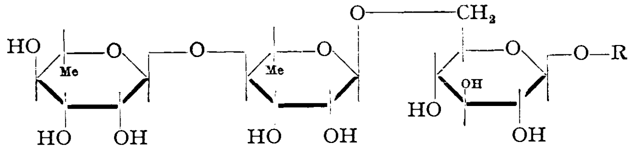
NOTES.

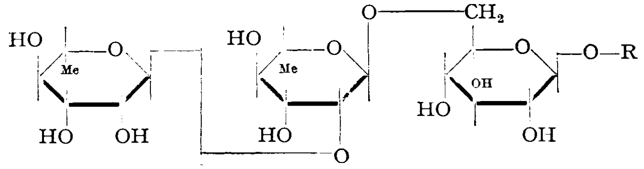
570. Solanum *Alkaloids. Part XI.* The Mode of Linkages in the Trisaccharide Moiety of Solamargine.*

By Lindsay H. Briggs and E. G. Brooker.

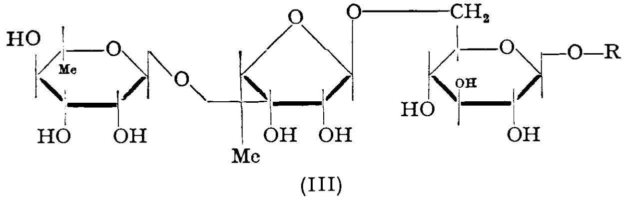
In Part VIII (*J.*, 1952, 3587) it was shown that solamargine from *Solanum marginatum* was a new trisaccharide derivative of solasodine of the structure, rhamnose-rhamnose-glucose-solasodine, with the trisaccharide joined to solasodine through the hydroxyl group at $C_{(3)}$. Solamargine exhibits no reducing properties, so that the three sugars are all joined through their potential aldehyde groups. Glucose is joined to solasodine through a β-linkage and from the ease of hydrolysis with 2% mineral acids the rhamnose units are also most probably similarly joined.



(I)



(II)



(III)

Quantitative oxidation of solamargine with periodate at 25°, illustrated in the Figure, showed that 5 mols. of periodate were consumed and 2 mols. of formic acid produced. Of the 96 possible structures for the trisaccharide moiety, including both pyranose and furanose forms of each sugar (but excluding the posibility of α- or β-linkages), only the three annexed structures (R = solasodine) could give the results actually obtained. Structures (I) and (III) cannot be distinguished by the rate of oxidation or by the identification of the hydroxy-acids formed by further oxidation and hydrolysis of the initial hexa-aldehyde

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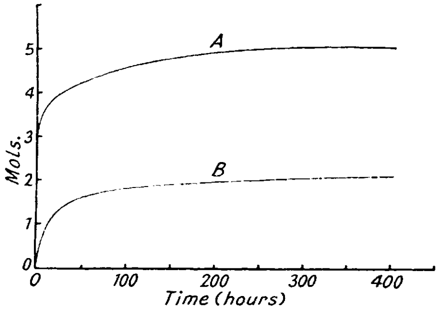
* Part X, *J.*, 1953, 2809.

produced by periodate oxidation. Also, they cannot be distinguished by methylation, hydrolysis, and identification of the methylated sugars, since the 2 : 3-di-*O*-methylrhamnose formed could exist in either of the theoretically interconvertible pyranose and furanose forms. However, it is most unlikely that rhamnose would occur in furanose form and even more unlikely that one molecule should exist in pyranose form and the other in furanose form. For these reasons (III) can be excluded.

Structures (I) and (II) could be distinguished by methylation. However, 1 : 2′-linkages in naturally occurring sugars are extremely rare (see Part X), so we prefer (I). This trisaccharide moiety is also that preferred for solanine and solasonine (Part X).

The same combination of sugars (two mols. of rhamnose and one of glucose) occurs in only one other glycoside, convallamarin (Voss and Vogt, *Ber.*, 1936, **69**, 2333), but the order of components and the nature of the linkages have not been determined.



A, Periodate consumed.
B, Formic acid produced.

Experimental.—Periodate oxidation of solamargine at 25°. By the procedure outlined in Part X (*loc. cit.*) anhydrous solamargine (0·5281 g.) was dissolved in 0·0243N-formic acid (75 c.c. 3 mols.), 0·0364N-sodium metaperiodate solution (150 c.c., 9 mols.) added, and the volume made up to 500 c.c. All solutions before mixing had been held at 25°. The final solution was held at 25° and aliquots were examined at intervals.

We are indebted to the Chemical Society and the Research Grants Committee of the University of New Zealand for continued grants and one of us (E. G. B.) for a University Research Fellowship.

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[*Received, April* 20*th*, 1953.]

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571. *α-Benzylidenepropiophenone and its Halogen Derivatives.*

By Robert D. Abell.

α-Benzylidenepropiophenone, prepared, with other products, by condensation of benzaldehyde with propiophenone in presence of hydrogen chloride (*J.*, 1901, **79**, 929), requires chemical treatment to render it chlorine-free. Kohler (*Amer. Chem. J.*, 1904, **31**, 642) obtained an intermediate chloro-ketone which he decomposed by heat. Condensation in presence of hydrogen chloride or bromide has now yielded β-chloro- and β-bromo-α-methyl-β-phenylpropiophenone, Hal·CHPh·CHMe·COPh, each in two isomeric forms, which differ slightly in their reactions.

Experimental.—α-Benzylidenepropiophenone (cf. Abell, *loc. cit.*). The dark product (A, see below), obtained by saturating a mixture of benzaldehyde (53 g.) and propiophenone (67 g.) with hydrogen chloride and storage of the mixture for 2 days, was slowly heated to 200° and kept at that temperature for some time. To obtain chlorine-free material, this product must then be boiled or steam-distilled with aqueous alkali for 10—12 hr. or boiled with alcoholic potassium acetate (20 g.) for 5—6 hr. Pouring the whole into water and removal of alcohol and unchanged reactants in steam gave a very dark, chlorine-free oil. When washed in light petroleum, dried, and distilled this afforded α-benzylidenepropiophenone as a yellow oil, b. p. 210—212°/20 mm.

Its phenylhydrazone formed lemon-yellow crystals, m. p. 128°. Kohler's record (*loc. cit.*) of m. p. 131° could not be repeated in many experiments.

β-*Chloro*-α-*methyl*-β-*phenylpropiophenone*. (*a*) To a solution of benzaldehyde (20 g.) in carbon disulphide (100 c.c.), saturated with hydrogen chloride, propiophenone (40 g.) was carefully added. After storage for several days, evaporation gave a dark oil which was dissolved in light petroleum (b. p. 40—60°), washed with water and then aqueous sodium carbonate, thoroughly dried ($CaCl_2$ or Na_2SO_4), and concentrated by evaporation (there is no decomposition if water is absent) until crystallisation occurred on cooling and scratching of a portion. Slow cooling of the bulk then gave β-*chloro*-α-*methyl*-β-*phenylpropiophenone* as rounded tufts of prisms, m. p. 79° (Found : Cl, 13·7. $C_{16}H_{15}OCl$ requires Cl, 13·7%), usually accompanied by the *isomer* in the form of large dense prisms, m. p. 68° (Found : Cl, 13·7%). If the second isomer does not crystallise spontaneously, it may be obtained from the mother-liquor on decantation. Mixtures of the two forms are readily separated by floating off the lighter form of m. p. 79°. Purification by crystallisation from light petroleum (or from alcohol, but less well owing to slow hydrolysis by water present) gave materials of the m. p.s quoted above. The whole product may, by repetition of these processes, be separated into the above-mentioned two forms, except for a small amount of readily soluble oil which yields the unsaturated ketone.

(*b*) The dark oil A (see p. 2834) similarly gave both isomers on treatment with light petroleum.

(*c*) The crystals of m. p. 79° were unchanged when heated at 80° for 1 hr. but decomposed at slightly above this temperature; those of m. p. 68° decomposed only at 200° (stable for 1 hr. at 95°).

The form of m. p. 79° gave 93·5% of its chlorine in the ionic form when boiled for 1 hr. with alcoholic potassium acetate (excess); with the isomer of m. p. 68° there was only 78·2% reaction on such treatment. In both cases α-benzylidenepropiophenone was regenerated.

The isomer of m. p. 79° (2·0 g.), when boiled for 3 hr. with phenylhydrazine (2 g.) in alcohol (55 c.c.), gave a dark, halogen-free viscous oil, stable at room temp. and giving Knorr's pyrazolone reaction. The isomer of m. p. 68°, on similar treatment, gave 4-*methyl*-1 : 3 : 5-*triphenylpyrazoline* as plates, m. p. 143° (Knorr's pyrazolone reaction positive) (Found : N, 8·9. $C_{22}H_{20}N_2$ requires N, 9·0%).

β-*Bromo*-α-*methyl*-β-*phenylpropiophenone*. (i) Passage of hydrogen bromide into a solution of propiophenone (67 g.) and benzaldehyde (53 g.) in carbon disulphide (100 c.c.) caused evolution of heat and separation of water. After 2 days the product was recovered. It partly crystallised. Addition of light petroleum gave a large yield of crystals, m. p. 93°. The mother-liquors and washings gave material, m. p. 80°, of which more was obtained on evaporation to half-volume. Further concentration and saturation with hydrogen bromide yielded further amounts of both isomers. The marked difference in solubility in light petroleum permitted finally complete separation of the β-*bromo*-α-*methyl*-β-*phenylpropiophenone* into the less soluble needles, m. p. 93° (Found : Br, 26·5. $C_{16}H_{15}OBr$ requires Br, 26·4%), and more soluble prisms, m. p. 80° (Found : Br, 26·5%). A small residue of dark oil yielded the unsaturated ketone.

(ii) A solution of α-benzylidenepropiophenone (50 g.) in carbon disulphide (100 c.c.), when saturated with hydrogen bromide, became dark and warm. After 24 hr., more carbon disulphide (100 c.c.) was added and the product isolated. This yielded the isomers, m. p. 93° (2 parts) and 80° (1 part). A similar experiment conducted in artificial light, gave only the isomer of m. p. 93°.

(iii) Reaction as in (*a*) but with hydrogen bromide in place of hydrogen chloride, and working up as in (i) gave only the isomer of m. p. 93° (perhaps owing to unsuitable lighting).

(iv) The isomer of m. p. 93° is dimorphous. A solution in hot carbon disulphide deposited long, flattened prisms resembling in form the isomer of m. p. 80° but melting at 93°. When kept in contact with the solution these prisms were replaced by the usual needles (m. p. and mixed m. p. 93°).

(v) The isomer of m. p. 93° decomposes at about 145°, the other isomer decomposes slightly above its m. p. (80°).

(vi) The isomer of m. p. 93° gave 98·8% of its bromine in the ionic form when boiled with alcoholic potassium acetate (excess) for 1 hour.

It did not react with hydroxylamine in alcohol when the solution was acid or neutral to methyl-orange (pH 5), but in solution just alkaline to phenolphthalein (pH 9) gave a halogen-free *substance* as prisms which soften at about 145° and are completely molten at 161° (unchanged on recrystallisation) (Found : 5·85. $C_{16}H_{15}ON$ requires N, 5·9%). This is also obtained when α-benzylidenepropiophenone is treated with hydroxylamine in acid solution and may be the oxime or 4-methyl-3 : 5-diphenyl*iso*oxazoline.

With hydrazine hydrate the isomer of m. p. 93° gave an alcohol-soluble oil and a small amount of sparingly soluble hexagonal plates (? the hydrazone), m. p. 220—221°, which contain bromine and do not give Knorr's pyrazolone test.

The same isomer (3·0 g.) and phenylhydrazine (2·2 g.), heated in alcohol (25 c.c.) for 1 hr., gave quantitatively 4-methyl-1 : 3 : 5-triphenylpyrazoline, m. p. 143° (Found : N, 8·9%).

TECHNICAL COLLEGE, BRADFORD. [*Received, January 5th*, 1953.]

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572. *Electric Moments and Intermolecular Hydrogen Bonds of Cyclic Amides and Oxazolidones : A Correction.*

By ERNST FISCHER.

RECENTLY (Fischer, *J.*, 1952, 4525) an attempt was made to estimate the contribution of bipolar mesomers to the structure of pyrrolid-2-one and of oxazolid-2-one. The author is indebted to Professor W. D. Kumler for pointing out an error in the " theoretical " moments then used, due to assignment of an incorrect value to the angle between the moment of the N–H bond and the resultant moment of the rest of the molecule.

In the pyrrolidone this angle plausibly has a value of between 110° (pyramidal arrangement of the three nitrogen valencies being accepted) and 124·5°, the H atom being assumed to lie in the plane of the ring. An intermediate value of 116° leads to a " theoretical" moment of *ca.* 3·0 D, without account being taken of mutual induction of the polar groups within the molecule. In the oxazolidone the corresponding figures are 102°, 104°, 103°, and 3·55 D. Combination of these " theoretical " moments with the experimental moments of 4·2 D for pyrrolidone and 5·1 D for oxazolidone leads to calculated contributions of bipolar mesomers (assumed to have a moment of 11 D) of 15% and 21%, respectively, and not 5% and 16% as reported previously. The main uncertainties concern the neglect of mutual induction within the molecules, as well as possible errors in the moment of the bipolar mesomer, in the valency angle mentioned above, and in the " experimental " moment of pyrrolid-2-one.

In the original communication attention was drawn to the parallelism between the contribution of bipolar mesomers and the tendency to association in benzene solutions. The present figures show this parallelism to be less pronounced.

WEIZMANN INSTITUTE OF SCIENCE,
REHOVOT, ISRAEL. [*Received, April 2nd*, 1953].

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573. *Free-radical Formation in Oxidations by Manganic Pyrophosphate.*

By ALAN Y. DRUMMOND and WILLIAM A. WATERS.

MANGANIC PYROPHOSPHATE was previously shown by us (*J.*, 1953, 435) to be a selective oxidising agent which slowly attacks most water-soluble aldehydes and ketones, 1 : 2-glycols α-hydroxy-acids, and a few other compounds, but not monohydric alcohols or olefins. Kinetic studies on which we are now engaged indicate that the exact courses of these oxidations depend very much upon the structural type of the organic compound involved. The following evidence indicates however that in each case the initial attack on the organic molecule, which may be represented as

$$(a)\quad \text{R–H} + \text{Mn}^{3+} \longrightarrow \text{R}\cdot + \text{Mn}^{2+} + \text{H}^{+}$$

leads to the formation of an *active* free radical.

1. *Catalysis of Vinyl Polymerisation.*—Manganic pyrophosphate solutions do not attack olefins. Consequently aqueous solutions of vinyl cyanide and of methyl methacrylate do not, in the absence of air, polymerise for a long time when added to neutral or acidified manganic pyrophosphate solutions; but if an oxidisable organic compound is added then the deposition of insoluble polymer is soon evident, even when the oxidation of the organic compound is quite slow. Decisive positive results have been obtained for the oxidations of the following compounds :

1 : 2-*Glycols*. Vinyl cyanide polymerisation is induced in the cold by the oxidation of

butane-1 : 2-diol, butane-2 : 3-diol, pinacol, erythritol, mannitol, or sorbitol. Of these only butane-2 : 3-diol and pinacol readily induced methyl methacrylate polymerisation, though with the others polymerisation was evident after 5 hours. Ethylene glycol and glycerol oxidised too slowly to induce visible polymerisation.

Aldehydes and ketones. With both monomers, positive results have been obtained for the oxidations of acetaldehyde, propaldehyde, butyraldehyde, acetone, ethyl methyl ketone, *cyclo*pentanone, 3-methyl*cyclo*pentanone, *cyclo*hexanone, and 4-methyl*cyclo*hexanone.

Carboxylic acids. Oxidation of oxalic, glycollic, lactic, tartronic, tartaric, malic, citric, or malonic acid induced polymerisations of both monomers. With oxalic and tartronic acids the induced polymerisation occurred rapidly; with glycollic acid the induced polymerisation of methyl methacrylate was evident only after 5 hours.

Phenols. Phenols, being oxidised, could not be tested in this way since they immediately gave dark precipitates.

To obviate effects due to oxygen, all tests were carried out in Thunberg tubes. Constant volumes of monomer, manganic pyrophosphate solution (*loc. cit.*), and dilute sulphuric acid were placed in the main Thunberg tube and about $1{\cdot}2 \times 10^{-3}$ mole of substrate in the side-tube. After evacuation the contents of the tubes were mixed and then kept at room temperature until precipitation was evident.

2. *Reduction of Mercuric Chloride.*—Active free radicals with $E_{(-e)}$ below *ca.* $+0{\cdot}6$ v are capable of reducing mercuric chloride to mercurous chloride (Merz and Waters, *J.*, 1949, S 15; Mackinnon and Waters, *J.*, 1953, 323). Though manganic pyrophosphate has a much higher redox potential the insolubility of mercurous chloride favours the occurrence of some reduction (*b*) in competition with further oxidation by the manganic salt (*c*).

$$(b)\quad R\cdot + Hg^{2+} \longrightarrow R^+ + Hg^+$$
$$(c)\quad R\cdot + Mn^{3+} \longrightarrow R^+ + Mn^{2+}$$

Though the reduction of mercuric chloride can be effected only by a limited group of free radicals, we have found that each one of the substrates listed in section (1) above does bring about some deposition of mercurous chloride when added to manganic pyrophosphate–mercuric chloride solutions at pH 0·8 and kept at 40° for a few hours. It is to be noted that this list includes compounds which do not give similar induced reductions when treated with Fenton's reagent, *e.g.*, acetone and pinacol.

In the case of oxalic acid it was found that copious precipitation of mercuric chloride results from the addition of only a few drops of manganic pyrophosphate solution to an aqueous oxalic acid–mercuric chloride mixture. Here the reduction $Mn^{3+} + (C_2O_4)^{2-} \longrightarrow Mn^{2+} + \cdot O_2C\cdot CO_2^-$ serves to catalyse the known oxalic acid–mercuric chloride chain reaction (Dhar, *J.*, 1917, **111**, 690; Cartledge, *J. Amer. Chem. Soc.*, 1941, **63**, 906; Weiss, *Discuss. Faraday Soc.*, 1947, **2**, 188). Dhar had reported some similar induced reductions of mercuric chloride during oxidations of α-hydroxy-acids by potassium permanganate.

One of us (A. Y. D.) thanks the D.S.I.R. for a Maintenance Grant.

The Dyson Perrins Laboratory, Oxford. [*Received, March* 16*th*, 1953.]

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574. *Observations on Exaltations of Molecular Refractions.*

By Ernst D. Bergmann and Ernst Fischer.

Everard, Kumar, and Sutton (*J.*, 1952, 2807) and Everard and Sutton (*J.*, 1952, 2816, 2817, 2818, 2821, 2836) studied the influence of conjugation on the molecular refraction and, in particular, on the distortion polarisation of compounds of the diphenyl, styrene, stilbene, and 1 : 4-diphenylbutadiene series (cf. Weizmann, *Trans. Faraday Soc.*, 1940, **36**, 928; Calvin and Alter, *J. Chem. Phys.*, 1951, **19**, 765; Curran and Palermiti, *J. Amer. Chem. Soc.*, 1951, **73**, 3733); an analogous study of substances of the above type and also of abnormal molecular refractions of coloured hydrocarbons has been carried out by Bergmann, Fischer, and Jaffe (*J. Amer. Chem. Soc.*, 1953, **75**, in the press). Additional data, related to some colourless or almost colourless substances, are reported in Table 1.

	$(R_D)_{calc.}$ (c.c.)	$(R_D)_{obs.}$ (c.c.)	Absorption max. (Å) (log E_m)
4-Methoxystilbene	67·2 *	68·5 ± 1·5	3150; 3250 [a]
p-Methoxybenzylideneaniline	64·5	71·0 ± 0·3	2230 (4·22); 2850 (4·24) (Fig. 1) [f]
Sorbic acid	31·2	34·0 ± 0·5	2540 (in alcohol) [b]
Triphenylene	83·0	81·5 ± 0·8	2500; 2580; 2740; 2840; 3000; 3220; 3280; 3340 [c]
Acenaphthene	51·5	52·0 ± 0·5	2470; 2670; 2780; 2810; 2850; 2890; 2920; 2960; 3000; 3040; 3080; 3130; 3170; 3220 [d]
3 : 4-Benzophenanthrene	83·0	83·5 ± 1	2180; 2290; 2620; 2720; 2810; 2950; 3030; 3150; 3250; 3540; 3710 [e]
Tetrabenzonaphthalene	113·0	122 ± 1	2320; 2680; 2870; 3010; 3380; 3500 [g]

* Based on $(R_D)_{obs.}$ 36·5 for styrene (Everard *et al.*, *loc. cit.*), which gives R_D 60·8 for stilbene. If the observed values for *cis*- (61·8) or *trans*-stilbene (65·6) (Everard *et al.*) are used, the above figure would be correspondingly higher.

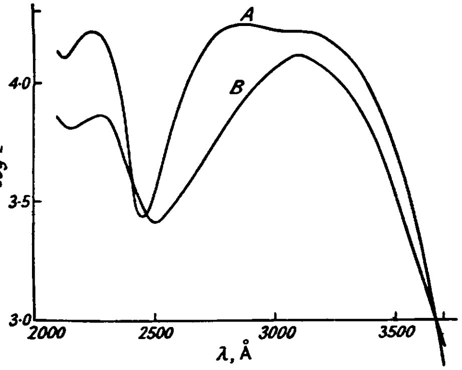
[a] Calvin and Alter, *loc. cit.*; cf. Ley, *Z. physikal. Chem.*, 1920, **94**, 405. [b] Hausser, Kuhn, Smakula, and Hoffer, *ibid.*, 1935, **29**, *B*, 371. [c] Clar and Lombardi, *Ber.*, 1932, **65**, 1411; Mohler and Sorge, *Helv. Chim. Acta*, 1939, **22**, 229. [d] Titeica, *Ann. Comb. liq.*, 1962, **11**, 445; *Chem. Abs.*, 1936, **30**, 6644; Seshan, *Proc. Indian Acad. Sci.*, 1936, **3**, 148. [e] Mayneord and Roe, *Proc. Roy. Soc.*, 1937, *A*, **158**, 634. [f] See Witkop, Patrick, and Kissman, *Ber.*, 1952, **85**, 949. [g] Bergmann, Fischer, and Jaffe, *loc. cit.*

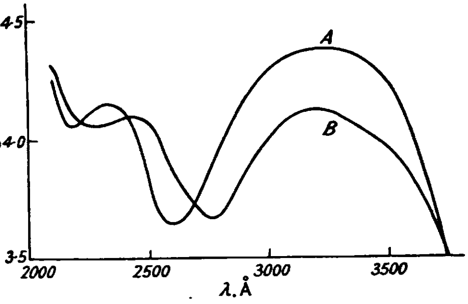
4-Methoxy-groups in systems of the stilbene type should exert a conjugation effect similar to that of amino-groups. In distinction to 4-aminostilbene and its *N*-dimethyl derivative (reported by Everard, Kumar, and Sutton, *loc. cit.*) *p*-methoxystilbene shows practically no effect of this kind; in *p*-methoxybenzylideneaniline (p-MeO·C_6H_4·CH:NPh) it is more pronounced. In this respect, Everard, Kumar, and Sutton's observation is of interest that the conjugation effect is much smaller for 4-methoxy- than for 4-dimethylamino-4′-nitrostilbene. This difference has also been noted by Bergmann and Weizmann (*Chem. Reviews*, 1942, **29**, 553); the methoxy-group has a smaller tendency to form structures such as (I) than the amino-group.

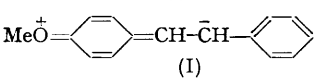
FIG. 1. p-*Methoxybenzylidene aniline* (*A*) *and ω-nitrosytrene* (*B*).

FIG. 2. 4-*Aminostilbene* (*A*) *and* 4-*dimethylaminostilbene* (*B*).

(*All in ethanol.*)







(I)

Unlike the coloured polycyclic hydrocarbons previously studied, the colourless compounds triphenylene, acenaphthene, and 3 : 4-benzophenanthrene show no exaltation of the molecular refraction, in spite of the extended conjugated systems. Tetrabenzonaphthalene shows a somewhat anomalous behaviour; this may be ascribed to the abnormal structure of this hydrocarbon, in which some of the carbon–carbon bonds appear to be non-aromatic, according to the *X*-ray analysis of the crystal structure ("intramolecular overcrowding") (G. Schmidt, personal communication). An open-chain analogue, sorbic acid, shows a slight exaltation of the molecular refraction.

As well as the molecular refractions, the absorption spectra of the above compounds have been measured. Those which have not been reported before are reproduced here. They may be of interest for a theoretical evaluation of the reported exaltations of the molecular refractions (see Sörensen, *Annalen*, 1940, **546**, 58).

Experimental.—The following materials were used. 4-Methoxystilbene, m. p. 136° (from *iso*propyl alcohol) (Orékhoff and Tiffeneau, *Bull. Soc. chim.*, 1925, **37**, 1410). *p*-Methoxybenzylideneaniline, m. p. 61—62° (from alcohol) (Knoevenagel, *Ber.*, 1898, **31**, 2606). Sorbic acid (commercial product, recrystallised from aqueous alcohol), m. p. 134. ω-Nitrostyrene, m. p. 60° (from methanol) (*Org. Synth.*, Coll. Vol. I, 1934, p. 413). Triphenylene, m. p. 198° (from *iso*propyl alcohol) (E. Bergmann, Fischer, and B. Pullman, *J. Chim. phys.*, 1931, **48**, 356). Acenaphthene (commercial product, purified *via* the picrate and recrystallised from alcohol), m. p. 95°. 3 : 4-Benzophenanthrene, m. p. 68° (from alcohol) (Szmuszkovicz and Modest, *J. Amer. Chem. Soc.*, 1950, **72**, 566). Tetrabenzonaphthalene, m. p. 218° (from toluene) (E. Bergmann, Fischer, and Pullman, *loc. cit.*). 4-Aminostilbene, m. p. 152° (from 80% methanol) (Pfeiffer and Sergiewskaja, *Ber.*, 1911, **44**, 1110). 4-Dimethylaminostilbene, m. p. 147° (from *iso*propyl alcohol) (Dey and Row, *J. Indian Chem. Soc.*, 1925, **1**, 285).

The method used for the determination of the molecular refraction has been described elsewhere (E. Bergmann, Fischer, and Jaffe, *loc. cit.*). The Table contains the molecular refractions, calculated from bond equivalents $(R_D)_{calc.}$ (Denbigh, *Trans. Faraday Soc.*, 1940, **36**, 926), the observed value $(R_D)_{obs.}$ and the absorption bands.

For the absorption spectra, the authors are indebted to Miss Hanna Weiler.

SCIENTIFIC DEPARTMENT, ISRAELI MINISTRY OF DEFENCE, TEL-AVIV.
WEIZMANN INSTITUTE OF SCIENCE, REHOVOTH.

[*Received, January* 30*th*, 1953.]

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575. *The Vapour Pressure and Improved Preparation of Methaneselenol.*

By G. E. COATES.

METHANESELENOL (CH_3·SeH), which was required for some experiments with trimethylgallium (Coates and Hayter, *J.*, 1953, 2519), is described by Baroni (*Atti Accad. Lincei*, 1930, **12**, 234), who prepared it from sodium hydrogen selenide and methyl iodide and gave its b. p. as 12°/758 mm. The reduction of dimethyl diselenide (Bird and Challenger, *J.*, 1942, 570) by sodium in liquid ammonia affords a more convenient preparative method.

The vapour pressure of methaneselenol, measured from −45° to +15°, is given by the equation $\log_{10}p = 6{\cdot}9500 - 1060/(t + 235)$ (where p is measured in mm. and t in degrees C). The average deviation of the pressures measured at 24 temperatures in this range from those calculated with the above equation is 0·8 mm. The b. p. is 25·5°. The latent heat of vaporisation is 6·20 ± 0·04 kcals./mole, the method of computation given by Thompson (*Chem. Reviews*, 1946, **38**, 1) being used with 228° C and 60 atm. as the critical temperature and pressure (values estimated by comparison with substances of similar constitution). The Trouton constant is thus 20·8. The latent heat of vaporisation is 6·48 kcal./mole, measured from the slope of the high-temperature (5—15°) part of the log p/T^{-1} graph, no corrections being made for deviations from perfect-gas laws.

Experimental.—Dimethyl diselenide (19 g., 0·1 mole) and sodium (4·6 g., 0·2 g.-atom) were added alternately to boiling liquid ammonia (150 c.c.). Ammonia was allowed to boil away from the resulting reddish-orange solution, which was protected from the atmosphere. Dilute sulphuric acid was slowly added to the solid residue, and the evolved gas was carried in a current of nitrogen through two drying tubes ($CaCl_2$) and condensed in a trap cooled in liquid oxygen. The product was transferred to a vacuum apparatus and was purified by fractional distillation. The only impurity detected was a little hydrogen selenide. The yield was nearly quantitative. The smell of methaneselenol is strong but not persistent.

THE UNIVERSITY, BRISTOL.

[*Received, March* 10*th*, 1953.]