

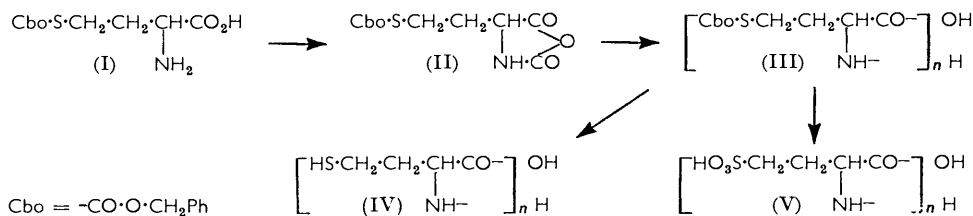
### 83. Syntheses of Poly-(S-alkyl-DL-homocysteines), Poly-DL-homocysteine, and Poly-DL-homocysteic Acid.

By MAX FRANKEL and DAVID GERTNER.

IN continuation of work<sup>1</sup> on the polymerisation of S-alkyl-L-cysteines, the polymerisation of S-alkyl-DL-homocysteines has been investigated.

The S-alkyl-DL-homocysteines were prepared by reducing DL-methionine with sodium in liquid ammonia and treating the homocysteine so prepared with excess of alkyl halides.<sup>2</sup> Passing carbonyl chloride into suspensions of them in dioxan at 50° gave the *N*-carboxyanhydrides which were polymerised in pyridine or dioxan solution or in bulk. Most of these polymers are more soluble in acetic acid, pyridine, and dimethylformamide than their lower homologues, the poly-(S-alkyl-L-cysteines).

Attempts to prepare poly-DL-homocysteine by reduction of poly-(S-benzyl-DL-homocysteine) with sodium in liquid ammonia gave impure products, so poly-DL-homocysteine was synthesised from poly-(S-benzyloxycarbonyl-DL-homocysteine) which was reduced more satisfactorily.<sup>3</sup> S-Benzyloxycarbonyl-DL-homocysteine (I) was prepared by the action of 1 mol. of benzyl chloroformate on DL-homocysteine in sodium hydrogen carbonate solution and was polymerised *via* its *N*-carboxyanhydride (II). Reduction of the resulting



polymer (III) yielded poly-DL-homocysteine (IV); this gave a positive nitroprusside reaction, and iodometric titration of the thiol groups showed the presence of 95% of the calculated amount. Oxidation of the polymer (III) in formic acid solution by excess of hydrogen peroxide gave poly-DL-homocysteic acid (V), hydrolysis of which by 20% hydrochloric acid gave only homocysteic acid.

*Experimental.* M. p.s were determined in a Fisher-Johns apparatus. The ascending method of paper chromatography in 80% phenol was used.

*S-Benzyloxycarbonyl-DL-homocysteine (I).* To DL-homocysteine (6.7 g.) dissolved in *N*-sodium hydrogen carbonate (75 ml.) at 0° benzyl chloroformate (8 g.) in ether (25 ml.) was added during 30 min. with stirring, which was continued for 1 hr.; then more ether (25 ml.) added and the whole stirred for a further 3 hr. The precipitate was filtered off and washed with ether, followed by water (yield, 2.9 g., 20%;  $R_F$  0.92; m. p. 230° on recrystallisation from water). If the filtrate was stirred for a further 3 hr. the total yield of *S-benzyloxycarbonyl-DL-homocysteine* was 35% [Found: C, 53.6; H, 5.8; N, 5.2; amino-N (Van Slyke), 5.2; S, 11.2.  $\text{C}_{12}\text{H}_{15}\text{NO}_4\text{S}$  requires C, 53.5; H, 5.6; N, 5.2; amino-N, 5.2; S, 11.9%].

*NS-Dibenzoyloxycarbonyl-DL-homocysteine.* To a solution of DL-homocysteine (6.8 g.) in 2*N*-sodium hydroxide (25 ml.) at 0° benzyl chloroformate (18 g.) and 2*N*-sodium hydroxide (50 ml.) were simultaneously added with stirring which was then continued for 2 hr. The solution was extracted with ether and acidified with hydrochloric acid. The NS-*dibenzoyloxycarbonyl-DL-homocysteine* which separated as an oil crystallised at 0° and was filtered off and washed with water; it (15 g., 75%) had m. p. 72–74° on recrystallisation from carbon tetrachloride (Found: N, 3.7.  $\text{C}_{20}\text{H}_{21}\text{NO}_6\text{S}$  requires N, 3.5%).

*N-Carboxyanhydride of S-benzyloxycarbonyl-DL-homocysteine (II).* Dry carbonyl chloride

<sup>1</sup> Frankel, Gertner, Jacobson, and Zilkha, *J.*, 1960, 1390.

<sup>2</sup> Armstrong and Lewis, *J. Org. Chem.*, 1951, 16, 749.

<sup>3</sup> Berger, Noguchi, and Katchalski, *J. Amer. Chem. Soc.*, 1956, 78, 4483.

was passed with stirring into a suspension of the acid (I) (1.2 g.) in dry dioxan (50 ml.) at room temperature for 90 min. The filtered solution was evaporated *in vacuo* at 30–40°, and the residue dissolved in dioxan (25 ml.) and evaporated once more. The *N*-carboxyanhydride, recrystallised from ether–light petroleum, had m. p. 75–76° (Found: N, 4.7.  $C_{13}H_{13}NO_5S$  requires N, 4.7%).

*Poly*-(*S*-benzyloxycarbonyl-DL-homocysteine) (III). Dry, freshly recrystallised *N*-carboxyanhydride (II) (0.5 g.) was dissolved in pyridine (10 ml.) and left for 2 days at room temperature, then heated on a water-bath for a few hr. The pyridine was evaporated *in vacuo*, and the residue washed with water and dried. The polymer was purified by dissolving it in a small volume of pyridine and reprecipitating it with ether. It is soluble in acetic acid, gives a positive biuret reaction, and softens around 160° [Found: C, 57.2; H, 5.3; N, 5.7; S, 12.1; amino-N (Van Slyke), 0.1.  $(C_{12}H_{13}NO_3S)_{50} \cdot H_2O$  requires C, 57.3; H, 5.2; N, 5.6; amino-N, 0.1; S, 12.7%].

*Poly*-DL-homocysteine (IV). *Poly*-(*S*-benzyloxycarbonyl-DL-homocysteine) (III) (0.5 g.) was suspended in liquid ammonia and sodium metal in small pieces added slowly with stirring until the blue colour persisted. A little ammonium chloride was added (to disappearance of the colour). The ammonia was evaporated at room temperature and then *in vacuo*. Boiled water (10 ml.) was added to the residue and the solution twice centrifuged. The aqueous solution was extracted with ether and acidified with hydrochloric acid. The polymer was collected, washed with water, and dried (yield 0.15 g.) (care has to be taken to prevent exposure to air to avoid oxidation) [Found: C, 41.2; H, 6.1; N, 11.8.  $(C_4H_7NOS)_n \cdot H_2O$  requires C, 41.0; H, 6.0; N, 12.0%].

*Poly*-DL-homocysteic acid (V). *Poly*-(*S*-benzyloxycarbonyl-DL-homocysteine) (III) (0.5 g.) was treated in 90% formic acid (25 ml.) with 30% hydrogen peroxide (2 ml.), with stirring for 2 hr. at room temperature. Evaporation to dryness *in vacuo*, dissolution of the residue in water (25 ml.), and evaporation to dryness again gave *poly*-DL-homocysteic acid which was washed with ether and dried. It gives a positive biuret reaction, is hygroscopic, soluble in water, acetic acid, and insoluble in acetone, and softens at 110° [Found: C, 29.8; H, 4.7; N, 8.5; S, 19.0.  $(C_4H_7NO_4S)_{50} \cdot H_2O$  requires C, 29.1; H, 4.3; N, 8.5; S, 19.4%]. Titration of the polymer with 0.1N-sodium hydroxide (Bromophenol Blue) showed 92% of the calculated sulphonic groups.

*S*-Benzoyl-DL-homocysteine. To DL-homocysteine (6.7 g.) in *N*-sodium hydrogen carbonate (50 ml.) at 0° benzoyl chloride (7 g.) in ether (25 ml.) was added with stirring simultaneously with further *N*-sodium hydrogen carbonate solution (50 ml.). After 2 hr. the precipitate of *S*-benzoyl-DL-homocysteine was filtered off and washed with cold water, ethanol, and ether (yield 3.5 g., 30%). It had m. p. 210° (recrystallised from water) and gave a negative nitroprusside reaction (on storage, a weak colour developed) (Found: C, 55.3; H, 5.4; N, 5.8; S, 13.2.  $C_{11}H_{13}NO_3S$  requires C, 55.3; H, 5.5; N, 5.9; S, 13.4%).

*N*-Carboxyanhydride of *S*-benzoyl-DL-homocysteine. The *N*-carboxyanhydride, prepared as above in 80% yield and recrystallised from ether–light petroleum, had m. p. 95–96° (Found: N, 5.1.  $C_{12}H_{11}NO_4S$  requires N, 5.3%).

*Poly*-(*S*-benzoyl-DL-homocysteine). The preceding *N*-carboxyanhydride (0.2 g.) was left in dry dioxan (15 ml.) with triethylamine (0.05 ml.) for 18 hr. at room temperature and then for 6 hr. on a boiling-water bath. The dioxan was removed *in vacuo*. The residual *poly*-(*S*-benzoyl-DL-homocysteine) gave a positive biuret reaction and was soluble in hot glacial acetic acid and dimethylformamide [Found: C, 59.8; H, 5.2; N, 6.3; amino-N (Van Slyke), 0.1.  $(C_{11}H_{11}NO_2S)_{60} \cdot H_2O$  requires C, 59.6; H, 5.0; N, 6.3; amino-N, 0.1%].

*Poly*-(*S*-benzyl-DL-homocysteine). *S*-Benzyl-DL-homocysteine was prepared by an exchange reaction of benzyl chloride with DL-methionine.<sup>4</sup> The *N*-carboxyanhydride was prepared as usual but in dry tetrahydrofuran (50 ml. per g.) for 1 hr. The solution was evaporated *in vacuo*, and the residue dissolved in tetrahydrofuran (25 ml.) and evaporated again. The *N*-carboxyanhydride, recrystallised from ether–light petroleum, had m. p. 57° (Found: N, 5.6.  $C_{12}H_{13}NO_3S$  requires N, 5.6%).

Polymers were obtained from the *N*-carboxyanhydride in a high vacuum and in pyridine [Found, for polymer prepared *in vacuo*: C, 63.5; H, 6.3; N, 6.8; S, 15.2.  $(C_{11}H_{13}NOS)_n \cdot H_2O$  requires C, 63.8; H, 6.3; N, 6.8; S, 15.5. Found, for polymer prepared in pyridine: N, 6.6%].

<sup>4</sup> Dekker and Fruton, *J. Biol. Chem.*, 1948, **173**, 471.

*Poly-(S-allyl-DL-homocysteine)*. The *N*-carboxyanhydride was prepared from *S*-allyl-DL-homocysteine as above and polymerised in pyridine. The *polymer* is soluble in acetic acid and gave a positive biuret reaction [Found: C, 53.4; H, 7.1; N, 8.7; amino-N (Van Slyke), 0.1. (C<sub>7</sub>H<sub>11</sub>ONS)<sub>90</sub>.H<sub>2</sub>O requires C, 53.4; H, 7.0; N, 8.9; amino-N, 0.1%].

*Poly-(S-ethyl-DL-homocysteine) (poly-DL-ethionine)*. The *N*-carboxyanhydride was prepared from DL-ethionine and polymerised in pyridine and in dioxan. The *polymer* from pyridine was recovered on evaporation *in vacuo* and trituration of the residue with ethanol [Found, for the pyridine polymer: C, 49.4; H, 7.4; N, 9.4; S, 21.6. (C<sub>6</sub>H<sub>11</sub>ONS)<sub>n</sub>.H<sub>2</sub>O requires C, 49.7; H, 7.6; N, 9.7; S, 22.1%. Found, for the dioxan polymer: N, 9.5%].

*Poly-(S-propyl-DL-homocysteine)*. The *polymer* was prepared from the *N*-carboxyanhydride of *S*-propyl-DL-homocysteine obtained as above, which was polymerised in pyridine [Found: N, 8.6; amino-N (Van Slyke), 0.2. (C<sub>7</sub>H<sub>13</sub>ONS)<sub>45</sub>.H<sub>2</sub>O requires N, 8.8; amino-N, 0.2%].

*Poly-(S-butyl-DL-homocysteine) (poly-DL-butionine)*. *Poly-(S-butyl-DL-homocysteine)* was prepared *via* the *N*-carboxyanhydride by polymerisation in pyridine [Found: C, 55.7; H, 8.8; N, 7.9. (C<sub>8</sub>H<sub>15</sub>ONS)<sub>n</sub>.H<sub>2</sub>O requires C, 55.5; H, 8.7; N, 8.1%].

*Note*. In calculating analytical detail for the indefinite polymers, *n* was taken as ∞ and the end-group (H<sub>2</sub>O), being insignificant, was neglected.

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## 84. A Grignard Reagent from *p*-Bromodimethylaniline.

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THE preparation of an ethereal Grignard reagent from *p*-bromodimethylaniline is difficult<sup>1</sup> but a moderately successful preparation has been described by Davies and Mann.<sup>2</sup> In tetrahydrofuran<sup>3</sup> reaction proceeds smoothly and the reagent so obtained may be used to prepare *p*-dimethylaminobenzoic acid in excellent yield.

*Experimental*.—*p*-Bromodimethylaniline (15 g.) reacted exothermally with magnesium (excess) in tetrahydrofuran (100 ml.) after initiation by a little ethyl iodide or iodine. Reaction was completed by 30 minutes' refluxing. Part (5 ml.) of the solution was added, after cooling, to solid carbon dioxide. More tetrahydrofuran (5 ml.) was added, followed by 2% acetic acid (55 ml.). The precipitate was recrystallised from ethanol, affording *p*-dimethylaminobenzoic acid (88%), m. p. and mixed m. p. 243° (Found: equiv., 165. Calc. for C<sub>8</sub>H<sub>10</sub>N·CO<sub>2</sub>H: equiv., 165) (Me ester, m. p. 102°).

Commercial (British Drug Houses Ltd.) tetrahydrofuran was freed from peroxides by refluxing it over aqueous ferrous sulphate acidified with sulphuric acid, then distilled through a short column of glass beads, dried (2 portions of CaCl<sub>2</sub>), refluxed over and distilled from sodium wire, and stored over fresh sodium wire in a dark bottle.

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<sup>1</sup> See, e.g., Kharasch and Reinmuth, "Grignard Reactions of Non-metallic Substances," Prentice-Hall, Constable, London, 1954, pp. 10–11, 41, 404, 896; Baeyer and Villiger, *Ber.*, 1903, **36**, 2794; Chamberlain and Dull, *J. Amer. Chem. Soc.*, 1928, **50**, 3088.

<sup>2</sup> Davies and Mann, *J.*, 1944, 276.

<sup>3</sup> Cf., e.g., Normant, *Compt. rend.*, 1954, **239**, 1510; Rosenberg, Gibbons, and Ramsden, *J. Amer. Chem. Soc.*, 1957, **79**, 2137; Metal and Thermit Corp., B.P. 776,933.

### 85. *The Conductance of Ferric and Cupric Stearates in Aliphatic Hydrocarbons.*

By C. M. FRENCH and E. R. MONKS.

AN attempt was recently made, using a Schering a.c. bridge, to investigate the conductometric behaviour of  $10^{-3}$ – $10^{-5}$ M-solutions in repeatedly fractionated n-heptane, n-decane, and n-dodecane of anhydrous and moist (2 molecules of water per metal atom) cupric and ferric stearate purified by recrystallisation. The specific conductances of the solvents were less than  $4 \times 10^{-14}$  ohm $^{-1}$  cm. $^{-1}$ , their dielectric constants between 1.93 and 2.14, and their viscosities between 0.24 and 1.14 centipoise. Conductances were not reproducible to a high degree of accuracy and, in the case of measurements at more than one temperature, depended on the rate of cooling. Equilibrium was attained very slowly, in some cases only after several hours. Similar observations have been recorded earlier<sup>1,2</sup> for analogous measurements on systems of this type, and are probably associated with a slow ionisation of the solute molecules, a slow exchange of ions and molecules between micelles formed by the solute, and variations in micelle structure. In each case in the present work, conductances were measured first at 65° and then at progressively lower temperatures, measurements being started 20 min. after the sample had been placed in the thermostat-bath at each selected temperature. In spite of very extensive precautions there was a considerable scatter of results and lack of reproducibility with some systems, and only the more distinct features, as summarised below, will therefore be reported.

(1) Conductances of all solutions were very much greater than those of the pure solvents (molar conductances of solutions were between  $10^{-4}$  and  $10^{-6}$  ohm $^{-1}$  cm. $^2$ ), indicating that ionisation, though not extensive, does occur in these solutions.

(2) The molar conductances of all solutions of ferric stearate were greater (up to 10-fold for anhydrous, and up to 100-fold for moist, solutions) than those of the same concentration of cupric stearate.

(3) Addition of 2 moles of water per mole of solute had little effect on the conductance of cupric stearate, but caused a significant (up to 10-fold) increase in that of ferric stearate solutions.

(4) Change of solvent had only a small effect on the conductance of either salt, heptane solutions being somewhat more conducting than those in the other two, more viscous solvents.

(5) Increase in temperature generally resulted in the usual increase in conductance, although some anhydrous solutions at concentrations greater than  $10^{-3}$ M had lower conductances at 65° than at 45°.

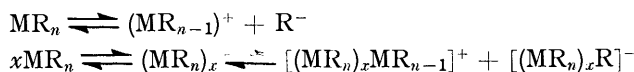
(6) Plots of the molar conductance  $\Lambda_m$  of the cupric stearate solutions against  $c^{\frac{1}{2}}$  gave curves with either clear minima or indications that one would occur at a concentration slightly greater than that measured here, and a typical example is shown in Fig. 1. In anhydrous solutions, increasing the dielectric constant of the solvent results in the expected shift of the minimum to higher concentrations, but little change occurs in the moist solutions. At concentrations below the conductance minimum,  $\log \Lambda_m - \log c$  plots were in many cases linear, with slope  $-\frac{1}{2}$ . There are thus indications of the formation of both ion-pairs and triple ions in these systems. Measurements in ferric stearate solutions were the least reproducible, but one clear feature was the presence of a maximum as well as a minimum, or a tendency towards one, in the conductance-concentration curves for the moist solutions (Fig. 2), although it is possible that this was due to some of the solute passing into colloidal rather than true solution at higher concentrations.

The lack of uniformity in conductometric behaviour from system to system is undoubtedly associated with the formation of micelles by the solute molecules in the

<sup>1</sup> Nelson and Pink, *J.*, 1954, 4412.

<sup>2</sup> Nesbitt and Pink, 2nd Internat. Congress Surface Activity, 1957, Vol. III, p. 13.

hydrocarbons, and the adsorption of ions on them. A complex pattern of behaviour may be expected, especially as concentration and temperature are varied. Among the factors to be noted which may influence the number and nature of conducting particles present are the series of equilibria of the type suggested by Burkin,<sup>3</sup> which, for the salt of an "n"-valent metal M, may be represented as:



The degree of aggregation  $x$  will depend on solute and solvent, and will increase with increase in concentration and decrease in temperature. However, the close proximity of

FIG. 1.  $\Lambda_m - c^{\frac{1}{2}}$  plot for cupric stearate "dihydrate" in *n*-decane at (A) 25°, (B) 45°, and (C) 65°.

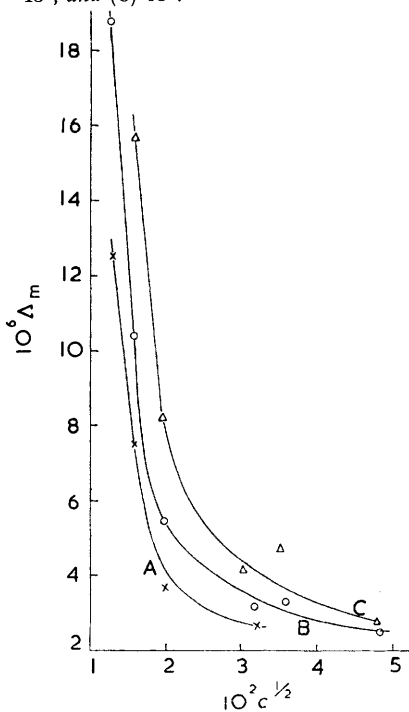
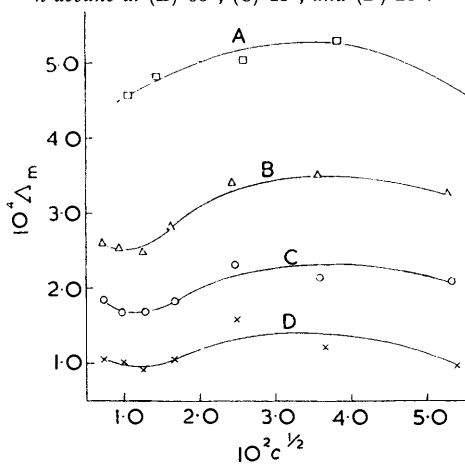


FIG. 2.  $\Lambda_m - c^{\frac{1}{2}}$  plot for ferric stearate "dihydrate": (A) in *n*-heptane at 45°; and in *n*-decane at (B) 65°, (C) 45°, and (D) 25°.



metal-carboxyl groups in the micelles would tend to increase ionisation in the micelles as compared with single molecules, and hence lead to an increase in conductance with increase in micellar complexity. This effect is opposite in direction to, and would be superimposed on, the normal ones resulting from temperature and concentration changes.

Such changes as the addition of small traces of water may bring about in the conductance of the present systems are probably to be ascribed to hydration of the solute molecules and their subsequent hydrolysis rather than to any changes in the dielectric constant of the medium. Again, however, a series of complex equilibria is possible, and until more precise data can be obtained with these systems attempts at detailed analysis of the results would be unprofitable.

The same factors would be expected to operate in solutions of these solutes in mixtures

<sup>3</sup> Burkin, *J.*, 1954, 71.

of hydrocarbons, and as expected, the conductometric behaviour of solutions of cupric and ferric stearates in three mixtures of heptane and dodecane follow the same general pattern as in single pure hydrocarbons. Such additional features as the commonly somewhat lower conductance in the mixed solvent than in the single constituent hydrocarbons, and the slightly greater variation in conductance on change of solvent, which was not always in the direction expected from the viscosity change, were not sufficiently well defined to be capable of analysis in these complex systems.

Finally, as might be expected, the conductometric behaviour of solutions, in n-heptane, of mixtures of cupric and ferric stearate did not differ markedly from that of the other systems, although the  $\Lambda_m-c^{1/2}$  curves were as a rule shallower and with less pronounced minima, and the conductances of all the anhydrous mixtures were less than those of the same concentration of ferric or of cupric salt alone. Conductances of moist mixtures were less than those of moist ferric stearate solutions in heptane. The conductance of anhydrous solute mixtures also decreased to a minimum as the composition of the solute reached equimolecular proportions, although an increase in conductance with change in solute composition was only observed in the moist solutions when the proportion of ferric stearate was more than 50% molar. The last phenomenon may also be associated with the nature of the solutes, Lawrence <sup>4</sup> having reported the occurrence of mutual peptisation of soaps in solutions containing mixtures of these solutes in non-polar solvents. This effect, with the consequent decrease in aggregation of solute molecules, would be expected to be a maximum for equimolecular mixtures, and also to reduce aggregation below that for a single pure solute of the same concentration. The observed conductance changes are thus not incompatible with these views on the nature of the solutions.

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<sup>4</sup> Lawrence, *J. Phys. Colloid Chem.*, 1948, **52**, 1510.

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## 86. *Surface Tensions of Some Molten Metal Nitrates and Nitrites.*

By C. C. ADDISON and J. M. COLDREY.

BECAUSE of their advantages as high-temperature solvents and reaction media, molten salts (particularly nitrates and chlorides) are being studied extensively, and their electrical properties, density, viscosity, vapour pressure, etc., interpreted in terms of ion association in the melt. Surface tension is also a sensitive measure of ion association, but has been less fully studied. This Note records the first measurements of the surface tensions of calcium, strontium, and barium nitrates; values for certain alkali-metal nitrates [and for silver, thallium(I), and ammonium nitrates], for which published data are scanty, have been redetermined. The surface tensions of sodium and potassium nitrites have been determined over a temperature range for comparison with the nitrates, since decomposition of molten nitrates usually produces nitrite in solution.

*Experimental.*—Surface tensions were measured by the maximum bubble pressure method by use of the apparatus shown in Fig. 1, and argon (British Oxygen Co. 99.98%) purified by

passage through Linde molecular sieve, grade 4A. The containing vessel and orifice tube were of Supremax glass, which showed no deformation below 750°. The orifice tube passed down the centre of the delivery tube (A) through which argon also passed continuously to provide a blanket of inert gas. Vertical movement of A and the orifice tube was controlled by a fine screw thread and vernier. Orifices of approx. 0.08 cm. internal diameter were used, and results calculated by using Sugden's correction factors.<sup>1</sup> The lagged steel furnace B (controlled by thermocouple T to  $\pm 1^\circ$ ) carried observation holes protected by mica windows through which bubble formation was observed; bubbles formed cleanly on the inside edge of the orifice. In most cases, tension values were determined at zero and at finite depths of immersion, and during both heating and

FIG. 1. Apparatus for determination of surface tension.

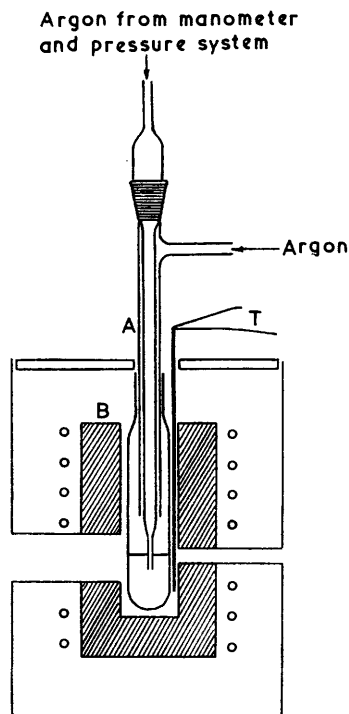
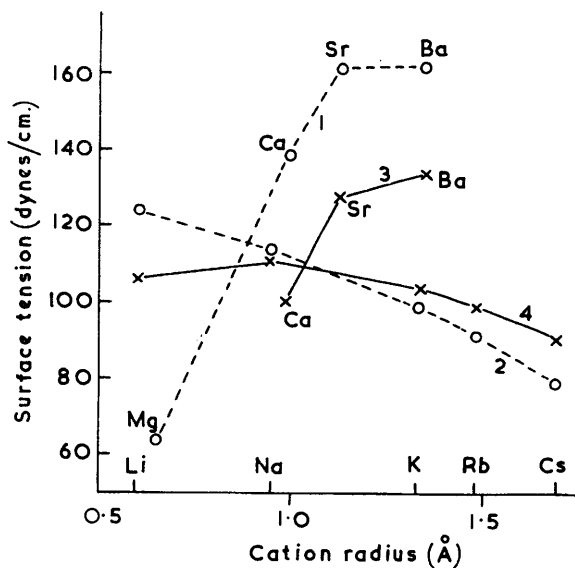


FIG. 2. Surface tensions of molten Group I and Group II chlorides and metal nitrates. (1) Group II chlorides at 1000°. (2) Group I chlorides at 800°. (3) Group II nitrates at 595° (Ba), 615° (Sr), or 560° (Ca). (4) Group I nitrates at 425°.



cooling of the melt. Results were reproducible within  $\pm 0.5$  dyne/cm. The apparatus was calibrated by using molten "AnalaR" sodium and potassium nitrates. The values given in Table 3, for comparison with the nitrites, are in good agreement with accepted values.<sup>2-6</sup>

Barium, silver, and ammonium nitrates, and sodium nitrite, were of "AnalaR" grade. The remainder were of reagent grade. The only salt containing appreciable impurity was potassium nitrite. Analysis for  $\text{NO}_2^-$  gave 95.3% purity; the remainder was nitrate and had a negligible effect on the surface tension of the nitrite (Table 3). The anhydrous salts were dried at 110° for several hours before use.

<sup>1</sup> Sugden, J., 1922, **121**, 858.

<sup>2</sup> Jaeger, Z. anorg. Chem., 1917, **101**, 1.

<sup>3</sup> Semenchenko and Shikhobalova, *Mineral Suir'e*, 1936, **11**, 27.

<sup>4</sup> Boardman, Palmer, and Heymann, *Trans. Faraday Soc.*, 1955, **51**, 277.

<sup>5</sup> Gromakev and Kostromin, *Uchenye Zapiski Kazan, Gosudarst. Univ. im. V.I. Ul'yanova-Lenina, Khim*, 1955, **115**, 93.

<sup>6</sup> Dahl and Duke, U.S.A.E.C., Publ. No. ISC-923, 1958.

*Results.* The liquid temperature range available with the alkaline-earth nitrates increases with atomic weight of the metal. The behaviour of the melts may be summarised as follows:

	Ca(NO <sub>3</sub> ) <sub>2</sub>	Sr(NO <sub>3</sub> ) <sub>2</sub>	Ba(NO <sub>3</sub> ) <sub>2</sub>
Clear, pale amber liquid, gas evolution negligible .....	555°	605°	595°
Small gas bubbles perceptible in melt .....	560	615	630
Gas evolution sufficient to interfere with tension measurement ...	575	635	675

Anhydrous magnesium nitrate decomposes almost immediately on melting. Only with barium nitrate was a determination of temperature coefficient feasible; results are given in Table 1. These values were unchanged when the melt was kept for some hours, even at 660°, so that the surface tension of molten barium nitrite must be very near to that of the nitrate. This is certainly the case for sodium and potassium nitrites (Tables 2 and 3).

TABLE 1. *Surface tension of molten barium nitrate.*

Temp.	Surface tension (dynes/cm.) *			Temp.	Surface tension (dynes/cm.) *		
	(a)	(b)	(c)		(a)	(b)	(c)
600°	134.6	134.4	134.8	640°	133.9	134.0	—
620	134.5	134.4	134.4	660	133.7	133.6	133.8

\* Depth of orifice immersion: (a) 0.5 cm., (b) 1.0 cm., (c) 1.5 cm.

TABLE 2. *Surface tensions of molten nitrites.*

NaNO <sub>2</sub>	Temp.	291°	308°	334°	355°	367°	384°
$\gamma$ (dynes/cm.) .....		120.2 *	120.0	118.9	118.0 *	117.6	116.8 *
KNO <sub>2</sub>	Temp.	445°	460°	470°	474°	480°	487°
$\gamma$ (dynes/cm.) .....		106.7 *	106.5	105.5 *	105.1	104.4 *	104.0
							501°
							103.7 *

\* Determined during the heating cycle: other values determined during subsequent cooling of the melt.

TABLE 3. *Surface tension constants.*

[ $\gamma = \alpha - \beta(t - t_0)$ , where  $t_0 =$  m. p. of salt.]

Salt	$t_0$	$\alpha$ (dynes/cm.) ( $\gamma$ at m. p.)	$\beta$ (temp. coeff., dynes cm. <sup>-1</sup> deg. <sup>-1</sup> )	Temp. range used	Lit. values (refs. in parentheses)	
					$\alpha$	$\beta$
Ca(NO <sub>3</sub> ) <sub>2</sub> ...	551°	101.5 (at 560°)	—	—	—	—
Sr(NO <sub>3</sub> ) <sub>2</sub> ...	605	128.4 (at 615°)	—	—	—	—
Ba(NO <sub>3</sub> ) <sub>2</sub> ...	595	134.8	0.015	600—660°	—	—
LiNO <sub>3</sub> .....	255	115.4	0.053	276—425	117.7 <sup>(2)</sup>	0.061 <sup>(2)</sup>
RbNO <sub>3</sub> ...	306	—	—	—	109.0 <sup>(2)</sup> , 109.1 <sup>(5)</sup>	0.074 <sup>(2)</sup> , 0.070 <sup>(5)</sup>
CsNO <sub>3</sub> .....	414	92.5	0.069	421—597	92.3 <sup>(2)</sup>	0.083 <sup>(2)</sup>
AgNO <sub>3</sub> .....	212	152.1	0.082	244—400	149.9 <sup>(6)</sup> , 170.2 <sup>(2)</sup>	0.069 <sup>(6)</sup> , 0.082 <sup>(2)</sup>
TlNO <sub>3</sub> .....	206	94.8	0.078	226—458	118.3 <sup>(2)</sup>	0.084 <sup>(2)</sup>
NH <sub>4</sub> NO <sub>3</sub> ...	170	101.9	0.105	170—220	99.5 <sup>(7)</sup>	0.062 <sup>(7)</sup>
NaNO <sub>2</sub> ...	277	121.2	0.041	291—384	119.6 <sup>(9)</sup> , 124.5 <sup>(10)</sup> , 122.7 <sup>(8)</sup>	0.07 <sup>(10)</sup> , 0.028 <sup>(9)</sup>
NaNO <sub>3</sub> ...	308	116.6	0.050	320—500	116.9 <sup>(4)</sup> , 109.9 <sup>(4)</sup>	0.057 <sup>(4)</sup>
KNO <sub>2</sub> .....	435	107.6	0.080	445—501	109.3 <sup>(8)</sup>	—
KNO <sub>3</sub> .....	334	110.8	0.073	350—520	109.9 <sup>(4)</sup> , 109.9 <sup>(4)</sup>	0.073 <sup>(4)</sup>

With all salts studied, surface tension varied linearly with temperature. The results are therefore given in Table 3 in terms of constants for the appropriate equations. The  $\alpha$  values for lithium and caesium nitrates confirm the single published values by Jaeger<sup>2</sup> though  $\beta$  differs somewhat. Jaeger's values<sup>2</sup> for the surface tension of thallos nitrate, however, are much higher than ours.

<sup>7</sup> Reh binder, *Z. phys. Chem.*, 1926, **121**, 103.

<sup>8</sup> Traube, *Ber.*, 1891, **24**, 3074.

<sup>9</sup> Bloom, Davis, and James, *Trans. Faraday Soc.*, 1960, **56**, 1179.

<sup>10</sup> Frame, Rhodes, and Ubbelohde, *Trans. Faraday Soc.*, 1959, **55**, 2039.



The significance of the surface-tension values for the molten salts of the metals of Groups I and II, in terms of ion-association, is clear from Fig. 2, in which the tensions for molten chlorides and nitrates are plotted against the ionic radius of the cations. The surface tension of the alkali-metal chlorides increases with decreasing ionic radius of the cation, and since covalency in these salts will reduce surface tension, one important factor responsible for the curvature of this graph at low ionic radii may well be the increasing covalency in the liquid state. It is noteworthy that this effect is much more pronounced in the molten nitrates, even when temperature difference is allowed for, and the surface tension of lithium nitrate is less than that for sodium nitrate at all temperatures. With the Group II metal chlorides the influence of cation radius is more than offset by the decrease in tension resulting from covalency, so that surface tensions actually decrease with decreasing cation radius. We now see that the Group II metal nitrates behave similarly, so that covalency is also pronounced in the molten nitrates.

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### 87. *The Infrared Spectra of Cobalt(III) Ethylenediamine Complexes.* *Part II.<sup>1</sup> Compounds containing the Thiocyanate Group.*

By M. E. BALDWIN.

THE infrared spectrum of the thiocyanate ion is characterised by three fundamental modes:<sup>2</sup> the C-N stretching mode  $\nu_1$  which occurs near 2050  $\text{cm}^{-1}$ , the doubly degenerate bending mode  $\nu_2$  near 480  $\text{cm}^{-1}$ , and the C-S stretch  $\nu_3$  at 750  $\text{cm}^{-1}$ .<sup>3</sup>

Cobalt(III)-ethylenediamine complexes containing ionic and co-ordinated thiocyanate have been examined in Nujol mulls in the region 2—20  $\mu$ . The absorption bands due to the thiocyanate group have been deduced by comparing the spectra of the complexes containing thiocyanate with those of the *cis*- and *trans*- $[\text{Co en}_2\text{Cl}_2]\text{Cl}$  given in Part I.<sup>1</sup> A number of the compounds were soluble in *NN*-dimethylformamide which was a useful solvent for the study of the C-N stretching region.

The frequencies recorded for the thiocyanate ion in complexes of the type  $[\text{Co en}_2\text{XY}]\text{SCN}$  were in good agreement with those found by Jones<sup>3</sup> for potassium thiocyanate and by Chamberlain and Bailar<sup>4</sup> for similar cobalt complexes. The C-S stretching frequency occurs in a region where there are bands due to the rocking of the ethylenediamine-NH<sub>2</sub> groups. On deuteration the NH<sub>2</sub> rocking frequency is shifted while the C-S stretching frequency is unaffected. The assignment of the C-S stretching band was confirmed from the unshifted bands in the spectra of three deuterated complex thiocyanate salts: *trans*- $[\text{Co en}_2\text{Cl}_2]\text{SCN}$ , *trans*- $[\text{Co en}_2\text{NCS}(\text{OH})]\text{SCN}$ , and  $[\text{Co en}_3](\text{SCN})_3$  (see Table 1).

The frequencies of absorption bands due to the co-ordinated isothiocyanate group in compounds of the type  $[\text{Co en}_2(\text{NCS})\text{Y}]\text{Z}$  are given in Table 2.

Chamberlain and Bailar have assigned a band in the region of 780  $\text{cm}^{-1}$  to the C-S stretch of the isothiocyanato-group in complexes of this type. A comparison of the spectra of compounds containing the isothiocyanato-ligand with those of the *cis*- and *trans*- $[\text{Co en}_2\text{Cl}_2]^+$  cations indicates that the band in the region of 830  $\text{cm}^{-1}$  is due to the isothiocyanato-group, while that in the 780  $\text{cm}^{-1}$  region is due to a vibration of the NH<sub>2</sub> group. Confirmation of these assignments was obtained by the deuteration of *trans*- $[\text{Co en}_2(\text{NCS})\text{OH}]\text{SCN}$ .

<sup>1</sup> Part I, Baldwin, *J.*, 1960, 4369.

<sup>2</sup> Herzberg, "Infrared and Raman Spectra," Van Nostrand, New York, 1945, p. 174.

<sup>3</sup> Jones, *J. Chem. Phys.*, 1956, **25**, 1069.

<sup>4</sup> Chamberlain and Bailar, *J. Amer. Chem. Soc.*, 1959, **81**, 6412.

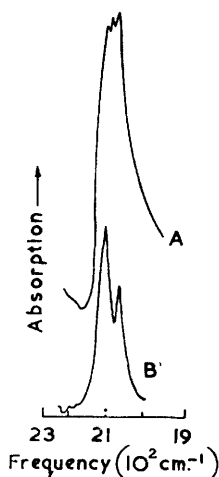
TABLE 1. *Frequencies (cm.<sup>-1</sup>) of absorption bands due to the thiocyanate ion in compounds of the type [Co en<sub>2</sub>XY]SCN.*

Complex cation	$\nu_1$ (mull)	$\nu_1$ (soln.)	$2\nu_2$	$\nu_3$
<i>trans</i> -[Co en <sub>2</sub> Cl <sub>2</sub> ] <sup>+</sup> .....	2046	—	939 } 927 }	754
<i>trans</i> -[Co en <sub>2</sub> Cl <sub>2</sub> ] <sup>+</sup> (D) .....	2053			758
<i>trans</i> -[Co en <sub>2</sub> NCS(Cl)] <sup>+</sup> .....	2053	2058	936	730
<i>trans</i> -[Co en <sub>2</sub> NCS(OH)] <sup>+</sup> .....	2041	2058	945	740
<i>trans</i> -[Co en <sub>2</sub> NCS(OH)] <sup>+</sup> (D) .....	2041			735
<i>trans</i> -[Co en <sub>2</sub> (NCS) <sub>2</sub> ] <sup>+</sup> .....	2070 <sup>a</sup>	2058	943	764
<i>cis</i> -[Co en <sub>2</sub> Cl <sub>2</sub> ] <sup>+</sup> .....	2058		938 } 930 }	746
<i>cis</i> -[Co en <sub>2</sub> NCS(NO <sub>2</sub> )] <sup>+</sup> .....	2045	2053	963 } 935 }	755
<i>cis</i> -[Co en <sub>2</sub> Cl(NO <sub>2</sub> )] <sup>+</sup> .....	2070		954 } 928 }	752
[Co en <sub>3</sub> ] <sup>3+</sup> .....	2066 } 2033 }	2053	945 } 926 }	757 } 745 }
[Co en <sub>3</sub> ] <sup>3+</sup> (D) .....	2053 } 2008 }			756 } 743 }

D = deuterated complex. <sup>a</sup> See Fig.TABLE 2. *Frequencies (cm.<sup>-1</sup>) of absorption bands attributed to the -NCS group in compounds of the type [Co en<sub>2</sub>(NCS)Y]Z.*

Confign.	Y	Z	$\nu_1$ (mull)	$\nu_1$ (soln.)	$\nu_3$
<i>trans</i>	Cl	SCN	2137	2105	833
<i>trans</i>	Cl	S <sub>2</sub> O <sub>6</sub>	2132, 2088		833
<i>trans</i>	NCS	NO <sub>2</sub>	2110		836
<i>trans</i>	NCS	Cl	2119		840
<i>trans</i>	OH	SCN	2128	2105	833
<i>trans</i>	NCS	SCN	2105	2101	835
<i>cis</i>	Cl	Cl	2141		824
<i>cis</i>	Cl	ClO <sub>4</sub>	2128		826 <sup>a</sup>
<i>cis</i>	NCS	Cl	2141, 2110		833, 823
<i>cis</i>	NCS	NO <sub>2</sub>	2123		835, 824
<i>cis</i>	NO <sub>2</sub>	NO <sub>2</sub>	2167, 2137	2110	<sup>b</sup>
<i>cis</i>	NO <sub>2</sub>	SCN	2128	2114	<sup>b</sup>
<i>cis</i>	OH <sub>2</sub>	S <sub>2</sub> O <sub>6</sub>	2146		833

<sup>a</sup> Reported by Chamberlain and Bailar <sup>4</sup> to be obscured by the broad absorption of the ClO<sub>4</sub><sup>-</sup> ion; however, ClO<sub>4</sub><sup>-</sup> shows no absorption between 1000 cm.<sup>-1</sup> and the very strong band at 620 cm.<sup>-1</sup>.<sup>5</sup>  
<sup>b</sup> Obscured by the strong absorption band of the co-ordinated nitro-group.<sup>6</sup>



*trans*-[Co en<sub>2</sub>(NCS)<sub>2</sub>]SCN: (A) solid mull;  
 (B) solution in NN-dimethylformamide.

<sup>5</sup> Miller and Wilkins, *Analyt. Chem.*, 1952, **24**, 1253.

<sup>6</sup> Chatt, Duncanson, Gatehouse, Nyholm, Tobe, Todd, and Venanzi, *J.*, 1959, 4073.

In trisethylenediaminecobalt(III) thiocyanate, the N-C stretching frequency is split into two sharp bands occurring at 2033 and 2066  $\text{cm}^{-1}$ . In solution in *NN*-dimethylformamide only one band at 2053  $\text{cm}^{-1}$  is observed. Similarly, in the solid mull, *trans*- $[\text{Co en}_2(\text{NCS})_2]\text{SCN}$  shows at least three bands close together at 2105, 2092, and 2070  $\text{cm}^{-1}$ . In solution the bands due to the N-C stretching in both the ionic and the co-ordinated thiocyanate appear at their characteristic frequencies, *viz.*, 2101 and 2058  $\text{cm}^{-1}$  (see Figure).

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## 88. *The Formation of Ferrocenium Thiocyanate in Mixed Aqueous Solvents.*

By T. D. SMITH.

ADDITION of ammonium thiocyanate to a solution of ferrocenium perchlorate in various non-aqueous solvents leads to the formation of a highly coloured, stable complex, though no reaction occurs in water. Adding of water destroys the colour owing to dissociation of the complex.

The ion  $\text{Fe}(\text{SCN})^{2+}$ , though readily formed in water, is also affected by solvent composition, and it has been suggested<sup>1</sup> that the increase in absorption of its aqueous solution with increasing concentration of acetone was due to the lower dielectric constants of the mixed media. Further, in solutions containing a large excess of thiocyanate, complexes of iron(III) containing more than one ligand exist.<sup>2</sup>

A recent study<sup>3</sup> showed that the ferrocenium ion is able to form stable yellow complexes with a variety of organic ligands.

*Experimental.*—A stock solution of ferrocenium perchlorate was prepared by electrolytic oxidation of ferrocene in ethanol, methanol, and acetone containing perchloric acid.<sup>4</sup> The concentration of the ferrocenium perchlorate in ethanol was adjusted so that when it was added to the other solvent the amount of ethanol in the resulting solution made no difference to the spectra of the solution. Solutions of thiocyanate were made from "AnalaR" ammonium thiocyanate in the appropriate solvent. The water content of the solutions was adjusted by adding weighed amounts of water to the organic solvent.

The acetone used was redistilled and dried over potassium carbonate. Redistilled methanol was distilled from magnesium turnings. Absolute alcohol was used without further purification. Dimethylformamide was purified by distillation. "AnalaR" glacial acetic acid was used as such.

Spectra were taken with a Hilger Uvispek spectrophotometer with a glass prism and glass cells.

*Results and Discussion.*—The absorption spectrum of an ethanolic ferrocenium solution containing an excess of thiocyanate (Fig. 1) illustrates the effect of water. The stoichiometry in ethanol solution, investigated by Job's method<sup>5</sup> (Fig. 2), indicates a 1:1 compound. Similar plots indicate that a 1:1 compound is formed also in all the other solvents mentioned. The absorption of the ferrocenium thiocyanate is dependent on the nature of the solvent, as shown by Fig. 3.

Adding water to methanol, ethanol, and acetone solutions of ferrocenium thiocyanate

<sup>1</sup> Baldwin and Svirbely, *J. Amer. Chem. Soc.*, 1949, **71**, 3326.

<sup>2</sup> Lister and Rivington, *Canad. J. Chem.*, 1955, **33**, 1572.

<sup>3</sup> Smith, *J. Inorg. Nuclear Chem.*, 1960, **14**, 290.

<sup>4</sup> Page and Wilkinson, *J. Amer. Chem. Soc.*, 1952, **74**, 6149.

<sup>5</sup> Job, *Ann. Chim. (France)*, 1928, **9**, 113.

decreases the intensity of absorption. The effect of the added water may be expressed in terms of the equilibrium constant  $K^n_{\text{solvent}}$  where

$$K^n_{\text{solvent}} = \frac{\gamma(\text{C}_5\text{H}_5)_2\text{FeSCN}}{\gamma(\text{C}_5\text{H}_5)_2\text{Fe}^+ \cdot \gamma\text{CNS}^-} \cdot \frac{\gamma^n\text{H}_2\text{O}}{\gamma_{\text{solvent}}} \cdot \frac{[(\text{C}_5\text{H}_5)_2\text{FeSCN}][\text{H}_2\text{O}]^n}{[(\text{C}_5\text{H}_5)_2\text{Fe}^+][\text{CNS}^-][\text{solvent}]}$$

and  $\gamma$  denotes an activity coefficient. First, for acetone–water mixtures, wavelengths were chosen at which Beer's law held for ferrocenium thiocyanate in pure acetone solution. Then, on the assumption that the molar extinction coefficient of the compound remained constant on addition of water and with wavelengths where the absorption of the free ferrocenium ion could be neglected, the concentration of the ferrocenium thiocyanate was estimated.

The values obtained for the concentration quotient  $K'_{\text{acetone}}$  for various additions of water are shown by Table 1 for  $n = 1$ . The values of the activity coefficients of the

TABLE 1.

$(\text{C}_5\text{H}_5)_2\text{FeSCN}$ ( $10^{-4}\text{M}$ )	$(\text{C}_5\text{H}_5)_2\text{Fe}^+$ ( $10^{-4}\text{M}$ )	$\text{NH}_4\text{CNS}$ ( $10^{-2}\text{M}$ )	$\text{H}_2\text{O}$ (M)	Acetone (M)	$K'_{\text{acetone}}$	$\frac{\gamma_{\text{H}_2\text{O}}}{\gamma_{\text{acetone}}} \cdot K_{\text{acetone}}$
0.765	0.235	1.000	2.78	13.4	67.5	—
0.495	0.506	1.000	8.34	12.0	67.9	81.0
0.408	0.592	1.000	11.12	11.3	67.9	77.3
0.325	0.675	1.000	13.9	10.4	64.2	69.0

compound and the ionic species under the varying solvent conditions are not known. However, the activities of the water in acetone and of acetone in water at the higher mole fractions of water may be determined from vapour-pressure data,<sup>6</sup> and the influence of the

FIG. 1. Absorption spectra (1 cm. cell) of  $2.00 \times 10^{-4}\text{M}$ -ferrocenium thiocyanate in ethanol containing (1) 0, (2) 2.78, (3) 5.56, (4) 13.9, and (5) 27.8 mol. of water.

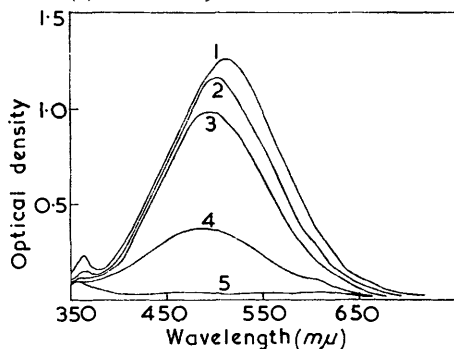
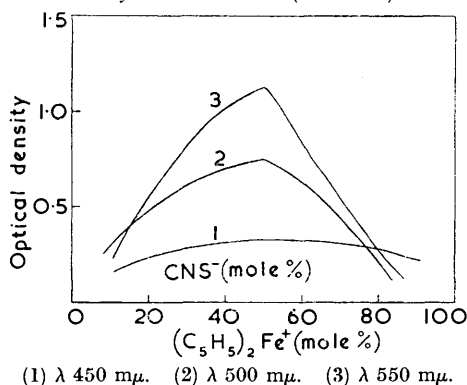


FIG. 2. Continuous-variation plot for ferrocenium thiocyanate in ethanol (1 cm. cell).



variation of the appropriate activities of the solvent system on  $K'_{\text{acetone}}$  is detailed by Table 1. Under the varying solvent conditions the activities of the ionic species and of the complex will change, especially in the region of low mole fractions of water.

Similar considerations resulting from the spectra of water–ethanol and water–methanol solutions of ferrocenium thiocyanate may be expressed in terms of the equilibrium constants  $K^n_{\text{ethanol}}$  and  $K^n_{\text{methanol}}$ . Again, the values of the activity coefficients of the compound and of the ionic species under the solvent conditions are not known. However, the values of the activity coefficients of water in alcohols and of the alcohols in water at the mole fractions concerned here have been determined by Butler *et al.*<sup>7</sup> The values of the concentration quotients  $K^{1'}_{\text{ethanol}}$  and  $K^{2'}_{\text{ethanol}}$  are shown in Table 2, as well as the

<sup>6</sup> International Critical Tables, Vol. III, p. 290, 1928.

<sup>7</sup> Butler, Thomson, and MacLennan, 1933, 674.

effect of the activity coefficients. The results for water-methanol system are shown in Table 3.

In the three solvent systems the activity coefficients of the solvent mixtures considerably affect the values of the concentration quotients, and variations resulting from the changing activity coefficients of the ionic species also occur. In each case the essential

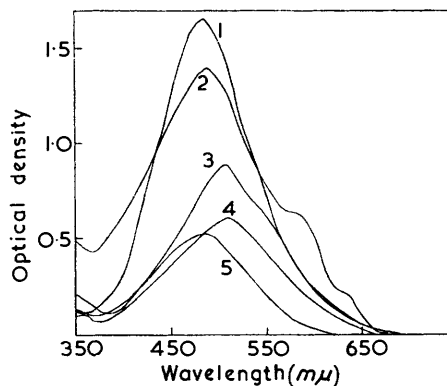


FIG. 3. Absorption spectra of  $1.00 \times 10^{-4}M$  ferrocenium thiocyanate in (1) acetone, (2) acetic acid, (3) methanol, (4) ethanol, and (5) dimethylformamide (1 cm. cell).

process involved in the dissociation of the compound is replacement of the thiocyanate ion by a water molecule. However, from the results it is impossible to elucidate the solvation of the organic molecules. For alcohol-water systems consistent results for the final

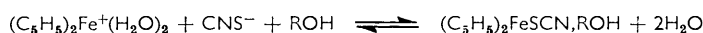
TABLE 2.

$(C_5H_5)_2FeSCN$ ( $10^{-4}M$ )	$(C_5H_5)_2Fe^+$ ( $10^{-4}M$ )	$NH_4CNS$ ( $10^{-3}M$ )	$H_2O$ (M)	$EtOH$ (M)	$K^1_{EtOH}$	$K^2_{EtOH}$	$\frac{\gamma^2_{H_2O}}{\gamma_{MeOH}} \cdot K^2_{EtOH}$
1.60	0.40	2.00	2.78	16.27	34.2	190	878
1.29	0.71	2.00	5.58	15.40	32.8	360	1150
0.94	1.06	2.00	8.34	14.25	25.9	384	944
0.45	1.55	2.00	13.9	12.80	15.6	438	701

TABLE 3.

$(C_5H_5)_2FeSCN$ ( $10^{-4}M$ )	$(C_5H_5)_2Fe^+$ ( $10^{-4}M$ )	$NH_4CNS$ (10M)	$H_2O$ (M)	$MeOH$ (M)	$K^1_{MeOH}$	$K^2_{MeOH}$	$\frac{\gamma^2_{H_2O}}{\gamma_{MeOH}} \cdot K^2_{MeOH}$
0.875	0.125	1.00	2.78	23.63	82.5	225	527
0.713	0.287	1.00	5.56	22.4	61.7	346	678
0.400	0.600	1.00	10.15	19.9	34.0	345	569
0.250	0.750	1.00	13.9	18.7	24.8	345	497

product in Tables 2 and 3 are obtained when  $n = 2$ . Bearing in mind the uncertainties of the state of solvation of the species in these solutions the following equilibrium process is tentatively proposed for the water-alcohol solutions:



The spectrophotometric data indicate that the maximum absorption in the solvents containing the C=O group is in the region 490  $m\mu$  whilst the maximum absorption in the alcohols occurs in the region 510  $m\mu$  which may be due to structural differences in these solvents.<sup>8</sup>

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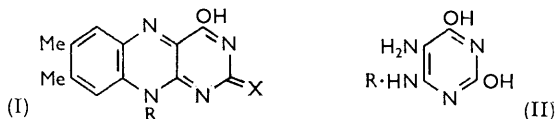
[Received, June 8th, 1960.]

<sup>8</sup> Chu, Fujii, and Li, *J. Amer. Chem. Soc.*, 1955, **77**, 2085.

### 89. Pteridine Derivatives. Part VIII.<sup>1</sup> A New Synthesis of Riboflavin and Related Isoalloxazines.

By R. M. CRESSWELL, THOMAS NEILSON, and H. C. S. WOOD.

THE synthesis of alloxazines by condensation of 4,5-diaminopyrimidines with the dimer of 3,4-dimethyl-*o*-benzoquinone has recently been described by Bardos, Olsen, and Enkoji.<sup>2</sup> In Part VII<sup>1</sup> of this series we described the synthesis of "lumiflavin 2-imine" (I; R = Me, X = NH) by a modification of this method. We have now extended the reaction to the synthesis of riboflavin and related isoalloxazines.



Condensation of 5-amino-4-D-ribitylamino-2,6-dihydroxy-1,2,4-triazine (II; R = D-ribityl) with the dimer<sup>2</sup> of 3,4-dimethyl-*o*-benzoquinone gave a 29% yield of riboflavin (I; R = D-ribityl, X = O), identified by mixed m. p., paper chromatography, and ultraviolet and infrared spectra. The pyrimidines (II; R = Me, CH<sub>2</sub>·CH<sub>2</sub>-OH, D-mannityl, and D-sorbityl) similarly gave the corresponding isoalloxazines (I). The 5-aminopyrimidines (II) were prepared by reduction of the 5-nitro-compounds<sup>3,4</sup> with sodium dithionite.

Lumiflavin (I; R = Me, X = O) and its 2-hydroxyethyl analogue were identified by comparison with authentic materials.<sup>5,6</sup> The D-sorbityl compound agrees in m. p. and optical rotation with that recorded by Euler *et al.*<sup>7</sup> although these authors do not give preparative or analytical details.

*Experimental.*—For general instructions see Part VII.<sup>1</sup>

*Riboflavin* (I; R = D-Ribityl, X = O). 5-Nitro-4-D-ribitylamino-2,6-dihydroxy-1,2,4-triazine<sup>3</sup> (0.25 g.) in water (10 c.c.) at 90° was treated with N-sodium hydroxide (5 c.c.), followed by sodium dithionite portionwise until the solution became colourless. Glacial acetic acid was added to the cooled solution to give pH 4, followed by dimeric 3,4-dimethyl-*o*-benzoquinone<sup>2</sup> (0.15 g.) in ethanol (10 c.c.). The mixture was heated for 30 min. on the steam-bath and finally acidified by 12N-hydrochloric acid. On cooling, riboflavin separated as orange needles (0.09 g., 29%), m. p. 288° (lit.,<sup>8</sup> 292°),  $[\alpha]_D^{23} - 116^\circ$  (c 0.53 in 0.1N-NaOH) (lit.,<sup>9</sup> -115°). The ultraviolet and infrared spectra were identical with those of an authentic sample.

The following isoalloxazines (orange needles) were prepared by similar methods, and where applicable the ultraviolet and infrared spectra of the products were compared with those of authentic materials: Lumiflavin (I; R = Me, X = O) (obtained from 4-methylamino-5-nitro-2,6-dihydroxy-1,2,4-triazine<sup>3</sup> in 40% yield), m. p. 325—326° (lit.,<sup>5</sup> 328°).

9-(2'-Hydroxyethyl)-6,7-dimethylisoalloxazine (I; R = CH<sub>2</sub>·CH<sub>2</sub>-OH, X = O) (from 4-(2'-hydroxyethylamino)-5-nitro-2,6-dihydroxy-1,2,4-triazine<sup>3</sup> 29%), m. p. 297—299° (lit.,<sup>6</sup> 300—301°).

9-D-Mannityl-6,7-dimethylisoalloxazine (I; R = D-mannityl, X = O) (from 4-D-mannitylamino-5-nitro-2,6-dihydroxy-1,2,4-triazine<sup>4</sup> 49%), m. p. 285° (Found: C, 52.4; H, 5.2; N, 13.5. C<sub>18</sub>H<sub>22</sub>N<sub>4</sub>O<sub>7</sub>·0.5H<sub>2</sub>O requires C, 52.1; H, 5.6; N, 13.5%),  $[\alpha]_D + 61^\circ$  (c 0.18 in 0.05N-NaOH),  $\lambda_{max}$  223 ( $\epsilon$  34,300), 266 ( $\epsilon$  37,000), 374 ( $\epsilon$  12,600), and 444 m $\mu$  ( $\epsilon$  13,500) at pH 1, 222 ( $\epsilon$  23,000), 270 ( $\epsilon$  26,700), 356 ( $\epsilon$  8900), and 445 m $\mu$  ( $\epsilon$  8500) at pH 13.

<sup>1</sup> Part VII, Cresswell, Hill, and Wood, *J.*, 1959, 698.

<sup>2</sup> Bardos, Olsen, and Enkoji, *J. Amer. Chem. Soc.*, 1957, **79**, 4704.

<sup>3</sup> Cresswell and Wood, *J.*, 1960, 4768.

<sup>4</sup> Cresswell, Neilson, and Wood, *J.*, 1960, 4776.

<sup>5</sup> Kuhn, Rudy, and Wagner-Jauregg, *Ber.*, 1933, **66**, 1950.

<sup>6</sup> Fall and Petering, *J. Amer. Chem. Soc.*, 1956, **78**, 377.

<sup>7</sup> Euler, Karrer, Malmberg, Schöpp, Benz, Becker, and Frei, *Helv. Chim. Acta*, 1935, **18**, 522.

<sup>8</sup> Kuhn, Reinemund, Weygand, and Ströbele, *Ber.*, 1935, **68**, 1765.

<sup>9</sup> Kuhn and Rudy, *Ber.*, 1935, **68**, 169.

6,7-Dimethyl-9-D-sorbitylisoalloxazine (I; R = D-sorbityl, X = O) (from 5-nitro-4-D-sorbitylaminouracil; <sup>4</sup> 23%), m. p. 275° (lit.,<sup>7</sup> 272°) (Found: C, 52.1; H, 5.5; N, 13.4. C<sub>18</sub>H<sub>22</sub>N<sub>4</sub>O<sub>7</sub>·0.5H<sub>2</sub>O requires C, 52.1; H, 5.6; N, 13.5%), [α]<sub>D</sub> -45° (c 0.18 in 0.05N-NaOH) (lit.,<sup>7</sup> -47.7°), λ<sub>max</sub> 222 (ε 27,500), 266 (ε 29,600), 374 (ε 10,000), and 444 (ε 11,400) at pH 1, 222 (ε 25,000), 270 (ε 28,100), 356 (ε 9900), and 449 mμ (ε 9700) at pH 13. With pyridine and acetic anhydride it gave the *acetate*, m. p. 238° (lit.,<sup>7</sup> 237°) (Found: C, 54.5; H, 5.9. C<sub>28</sub>H<sub>32</sub>N<sub>4</sub>O<sub>12</sub>·C<sub>2</sub>H<sub>5</sub>·OH requires C, 54.4; H, 5.8%).

The authors thank the British Empire Cancer Campaign for a research grant, and the D.S.I.R. for a Research Studentship (to R. M. C.).

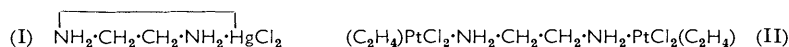
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GLASGOW.

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## 90. The Infrared Spectra and Structures of the Complexes Dichloro(ethylenediamine)-zinc, -cadmium, and -mercury.

By G. NEWMAN and D. B. POWELL.

THE usual complexes of zinc(II) and cadmium(II) with ethylenediamine contain 2 or 3 chelated ligands, such as [Cd en<sub>3</sub>]Cl<sub>2</sub>.<sup>\*</sup> Insoluble compounds have been prepared of the type M enCl<sub>2</sub> (M = Zn, Cd, Hg), by addition of ethylenediamine to solutions of the respective chlorides. It has been suggested<sup>1</sup> that the mercury complex contains a chelated ethylenediamine group, as in (I). This is supported by Sutton's ultraviolet spectroscopic measurements.<sup>2</sup>



The infrared spectra of these compounds (Figs. 1*b*, 1*c*, 1*d*) are much simpler than that of the chelated [Cd en<sub>3</sub>]Cl<sub>2</sub> (Fig. 1*a*), and very similar to that of compound (II) (Fig. 1*e*) when allowance is made for the absorption peaks due to ethylene. Compound (II) contains a bridging ethylenediamine group with the *trans*-configuration, and a fairly complete assignment of the absorption bands to the fundamental vibrations has been made on this basis.<sup>3</sup>

In the Table the absorption frequencies for dichloro(ethylenediamine)-zinc, -cadmium, and -mercury are compared with those obtained for the platinum compound (II). In spite of some quite large frequency changes, the corresponding absorption bands can be

### Infrared absorption frequencies (cm.<sup>-1</sup>) of ethylenediamine complexes.

Zn enCl <sub>2</sub>	Cd enCl <sub>2</sub>	Hg enCl <sub>2</sub>	(II)	Assignment
1575	1612	1610	1551	δNH <sub>2</sub> scissors
1455	1483	1490	1452	δCH <sub>2</sub> scissors
1377	1374?	1374?	1375	δCH <sub>2</sub> wag
1339	1334	1351	1336	δNH <sub>2</sub> wag
1278	1278	1278	1280	δCH <sub>2</sub> twist
1140	1099	1180	1190	δNH <sub>2</sub> twist
1008	1017	1007	1052?	ν skeletal
792	847	820	752	δCH <sub>2</sub> rock
665	} 540	683	653	δNH <sub>2</sub> rock
(630)				

readily identified, and there seems no doubt that the ethylenediamine group in all these compounds has the same configuration. An interesting feature of the spectra (1*b*, *c*, and

\* The symbol en represents the ethylenediamine molecule.

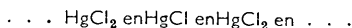
<sup>1</sup> O'Brien, *J. Amer. Chem. Soc.*, 1948, **70**, 2771.

<sup>2</sup> Sutton, *Austral. J. Chem.*, 1959, **12**, 637.

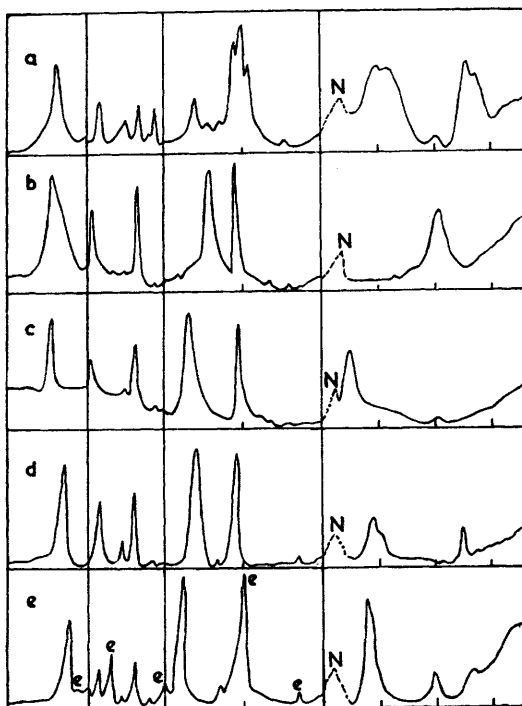
<sup>3</sup> Powell and Sheppard, *J.*, 1959, 3089.

d) is the prominence of the skeletal stretching vibration near  $1000\text{ cm}^{-1}$ . This vibration was difficult to detect in the spectrum of compound (II), and is obscured by the strong absorption in this region due to the ethylene group.

Chelate structures for dichloro(ethylenediamine)-zinc, -cadmium, and -mercury would clearly be inconsistent with this infrared evidence, and the most probable structures would be polymeric chains with ethylenediamine molecules joined to different metal atoms, *viz.*,



Such a structure has been found<sup>4,5</sup> for the dioxan-mercuric chloride complex,  $\text{Hg}(\text{C}_4\text{H}_8\text{O}_2)_2\text{Cl}_2$ , and would account for the insolubility of these compounds. With the



*Infrared absorption spectra of complexes:*  
 a,  $[\text{Cd en}_3]\text{Cl}_2$ ; b,  $\text{Cd enCl}_2$ ; c,  $\text{Zn enCl}_2$ ;  
 d,  $\text{Hg enCl}_2$ ; and e, (II).  
 (1)  $1750$ — $1500$  and  $1250$ — $400\text{ cm}^{-1}$ ,  
 Nujol mulls;  $1500$ — $1250\text{ cm}^{-1}$ , hexa-  
 chlorobutadiene mull.  
 (2) Absorption marked N is due to Nujol;  
 absorption peaks marked "e" in 1(e)  
 are due to ethylene.

cadmium chloride complex, the low, variable values obtained for the C, H, and N determinations probably arise from the formation of chains of fairly low molecular weight and terminated by  $\text{CdCl}_2$  groups. The infrared spectrum of another known<sup>1</sup> mercuric chloride complex,  $(\text{HgCl}_2)_2\text{en}$ , also has a *trans*-bridging ethylenediamine group. This compound with the ethylenediamine group bridging two mercuric chloride molecules would probably represent the first stage in the building of the polymeric chain, which reaches the limiting case with the compound  $\text{Hg enCl}_2$ .

*Experimental.*—All spectra were obtained with a Hilger H.800 spectrometer with rock-salt and potassium bromide optics. The samples were examined as dispersions in liquid paraffin and hexachlorobutadiene.

$\text{Hg enCl}_2$  and  $(\text{HgCl}_2)_2\text{en}$  were prepared by O'Brien's method.<sup>1</sup>  $\text{Cd enCl}_2$  was prepared in the same manner as its mercury analogue; aqueous ethylenediamine (*ca.*  $1\text{M}$ ) was added to

<sup>4</sup> Tarte and Laurent, *Bull. Soc. chim. France*, 1957, 403.

<sup>5</sup> Hassel and Hvoslef, *Acta Chem. Scand.*, 1954, 8, 1953.



aqueous 1M-cadmium chloride, giving a white insoluble precipitate, which was washed successively with water, alcohol, and ether, and dried *in vacuo* ( $P_2O_5$ ) (Found: C, 9.1, 8.8; H, 3.2, 3.0; N, 10.5. Cd enCl<sub>2</sub> requires C, 9.9; H, 3.3; N, 11.5%). Zn enCl<sub>2</sub> can be obtained as a white precipitate, on addition of 1 mole of ethylenediamine in 20% aqueous alcohol (v/v) to an alcoholic solution containing 1 mole of anhydrous zinc chloride (Found: C, 11.9; H, 4.2. Zn enCl<sub>2</sub> requires C, 12.2; H, 4.1%).

Difficulty was experienced in repeating the last preparation and conditions appear to be critical for the formation of this complex. In the spectrum shown (Fig. 1*d*) the shoulder at 630 cm.<sup>-1</sup> may be due to impurity, as its intensity varied with different preparations, and was decreased by repeated washing with water.

One of the authors (G. N.) thanks the Department of Scientific and Industrial Research for a maintenance grant.

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### 91. *The Action of N-Bromosuccinimide on 1,2,3,4-Tetraphenylcyclobutane.*

By W. BAKER, (MISS) J. W. HILPERN, and J. F. W. McOMIE.

IN an attempt to introduce one or two double bonds into the four-membered ring of 1,2,3,4-tetraphenylcyclobutane, a solution of this compound in carbon tetrachloride was treated with *N*-bromosuccinimide. The product was shown to be 1,2,3,4-tetraphenylbuta-1,3-diene, presumably formed by bromination followed by dehydrobromination with concurrent ring-opening.

The tetraphenylcyclobutane was prepared in 20% yield by ultraviolet irradiation of stilbene. Previously this compound had been made in low yield by exposure of stilbene to sunlight<sup>1</sup> for 2 years and in 7% yield by using ultraviolet light.<sup>2</sup> The cyclobutane is known to have the *cis-anti-cis*-structure.<sup>3</sup>

*Experimental.*—1,2,3,4-Tetraphenylcyclobutane. Stilbene (20 g.) in warm benzene (150 ml.) was irradiated in an atmosphere of nitrogen for 48 hr. in an annular Pyrex glass vessel (5.5 cm. internal diameter) surrounding a Hanovia U.V.S. 500 ultraviolet lamp. After evaporation of the solvent, the residue was shaken with ether and filtered. The insoluble portion was crystallised four times from ethanol, giving 1,2,3,4-tetraphenylcyclobutane (4 g.), m. p. 162—163° (lit., 163°). Stilbene (3 g.) was obtained from the ether extract.

1,2,3,4-Tetraphenylbuta-1,3-diene. A mixture of the cyclobutane (1 g.), *N*-bromosuccinimide (0.4 g.), dibenzoyl peroxide (40 mg.), and carbon tetrachloride was boiled gently under reflux for 1 hr. After being filtered the solution was evaporated under reduced pressure and the residue purified by chromatography on alumina with benzene as solvent. The material which formed a yellow band (violet under ultraviolet light) was eluted with benzene and purified by four-fold crystallisation from benzene, giving 1,2,3,4-tetraphenylbuta-1,3-diene (0.4 g., 40%), m. p. and mixed m. p. with an authentic<sup>4</sup> specimen, 183—184° (Found: C, 93.9; H, 6.5. Calc. for C<sub>28</sub>H<sub>22</sub>: C, 93.8; H, 6.2%). The infrared spectrum of the product was identical with that of a sample kindly supplied by Professor J. Coops.

THE UNIVERSITY, BRISTOL.

[Received, June 24th, 1960.]

<sup>1</sup> Ciamician and Silber, *Ber.*, 1902, **35**, 4128.

<sup>2</sup> Pailer and Müller, *Monatsh.*, 1948, **79**, 615.

<sup>3</sup> Dunitz, *Acta Cryst.*, 1949, **2**, 1.

<sup>4</sup> Coops, Hoijtink, Kramer and Faber, *Rec. Trav. chim.*, 1953, **72**, 765.

92. *Submicro-methods for the Analysis of Organic Compounds*  
*Part XIII.\* The Cryoscopic Determination of Molecular Weight.*

By R. BELCHER, M. SOBOTKA, and W. I. STEPHEN.

THE cryoscopic method for the determination of molecular weight<sup>1</sup> appeared to be very suitable for adaption to the submicro-scale because of the favourable depression of the melting point of camphor, the solvent which is generally used. Because of the small quantities involved it is necessary to use capillaries instead of the comparatively wide tubes used on the microscale and the main problem was the weighing and transference of the sample without loss to the weighed camphor. This was overcome by weighing the capillary, transferring the camphor to it and reweighing the added camphor on the *micro-balance*. To transfer the sample quantitatively after weighing on the *submicro-balance*, a new technique described in the experimental section was developed. This has certain limitations but has proved satisfactory for a wide range of organic compounds.

Several methods of heating the capillary were examined, including the use of a conventional oil-bath, but in this medium it was not only difficult to make accurate observations of the melting and crystallising points of the solution in the narrow tube, but also the tube could not be shaken. The preferred method makes use of a commercial electrical melting-point apparatus, which provides adequate magnification of the tube and its contents; moreover, the possibility of moving the tube in the apparatus enables the solute to be thoroughly mixed with solvent during the melting process.

Since the method involves temperature differences only, this type of apparatus can be used provided that the rates of heating and cooling at temperatures in the immediate vicinity of the melting and crystallising point are controlled. In the present work, the crystallisation temperature was found to be more easily observed than the melting point and therefore was used throughout the study. Observations of the crystallisation of pure camphor indicated that the rate of cooling of the apparatus was very critical. When the temperature of the heating block was raised to 5° above the melting point of camphor, *i.e.*, to about 185°, and the current to the heating element was then cut off, so that a rapid cooling rate was established, the characteristic fine network of camphor crystals appeared at 180°. However, when the cooling rate was adjusted by rheostat control so that the temperature fell 1° per minute, crystallisation occurred at 176°. An intermediate cooling rate of 1° per 20 seconds gave a crystallisation point of 178·4—178·6°. This rate of cooling was sufficiently slow to allow observation of the crystallisation temperature to be made within 0·2°. Similar differences in temperature were observed for the crystallisation points of a solution of acetanilide in camphor so that the actual depression of the crystallisation point of camphor was constant for a particular rate of cooling.

Determination of the cryoscopic constant of camphor by using acetanilide as solute gave values for 36 to 40, depending on the cooling rate. When this was standardised during any one series of determinations the molecular depression remained constant.

In preliminary experiments the capillaries were made with rounded ends. A series of qualitative tests with acetanilide as solute gave abnormal but constant values for the crystallisation temperature. These were attributed to the formation of eutectic mixtures of acetanilide and camphor, and true solutions were not obtained. When flat-ended tubes were used and agitated in the apparatus, the loosened platinum wire acted as a stirrer and the contents of the tube were adequately mixed. This completely prevented the formation of the low-melting eutectics and was adopted in all the quantitative work.

\* Part XII, *J.*, 1960, 3830.

<sup>1</sup> Le Fèvre, *Nature*, 1930, **126**, 760; Le Fèvre and Tideman, *Nature*, 1931, **127**, 972; Le Fèvre and Webb, *J.*, 1931, 1211; Le Fèvre and Tideman, *J.*, 1931, 1729.

Results for a number of organic compounds are given in the Table. The weights of sample ranged from 30 to 96  $\mu\text{g.}$ , dissolved in sufficient camphor to give solutions of 0.2—0.3M-concentration. Camphor was the only solvent examined in the present work, but it is reasonable to suppose that the method can be applied with other solvent systems.<sup>2</sup>

The procedure which has been developed for weighing the sample can only be used with solid organic compounds which melt without decomposition. Many organic compounds sublime without melting when heated, but a sufficient weight of sublimate can be collected on the sampling wire when the end of the wire is held over the heated compound. More care is then necessary in handling the wire, especially when the sublimate is light and bulky.

*Experimental.—Apparatus.* Gallenkamp electrically heated melting-point apparatus, single melting-point tube type.

Anschutz thermometer, 145—205° range. Gas-heated aluminium block with 0—360° thermometer.

Capillary tubes, approximately 50 mm. long, of 2 mm. internal-diameter at the open end, tapering to 0.5—0.6 mm. at the sealed end. Drawn from *clean*, hard glass tubing.

Platinum cup. A depression of about 3 mm. diameter, and 2 mm. depth is made in the centre of a 10 mm. square of thin platinum sheet. A handle of platinum wire is welded on.

*Reagent:* Camphor (microanalytical reagent grade).

*Determination of cryoscopic constant of camphor.* A submicro-capillary tube is charged with about 1 mg. of camphor by Pregl's technique<sup>3</sup> for inserting the camphor into the bottom of the tube. A 15 mm. length of platinum wire (0.03 mm. diam.) is added and the tube is sealed about 2 mm. above the wire by means of a very fine flame from an oxy-coal gas hand-torch. Another tube, but of known weight, is similarly charged with camphor and is reweighed on a microbalance. A crystal of acetanilide is put into a small platinum cup placed on an aluminium heating block. The acetanilide is heated to slightly above its m. p. and one end of another similar piece of platinum wire whose weight has been determined by means of the submicrobalance is touched against the molten substance and then immediately withdrawn. The weight of substance adhering to the tip of the wire is found by reweighing the wire. The wire is placed sample-end first in the capillary which is sealed off as before.

The capillary containing camphor alone is placed in the m. p. apparatus previously heated to 175°. Heating is continued until a temperature 5° above the m. p. is reached. The current to the heating element is reduced to a value which gives a cooling rate of approx. 1° per 20 sec., and the temperature at which the first crystals appear in the clear melt is read to 0.1°. The camphor is again melted and cooled, the process being repeated three times. The crystallisation temperature should be reproducible to  $\pm 0.1^\circ$ . A similar procedure is applied to the tube containing the acetanilide, after the temperature of the apparatus has been allowed to drop to about 160°, but during the melting process the tube is raised and rotated in the apparatus, so that the platinum wire moves about in the tube and mixes the contents thoroughly.

*Determination of molecular weights of organic compounds.* The procedure described above was repeated with other organic compounds which can be melted without decomposition (see Table).

Substance *	Molecular weight		Substance *	Molecular weight	
	Theory	Found		Theory	Found
8-Hydroxyquinoline	145.2	144, 149, 148, 144	Phenacetin .....	179.2	183
Benzoic acid .....	122.1	119, 127, 124	Acetanilide .....	135.2	134
Cinnamic acid .....	148.2	142	<i>p</i> -Chlorobenzoic acid .....	156.7	155
Sulphonal .....	228.3	235	Hippuric acid † .....	179.2	167
<i>p</i> -Nitroaniline .....	138.1	132	Trifluoroacetanilide .....	189.1	186
<i>m</i> -Dinitrobenzene ...	168.1	172	2,2'-Bistrifluoromethylazobenzene	318	307

\* All were of Microanalytical Standard Grade except the last.

† This substance appeared to decompose during the determination.

<sup>2</sup> Pirsch, *Angew. Chem.*, 1938, 51, 73.

<sup>3</sup> Pregl, "Die Quantitative Organische Mikroanalyse," 3rd edn., Springer Verlag, Berlin, 1930.

We are indebted to Mr. P. Gouverneur, Royal Dutch Shell Co., Amsterdam, for independently checking the procedure. One of us (M. S.) thanks the British Council for financial support.

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### 93. NN'-Di(cyclohepta-2,4,6-trienyl)urea, alias Tropylium Isocyanate.

By W. VON E. DOERING and L. E. HELGEN.

DEWAR and PETTIT achieved an elegant, generally applicable synthesis of the tropylium ion in 1955 by a Curtius reaction with cyclohepta-2,4,6-trienecarboxylic acid (norcaradienecarboxylic acid).<sup>1,2,3</sup> Two intermediates were isolated. One, a liquid, was formulated as the covalent isocyanatonorcaradiene and synthesized independently by *rapid* addition of an excess of aqueous sodium cyanate to aqueous tropylium fluoroborate.<sup>3</sup> The other was water-insoluble, high-melting, crystalline, and, it was asserted, isomeric with the former, and it was formulated as the salt-like tropylium isocyanate: it was synthesized by *slow* addition of aqueous sodium cyanate to aqueous tropylium fluoroborate. Both products were transformed into tropylium bromide on treatment with hydrogen bromide.<sup>2</sup>

Of less importance than the synthesis of tropylium ion itself, the disclosure of a pair of valency tautomers related as covalent and ionic isomers was nonetheless striking, the more so because the two isomers appeared capable of indefinite existence, either alone or in contact with each other. Since a closed system composed of a liquid and a solid isomer can be at equilibrium at a given pressure at only one temperature, it is clear that the two isomers are *not* in equilibrium. However, the synthesis of both of them under essentially identical conditions from an aqueous solution of tropylium fluoroborate and sodium cyanate demands the establishment of equilibrium in water. The probability of satisfying these conditions seemed sufficiently small to call into question the structure and, thereby, the number of the components in the system.

The structure, isocyanatonorcaradiene (cyclohepta-2,4,6-triene isocyanate<sup>4</sup>), assigned to the liquid isomer is corroborated by the finding of a nuclear magnetic resonance spectrum very similar to that of methyl cyclohepta-2,4,6-trienecarboxylate<sup>4</sup> and a very strong infrared band at 4.4  $\mu$ .<sup>5</sup>

However, the structure of tropylium isocyanate assigned to the solid is incorrect. Elemental analysis is in better accord with the formula C<sub>15</sub>H<sub>16</sub>N<sub>2</sub>O than with C<sub>8</sub>H<sub>7</sub>NO. The ultraviolet spectrum  $\lambda_{\max}$  256 (log  $\epsilon$  3.9) and  $\lambda_{\min}$  222 m $\mu$  (log  $\epsilon$  3.5) is in better accord with that of cycloheptatriene (tropilidene)<sup>6</sup> than with that of the tropylium ion.<sup>7</sup> The infrared spectrum shows no absorption at 4.63  $\mu$  characteristic of the cyanate ion. An independent synthesis of the solid was effected by mixing an aqueous solution of tropylium

<sup>1</sup> Dewar and Pettit, *Chem. and Ind.*, 1955, 199.

<sup>2</sup> Dewar and Pettit, *J.*, 1956, 2021.

<sup>3</sup> Dewar and Pettit, *J.*, 1956, 2026.

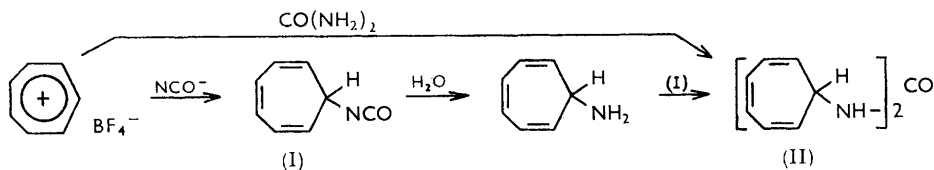
<sup>4</sup> Doering, Laber, Vanderwahl, Chamberlain, and Williams, *J. Amer. Chem. Soc.*, 1956, **78**, 5448.

<sup>5</sup> Davison, *J.*, 1958, 3712.

<sup>6</sup> Doering and Knox, *J. Amer. Chem. Soc.*, 1953, **75**, 297.

<sup>7</sup> Doering and Knox, *J. Amer. Chem. Soc.*, 1954, **76**, 3203.

bromide and urea.<sup>8</sup> Its m. p. and infrared spectrum were identical with those of the product prepared by Dewar and Pettit's method from tropylium bromide or fluoroborate and potassium cyanate shows the substance to be a ditropyliurea. A tentative decision between the symmetrical and the unsymmetrical formulation is based on the feeling that Dewar and Pettit's reaction would most probably lead to the symmetrical derivative. Irrespective of whether addition of the aqueous sodium cyanate is gradual or rapid, the



initial product is the isocyanate (I). During the gradual addition there is ample opportunity for this to be hydrolysed to the still unknown aminocycloheptatriene *via* the carbamic acid and this with unchanged isocyanate (I) then leads to the symmetrical urea.

Correction of this structure leads to a few minor revisions in Dewar and Pettit's work. The formation of the urea in the Curtius reaction must have depended on the presence of variable amounts of water. In this connection, the observation that "the individual yields of the solid isomer varied from 0% to 50%" is relevant.<sup>2</sup> Conversion of the urea into tropylium bromide by hydrogen bromide should doubtless be reformulated as an example of the general reaction of *N*-cycloheptatrienyl amides with hydrogen bromide.<sup>8</sup> Discussion of valency tautomerism in this series becomes superfluous.

*Experimental.*—*NN'*-*Di(cyclohepta-2,4,6-trienyl)urea*. (a) As recorded by Dewar and Pettit,<sup>3</sup> potassium cyanate (0.34 g.) in water (10 g.) was added dropwise in 10 min. to a stirred solution of tropylium bromide (1.00 g.) in water (10 g.). When the addition was about half-complete, crystals began to appear. After being stirred for 3 hr., the mixture was filtered to yield colourless crystals of the *urea*, m. p. 186.5—188.0° (0.23 g., 46%). Four recrystallizations from ethyl acetate raised the m. p. to 190—191° (Found: C, 74.8; H, 6.9; N, 11.6.  $\text{C}_{15}\text{H}_{16}\text{N}_2\text{O}$  requires C, 75.0; H, 6.7; N, 11.7%).

(b) Reaction with tropylium fluoroborate in place of the bromide gave the same product, m. p. and mixed m. p. 190—191° (Found: C, 75.0; H, 7.0; N, 11.8%).

(c) No visible change followed the addition of urea (0.18 g.) in water (3 g.) to a stirred solution of tropylium bromide (1.01 g.) in water (10 g.) until further addition of sodium hydrogen carbonate (0.49 g.) in water (5 g.). After an immediate precipitation, evolution of gas, and decolorisation, the mixture was stirred for 3 hr. and filtered to yield the urea, m. p. and mixed m. p. 189—190° (after one recrystallization from ethyl acetate). The infrared spectra of all these samples were superimposable.

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<sup>8</sup> Doering and Knox, *J. Amer. Chem. Soc.*, 1957, **79**, 4127.

### 94. *Supinine from the Seeds of Trichodesma zeylanicum, R.Br.*

By J. O'KELLY and K. SARGEANT.

THE alkaloid supinine, the pharmacology of which is at present of interest in Australia as the probable causative agent in the heliotrope poisoning of sheep,<sup>1,2</sup> has previously been obtained in low yields from *Heliotropium supinum*, L., *Heliotropium europaeum*, L., and *Tournefortia sarmentosa*, Lam.<sup>3</sup>

We now report its isolation, in about 1% yield, from the dried seeds of *Trichodesma zeylanicum*. These seeds were collected in Tanganyika where the plant is a common weed. They contain in all about 2% of basic material. Paper chromatography in a variety of solvent systems suggests that this basic material is almost entirely supinine although at least two other bases are present in minor quantities.

Only small amounts of alkaloidal *N*-oxides occur in the seeds. This was shown by the very small increase in the content of chloroform-soluble bases after the reduction of a chloroform-insoluble basic extract with zinc dust and sulphuric acid.

*Experimental.*—Finely ground *Trichodesma zeylanicum* seeds (740 g.) were extracted with absolute alcohol in a Soxhlet apparatus for 8 hr. (12 changes). The extract (1200 ml.), after dilution with water (400 ml.), was made acidic to Congo Red paper with citric acid, concentrated to 200 ml. under reduced pressure, exhaustively extracted with ether and chloroform, and basified with an excess of sodium carbonate, and the total bases (15.3 g.) were extracted with chloroform. Crystallisation from ethyl acetate gave colourless needles (7.0 g.), m. p. 138—142°, which, after several recrystallisations from ethyl acetate and finally methanol, had m. p. 147—148.5°,  $[\alpha]_D^{21} - 13.4^\circ$  (*c* 2.4 in EtOH) (Found: C, 63.4, 63.3; H, 8.9, 8.9; N, 5.1, 5.2. Calc. for C<sub>15</sub>H<sub>25</sub>NO<sub>4</sub>: C, 63.6; H, 8.9; N, 4.9%). This product was shown to be supinine, by a mixed m. p. determination and by comparison of infrared absorption spectra.

Paper chromatography of the crude bases in butan-1-ol-acetic acid-water,<sup>2</sup> with potassium iodobismuthate in acetic acid as the spray reagent,<sup>4</sup> showed the presence of at least three constituents. The major one had  $R_F$  0.34. The two others had  $R_F$  0.04, and 0.63 respectively and were present in very much smaller amounts. The major spot, which had the same  $R_F$  value as pure supinine, was not resolved in the following solvent systems: (1) butan-1-ol-hydrochloric acid-water on paper impregnated with potassium chloride;<sup>4</sup> (2) cyclohexane-diethylamine on paper impregnated with formamide;<sup>5</sup> (3) butan-1-ol-citric acid-water on paper impregnated with sodium dihydrogen citrate.<sup>6</sup>

The sodium carbonate solution left after the removal of the bases was acidified to 2N with sulphuric acid. The resultant solution was stirred with zinc dust for 24 hr., basified with sodium carbonate, and extracted with chloroform. The gum obtained (0.5 g.), when submitted to paper chromatography in butan-1-ol-acetic acid-water, appeared to have approximately the same composition as the mixture of bases already examined.

Thanks are offered to Dr. W. D. Raymond who kindly supplied the plant material, and to Mrs. H. C. Crowley and Dr. C. C. J. Culvenor who provided a sample of supinine isolated from *Heliotropium supinum*.

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<sup>1</sup> Bull, Dick, Keast, and Edgar, *Austral. J. Agric. Res.*, 1956, **7**, 281; Gallagher, *Biochem. Pharmacol.*, 1960, **3**, 220.

<sup>2</sup> Crowley and Culvenor, *Austral. J. Chem.*, 1959, **12**, 694.

<sup>3</sup> Leonard, in Manske's "The Alkaloids," Academic Press, London, 1960, Vol. VI, p. 44.

<sup>4</sup> Munier, Machebouef, and Cherrier, *Bull. Soc. Chim. biol.*, 1952, **34**, 204.

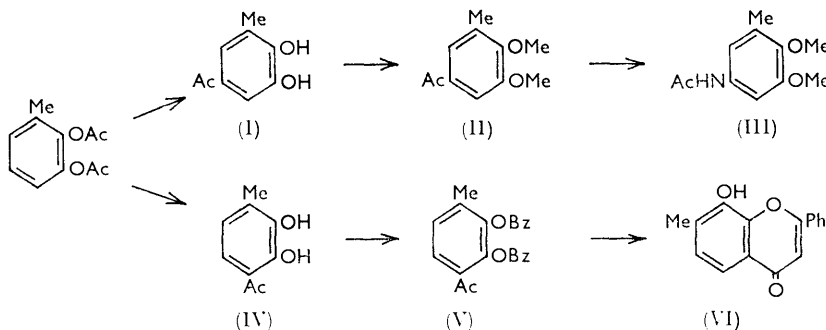
<sup>5</sup> Waldi, *Arch. Pharm.*, 1959, **292**, 206.

<sup>6</sup> Curry and Powell, *Nature*, 1954, **173**, 1143.

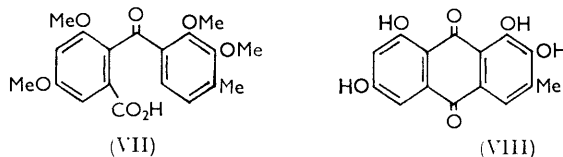
## 95. Naturally Occurring Quinones. Part IV.<sup>1</sup> A Synthesis of Alaternin.

By J. C. LOVIE and R. H. THOMSON.

THE bark of *Rhamnus alaternus* L. contains an abundant mixture of hydroxyanthraquinone glycosides, of which emodin is the principal aglycone. A second pigment, alaternin, was isolated by Briggs and his co-workers<sup>2</sup> who deduced from chemical and spectroscopic evidence that it was a *C*-methyl derivative of 1,2,6,8-tetrahydroxyanthraquinone. On the assumption that the methyl group occupies the usual  $\beta$ -position, two structures are possible, the hydroxyemodin (VIII) being favoured on phytochemical grounds. This view is supported by the recent observation<sup>3</sup> that alaternin readily condenses with alkaline formaldehyde and we have now established structure (VIII) by synthesis.



An earlier attempt<sup>1</sup> to form 1,2,6,8-tetrahydroxy-3-methylanthraquinone by direct condensation of 3,5-dimethoxyphthalic anhydride with 3-methylcatechol was unsuccessful but our object has now been achieved by stepwise condensation of 3,5-dimethoxybenzoic ester with 2,3-dimethoxy-4-methylbenzoyl chloride. The latter was obtained *via* Fries rearrangement of 3-methylcatechol diacetate which gave a mixture of the two ketones (I) and (IV), containing 15–20% of the 1,2,3,4-isomer. Direct *C*-acetylation of 3-methylcatechol by boron trifluoride-acetic acid gave the ketone (I) with only a trace of the other isomer. The orientations are based on the infrared spectra of the isomers, the steam-volatility of the *o*-hydroxy-ketone, and the transformations shown in the formulae. The anilide (III), obtained from the ketone (I) by Beckmann rearrangement of the oxime of its dimethyl ether (II), was identical with the product obtained by reductive acetylation of



3-methyl-5-nitroveratrole.<sup>4</sup> The *o*-hydroxy-ketone (IV) formed a dibenzoate (V) in pyridine solution which underwent a normal Baker-Venkataraman rearrangement to give the flavone (VI).

Methylation of the hydroxy-ketone (IV), followed by oxidation with hypobromite,

<sup>1</sup> Part III, *J.*, 1959, 4139.

<sup>2</sup> Briggs, Jacobs, and Nicholls, *J.*, 1953, 3069.

<sup>3</sup> Dave, Joshi, Patwardhan, and Venkataraman, *Tetrahedron Letters*, 1959, No. 6, 22.

<sup>4</sup> Majima and Okazaki, *Ber.*, 1916, **49**, 1482.

yielded 2,3-dimethoxy-4-methylbenzoic acid which was used to acylate 3,5-dimethoxybenzoic ester. The resulting keto-acid (VII) was converted into 1,2,6,8-tetrahydroxy-3-methylanthraquinone (VIII) by brief treatment in molten aluminium chloride-sodium chloride. A sample of natural alaternin was not available to us but the infrared spectra of the natural and the synthetic material were kindly compared for us by Professor L. H. Briggs who reported that "there appears to be no significant difference between these two spectra and in our opinion the two compounds are identical."

*Experimental.*—3-Methylcatechol diacetate crystallised from light petroleum (b. p. 50—60°) in plates, m. p. 69° (Found: C, 63.4; H, 5.9.  $C_{11}H_{12}O_4$  requires C, 63.5; H, 5.8%).

*Fries rearrangement.* 3-Methylcatechol diacetate (20 g.) was added to a molten mixture of anhydrous aluminium chloride (100 g.) and sodium chloride (20 g.) at 140°. The mixture was kept at 200° with continuous stirring for 30 min., cooled, and poured on ice and concentrated hydrochloric acid. Steam-distillation gave a yellow solid (3 g.) which after crystallisation from light petroleum (b. p. 50—60°) and sublimation at 60°/10 mm. afforded 2,3-dihydroxy-4-methylacetophenone as pale yellow plates, m. p. 70° (Found: C, 64.9; H, 6.1.  $C_9H_{10}O_3$  requires C, 65.0; H, 6.0%),  $\nu_{\max.}$  (in KBr) 1640 (chelated CO), 727 and 796  $cm^{-1}$  (two adjacent ring C-H). The *dibenzoate* formed plates, m. p. 152—153° (from alcohol) (Found: C, 73.5; H, 4.8.  $C_{23}H_{18}O_5$  requires C, 73.8; H, 4.8%). The 2,4-dinitrophenylhydrazone crystallised from acetic acid in red needles, m. p. 288° (decomp.) (Found: C, 52.0; H, 4.2; N, 16.2.  $C_{15}H_{14}N_4O_6$  requires C, 52.0; H, 4.0; N, 16.2%). 3,4-Dihydroxy-5-methylacetophenone (8 g.) separated from the residual steam-distillation liquor on cooling. It crystallised from water (charcoal) in plates, m. p. 197—199° (Found: C, 64.9; H, 6.0%),  $\nu_{\max.}$  (in KBr) 1650 (CO), 862 and 882  $cm^{-1}$  (isolated ring C-H). The 2,4-dinitrophenylhydrazone formed red plates (from acetic acid), m. p. 268—270° (decomp.) (Found: C, 52.0; H, 4.0; N, 16.0%).

3,4-Dihydroxy-5-methylacetophenone was also obtained by warming 3-methylcatechol (3 g.) in boron trifluoride-acetic acid (15 ml.) at 60—70° for 3 hr. The mixture, after dilution with water (50 ml.) and addition of concentrated hydrochloric acid (5 ml.), was boiled for a few minutes and the resulting product (2.5 g.) collected. It crystallised from water (charcoal) in plates, m. p. and mixed m. p. 197—199°. Steam-distillation of the crude product yielded only a trace of the 1,2,3,4-isomer, m. p. and mixed m. p. 69—70°.

2,3-Dimethoxy-4-methylbenzoic acid. A solution of 2,3-dihydroxy-4-methylacetophenone (12 g.) in acetone (150 ml.) was refluxed for 9 hr. with dimethyl sulphate (25 ml.) and anhydrous potassium carbonate (80 g.). Working up gave the dimethoxy-ketone (11 g.), b. p. 138—140°/30 mm. This oil (1 g.) in dioxan (25 ml.) was treated with potassium hydroxide (3.5 g.) in water (13 ml.) containing bromine (1 ml.). After 1 hr., the solution was refluxed for 1 hr., and cooled. Sodium hydrogen sulphite (0.25 g.) and 8% aqueous potassium hydroxide solution (8 ml.) were then added, and the mixture was extracted thrice with ether. Acidification of the aqueous phase precipitated 2,3-dimethoxy-4-methylbenzoic acid (1 g.) which crystallised from water (charcoal) in needles, m. p. 125° (Found: C, 61.4; H, 6.5.  $C_{10}H_{12}O_4$  requires C, 61.2; H, 6.1%).

3,4-Dimethoxy-5-methylbenzoic acid. 3,4-Dihydroxy-5-methylacetophenone (4.5 g.) in acetone (100 ml.) was refluxed for 6 hr. with dimethyl sulphate (5 ml.) and potassium carbonate (20 g.). The dimethoxy-ketone crystallised from light petroleum (b. p. 50—60°) in needles, m. p. 47—48° (Found: C, 68.0; H, 7.4.  $C_{11}H_{14}O_3$  requires C, 68.1; H, 7.2%). The *oxime* crystallised from light petroleum (b. p. 50—60°) (charcoal) in needles, m. p. 89—90° (Found: C, 63.0; H, 7.3; N, 6.6.  $C_{11}H_{15}NO_3$  requires C, 63.2; H, 7.2; N, 6.7%). Hypobromite oxidation of the dimethoxy-ketone, as above, afforded 3,4-dimethoxy-5-methylbenzoic acid, separating from water in needles, m. p. 151° (Found: C, 61.2; H, 6.2%).

3,4-Dimethoxy-5-methylacetanilide. (a) A mixture of 3,4-dimethoxy-5-methylacetophenone oxime (0.5 g.) and polyphosphoric acid (8 ml., 16.8 g.) was heated at 100° for 10 min., cooled, and poured into water (80 ml.). The *anilide* crystallised from light petroleum (b. p. 80—90°) in needles, m. p. 122° (Found: C, 63.0; H, 7.3; N, 6.5.  $C_{11}H_{15}NO_3$  requires C, 63.2; H, 7.2; N, 6.7%).

(b) A solution of 3-methyl-5-nitroveratrole<sup>4</sup> (0.25 g.) in acetic anhydride (10 ml.) containing platinum oxide (0.05 g.) was shaken in hydrogen until absorption ceased. After filtration and removal of the solvent *in vacuo*, the residue crystallised from light petroleum (b. p. 80—



90°) (charcoal) in needles, m. p. 121° not depressed by admixture with the product obtained as in (a).

**8-Hydroxy-7-methylflavone.** Pulverised potassium hydroxide (0.7 g.) was added to a solution of 2,3-dibenzoyloxy-4-methylacetophenone (2 g.) in pyridine (7.5 ml.) at 50°. After being stirred at this temperature for 15 min. the mixture was cooled and acidified with 2*N*-acetic acid, to precipitate 2,3-dihydroxy-4-methyldibenzoylmethane which separated from aqueous alcohol in yellow needles, m. p. 122—123° (Found: C, 70.8; H, 5.3. C<sub>16</sub>H<sub>14</sub>O<sub>4</sub> requires C, 71.1; H, 5.2%),  $\nu_{\max}$ . (in KBr) 1610 (CO of chelated  $\beta$ -diketone). This diketone (1 g.) in glacial acetic acid (30 ml.) was heated with concentrated sulphuric acid (1 ml.) on the steam-bath for 1½ hr., cooled, and poured on ice. The solid was collected and chromatographed in acetone on a magnesia column. The pale yellow flavone obtained on evaporation of the eluant crystallised from aqueous acetic acid in needles, m. p. 257—258° (Found: C, 75.7; H, 4.9. C<sub>16</sub>H<sub>12</sub>O<sub>3</sub> requires C, 76.2; H, 4.8%). The methyl ether crystallised from aqueous alcohol in pale yellow needles, m. p. 138—139° (Found: C, 76.5; H, 5.4; OMe, 10.8. C<sub>17</sub>H<sub>14</sub>O<sub>3</sub> requires C, 76.7; H, 5.3; OMe, 11.7%),  $\lambda_{\max}$ . (in EtOH) 260, 297, and 300  $\mu$  ( $\log \epsilon$  4.37, 4.29, 4.28 respectively); 8-methoxyflavone has  $\lambda_{\max}$ . 266, 299, and 301  $\mu$  ( $\log \epsilon$  4.33, 4.06, 4.05 respectively).

**3,5-Dimethoxy-2-(2,3-dimethoxy-4-methylbenzoyl)benzoic acid.** 2,3-Dimethoxy-4-methylbenzoic acid (3 g.) was refluxed for 30 min. with thionyl chloride (3 ml.). Excess of reagent was then removed under reduced pressure and the residual acid chloride was added in dry tetrachloroethane (20 ml.) to ethyl 3,5-dimethoxybenzoate (4 g.) in the same solvent (30 ml.). The mixture was stirred in an ice-bath while anhydrous aluminium chloride (2.7 g.) was added, in portions, during 30 min. After 2 hr. the ice-bath was removed and stirring was continued at room temperature overnight. The mixture was then poured on ice and concentrated hydrochloric acid. The aqueous phase was extracted with ether, and the organic phase steam-distilled to remove solvent, then extracted with ether. The combined ether solutions were evaporated, leaving a brown oil which gave a positive ferric reaction. Remethylation was effected by refluxing a solution of the oil in acetone with dimethyl sulphate (10 ml.) and anhydrous potassium carbonate (20 g.). The product, isolated in the usual way, was then hydrolysed by boiling with 2*N*-aqueous sodium hydroxide (150 ml.). The acid (4 g.) obtained on acidification crystallised from water in needles, m. p. 157° (Found: C, 63.1; H, 5.6. C<sub>19</sub>H<sub>20</sub>O<sub>7</sub> requires C, 63.3; H, 5.6%),  $\nu_{\max}$ . (in KBr) 1695 (carboxyl CO), 1660 cm.<sup>-1</sup> (diaryl CO).

**1,2,6,8-Tetrahydroxy-3-methylanthraquinone.** The above acid (1 g.) was added to a molten mixture of anhydrous aluminium chloride (10 g.) and sodium chloride (2 g.) at 120°. The temperature was rapidly raised to 180—190° and maintained for 3 min. with continuous stirring. After cooling, the mixture was poured on ice and concentrated hydrochloric acid, and after a few minutes' boiling the resulting precipitate was collected. Crystallisation from glacial acetic acid, followed by sublimation at 200—20°/2 × 10<sup>-5</sup> mm., afforded red plates, m. p. 320—321° (Kofler (lit.,<sup>2</sup> 310°) (0.4 g.) (Found: C, 61.6; H, 3.7. Calc. for C<sub>15</sub>H<sub>10</sub>O<sub>6</sub>: C, 62.9; H, 3.5%). Despite repeated attempts, including purification through the tetra-acetate, a satisfactory carbon analysis could not be obtained.  $\nu_{\max}$ . (in Nujol) were at 758.5, 825.1, 863.5, 894.6w, 934.6, 1033, 1087, 1106, 1167, 1205, 1277, 1312, 1577, 1618, 3175, 3344. Natural alaternin has  $\nu_{\max}$ . 759.6, 826.4, 862.8, 886.1w, 905.3w, 934.6, 1033, 1087, 1107, 1206, 1277, 1319, 1572, 1613, 1686w, 3195, 3367. The tetra-acetate separated from alcohol in bright yellow needles, m. p. 222—223° (lit.,<sup>2</sup> 224°) (Found: C, 61.0; H, 4.2; Ac, 37.1. Calc. for C<sub>23</sub>H<sub>18</sub>O<sub>10</sub>: C, 60.8; H, 4.0; Ac, 37.9%). The tetramethyl ether also crystallised from alcohol in yellow needles, m. p. 182° (lit.,<sup>2</sup> 181—182°) (Found: C, 66.8; H, 5.5; OMe, 37.2. Calc. for C<sub>19</sub>H<sub>18</sub>O<sub>6</sub>: C, 66.7; H, 5.2; OMe, 36.3%),  $\lambda_{\max}$ . (in EtOH) 223, 277, and 365  $\mu$  ( $\log \epsilon$  4.30, 4.45, 3.81 respectively).

We thank Professor L. H. Briggs for the infrared data on alaternin, Dr. H. F. Bondy for supplies of 3-methylcatechol and Dr. T. H. Simpson for a sample of 8-methoxyflavone. One of us (J. C. L.) is grateful to the Department of Scientific and Industrial research for a Research Studentship.

**96.** *An Insect Repellant from Black Cocktail Ants.*

By C. W. L. BEVAN, A. J. BIRCH, and H. CASWELL.

*Crematogaster (Atopogyne) africana* Mayr. are a common West African species of black cocktail ant; they live on trees in roughly spherical carton nests made of chewed vegetable fibres mixed with a secretion of the maxillary glands of the workers.<sup>1</sup> When disturbed or crushed they give off a characteristic smell. This has been identified as due to hex-2-enal, which is an insect repellant also secreted by the cockroach *Eurycotis floridana*.<sup>2</sup>

*Experimental.*—Ants (100 g.) from a nest which was used as the source of specimens for identification were macerated under light petroleum (b. p. 60—80°; 100 ml.). This extract was then shaken with Brady's reagent, and the precipitated dinitrophenylhydrazone recrystallised from methanol; it had m. p. and mixed m. p. (with a synthetic specimen<sup>3</sup> of hex-2-enal dinitrophenylhydrazone) 142—143°. The infrared spectra of the dinitrophenylhydrazones taken in a Nujol film were identical; the ultraviolet absorption [ $\lambda_{\max}$ , 372 m $\mu$  ( $\log \epsilon$  4.5) in chloroform] was consistent with that recorded<sup>4</sup> for hexenal dinitrophenylhydrazone.

We are indebted to Dr. Pearson of the Commonwealth Institute of Entomology for identification of the ants.

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<sup>1</sup> Skaife, "African Insect Life," Longmans, Green and Co., London, 1953, p. 371.

<sup>2</sup> Roth, Niegisch, and Stahl, *Science*, 1956, **123**, 670.

<sup>3</sup> Ohoe and Hori, *J. Chem. Soc. Japan*, 1952, **73**, 275.

<sup>4</sup> Braude and Jones, *J.*, 1945, 498.