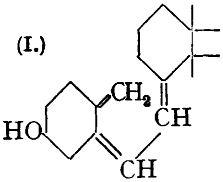
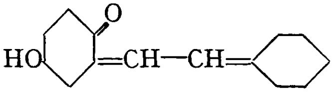
NOTES

Preliminary Note on the Synthesis of Compounds Related to the Antirachitic Vitamins. The Condensation of cyclo*Hexylideneacetaldehyde with 4-Hydroxy*cyclo*hexanone.* By John B. Aldersley and G. Norman Burkhardt.

As the first stage in an investigation directed to the synthesis of compounds of the general formula (I), containing the conjugated system of calciferol, the ketone (II) has been obtained by condensation of *cyclo*hexylideneacetaldehyde [b. p. 80—85°/16 mm.; main absorption band, in alcohol, λ = 2390 A., ε = 9,100; *semicarbazone*, m. p. 205° (Found: C, 59·4; H, 7·9; N, 22·7. $C_9H_{15}ON_3$ requires C, 59·6; H, 8·3; N, 23·2%); $\lambda_{max.}$ = 2720 A., $\varepsilon_{max.}$ = 28,000] with 4-acetoxy*cyclo*hexanone [b. p. 121—124°/11 mm.; *semicarbazone*, m. p. 182—183° (Found: N, 19·8. $C_9H_{15}O_3N_3$ requires N, 19·7%)] in presence of excess of aqueous sodium hydroxide. The product was characterised by its absorption spectrum (λ = 3060 A., ε = 10,530, in alcohol), its *phenylurethane*, m. p. 180° (Found: C, 74·6; H, 7·5; N, 4·2. $C_{21}H_{25}O_3N$ requires C, 74·5; H, 7·4; N, 4·1%), and its 2 : 4-*dinitrophenylhydrazone*, m. p. 170—171° (Found: N, 13·9. $C_{20}H_{24}O_5N_4$ requires N, 14·0%). Preliminary experiments on the replacement of the carbonyl oxygen by an exocyclic methylene group have given a product having an absorption maximum at 2690 A., which compares favourably with that exhibited by calciferol (2650 A.).

(I.)





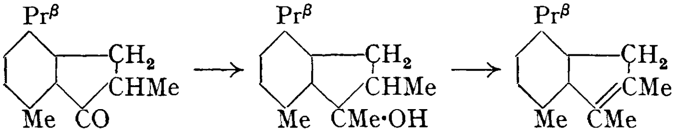
(II.)

*cyclo*Hexylideneacetaldehyde was obtained together with its isomer, *cyclo*hexenylacetaldehyde [b. p. 58—62°/16 mm.; *semicarbazone*, m. p. 186° (Found: C, 59·8; H, 8·1. $C_9H_{15}ON_3$ requires C, 59·6; H, 8·3%)], by the ozonolysis of 1-allyl*cyclo*hexanol (Mazurewitsch, *J. Russ. Phys. Chem. Soc.*, 1911, **43**, 973), separation of the products being effected by fractional distillation.

4-Acetoxy*cyclohexanone* was prepared by chromic anhydride oxidation of quinitol monoacetate (4-acetoxy*cyclo*hexanol), which in its turn was obtained in good yield by the partial hydrolysis of *trans*-quinitol diacetate.—The University, Manchester. [*Received, February* 10*th*, 1938.]

The Preparation of 1 : 2 : 7-*Trimethyl*-4-iso*propylindene and* 1 : 2 : 7-*Trimethyl*-4-iso*propylhydrindene.* By C. L. CARTER and S. N. SLATER.

THESE two compounds were prepared during an attempt to synthesise an azulene which was undertaken before the work of Pfau and Plattner appeared (*Helv. Chim. Acta*, **1936**, **19**, 858; **1937**, **20**, 224). 2 : 7-Dimethyl-4-*iso*propyl-1-hydrindone (Cook, Hewett, Mayneord, and Roe, J., **1934**, 1727) on treatment with methylmagnesium iodide yielded 1 : 2 : 7-*trimethyl*-4-iso*propylindene*, the tertiary alcohol first formed losing the elements of water :



Catalytic hydrogenation yielded 1 : 2 : 7-*trimethyl*-4-iso*propylhydrindene*. Attempts at dehydrogenation were unsuccessful.

The Grignard reagent prepared from methyl iodide (14 g.) and magnesium (2·4 g.) in ether (30 c.c.) was cooled in ice, and 2 : 7-dimethyl-4-*iso*propyl-1-hydrindone (10 g.) in ether (20 c.c.) added during 2 hours. After 2 hours' boiling, the product was decomposed with ice and concentrated hydrochloric acid and extracted with ether. The extract was freed from iodine by sodium bisulphite, most of the solvent removed, and the yellow oil steam-distilled. The distillate, dried in ether and distilled in a vacuum, had b. p. 154—157°/17 mm., $d_{25^\circ}^{25^\circ}$ 0·9574, $n_D^{25^\circ}$ 1·5428 (Found : C, 90·6; H, 10·4. $C_{15}H_{20}$ requires C, 90·0; H, 10·0%).

1 : 2 : 7-*Trimethyl*-4-iso*propylindene* (5 g.) in alcohol was hydrogenated in the presence of freshly prepared palladised norit (0·5 g.). After 6 hours an absorption of 585 c.c. (corresponding with one double bond) took place. The product was removed and distilled in a vacuum, yielding 1 : 2 : 7-*trimethyl*-4-iso*propylhydrindene* as a clear, mobile, slightly yellow oil, b. p. (redistilled) 154—155°/29 mm., $d_{25}^{25^\circ}$ 0·9250, $n_D^{25^\circ}$ 1·5112 (Found : C, 88·85; H, 10·8. $C_{15}H_{22}$ requires C, 89·1; H, 10·9%).—UNIVERSITY OF OTAGO, NEW ZEALAND. [*Received, March 25th,* 1938.]

Thixotropic Behaviour of Silica Gels. By HERBERT FREUNDLICH and DAVID W. GILLINGS.

IT has generally been considered that silica gels do not show any thixotropy (see, for instance, H. Freundlich ." Thixotropy," Hermann, Paris, note 13 in bibliography). In agreement with this consideration, no liquefaction of silica gels by ultrasonic waves has previously been noted (Freundlich, Rogowski, and Söllner, *Kolloid Beih.*, 1933, **37**, 215).

In the course of experiments on the reduction of viscosity of colloidal solutions by ultrasonics, we have found that these observations apply only to the acid gels, as they are formed when solutions of sodium silicate are mixed with an excess of hydrochloric acid. By dialysis of these sols, we obtained a product, slowly coagulating to a gel, which could be liquefied by shaking, or by ultrasonics, and returned to the gel state after the disturbance ceased.

As far as our experiments go, all these thixotropic gels were weakly alkaline, at the p_H range 8·5—9·5. This is the range at which Freundlich and Cohn (*Kolloid-Z.*, 1926, **39**, 28) showed that silica sols could be coagulated by electrolytes.—THE SIR WILLIAM RAMSAY AND RALPH FORSTER LABORATORIES OF CHEMISTRY, UNIVERSITY COLLEGE, LONDON, W.C.1. [*Received, February 23rd,* 1938.]

The Reaction between Disodium Phthalocyanine and Methyl Alcohol. By CHARLES E. DENT.

COLD methyl alcohol rapidly and completely eliminates the sodium from disodium phthalocyanine (Barrett, Dent, and Linstead, J., **1936**, 1719). The change within a few seconds from a thin suspension of the crystalline disodium phthalocyanine (1 part) in methyl alcohol (4 parts) to a thick paste of finely divided, amorphous, metal-free phthalocyanine is so marked that it can be used as a test for either compound. The final mixture is strongly alkaline. The reaction can be followed under a microscope with minute quantities of reagents, the dull green smear first produced rapidly changing to the bright blue colour of the dispersed metal-free pigment.

The reaction appears to be specific for methyl alcohol. Dilution with water or ethyl alcohol to 50% slows the reaction slightly. Many reagents, *e.g.*, wet ethyl alcohol, dilute acids, are known to cause sodium elimination (Barrett, Dent, and Linstead, *loc. cit.*), but in no case do they react with sufficient vigour to produce the above remarkable change in physical form.

A wide range of hydroxylic and other compounds has been brought into reaction with disodium phthalocyanine under various conditions and as mixtures. Only ethyl, butyl, and *n*-propyl alcohols gave, in decreasing order, any similar reactivity and then only on prolonged standing. Disodium phthalocyanine thus appears to be a very valuable " spot " reagent for methyl alcohol.

The author thanks Imperial Chemical Industries, Limited, and the Directors of the Dyestuffs Group for permission to publish this note.—[*Received, February* 14th, 1938.]

The Transition Temperatures of Lithium Chloride Hydrates. By Malcolm P. Applebey and Ralph P. Cook.

Recent determinations of the transition temperatures $LiCl \rightleftharpoons LiCl,H_2O$ and $LiCl,H_2O \rightleftharpoons LiCl,2H_2O$ show greater discrepancies than would be expected from the estimated accuracy of individual determinations. For the upper transition temperature, Applebey, Crawford, and Gordon (J., 1934, 1665) obtained a value of 93·5° ± 0·5° from measurements of solubility, density, and vapour pressure of saturated solutions, and from cooling curves, whereas Friend, Hale, and Ryder (J., 1937, 970) from solubility measurements give a transition temperature of 96°. The lower transition temperature determined by Applebey, Crawford, and Gordon is 19·1° ± 0·25° from solubility and density of saturated solutions and cooling curves, also in poor agreement with Friend and Colley's value (J., 1931, 3148) of 18° obtained by solubility measurements, and with the determination by Benrath (*Z. anorg. Chem.*, 1932, **205**, 417), who found the temperature of continued coexistence of the two solids with the saturated solution to be 20°. In view of these discrepancies, we have made some measurements by the dilatometric method.

The lithium chloride used contained a small amount of insoluble matter and traces of sulphate and of calcium salts. It was recrystallised from water and a product was obtained which was free from sulphate and contained only 0·02% of calcium. The monohydrate and dihydrate were prepared by crystallisation at appropriate temperatures, and the anhydrous salt by drying the monohydrate in an air-oven at 120—150°.

A mixture of approximately equal amounts of the two forms was confined in the bulb of the dilatometer by toluene at the lower temperatures, and by *m*-xylene at the higher temperatures. These liquids were purified by agitation with mercury to remove traces of sulphur, followed by distillation. The dilatometers were immersed in electrically regulated thermostats, the constancy of which at both temperatures was better than ± 0·01°; transformer oil was used for the bath liquid at the upper temperature. Temperatures were read by a Beckmann thermometer calibrated against a thermometer standardised by the N.P.L., and the rate of change of volume at a series of constant temperatures was observed. Measurements at temperatures comparatively remote from the transition point were taken over periods of an hour or more; close to the transition point the measurements extended over period varying from 4 to 24 hours. The readings obtained were as follows (A and B refer to two dilatometers charged with salt from separate preparations) :

Temp.	19·23°	19·18°	19·13°	19·10°	19·09°	19·08°	19·05°	19·03°	18·98°
Rate, cm./hr. A ...	+17·4	+11·7	+5·5	—	—	0·00	—	−1·0	−7·8
Rate, cm./hr. B ...	—	—	—	+2·0	+0·45	+0·27	−1·7	—	—
Temp.	93·73°	93·63°	93·53°	93·48°	93·43°	93·42°	92·93°	92·44°	
Rate, cm./hr. ...	+4·7	+1·4	+0·12	−0·12	−0·85	−1·4	−4·7	−7·7	

From these measurements we conclude that the transition temperatures for the sample of salt used are 93·51° ± 0·03° for $LiCl \rightleftharpoons LiCl,H_2O$ and 19·07° ± 0·02° for $LiCl,H_2O \rightleftharpoons LiCl,2H_2O$. A correction may be applied for the small quantity of calcium present as impurity. Assuming that this is present as completely dissociated calcium chloride, and taking the heats of reaction as

$LiCl + H_2O \longrightarrow LiCl,H_2O$: $\Delta H = -$ 4950 (Applebey, Crawford, and Gordon, *loc. cit.*)
$LiCl,H_2O + H_2O \longrightarrow LiCl,2H_2O$: $\Delta H = -$ 3162 (Bogorodski, *J. Russ. Phys. Chem. Soc.*, 1893, **25**, 320)

we find a correction of + 0·04° in each case. Our final conclusion, therefore, is that the most probable values of the transition temperatures are 93·55° and 19·1° with an uncertainty of not more than ± 0·05° in each case.—Billingham. [*Received, February* 21st, 1938.]