NOTES.

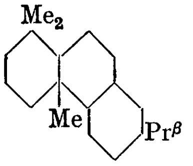
The Identity of α-Dihydrophyllocladene with Iosene. By Lindsay H. Briggs.

It has been shown previously that the lignite hydrocarbons, iosene, bombiccite, branchite, hofmannite and the hydrocarbon from Terni lignite are identical (Ciusa and Galazzi, *Gazzetta*, 1921, **51**, i, 55; Ciusa and Croce, *ibid.*, 1922, **52**, i, 125; Soltys, *Monatsh.*, 1929, **53—54**, 175).

Professor Ciusa has kindly forwarded samples of bombiccite and the hydrocarbon from Terni lignite. These do not depress the melting point of the diterpene derivative, α-dihydrophyllocladene (identical with dihydrodacrene and dihydrosciadoptiene; Briggs, this vol.

p. 830), so the latter also is identical with iosene (the name iosene is preferred to the prior synonyms). The rotation, $[\alpha]_D^{22°}$ + 23·25° (c = 1·118 in absolute alcohol) (Nishida and Uoda, *J. Agric. Chem. Soc. Japan*, 1936, **12**, 308, give $[\alpha]_D^{20°}$ + 22·8° in chloroform), also agrees with that recorded for iosene by Soltys, $[\alpha]_D^{22°}$ + 23·75° (absolute alcohol). This observation is of interest to palæobotany as a link between living and fossil plant products.

On the basis of selenium dehydrogenation of iosene to retene, Soltys (*loc. cit.*) has proposed alternative formulæ for iosene. Although no conclusive evidence is yet available, the annexed formula for the carbon skeleton of iosene is equally compatible with the evidence of dehydrogenation, it conforms with the isoprene rule, and has the advantage of falling into line with the structures of abietic acid and fichtelite (Ruzicka and Waldman, *Helv. Chim. Acta*, 1935, **18**, 611). The position and nature of the fourth ring are unknown, but Soltys's suggestion that it is 3-membered does not harmonise with the absence of reactivity towards bromine.—AUCKLAND UNIVERSITY COLLEGE, AUCKLAND, NEW ZEALAND.



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The Spontaneous Polymerisation of Liquid Propaldehyde. By ERNEST J. BUCKLER.

IT does not seem to have been recorded hitherto that pure liquid propaldehyde is an unstable substance, liable to sporadic polymerisation. In the course of work on this substance, specimens either were taken from B.D.H. samples or were obtained by the oxidation of propyl alcohol with chromic acid. Their stability was not improved by rigorous drying, or careful fractional distillation in air, or evaporative distillation in a vacuum; in fact, intensive purification seemed rather to favour polymerisation. It seemed immaterial whether the substance was stored in Pyrex or in soda-glass, in air, inert gas, or a vacuum, in the light or in the dark, but polymerisation occurred more readily the lower the temperature at which it was stored.

The mobile aldehyde first became viscous, and insoluble in water; its vapour pressure at 0° fell from 105 mm. to 10 mm. Hg, and its aldehydic properties became less pronounced. The product had no definite boiling point, and its molecular weight in benzene, as found by the cryoscopic method, indicated that the mean number of propaldehyde units per molecule was 2·8.

In the next stage, which may occur spontaneously at room temperature, or more rapidly on heating, the liquid darkens, and divides into two layers, the lower one of which was found to be water, containing a little unchanged aldehyde. This suggests that an aldol condensation had occurred, followed by elimination of water.

The upper layer was submitted to evaporative distillation in a vacuum, until a dark brown, involatile, viscous liquid remained, whose empirical formula corresponded to that of methylethylacraldehyde (Found: C, 73·2; H, 11·1. Calc. for $C_6H_{10}O$: C, 73·5; H, 10·2%). It had no definite boiling point, and no aldehydic properties, and its molecular weight in benzene was 265, which implied a mean association of 2·7 methylethylacraldehyde units. Its empirical formula, molecular weight, and chemical properties were not altered by heating at 120° in a vacuum for 48 hours (Found: C, 73·6; H, 11·1%).

The volatile portion of the upper layer was a colourless liquid, with no definite boiling point, and no aldehydic properties, and had an empirical formula corresponding most closely to that of propaldehyde (Found: C, 63·4; H, 10·3. Calc. for C_3H_6O: C, 62·1; H, 10·3%). Its molecular weight in benzene increased as the solution became more concentrated, and indicated a mean association of 2·8 propaldehyde units. This polymer seemed to be of the aldol type, since when it was heated for a short time in a vacuum at 120°, water separated, and the residue had the same composition and properties as the involatile oil previously described. Neither commercial firms, nor ourselves, have found any effective stabiliser for the aldehyde.

The author's thanks are due to the Chemical Society, and the Department of Scientific and Industrial Research for grants, and to Prof. R. G. W. Norrish, F.R.S., for helpful advice and criticism.—THE DEPARTMENT OF PHYSICAL CHEMISTRY, CAMBRIDGE. [*Received, May* 13*th*, 1937.]

The Alkaloid of Solanum Auriculatum, *Ait.* By A. R. ANDERSON and LINDSAY H. BRIGGS.

GRESHOFF (*Ber.*, 1890, **23**, 3541; *Ber. Deut. pharm. Ges.*, 1899, **9**, 214) found that *Solanum auriculatum* Ait. is rich in " solanine," and a gluco-alkaloid sintering at 256° and slowly decomposing above 272° has now been obtained from the unripe berries by the method used by Oddo

(*Gazzetta*, 1911, **41**, i, 490) for the isolation of solanine-s from *S. sodomeum*. This alkaloid did not depress the decomposition point of solanine-s; with which it may be identical, since it gave the same colour reactions with alcoholic sulphuric acid. The aglucone, obtained by hydrolysis with alcoholic hydrogen chloride, separated from alcohol in needles, m. p. 216—219°, which raised the m. p. (197·5—199·5°) of authentic solanidine-s to 212·5—216·5° but depressed that of solanidine-t by 20°. It is probably an isomorphous form of solanidine-s, since it gave the same colour reactions and afforded derivatives melting at the same temperatures as those obtained from the lower-melting specimen, and no depression in m. p. was observed on admixture of the respective pairs. The following derivatives were prepared from both specimens and the melting points recorded by Oddo (*loc. cit.*) are given in parentheses: Hydrochloride, 309·5° decomp. (302—303° decomp.); hydrobromide, 283° decomp. (283—284° decomp.); picrate, 141·5—142° (decomp.), after sintering at 136° (144—145°); *o*-nitrobenzoate, 219° decomp. (222°).

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The Polymorphism of Chalkone. By R. J. W. LE FÈVRE.

DURING the preparation of chalkone for work already described (J., 1933, 344), it was noticed that the m. p. of apparently pure specimens of chalkone could be materially altered by a single fusion. Later, following Weygand and his collaborators (*Ber.*, 1929, **62**, 2603, and other papers), a sample with m. p. *ca.* 30° was obtained by seeding a melt with a minute crystal of dibenzoylmethane, and its polarisation in benzene solutions compared at 25° with that of the normal form, m. p. *ca.* 58°. The incidental measurements are recorded below; f_1, ε, and $d_{4^\circ}^{25^\circ}$ refer respectively to the molar fractions of the solute in the solutions, to the dielectric constants, and to the densities. Since the last two properties are linear with f_1, the expressions $\varepsilon = \varepsilon_2 (1 + \alpha f_1)$ and $d = d_2(1 + \beta f_1)$ are applicable.

	f_1.	ϵ.	$d_{4^\circ}^{25^\circ}$.	$\alpha\epsilon_2$.	βd_2.
Benzene	0	2·2725	0·87380	—	—
Chalkone, m. p. 58—59°	0·01201	2·4385	0·87968	13·819	0·4895
	0·01751	2·5128	0·88230	13·722	0·4854
	0·02205	2·5751	0·88451	13·723	0·4857
	0·02811	2·6589	0·88749	13·746	0·4870
Chalkone, m. p. *ca.* 30°	0·01501	2·4801	0·88101	13·831	0·4803
	0·02261	2·5806	0·88476	13·627	0·4847
	0·02565	2·6255	0·88636	13·762	0·4897
	0·02959	2·6799	0·88830	13·768	0·4900

The essential constancy of $\alpha\varepsilon_2$ and βd_2 for the two solutes suggests that they are polymorphs and not geometrical isomerides. These results thus confirm those recently published by Eisenlohr and Metzner (*Z. physikal. Chem.*, 1937, **178**, *A*, 350) relating to chalkone modifications of m. p. 49°, 57°, and 59°, for which moments 3·02, 2·98, and 3·00 D respectively were reported.

Calculated from the equation ${}^{\infty}P_1 = A(M_1 - B\beta d_2) + C\alpha\varepsilon_2$ (cf. J., 1936, 491) with the data tabulated above (mean $\alpha\varepsilon_2 = 13{\cdot}750$, mean $\beta d_2 = 0{\cdot}4865$), ${}^{\infty}P_1 = 257{\cdot}8_8$ c.c. (for the benzene used, $A = 0{\cdot}34085$, $B = 89{\cdot}265$, $C = 14{\cdot}670$). Auwers and Eisenlohr (*J. pr. Chem.*, 1911, **84**, 67) found $n_{\mathrm{D}}^{62\cdot3^\circ}$ 1·6458 and $d_{4^\circ}^{62\cdot4^\circ}$ 1·0712, whence $[R_L]_{\mathrm{D}} = 70{\cdot}5$. The present measurements, therefore, correspond to a moment of $3{\cdot}0_1$D units; the good agreement with Eisenlohr and Metzner's result suggests that Bergmann's value for chalkone (2·92 D) (J., 1936, 402) is somewhat low.—UNIVERISTY COLLEGE, LONDON. [*Received, May 13th*, 1937.]