright and characteristic in aqueous and alcoholic solutions.

On a larger scale bromomeconin (120 g.) gave bromonormeconin (87 g.) in 81% yield. The preparation of the dibenzyl ether of this phenol was unsuccessfully attempted under 18 sets of conditions; it was required for a synthesis of a pure nornarcotine. These trials were abandoned when it became clear that nornarcotine was not to be identified with vitamin C.

A curious property of bromonormeconin is that, whilst the addition of dilute hydrochloric acid to an alcoholic solution does not precipitate it, the addition of aqueous ammonia causes a rapid separation of a substance, possibly an ammonium salt, which yields bromonormeconin on treatment with acid.

The *diacetyl* derivative, obtained by heating the phenol (10 g.) with acetic anhydride (15 c.c.) and pyridine (5 drops) on the steam-bath for 90 minutes, crystallised from alcohol in fine, white, prismatic needles, m. p. 152° (Found: C, 43·9; H, 2·9. $C_{12}H_9O_6Br$ requires C, 43·8; H, 2·7%). The *dibenzoyl* derivative, prepared by the pyridine–benzoyl chloride method, crystallised from alcohol (charcoal) in white rods, m. p. 104—105° (Found: C, 58·2; H, 2·8. $C_{22}H_{13}O_6Br$ requires C, 58·3; H, 2·9%) (yield, 6 g. from 5 g. of bromonormeconin).

6-*Bromo*-O-3 : 4-*diphenylmethylenenormeconin*.—Diphenylmethylenation of bromonormeconin according to the method of Bradley, Robinson, and Schwarzenbach (J., 1930, 793) furnished the desired product, but the yield, though still poor, was improved by adoption of the following method: A mixture of bromonormeconin (4 g.), diphenyldichloromethane (4 g.), and pyridine (20 c.c.) was kept at room temperature for 24 hours and then heated on the steam-bath for 30 minutes. After the addition of water, the oil was collected and boiled with an excess of 5% aqueous potassium hydroxide, and the filtered solution then acidified. The reddish-coloured gum that separated was collected and became crystalline in contact with alcohol. The substance crystallised from this solvent in white prisms, m. p. 160° (Found: C, 61·5; H, 3·4. $C_{21}H_{13}O_4Br$ requires C, 61·6; H, 3·2%). This derivative furnished benzophenone and bromonormeconin when it was heated on the steam-bath with a mixture of acetic and concentrated hydrochloric acids.

On condensation with cotarnine in boiling alcoholic solution the substance furnishes a base having the properties to be anticipated for a diphenylmethylene ether of a bromonorgnoscopine. There is little doubt that a homogeneous nornarcotine could be synthesised along these lines, but, as the research was initiated under a misapprehension already implied, it was considered unnecessary to pursue the matter further.

Although the reduction of bromomeconin to meconin can be effected, we have not yet found the conditions necessary for the formation of normeconin from its bromo-derivative.—THE DYSON PERRINS LABORATORY, OXFORD UNIVERSITY. [*Received, June 7th,* 1934.]

Dimethylthallium Methoxide. By R. C. MENZIES and A. R. P. WALKER.

Dimethylthallium methoxide has been obtained, by double decomposition between thallous methoxide and dimethylthallium bromide in methyl alcohol, as a crystalline solid, m. p. 177—181°, which superficially darkens in air. It is sparingly soluble in light petroleum. It is also soluble in water, in which solvent hydrolysis is so complete that the thallium content may be accurately estimated by titration of the resulting dimethylthallium hydroxide with standard alkali (compare J., 1928, 186; 1932, 2605; Sidgwick and Sutton, J., 1930, 1465) [Found: C, 13·75, 13·5; H, 3·4, 3·4; Tl, 77·1, 77·0 (by titration), 77·1 (as sulphate). C_3H_9OTl requires C, 13·6; H, 3·4; Tl, 77·0%].

On attempted distillation in a vacuum, it decomposed at 120—130° with sufficient rapidity to project the cork and thermometer some distance into the air. The differences between dimethylthallium ethoxide, a liquid easily distilled in a vacuum and completely miscible both with water and with all the organic solvents tried (J., 1930, 1573), and methoxide thus resemble those between thallous ethoxide and methoxide (Sidgwick and Sutton, *loc. cit.*) and between aluminium ethoxide and methoxide (Gladstone and Tribe, J., 1876, **29**, 160; 1881, **39**, 3).

All three pairs constitute exceptionally well-marked examples of the familiar high melting points of many methyl as contrasted with the corresponding ethyl compounds.—THE UNIVERSITY, BRISTOL. [*Received, June 7th,* 1934.]