961. *Nucleophilic Displacements in Organic Sulphites. Part IV.* The Effects of Added Salts on the Solubility of Ethylene Sulphite.*

By E. D. Davies and J. G. Tillett.

Added salts have marked specific effects on the rate of acid-catalysed hydrolysis of ethylene sulphite. Since interpretation of these data involves consideration of the activity coefficients of initial and transition states for the reaction, the corresponding effects on the activity coefficient of ethylene sulphite have been estimated by determining its solubility at 25° in aqueous solutions of various uni-univalent electrolytes.

Experimental.—Ethylene sulphite had b. p. 88°/52 mm., n_D^{25} 1·4450. The salts used were either " AnalaR " or were recrystallised and dried. Tetraethylammonium perchlorate was prepared from the corresponding hydroxide.

Excess of ethylene sulphite was added to a known volume of salt solution. The mixture was placed in a thermostat for 1 hr. and vigorously stirred. It was then allowed to settle; portions (5 ml.) of the aqueous layer were removed and titrated with 0·905M-sodium hydroxide, thymolphthalein being used as indicator. The results are given in the Table:

Salt	[Salt] (M)	NaOH (ml.)	$S_i°/S_i$	log $S_i°/S_i$	K
None	—	17·80	—	—	—
NaCl	1·0	14·50	1·228	0·0890	0·089
NaCl	2·0	12·15	1·465	0·1659	0·083
NaCl	3·0	10·00	1·780	0·2504	0·081
NaBr	1·0	16·40	1·085	0·0356	0·0356
NaBr	2·0	15·30	1·163	0·0657	0·0329
$NaClO_4$	2·0	46·11	0·3860	−0·4134	−0·207
$NaO·SO_2·C_7H_7$	1·0	32·07	0·5550	−0·2556	−0·256
Et_4NClO_4	0·1	17·91	0·9940	−0·0026	−0·026
KI	1·0	19·84	0·8973	−0·0471	−0·047
Et_4NCl	1·0	20·53	0·8670	−0·0620	−0·062
KCl	1·0	15·66	1·137	0·0557	0·056

The solubility of ethylene sulphite was 18·0 g./100 ml. The effect of added salts on the activity coefficient of a non-electrolyte is given [1] by the equations:

$$\log f_i/f_i° = \log S_i°/S_i = k_s c_s + k_i(S_i - S_i°)$$

Here $f_i°$ and f_i are the activity coefficients in the pure solvent and in the solvent with added salt; $S_i°$ and S_i are the corresponding solubilities; c_s is the concentration of the salt; k_s is the salting-out parameter, *i.e.*, the parameter which takes into account interaction between ions and non-electrolytes; and k_i is the self-interaction parameter.

If $S_i°$ and S_i are low, the last term may be neglected and the following relationship holds:

$$\log f_i/f_i° = \log S_i°/S_i = k_s c_s$$

In the present case this assumption cannot be made, but the Setchenow equation, which is of similar form, would be expected to hold, *viz.*:

$$\log S_i°/S_i = K c_s$$

where K is the Setchenow constant. Values of K are calculated from the results and indicated in the table.

The results show that sodium chloride, sodium bromide, and potassium chloride decrease the solubility of ethylene sulphite in water, *i.e.*, they salt-out this ester. Sodium perchlorate, sodium toluene-*p*-sulphonate, potassium iodide, and tetraethylammonium chloride have the opposite effect, whereas tetraethylammonium perchlorate has hardly any effect.

* Parts I—III, preceding papers.

[1] Long and McDevitt, *Chem. Rev.*, 1952, **51**, 119.

The salting-in of ethylene sulphite by perchlorate ions is in accord with the observed salting in by perchlorate ions of ethyl acetate,[2] ethyl methyl ketone,[3] and γ-butyrolactone.[4]

The salting in by the tetraethylammonium chloride is to be expected because of the large size of the cation, but the negligible effect of the corresponding perchlorate is unexpected.

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[2] Waind, *J.*, 1954, 2879.
[3] Duclaux and Derand-Gasselin, *J. Chim. phys.*, 1938, **35**, 189.
[4] Long, McDevitt, and Dunkle, *J. Phys. Colloid Chem.*, 1951, **55**, 814.

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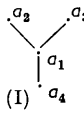
962. *A Rapid Method for the Calculation of the Molecular-orbital Secular Equation.*

By D. S. URCH.

MANY applications of molecular-orbital theory require the construction of a determinant whose roots give the first approximation to the energy levels of the system under consideration. For large molecules and molecules including hetero-atoms this is difficult and tedious. The following simple direct method for the calculation of the secular equation has therefore been devised. Its extension to include variable parameters is simple and is also described.



(I)

Definition of Symbols.—Common symbols have their usual meaning.[1] If r is a hetero-atom and s is a carbon atom, then let

$$x = (H_{rr} - ES_{rr})/H_{rs} = (\alpha_c - E)/\beta$$
$$h.\beta = (H_{rr})_{\text{hetero-atom}} - (H_{rr})_{\text{carbon atom}}; \quad k.\beta = H_{rs}$$

Consider the system (I) which is a portion of any given molecular orbital of energy x, with coefficients a_r at the rth atom. This system can be considered as an isolated system about a_1 since atom 1 is assumed to interact only with its immediate neighbours, $a_{2,3,\&4}$. It is then possible to write

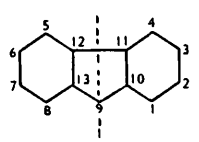
$$a_2 + a_3 + a_4 + a_1.x = 0 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

by using the normal simplifications.[2] It is more convenient if x, as used in this paper, has the value normally ascribed to $-x$. Thus for the roots of the final equation positive values of x are bonding (normally negative roots) and negative values are anti-bonding (normally positive roots).

Thus
$$\sum_{+\neq 1} a_r = a_1.x \text{ (r adjacent to 1)} \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

Equation (1) has the same array of coefficients as would occur in the corresponding line in the secular determinant.

It is possible to write equations of the same form as (1) or (2) about every atom in the molecule. Thus all the coefficients can be evaluated in terms of a few. As there are n atoms in the molecule there will be n equations so that finally all the coefficients can be eliminated leaving an equation in x alone. This is the same equation as would have been obtained by the solution of the secular determinant [(eqn. (3)].



(II)

Variable parameters (*e.g.*, about a hetero-atom) are best considered about the last atom in order that over-complicated expressions be not carried from atom to atom.

Fluorenyl System.—As an example, consider the fluorenyl system (I). The simplifying effect of symmetry is used whenever possible. The broken line is the axis of symmetry.

[1] Coulson, " Valence," Oxford Univ. Press, 1952, p. 60.
[2] Huckel, *Z. Physik*, 1931, **70**, 204, 227.

Anti-symmetric levels. These are the same as the anti-symmetric levels of diphenyl.

Symmetric levels. *A*. For a homo-atomic system:

Let $$a_2 = a_7 = m; \quad a_3 = a_6 = n$$

Now apply eqn. (2) successively around the molecule:

About atom 3 (or 6) $a_2 + a_4 = a_3.x \;\; \therefore a_4 = n.x - m = a_5$

About atom 2 (or 7) $a_1 + a_3 = a_2.x \;\; \therefore a_1 = m.x - n = a_8$

About atom 4 (or 5) $a_3 + a_{11} = a_4.x \;\; \therefore a_{11} = n(x^2 - 1) - m.x = a_{10}$

About atom 1 (or 8) $a_2 + a_{10} = a_1.x \;\; \therefore a_{12} = m(x^2 - 1) - n.x = a_{13}$

About atom 11 (or 12) $a_4 + a_{12} + a_{10} = a_{11}.x$

$$\therefore (nx - m) + n(x^2 - 1) - mx + m(x^2 - 1) - nx = x[n(x^2 - 1) - mx]$$

$$\therefore m = \frac{(x - 1)(x^2 - 1)}{2(x^2 - 1) - x}.n = kn$$

About atom 10 (or 13) $a_9 + a_{11} + a_1 = a_{10}.x$

$$\therefore a_9 = m.x(x^2 - 1) - n.x^2 - n(x^2 - 1) + m.x - m.x + n$$

$$\therefore a_9 = (x^2 - 1)(m.x - 2n)$$

About atom 9 $a_{13} + a_{11} = a_9.x \;\; \therefore a_9 = 2[m(x^2 - 1) - n.x]/x$

thus $(x^2 - 1)(m.x - 2n) = 2[m(x^2 - 1) - n.x]/x$

or $(x^2 - 1)(k'.x - 2n) = 2[k'(x^2 - 1) - x]/x$

Hence $$x(x^2 - 1).(k'.x - 2n) - 2[k'(x^2 - 1) - x] = 0 \quad . \quad . \quad . \quad . \quad (3)$$

$$\text{when } k' = \frac{(x - 1).(x^2 - 1)}{2(x^2 - 1) - x}$$

B. For a hetero-atomic system: Let atom 9 be the hertero-atom. The parameters h and k can now be included (others for the inductive effect on neighbouring atoms could be added if desired).

Equations are evaluated as before but about atoms 9, 10, and 13 the parameters must be included. Thus, about atom 10 (or 13)

$$a_9.k + a_{11} + a_1 = a_{12}.x \;\; \therefore a_9.k = (x^2 - 1).(m.x - 2n)$$

about atom 9 $$k.(a_{13} + a_{10}) = a_9.(x - h)$$

$$\therefore a_9k = k^2.2[m(x^2 - 1) - nx]/(x - h)$$

$$\therefore \frac{k^2}{(x - h)} = \frac{(x^2 - 1)(k'x - 2)}{2[k'(x^2 - 1) - x]} \quad . \quad . \quad . \quad . \quad . \quad (4)$$

The above equations have been arrayed in a formal manner. In practice it is possible to step round a molecule very quickly and write the coefficients beside the diagram. This method is very much easier and quicker than the construction and solution of the determinant and enables coefficients to be found directly for any orbital at any atom with no extra labour.

The inclusion of continuously variable parameters instead of guessed digits for hetero-atomic factors enables the variation of energy levels to be observed as in (II), in which various fixed values have been given to h and the effect of the variation of k upon the energy levels of the π electrons over the whole molecules has been found in each case from eqn. (4).

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963. *Characterisation of Thiols by Means of their* p-p'-*Nitrophenylazobenzoyl Derivatives.*

By El S. Amin.

p-p'-NITROPHENYLAZOBENZOYL CHLORIDE, already used for identification and separation of alcohols [1] and amines,[2] has now been applied for those purposes to thiols. The chloride with nine thiols has given the thiol-esters in fairly good yields on reaction in pyridine–benzene at convenient temperatures. The esters have sharp melting points in a convenient range, in contrast to other reagents,[3] and crystallise well. Occasionally contaminating nitrophenylazobenzoic acid requires chromatographic removal. The esters are brightly coloured, which assists in chromatographic separations, some examples of which are recorded below. The technique has been used to confirm [4] the presence of methanethiol in the Egyptian radish.

Experimental.—Evaporations were effected under reduced pressure at 50°. M. p.s were determined on a Kofler microscope stage.

Preparation of the thiol-esters. The thiol (0·5 mmole) and *p-p'*-nitrophenylazobenzoyl chloride [1] (0·725 mmole) were kept in 1 : 1 pyridine–benzene (30 ml.) at 5°, room temperature, or 50° (according to the b. p. of the thiol) for 1—2 days. The mixture was then treated with water and extracted with 1 : 1 benzene–ether (50 ml.). The extract was washed with 20% sulphuric acid, filtered, washed with water, aqueous sodium carbonate, and water, concentrated to *ca.* 20 ml., and filtered through activated alumina. The main, lower red band was eluted with benzene, and the product recrystallised from ethanol or acetone (as needles). The p-p'-*nitrophenylazo(thiolbenzoates)* shown in the Table were thus prepared in 80—85% yield.

Hydrolysis by potassium hydroxide (1 mol.) in 2-methoxyethanol for a few hr. at room temperature or 1—2 days at 5° regenerated the thiol

Thiol-esters, $NO_2{\cdot}C_6H_4{\cdot}N_2{\cdot}C_6H_4{\cdot}CO{\cdot}SR$

R	Colour	Solvent	M. p.	Found N (%)	Formula	Reqd. N (%)
Me	Red	Ethanol	162°	14·0	$C_{14}H_{11}O_3N_3S$	14·0
Et	Red	EtOH	154	13·2	$C_{15}H_{13}O_3N_3S$	13·3
Pr^n	Orange	EtOH	146	12·9	$C_{16}H_{15}O_3N_3S$	12·8
Bu^n	,,	EtOH	134	12·5	$C_{17}H_{17}O_3N_3S$	12·7
n-C_5H_{11}	,,	$COMe_2$	130	11·6	$C_{18}H_{19}O_3N_3S$	11·8
n-C_6H_{13}	,,	EtOH	124	11·1	$C_{19}H_{21}O_3N_3S$	11·1
n-C_7H_{15}	,,	$COMe_2$	125	11·2	$C_{20}H_{23}O_3N_3S$	11·0
n-C_9H_{19}	Orange-yellow	EtOH	125	10·3	$C_{22}H_{27}O_3N_3S$	10·0
Ph	Orange	EtOH	224	11·3	$C_{19}H_{13}O_3N_3S$	11·8
p-C_6H_4Me	,,	EtOH	172	11·5	$C_{20}H_{15}O_3N_3S$	11·1
CH_2Ph	,,	EtOH	169	11·0	$C_{20}H_{15}O_3N_3S$	11·1

Chromatography. The two layers formed by a 15 : 1 : 3 v/v mixture of decane, nitromethane, and dimethylformamide were separated. A tube (*ca.* 40 cm. long, 2 cm. in diameter) was half-filled with the decane layer. A 1 : 1 w/w mixture (40 g.) of the other layer and kieselguhr (dried at 110°) was made into a sludge with the decane layer (40 c.c.) and added to the column. When the column had drained, the thiol-ester (15 mg.) in the decane layer was added and the chromatogram was developed with the decane layer under slight suction. Materials eluted were recrystallised from ethanol. The following results are typical.

(i) A mixture of the esters (1 mg. each) from methane-, propane-1-, pentane-1-, and nonane-1-thiol was chromatographed on a 10 × 2 cm. column. Eluent fractions were 1 c.c. each. Fractions 1—10 yielded nonyl ester (0·6 mg.), fractions 11—23 pentyl ester (0·7 mg.), fractions 24—50 propyl ester (0·5 mg.), and fractions 55—80 methyl ester (0·7 mg.), all identified by m. p. and mixed m. p.

(ii) A mixture of the esters (1 mg. each) from ethane-, propane-1-, butane-1-, pentane-1-, and

[1] Hecker, *Chem. Ber.*, 1955, **88**, 1666; Amin and Hecker, *ibid.*, 1956, **89**, 695.
[2] Amin, *J.*, 1957, 3764.
[3] Bost, Turner, and Norton, *J. Amer. Chem. Soc.*, 1932, **54**, 1985; Wertheim, *ibid.*, 1929, **51**, 3661.
[4] Nakamura, *Biochem. Z.*, 1925, **164**, 31.

hexane-1-thiol were chromatographed on kieselguhr impregnated with dimethyloxosilane,[2] the solvents being 5 : 5 : 3-v/v formamide–nitromethane–nonane, in a 11·8 × 2 cm. column. Eluent fractions were: nos. 1—10, 3 ml.; nos. 11—25, 4 ml.; nos. 26—31, 5 ml. each. Photometric readings showed slight overlap for the pairs ethyl–propyl, propyl–butyl, and butyl–pentyl, but a gap of 6 fractions (4 ml. each) between the pentyl and the hexyl ester.

Examination of Strophanum sativum Egyptiacum. Radish roots (5 kg.) were crushed with pure sand at 0° and extracted with light petroleum (b. p. 30—50°) at 5°. The petroleum extract (5 l.) was dried (Na_2SO_4), mixed with dry benzene (5 l.), *p-p'*-nitrophenylazobenzoyl chloride (0·5 g.), and pyridine (10 ml.), and was kept at 5° for a week. The solution was then warmed in a closed vessel at 30—60° for 6 hr., concentrated to 250 ml., washed with 20% sulphuric acid, filtered, washed in turn with water, sodium carbonate solution, and water, and placed on an alumina column. Of the two coloured bands produced the lower was eluted with benzene, giving 50·4 mg. of material which on hydrolysis gave the odour of methanethiol. The upper band on elution (5·8 mg.) and hydrolysis gave no foul smell.

The substance from the lower band (40 mg.) was subjected to partition chromatography on kieselguhr–dimethyloxosilane with formamide–nitromethane–nonane, giving two bands. Elution of the main lower band and recrystallisation from ethyl alcohol gave red needles (26 mg.), m. p. 162° alone or mixed with the methyl thiol ester (Found: N, 14·0%).

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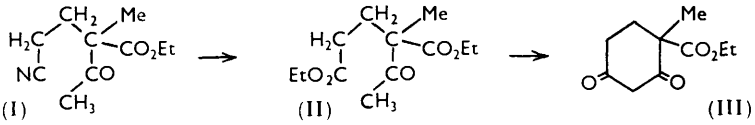
964. *Preparation of Ethyl* 1-*Methyl*-2 : 4-*dioxo*cyclo*hexane*-1-*carboxylate.*

By S. M. MUKHERJI, R. K. SHARMA, and O. P. VIG.

ETHYL 1-METHYL-2 : 4-DIOXO*cyclo*HEXANE-1-CARBOXYLATE (III), first prepared 20 years ago,[1] has been prepared by us by a more convenient method as an intermediate in a projected synthesis of artificial steroid gonadogens and we now record it in view of the recent publication of Stetter and Milbers [2] on analogous *cyclo*hexanediones. Ethyl methyl-



acetoacetate [3] with acrylonitrile [4] and 30% methanolic potassium hydroxide in *tert.*-butyl alcohol gave the nitrile ester (I) which on alcoholysis [5] gave a 79% yield of diethyl α-methyl-α-acetylglutarate (II). Alcohol-free potassium *tert.*-butoxide cyclised this in 70·4% yield to the monoester (III).

Experimental.—Ethyl α-methyl-α-2-cyanoethylacetoacetate (I). To ethyl methylacetoacetate [3] (160 g.) and 30% methanolic potassium hydroxide (9 c.c.) in *tert.*-butyl alcohol (300 c.c.) was added acrylonitrile (90 g.) dropwise with stirring at 30—35°. The solution was then neutralised and worked up in the usual manner. The *ester* (I) was obtained at 142—146°/5 mm. (yield 145 g., 66·2%) (Found: C, 60·9; H, 7·4. $C_{10}H_{15}O_3N$ requires C, 60·9; H, 7·7%).

Diethyl α-methyl-α-acetylglutarate (II). A solution of ethyl α-methyl-α-2-cyanoethylacetoacetate (II) (145 g.) in absolute alcohol (300 c.c.) was saturated with dry hydrogen chloride in 8 hr. The temperature was kept below 0° and the contents were continuously and efficiently stirred throughout and later set aside overnight. After removal of most of hydrogen chloride at 40° at the water-pump the contents were poured into an excess of ice-cold 20% sodium carbonate solution in a thin stream and at once extracted with ether (3 × 300 c.c.). The

[1] Lin and Robinson, *J.*, 1938, 2006.
[2] Stetter and Milbers, *Chem. Ber.*, 1958, **91**, 374.
[3] Folkers and Adkins, *J. Amer. Chem. Soc.*, 1931, **53**, 1416.
[4] Misra and Shukla, *J. Indian Chem. Soc.*, 1952, **29**, 201.
[5] Kimbal, Jefferson, and Pikes, *Org. Synth.*, Coll. Vol. II, 1946, p. 284.

ether extract was washed free from alcohol with ice-cold 5% sodium chloride solution and then shaken with ice-cold 10% sulphuric acid solution (300 c.c.). This was repeated twice and the acid layer containing the imidate was separated and heated at 50° for ½ hr. in order to hydrolyse it. It was cooled and extracted with ether. The acid solution was again heated at 80—90° and extracted with ether. All the ether extracts were combined, washed first with sodium carbonate solution, then with water, and dried (Na_2SO_4). After removal of the ether the residue was fractionated, giving the diester (II), b. p. 132—134°/5 mm. (142 g., 79·1%) (Found: C, 59·4; H, 8·4. $C_{12}H_{20}O_5$ requires C, 59·0; H, 8·25%).

Ethyl 1-methyl-2 : 4-dioxocyclohexane-1-carboxylate (III). The diester (II) (70 g.) in dry ether (200 c.c.) was added dropwise with swirling to a suspension of alcohol-free potassium *tert.*-butoxide (from 12·5 g. of potassium) in dry ether (500 c.c.). The mixture which soon solidified was refluxed for 3 hr. and cooled, and 3% sodium hydroxide solution (200 c.c.) was added. The aqueous layer after being extracted with ether (2 × 100 c.c.) was acidified with dilute hydrochloric acid and the separated oil extracted with ether. This ether extract was washed with water, dried, and evaporated. The diketo-ester (III) obtained had b. p. 145—148°/5 mm., m. p. 85° (from benzene) lit.,[1] m. p. 81·5—82·5° (40 g., 70·4%) (Found: C, 61·0; H, 6·9. Calc. for $C_{10}H_{14}O_4$: C, 60·6; H, 7·1%).

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965. *Reactions of Disodium Pentacyanoamminoferrate with Aromatic Amines. Part III.*[1] *The Preparation of 2 : 7-Dimethylphenazine from p-Toluidine.*

By E. F. G. HERINGTON.

THE reaction of disodium pentacyanoamminoferrate $Na_2[Fe(CN)_5NH_3]$ with many aromatic amines gives highly coloured solutions [1-3] containing ions of the general structure $[Fe(CN)_5NHR]^{3-}$ which are stable, but reaction of excess of the salt with *p*-toluidine gives a complex which decomposes and deposits a brown solid from the solution. A sample of 2 : 7-dimethylphenazine has been separated by chromatography from this crude product in a yield of 40% of the weight of *p*-toluidine taken.

Bamberger and Ham [4] obtained the heterocyclic base by reaction of *p*-nitrosotoluene with concentrated sulphuric acid. Their observation that 2 : 7-dimethylphenazine is not formed by the action of *p*-toluidine on *p*-nitrotoluene in the presence of sodium hydroxide although phenazine is formed by the action of aniline on nitrobenzene under similar conditions has been confirmed in the present study.

The following compounds may be mentioned as some of the products identified when *p*-toluidine in aqueous solution is oxidized by various reagents: *p*-azotoluene, 4 : 4′-dimethylazobenzene, 4-amino-2 : 5-toluquinone di-*p*-tolylimine, 4-*p*-toluidino-2 : 5-toluquinone di-*p*-tolylimine, 2 : 7-dimethyl-3-*p*-toluidinophenazine, and di-*p*-tolylamine.

However, direct oxidation of *p*-toluidine to 2 : 7-dimethylphenazine has only been reported to take place photochemically,[5] so the action of disodium pentacyanoamminoferrate appears to be unique.

The mechanism of the formation of 2 : 7-dimethylphenazine by the reaction of disodium pentacyanoamminoferrate with *p*-toluidine is probably as follows. The first step is the replacement of ammonia by *p*-toluidine [equation (1)] and this is then followed by the reaction shown in equation (2).

$$Na_2[Fe(CN)_5NH_3] + H_2N{\cdot}C_6H_4Me = Na_2[Fe(CN)_5H_2N{\cdot}C_6H_4Me] + NH_3 \quad (1)$$

$$Na_2[Fe(CN)_5H_2N{\cdot}C_6H_4Me] + NaOH = Na_3[Fe(CN)_5HN{\cdot}C_6H_4Me] + H_2O \quad (2)$$

[1] Part II, Herington, *J.*, 1958, 4683.
[2] Herington, *Nature*, 1955, **176**, 80.
[3] Herington, *J.*, 1956, 2747.
[4] Bamberger and Ham, *Annalen*, 1911, **382**, 82.
[5] Malaviya and Dutt, *Proc. Acad. Sci. United Provinces Agra Oudh, India*, 1935, **4**, 319; *Chem. Abs.*, 1936, **30**, 1056.

The resulting pentacyanoferrate complex is unstable, and as a result two of the complex radicals shown in equation (2) react to yield 2-amino-5 : 4′-dimethyldiphenylamine; for a discussion of the similar instability of the ion $[Fe(CN)_5HN{\cdot}C_6H_5]^{3-}$ see Part II.[1] The 2-amino-5 : 4′-dimethyldiphenylamine then reacts to give the ion $[Fe(CN)_5,NH{\cdot}C_6H_3Me{\cdot}HN{\cdot}C_6H_4Me]^{3-}$ which is oxidized further to close the central ring and to yield 2 : 7-dimethylphenazine.

Support for this mechanism was obtained when it was shown that disodium pentacyanoamminoferrate reacts with 2-amino-5 : 4′-dimethyldiphenylamine to give material containing 2 : 7-dimethylphenazine. Ring closure occurred in this reaction at room temperature, whereas hitherto it had been necessary to heat *o*-aminodiphenylamines with litharge to a very high temperature in order to obtain phenazines.[6]

Experimental.—Oxidation of p-*toluidine.* A solution of disodium pentacyanoamminoferrate[3] (2·5 g.), in 0·025N-sodium hydroxide (70 ml.), was poured on finely pulverized *p*-toluidine (0·25 g.), and the mixture was shaken for 7 days. The solid (0·16 g.) was then removed from the muddy green solution, washed with water, and dried in a vacuum over calcium chloride It gave a strong green colour with concentrated sulphuric acid in the cold, and a red solution when heated.

The solid in benzene (20 ml.) was passed through activated alumina (20 × 1·8 cm.). Washing with benzene removed successively a diffuse band (fraction 1), a yellow band (fraction 2), and a light brown band (fraction 3). Other fractions were washed out but were not examined.

4 : 4′-*Dimethylazobenzene.* The solid (0·002 g.) in fraction 1 had m. p. 140° and gave a yellow colour with concentrated sulphuric acid in the cold. It was shown to be 4 : 4′-dimethylazobenzene by a comparison of its infrared spectrum with that of a sample prepared by the reaction between *p*-nitrosotoluene and *p*-toluidine.

2 : 7-*Dimethylphenazine.* Fraction 3 from the crude product was rechromatographed on activated alumina. The yellow solution obtained was combined with fraction 2 and after removal of the benzene yielded 0·1 g. of solid [Found: C, 80·5; H, 6·4; N, 13·2%; *M* (Rast), 215. Calc. for $C_{14}H_{12}N_2$: C, 80·8; H, 5·8; N, 13·5%; *M*, 208]. This dissolved in concentrated sulphuric acid to give a strong red colour which yielded a bright yellow solution on dilution with water (characteristic of phenazine derivatives). It had m. p. 162° alone or mixed with 2 : 7-dimethylphenazine (m. p. 163°) prepared from *p*-nitrosotoluene, and the infrared spectra of these materials were identical.

p-Tolylhydroxylamine was prepared according to the second method described by Bamberger and Rising.[7] *p*-Nitrosotoluene (3·8 g.), made therefrom,[8] was introduced in glacial acetic acid (12 ml.) into ice-cold concentrated sulphuric acid (12 ml.) with stirring. After ½ hr. the product was poured on ice (50 g.) and water (50 g.). Bamberger and Ham [4] reported that the product obtained from this reaction was complex and contained at least six components which were difficult to separate. In the present experiments 2 : 7-dimethylphenazine *N*-oxide was isolated from the crude product by chromatography. The acid aqueous solution was filtered and extracted with benzene and the extract was passed through activated alumina (16 × 1·8 cm.). The chromatogram was developed with benzene and the first (yellow) and the second (orange) fraction (purplish on the column) were rejected. The third (yellow-orange) fraction contained slightly impure 2 : 7-dimethylphenazine *N*-oxide, m. p. 199° (lit.,[4] m. p. 204—205°). The oxide (0·1 g.) was treated in concentrated hydrochloric acid with a concentrated hydrochloric acid solution of stannous chloride. The green precipitate [4] was filtered off and boiled with 20% sodium hydroxide solution, and the resulting 2 : 7-dimethylphenazine was removed; it had m. p. 163° (Bamberger and Ham give m. p. 163°).

The chromatogram showed at least 9 other bands, indicating the complexity of the material.

2-*Amino*-5 : 4′-*dimethyldiphenylamine.* 4 : 4′-Dimethylhydrazobenzene [9] was isomerized to 2-amino-5 : 4′-dimethyldiphenylamine by the action of hydrochloric acid as reported by Täuber.[10]

[6] Campbell, Le Fèvre, Le Fèvre, and Turner, *J.*, 1938, 404; Mikhailov and Blokhina, *Izvest. Akad. Nauk S.S.S.R., Otdel. Khim. Nauk*, 1950, 304; *Chem. Abs.*, 1950, **44**, 9452.

[7] Bamberger and Rising, *Annalen*, 1901, **316**, 280.

[8] Wieland and Roseeu, *Ber.*, 1915, **48**, 1117.

[9] Cf. Hickinbottom, " Reactions of Organic Compounds," Longmans, Green and Co., London, 1941, p. 320.

[10] Täuber, *Ber.*, 1892, **25**, 1019.

Oxidation of 2-amino-5 : 4'-dimethyldiphenylamine by $Na_2[Fe(CN)_5NH_3]$ *and separation of the products.* The conditions were those described for the reaction of *p*-toluidine with $Na_2[Fe(CN)_5NH_3]$. The solid obtained was passed in benzene through alumina. The pink material in the first band was rejected, but the yellow solution which followed yielded 0·04 g. of solid (16% of the wt. of amine), m. p. 162° not depressed when mixed with 2 : 7-dimethylphenazine prepared from *p*-nitrosotoluene. The infrared spectra of these two specimens were identical.

A preliminary note on this work has been published.[2] The work described formed part of the research programme of the Chemical Research Laboratory and this note is published by permission of the Director.

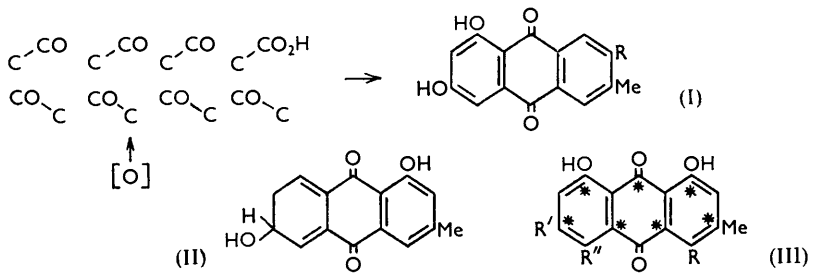
NATIONAL CHEMICAL LABORATORY,
TEDDINGTON, MIDDLESEX.

[*Received, June 16th,* 1958.]

966. *Studies in Relation to Biosynthesis. Part XIX.* The Biosynthesis of Helminthosporin.*

By A. J. BIRCH, A. J. RYAN, and HERCHEL SMITH.

IN 1953 it was suggested[1] that the structures of a large group of anthraquinones were consistent with a phytochemical synthesis by a process involving head-to-tail linkage of acetic acid units and appropriate cyclisation and secondary reactions. The example most closely related to this scheme is the anthraquinone acid, endocrocin (I; R = CO_2H), from *Nephromopsis endocrocea*[2] and *A. amstelodami*,[3] which would be formed from eight acid units with the introduction of one quinone-oxygen atom. Apart from decarboxylated analogues, *e.g.*, emodin (I; R = H), many variants of the same anthraquinone skeleton are known which are characterised by absence of oxygen substituents in the " expected " positions or possessing " additional " oxygen substituents, or both. These can be rationalised on the basis of oxidations, reductions, and dehydrations which are either known to occur in vital systems or have laboratory or biological analogies (for a discussion see ref. 4).



Originally it was our intention to study, by feeding experiments with $CH_3 \cdot {}^{14}CO_2H$, the biosynthesis of flavoskyrin[5] (II) in *P. islandicum* Sopp. This substance is readily transformed by acid into chrysophanic acid (III; R = R' = R'' = H) which is known to form a tetranitro-derivative suitable for scission by the bromopicrin method either directly or after conversion into 3-hydroxy-2 : 4 : 6-trinitrobenzoic acid.[6] We were, however, unable to obtain a culture of this organism and therefore turned to similar studies with *H. graminium* Rabenhorst. Although this organism is reported[7] to give abundant yields

* Part XVIII, *J.*, 1958, 4582.

[1] Birch and Donovan, *Austral. J. Chem.*, 1953, **6**, 360.
[2] Asahina and Fusikawa, *Ber.*, 1935, **68**, 1558.
[3] Ashley, Raistrick, and Richards, *Biochem. J.*, 1939, **33**, 1291, and references there cited; Shibata and Natori, *Pharm. Bull.* (*Japan*), 1953, **1**, 160.
[4] Birch, *Fortschr. Chem. org. Naturstoffe*, 1957, **16**, 186.
[5] Howard and Raistrick, *Biochem. J.*, 1955, **59**, 475.
[6] Léger, *Compt. rend.*, 1912, **154**, 281; *J. Pharm. Chim.*, 1912, **5**, 281.
[7] Charles, Raistrick, Robinson, and Todd, *Biochem. J.*, 1933, **27**, 499.

of helminthosporin (III; R = R′ = H, R″ = OH) and catenarin (III; R = R″ = H, R′ = OH), in our hands it gave a complex mixture of pigments from which we obtained a small quantity of helminthosporin as the only recognisable product. Owing to the lack of material the only degradation we were able to carry out on the labelled helminthosporin from $CH_3 \cdot {}^{14}CO_2H$ was Kuhn–Roth oxidation. Examination of the resultant acetic acid by pyrolysis of the lithium salt [8] showed that all the radioactivity was located on the carboxyl group and that this constituted one-seventh of the activity of the labelled helminthosporin. This result is in accord with the distribution of activity (III; labelled atoms *) postulated on the basis of the suggested biosynthesis. Taken in conjunction with earlier work showing the biosynthesis of a number of mould and plant [9] products through head-to-tail linkage of acetic acid units, it provides strong presumptive evidence that a large number of anthraquinones are formed in Nature by a similar process.

Experimental.—General directions are as for Part XVII.[9]

[^{14}C]*Helminthosporin. H. graminium* Rabenhorst was grown as described earlier. After 28 days $CH_3 \cdot {}^{14}CO_2Na$ (0·3 mc) in water was added to the culture medium. After a further 21 days the cultures were harvested. The dried mycelium was exhausted by percolation with chloroform, and the resulting bright red solid (16 g. from 18 l. of medium) was de-fatted with boiling light petroleum (b. p. 40—60°). The residue (12 g.) was dissolved in ethyl acetate had separated into fractions soluble in aqueous sodium hydrogen carbonate, sodium carbonate, and sodium hydroxide, denoted A, B, and C respectively. Fraction A was a red solid (0·25 g.) which was not examined further. Fraction B was expected to contain catenarin; it was treated with acetic anhydride in pyridine, and the product chromatographed in ether on Florisil, but no recognisable product was obtained. Fraction C (1·2 g.) had m. p. 190—210°. It was acetylated and chromatographed on Florisil as for fraction B. The fraction of m. p. 218—220° (lit.,[7] m. p. for helminthosporin triacetate 226—227°) was hydrolysed by 10% aqueous sodium hydroxide. The product was recrystallised from ethyl acetate, to give helminthosporin (0·118 g.; 9×10^{-5} mc), m. p. 220—221° (lit.,[7] m. p. 223—224°) (Found: r.m.a., 277×10^3). Kuhn–Roth oxidation gave acetic acid, collected as lithium acetate which was pyrolysed to $BaCO_3(Me)$ (Found: r.m.a., 0), and $BaCO_3(CO_2H)$ [Found: r.m.a.; 399×10^2; (1C, 396×10^2)].

This work was carried out during the tenure of a C.S.I.R.O. Overseas Studentship (by A. J. R.). We are grateful to the Rockefeller Foundation and the Distillers Co. Ltd. for financial support and to Imperial Chemical Industries Limited for the loan of counting equipment. We also thank Miss M. Hay for mycological work.

THE UNIVERSITY, MANCHESTER, 13. [*Received, June 20th*, 1958.]

[8] Cornforth, Hunter, and Popjak, *Biochem. J.*, 1953, **54**, 597.
[9] Part XVII, *J.*, 1958, 4576, and references there cited.

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967. *Hydroaromatic Steroid Hormones. Part VII.** (±)-17*a*-Ethynyl-17*a*-hydroxy-D-homo-18 : 19-bisnorandrost-4-en-3-one.†

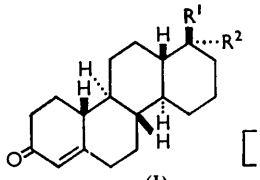
By A. J. BIRCH, G. A. HUGHES, and HERCHEL SMITH.

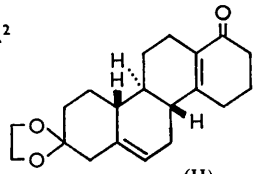
IT has been reported [1] that D-homo-18 : 19-bisnortestosterone (I; R^1 = OH, R^2 = H) is non-androgenic but possesses a high myotrophic activity. These properties are highly desirable in an anabolic agent. In Part V † we confirmed the absence of androgenic activity in the ketol (I; R^1 = OH, R^2 = H) and the propionate (I; R^1 = Et·CO_2, R^2 = H), but recent tests on the same two compounds carried out by Benger's Laboratories, Holmes Chapel, failed to substantiate the claimed myotrophic activity. As part of an attempt to determine whether any hormones based on D-homo-18 : 19-bisnorandrostane retain biological activity we have synthesised the ethynyl alcohol [I; R^1 = OH (or C:CH), R^2 = C:CH (or OH)]. The choice of this compound was due partly to the relatively low structural

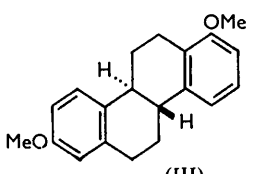
* Part VI, Birch, Pride, and Smith, *J.*, 1958, 4688.
† Nomenclature as for Part V, *J.*, 1956, 4909.
[1] Johnson, Dehn, and Chinn, *J. Org. Chem.*, 1954, **19**, 670.

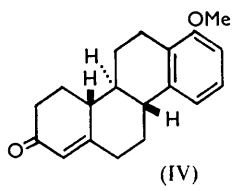
requirement for progestational activity which is apparent from the high activity of 8β-[2] and 8β : 14α-progesterone,[3] partly to the enhancement of activity in 19-norprogesterone,[4] and partly to the claim [5] that 17α-ethynyl-19-nortestosterone is a highly potent gestogen.

The synthesis of the alcohol [I; R^1 = OH (or C:CH), R^2 = C:CH (or OH)] is based on the ketone (II) obtained as an intermediate in the synthesis of the alcohol (I; R^1 = OH,


(I)


(II)


(III)


(IV)

R^2 = H). Reduction of this ketone with lithium in liquid ammonia gave a saturated ketone: no evidence for the formation of a less stable *cis*-isomer (cf. ref. 6) was obtained. Reaction of the latter ketone with lithium acetylide in liquid ammonia, followed by acid hydrolysis, gave the required alcohol. It has no androgenic or myotrophic activity but has not yet been tested for progestational activity. The stereochemistry at the 17*a*-position is not proved, but it is probable that the hydroxyl group has the β-configuration by analogy with the addition of alkali-metal acetylides to 17-oxo-steroids [7] and to a 9-methyl*trans*-decal-1-one. After the completion of this work, Nelson and Garland [8] reported the synthesis of what were claimed to be 18 : 19-bisnorprogesterone and 14α-hydroxy-18 : 19-bisnorprogesterone, neither of which showed progestational activity.

During our work intermediate stages in the synthesis of the ketol (I; R^1 = OH, R^2 = H) have been re-investigated. Selective reduction of the 1 : 3 : 4-substituted benzene ring in the chrysene (III) depends, not only upon the amount of reducing agent, but also on the quality of the liquid ammonia. Reproducible yields (*ca.* 68%) of the ketone (IV) (obtained by acid-hydrolysis and base-catalysed rearrangement of the reduction product) were obtained with 30—35 atom-equiv. of lithium and with ammonia distilled from sodium.

Experimental.—(±)*17a-Ethynyl-17a-hydroxy-*D*-homo-18 : 19-bisnorandrost-4-ene-3-one* [I; R^1 = OH (or C:CH), R^2 = C:CH (or OH)]. 10-Ethylenedioxy-1 : 2 : 3 : 4 : 5 : 6 : 7 : 9 : 10 : 11 : 12 : 13 : 15β : 16α-tetradecahydro-3-oxochrysene (II) (290 mg.) in tetrahydrofuran (20 c.c.) was added dropwise with stirring to a solution of lithium (5—10 mg.) in liquid ammonia (200 c.c.; distilled from sodium), until the blue colour was discharged. Lithium (*ca.* 2 mg.) was added and the solution was decolorised by the addition of more of the tetrahydrofuran solution. The process was repeated until the liquid ammonia remained pale blue after addition of all the ketone solution. The mixture was stirred for 10 min., the blue colour was discharged with sodium nitrite, and water (100 c.c.) was added. The product was recrystallised from light petroleum (b. p. 60—80°) to give a ketone (176 mg.), m. p. 108—111°, $\nu_{max.}$ in carbon disulphide 1710, 1110, and 1050 cm.$^{-1}$. This ketone in tetrahydrofuran (30 c.c.) was added with stirring to a solution of lithium acetylide (from the metal, 250 mg.) in liquid ammonia (30 c.c.) at −70°. The mixture was stirred for 45 min. at this temperature. After 9 hr. ice-water (40 c.c.), was added, and the mixture extracted with ether–ethyl acetate (1 : 1). The product, which showed no ketonic infrared bands, was refluxed in glacial acetic acid (7·5 c.c.) and water (7·5 c.c.) for 45 min. under nitrogen. The solution was poured on a slurry of potassium hydrogen carbonate in water, and the product was collected with ether–ethyl acetate (1 : 1). It was dissolved in benzene (10 c.c.) and chloroform (2·5 c.c.) and adsorbed on Florex (Floridin Co., Warren, Pennsylvania) from which it was eluted with benzene and benzene

[2] Djerassi, Manson, and Segaloff, *J. Org. Chem.*, 1956, **21**, 490.
[3] Barber and Ehrenstein, *Annalen*, 1957, **603**, 89.
[4] Djerassi, Miramontes, and Rosenkrantz, *J. Amer. Chem. Soc.*, 1953, **75**, 4440.
[5] Hertz, Raffelt, and Tuller, *Endocrinology*, 1954, **54**, 228.
[6] Birch, Smith, and Thornton, *J.*, 1957, 1339.
[7] Cf., *e.g.*, Reichstein and Meystre, *Helv. Chim. Acta*, 1939, **22**, 728; Reichstein and Gatzi, *ibid.*, 1938, **21**, 118; and Part VI of our series.
[8] Nelson and Garland, *J. Amer. Chem. Soc.*, 1957, **79**, 6313.

containing increasing proportions of chloroform up to 50% by volume. Recrystallisation from ethanol–tetrahydrofuran gave (±)-17*a*-*ethynyl*-17*a*-*hydroxy*-D-*homo*-18 : 19-*bisnorandrost*-4-*en*-3-*one* (56 mg.), m. p. 232—235° (Found: C, 80·6; H, 8·6. $C_{20}H_{26}O_2$ requires C, 80·5; H, 8·8%), $\nu_{max.}$ (Nujol mull) 3360, 3280, 1670, and 1180 cm.$^{-1}$.

We are indebted to Dr. L. Golberg (Benger's Laboratories, Holmes Chapel, Cheshire) for the biological tests, and to the D.S.I.R. for a Maintenance Grant (to G. A. H.).

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968. *The Indole Alkaloids. Part II.* Vobtusine and Voacangine from* Voacanga dregei.

By B. O. G. SCHULER, A. A. VERBEEK, and F. L. WARREN.

VOBTUSINE, m. p. 286°, was first isolated by Janot and Goutarel [1] from *Voacanga afrikana* Staph. and *V. thoursii* Roem and Schultes (var. *obtusa* K. Schum); they assigned to it the formula $C_{21}H_{26}O_3N_2$ or $C_{20}H_{26}O_3N_2$. Stauffacher and Seebeck [2] recently re-isolated this alkaloid from *V. afrikana* and recorded m. p. 302—305° ± 5°.

The bark of *V. dregei* was previously extracted by Rindl and Groenewoud [3] who reported no crystalline alkaloid. We have now isolated vobtusine as the sole alkaloid of the root bark, whilst from the aerial bark it is obtained in smaller yield and mixed with larger quantities of voacangine.[4]

Vobtusine, for which we find m. p. 305—306° (decomp.), is now assigned the formula $C_{42}H_{50}O_7N_4$ on the basis of molecular-weight determinations. The double formula includes an additional 1 H_2O and avoids the use of $\frac{1}{2}H_2O$ in the formulæ for the alkaloid, the hydrochloride, $C_{42}H_{52}O_7N_4Cl_2,2C_2H_6O$, and the hydrobromide, $C_{42}H_{52}O_7N_4Br_2$. The alkaloid contains two methoxyl groups but no *C*- or *N*-methyl group. In concentrated nitric acid it dissolves to a deep blue solution. Its infrared spectrum shows bands at 1681 and 1608 cm.$^{-1}$, previously reported,[1] which are assigned to a possible amide group and a benzene nucleus respectively, and an additional band now found at 3335 cm.$^{-1}$ indicates a bonded $-NH-$ grouping. Vobtusine with selenium gives quinoline which was identified as picrate and styphnate. Under similar conditions voacangine gives 3-ethyl-5-methylpyridine (isolated as picrate) which was previously isolated on fusion of voacangine with potassium hydroxide.[5]

Despite the close association of vobtusine with voacangine in the plant, the alkaloids seemingly differ considerably in structure, and the indole double bond may not be present in vobtusine since the ultraviolet spectrum is not that of a typical indole. This double bond may be involved in the formation of the double molecule.

Experimental.—Extraction. The ground and dried aerial bark of *V. dregei* from the South Coast, Natal, was extracted with hot alcohol containing 2% of acetic acid. The extract was concentrated and poured into water. The mixture was filtered, made basic with ammonia, and extracted with chloroform. The chloroform extract was concentrated, ethanol was added, and solution was boiled until free from chloroform, filtered from the crystalline solid (vobtusine, yield 0·1%), and evaporated to dryness. The residual gum was ground with plaster of Paris, air-dried, and extracted with light petroleum. The petroleum extract gave a gum which crystallised from methanol to give voacangine (0·15% yield), m. p. 137—138°, $[\alpha]_D^{20}$ −42° (*c* 1 in chloroform) (Found: C, 71·5; H, 7·8; N, 7·6. Calc. for $C_{22}H_{28}O_3N_2$: C, 71·7; H, 7·7; N, 7·6%). Chromatography gave no other alkaloids. The root bark gave only vobtusine, in 0·5% yield.

* Part I, *J.*, 1956, 215.

[1] Janot and Goutarel, *Compt. rend.*, 1955, **240**, 1719.
[2] Stauffacher and Seebeck, *Helv. Chim. Acta*, 1958, **41**, 169.
[3] Rindl and Groenewoud, *Trans. Roy. Soc. S. Africa*, 1932, 55.
[4] Janot and Goutarel, *Compt. rend.*, 1955, **240**, 1800.
[5] *Idem, ibid.*, 1953, **237**, 1718.

Vobtusine. The solid in chloroform was added to boiling methanol and the mixture boiled until free from chloroform to give crystals of vobtusine, m. p. 305—306° (decomp.), $[\alpha]_D^{20}$ −321° (*c* 1 in chloroform) [Found: C, 69·8; H, 7·2; N, 7·6; OMe, 7·8%; *M* (ebullioscopic in $CHCl_3$), 686 ± 60. Calc. for $C_{42}H_{50}O_7N_4$: C, 69·8; H, 7·0; N, 7·8; OMe, 8·6%; *M*, 722·9].

Dry hydrogen chloride was passed into a solution of vobtusine in chloroform, and the solution evaporated to a gummy *hydrochloride* which crystallised from ethanol in prisms, m. p. 242—244° (Found: C, 62·2; H, 7·2; N, 6·0; Cl^-, 8·2. $C_{42}H_{52}O_7N_4Cl_2,2C_2H_6O$ requires C, 62·2; H, 7·2; N, 6·3; Cl, 8·0%).

One drop of hydrobromic acid was added to a suspension of vobtusine in methanol, and the mixture shaken until all the solid had dissolved. Addition of ether gave a white amorphous precipitate which crystallised slowly from acetone to give prisms of *vobtusine hydrobromide*, decomp. 290° (Found: C, 57·4; H, 6·0; N, 6·1. $C_{42}H_{52}O_7N_4Br_2$ requires C, 57·0; H, 5·9; N, 6·3%).

Vobtusine in chloroform was mixed with alcoholic picric acid, the solvent removed, the solid dissolved in alcohol, and water added. A picrate was precipitated as a heat-labile, amorphous powder, m. p. 206—210° (Found: C, 54·3; H, 5·2; N, 10·8. Calc. for $C_{54}H_{56}O_{21}N_{10}$: C, 54·8; H, 4·8; N, 11·8%).

Selenium dehydrogenation of vobtusine. Vobtusine (4 g.) and selenium (6 g.) were heated at 320—340° for 15 min. The cooled, powdered, product was exhaustively extracted with benzene, and the solution shaken with 2% acetic acid, 5% sulphuric acid, and 2N-ammonia, to give a slightly basic, basic, acid, and neutral (benzene residue) fractions. Both basic fractions were chromatographed in benzene over alumina to give a yellow oil. This oil gave a picrate which crystallised twice from methanol to give yellow needles, m. p. 200—202°, undepressed on admixture with quinoline picrate (Found: C, 50·0; H, 3·2. Calc. for $C_{15}H_{10}O_7N_4$: C, 50·3; H, 2·9%). The oil also gave a styphnate which crystallised twice from methanol to give needles, m. p. 207—209°, undepressed on admixture with quinoline styphnate (Found: C, 47·8; H, 2·7; N, 14·8. Calc. for $C_{15}H_{10}O_8N_4$: C, 48·1; H, 2·7; N, 15·0%).

Selenium dehydrogenation of voacangine. Voacangine and selenium were heated to 350° for 15 min. The ether extract of the ground mass gave an oil, b. p. 220°/700 mm., from which was obtained a picrate, m. p. 187—188° (Found: C, 48·1; H, 4·0. Calc. for $C_{14}H_{14}O_7N_4$: C, 48·0; H, 4·0%). 3-Ethyl-5-methylpyridine picrate has m. p. 187—188°.[5]

The authors acknowledge with thanks bursaries (to B. O. G. S. and A. A. V.), and grants from the S.A. Council for Scientific and Industrial Research.

DEPARTMENT OF CHEMISTRY AND CHEMICAL ENGINEERING, UNIVERSITY OF NATAL,
PIETERMARITZBURG, SOUTH AFRICA. [*Received, June 23rd*, 1958.]

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969. *The Reaction of Ethyl Diazoacetate with Thionaphthen.*

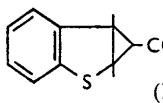
By G. M. BADGER, H. J. RODDA, and JENNETH M. SASSE.

THIONAPHTHEN and ethyl diazoacetate have been reported[1] to yield ethyl 2 : 3-dihydrothionaphthen-2 : 3-yleneacetate (I; R = Et). Further examination of the reaction leading to this ester has shown that at least three addition products are formed and that a compound previously isolated as its amide from the mixture of acids formed by hydrolysis and reductive desulphurisation of the adduct mixture, and thought to be 2-*cyclo*hexyl*cyclo*propanecarboxylic acid, is not this substance but is probably an ethyl*cyclo*heptanecarboxylic acid. 2-*cyclo*Hexyl*cyclo*propanecarboxylic acid should therefore be deleted from the literature.

Vacuum-distillation of the ester adduct from thionaphthen and ethyl diazoacetate gave two fractions, b. p. 86°/0·01 mm. and 98—110°/0·01 mm. respectively. The lower-boiling fraction, on alkaline hydrolysis, gave a mixture of acids from which the major constituent, 2 : 3-dihydrothionaphthen-2 : 3-yleneacetic acid-A (I; R = H; for designation see below), m. p. 148°, identical with that previously isolated,[1] was separated. Reductive desulphurisation of the mixed acids gave γ-phenylbutyric acid as the major product. The residues,

[1] Badger, Christie, Rodda, and Pryke, *J.*, 1958, 1179.

after separation of this acid, were treated with thionyl chloride and then aqueous ammonia, giving a small yield of an amide, m. p. 148°, identical with that product previously erroneously described as 2-*cyclo*hexyl*cyclo*propanecarboxyamide. In the earlier study[1] the total desulphurised acid was treated with thionyl chloride and aqueous ammonia; it has been shown that γ-phenylbutyric acid does not form an amide under these conditions, and the amide, m. p. 148°, was therefore the only acid derivative then isolated. This compound has now been found to be identical with the amide of an acid obtained by the hydrolysis and reduction of the adduct from ethyl diazoacetate and ethylbenzene; it is therefore probably an ethyl*cyclo*heptanecarboxyamide, the corresponding acid arising from the hydrolysis and reductive desulphurisation of a small amount of adduct formed by addition of ethyl diazoacetate to the benzo-ring of thionaphthen.



(I)

The higher-boiling fraction of the ester adduct (above) gave on hydrolysis 2 : 3-dihydrothionaphthen-2 : 3-yleneacetic acid-B (I; R = H), m. p. 182°. Reductive desulphurisation of this acid gave γ-phenylbutyric acid.

In keeping with the above results, freshly prepared W-7 Raney nickel reduced *trans*-2-phenyl*cyclo*propanecarboxylic acid to γ-phenylbutyric acid despite the previous failure[1] to achieve this reduction.

The 2 : 3-dihydrothionaphthen-2 : 3-yleneacetic acids-A and -B have very similar ultraviolet spectra, and as both gave γ-phenylbutyric acid on desulphurisation they must be stereoisomers. It has not been possible to assign unequivocally geometrical configurations to these acids, but it has been shown by paper chromatography that acid-B can be isomerised to acid-A *via* the acid chloride,[2] and that the reverse isomerisation does not occur. This indicates that acid-A is conformationally the more stable, a condition which would be fulfilled if this were the *trans*-acid with the smaller steric interaction between the ethoxycarbonyl group and the main bulk of the molecule.

Experimental.—2 : 3-*Dihydrothionaphthen*-2 : 3-*yleneacetic acid.* The crude adduct,[1] b. p. 126—160°/0·5 mm. (8·9 g.), was redistilled to give two fractions: (i) b. p. 86°/0·01 mm. (6·32 g.), and (ii) b. p. 98—110°/0·01 mm. (1·83 g.). Fraction (i) was chromatographed on alumina with light petroleum, then hydrolysed, and 2 : 3-dihydrothionaphthen-2 : 3-yleneacetic acid-A (1·3 g.) was isolated. It had m. p. 148°, unchanged on repeated recrystallisation; it showed only one spot on paper chromatography[3] (with butanol–ammonium carbonate buffer as solvent), R_F 0·55, and was identical with that previously isolated.[1] Fraction (ii) was similarly chromatographed and the material eluted with benzene, then hydrolysed, and the product recrystallised from light petroleum to give 2 : 3-*dihydrothionaphthen*-2 : 3-*yleneacetic acid-B* (0·35 g.), m. p. 182°, R_F 0·29 (Found: C, 62·4; H, 4·3; O, 16·4; S, 16·4. $C_{10}H_8O_2S$ requires C, 62·5; H, 4·3; O, 16·6; S, 16·7%). Its ultraviolet light absorption in 95% ethanol was very similar to that of the A-isomer and showed $\lambda_{max.}$ (log ε in parentheses) at 250 (3·92), 264 (3·73), and 292 mμ (3·16). Its 4-*phenylphenacyl ester* formed needles, m. p. 163° (Found: C, 74·4; H, 5·0; O, 12·8; S, 8·2. $C_{24}H_{18}O_3S$ requires C, 74·6; H, 4·7; O, 12·4; S, 8·3%).

Desulphurisations. The above A-acid (1·2 g.), in 1% aqueous sodium carbonate, was treated with W-7 Raney nickel (from 15 g. of alloy). The resulting oil showed only one spot on paper chromatography, but distillation gave fractions (i) b. p. 104°/0·01 mm. (0·3 g.) and (ii) b. p. 108—120°/0·01 mm. (0·61 g.). The latter solidified and gave γ-phenylbutyric acid (0·22 g.), m. p. 48—49°, identified by its infrared spectrum, its R_F (0·64), and by mixed m. p. The mother-liquors were added to fraction (i), which was treated with excess of thionyl chloride and then ammonia, to give an amide (20 mg.), m. p. 148°, not depressed on admixture with the amide previously obtained[1] (Found: C, 71·4, 71·3, 71·2; H, 11·2, 10·9, 10·8; N, 8·3. Calc. for ethyl*cyclo*heptanecarboxyamide, $C_{10}H_{19}ON$: C, 71·0; H, 11·3; N, 8·3%).

Desulphurisation of the B-acid (0·4 g.) gave an acid (0·32 g.; m. p. 37—40°) which showed only one spot on paper chromatography. Recrystallisation from water gave γ-phenylbutyric acid, m. p. and mixed m. p. 49°. Its identity was confirmed by paper chromatography (R_F 0·64) and by infrared spectroscopy.

[2] Cf. Burger and Yost, *J. Amer. Chem. Soc.*, 1948, **70**, 2198.

[3] Block, Durrum, and Zweig, "Paper Chromatography and Paper Electrophoresis," Academic Press, New York, 1955.

Reduction of trans-2-*phenyl*cyclo*propanecarboxylic acid with Raney nickel.* *trans*-2-Phenyl-*cyclo*propanecarboxylic acid (0·2 g.) was treated with freshly prepared W-7 Raney nickel (from 2·5 g. of alloy) in 1% aqueous sodium carbonate (25 c.c.) and stirred on the steam-bath for 1 hr. The resulting oil (0·2 g.) gave a solid (0·07 g.) which on recrystallisation from water formed plates, m. p. 48—49°, not depressed on admixture with authentic γ-phenylbutyric acid.

Reaction of ethyl diazoacetate with ethylbenzene. Ethyl diazoacetate (16 g.) in ethylbenzene (15 g.) was added dropwise, with stirring, to copper powder (0·5 g.) and ethylbenzene (30 g.) during 5 hr. at 145° (bath). More copper (0·5 g.) was added during the next 4 hr. Distillation gave ethylbenzene (34 g.) and fractions (i) b. p. 67—70°/0·4 mm. (1·5 g.), (ii) b. p. 74—78°/0·4 mm. (1·44 g.), and (iii) b. p. 140°/0·3 mm. (4 g.). Hydrolysis of fraction (i) gave fumaric acid. Hydrolysis of part of fraction (ii) (1 g.) gave a semisolid acid (0·5 g.). Washing with light petroleum (b. p. <40°) gave fumaric acid (0·02 g.), and the remaining oil (0·44 g.) was hydrogenated, in 1% aqueous sodium carbonate, over W-7 Raney nickel. Treatment of the resulting acid (0·4 g.) with thionyl chloride, and then ammonia, gave ethyl *cyclo*heptanecarboxyamide, identical (mixed m. p., infrared spectra) with the product described above.

UNIVERSITY OF ADELAIDE, SOUTH AUSTRALIA. [*Received, June 27th*, 1958.]

970. 1-*Ethyl*-3-*methyl*cyclo*pentadiene.*

By D. A. H. TAYLOR.

1-ETHYL-3-METHYL*cyclo*PENTADIENE has been prepared [1] by the decarboxylation of β-(2-carboxy-4-methyl*cyclo*pentadienyl)propionic acid, produced by self-condensation of lævulic acid. A specimen was required and was prepared by the action of ethylmagnesium bromide on 3-methyl*cyclo*pent-2-en-1-one. Although it reacted readily with the usual reagents for *cyclo*pentadiene, including maleic anhydride, crystalline products were not obtained, which suggests that it is a mixture of double-bond isomers.

The ultraviolet absorption maximum in hexane [$\lambda_{max.}$ 241 mμ (log ε 4·5)] agrees in position with the value $\lambda_{max.}$ 238 mμ (log ε 3·5) reported for *cyclo*pentadiene.[2] The larger extinction coefficient of our compound suggests that it may have an exocyclic double bond; thus the expected values [3] for 3-ethylidene-1-methyl*cyclo*pentene are $\lambda_{max.}$ 242 mμ (log ε > 4). In this case, isomerisation must precede reaction as a *cyclo*pentadiene.

Experimental.—1-*Ethyl*-3-*methyl*cyclo*pentadiene.* To the Grignard solution prepared from ethyl bromide (56 g.), magnesium (12 g.), and ether was added 3-methyl*cyclo*pent-2-en-1-one (48 g.).[4] The solution was decomposed with ammonium chloride solution, washed, and dried, and the ether evaporated. The residue was distilled, 1-ethyl-3-methyl*cyclo*pentadiene (15 g.) being collected as a liquid, b. p. 58°/50 mm., n_D^{20} 1·4688. No polymerisation occurred on redistillation at this pressure (Found: C, 88·7; H, 11·0. Calc. for C_8H_{12}: C, 88·9; H, 11·1%).

The high-boiling residue was unchanged when heated.

UNIVERSITY COLLEGE, IBADAN, NIGERIA. [*Received, June 30th*, 1958.]

[1] Duden and Freydag, *Ber.*, 1903, **36**, 944.
[2] Scheibe, *Ber.*, 1926, **59**, 1333.
[3] Woodward, *J. Amer. Chem. Soc.*, 1942, **64**, 72; Fieser and Fieser, " Natural Products related to Phenanthrene," 3rd Edn., Reinhold, New York, 1949, p. 185.
[4] Acheson and Robinson, *J.*, 1952, 1127.

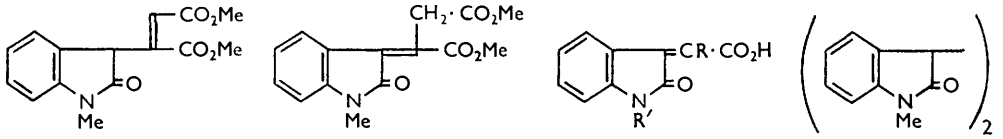
971. *Michael Addition of* 1-*Methyloxindole and Dimethyl Acetylenedicarboxylate.*

By J. A. BALLANTINE, R. J. S. BEER, and ALEXANDER ROBERTSON.

DURING an investigation of possible synthetical routes to γ-(5-hydroxy-3-indolyl)-α-3-oxindolyl-γ-oxobutyric acid, a degradation product of violacein,[1] attempts were made to effect a Michael reaction between 1-methyloxindole and dimethyl acetylenedicarboxylate in the presence of sodium methoxide. The two coloured compounds isolated gave almost identical analytical results, consistent with either of the expected products (I) or (II), and

[1] Ballantine, Barrett, Beer, Boggiano, Clarke, Eardley, Jennings, and Robertson, *J.*, 1957, 2222.

had ultraviolet absorption spectra very similar to those of α-3-oxindolylidenepropionic acid [2] (III; R = Me, R′ = H) and β-benzyl-α-(1-methyl-3-oxindolylidene)propionic acid [3]



(I) (II) (III) (IV)

(III; R = CH_2·COPh, R′ = Me). The coloured products are therefore regarded as different forms, possibly geometrical isomers, of dimethyl (1-methyl-3-oxindolylidene)succinate (II).

A third, colourless product is formulated as the bisoxindolyl (IV) in accordance with the analytical data and with its ultraviolet absorption spectrum ($\lambda_{max.}$ 253 mμ, log ε 4·13, in alcohol) which resembles that of 1-methyloxindole ($\lambda_{max.}$ 251 mμ, log ε 4·00). A compound with identical properties and infrared absorption spectrum was obtained by reduction of 1 : 1′-dimethyl*iso*indigotin [4] with zinc and acetic acid.

Ultraviolet absorption spectra.

Compound	$\lambda_{max.}$ (log ε)	$\lambda_{min.}$ (log ε)
Red product, m. p. 81°	261(4·40), 306(3·76)	232(3·83), 281(3·49)
Yellow product, m. p. 86°	263(4·42), 307(3·79)	234(3·85), 281(3·52)
(III; R = Me, R′ = H) [2]	262(4·38), 295(3·90)	230(3·85), 277(3·78)
(III; R = CH_2·CO·Ph, R′ = Me) [3]	258(4·37), 304(3·73)	224(4·08), 286(3·69)

Experimental.—Dimethyl (1-*methyl*-3-*oxindolylidene*)*succinate* (II). A solution of 1-methyloxindole (2·0 g.) in methanol (20 ml.) containing sodium methoxide (from 0·5 g. of sodium) was cooled to −5° and stirred (nitrogen atmosphere) whilst dimethyl acetylenedicarboxylate (2 ml.),[5] dissolved in a little methanol, was gradually added. The vessel was then sealed and kept at room temperature. After 30 days, the separated crystalline solid was removed and the filtrate poured into water, acidified, and extracted with ether. The gummy residue left after evaporation of the ether was extracted with light petroleum (b. p. 40—60°) and the combined extracts on concentration deposited a mixture (150 mg.) of the yellow and the red form of *dimethyl* (1-*methyl*-3-*oxindolylidene*)*succinate*, which were separated mechanically. The red form was freed from traces of the yellow form by digestion with a little warm light petroleum, and was thus obtained as dense prisms, m.p. 81° (Found: C, 62·1; H, 5·1; N, 4·7; OMe, 21·6. $C_{15}H_{15}O_5N$ requires C, 62·3; H, 5·2; N, 4·8; OMe, 21·5%) The yellow form separated from light petroleum in bright yellow needles, m.p. 86° (Found: C, 62·1; H, 5·1; N, 4·7; OMe, 21·4%) The red form was converted into the yellow by recrystallisation from light petroleum (b. p. 40—60°).

The solid which separated from the reaction mixture formed prisms (from methanol), m. p. 270° (decomp.) (Found: C, 74·0; H, 5·3; N, 9·4. $C_{18}H_{16}O_2N_2$ requires C, 73·8; H, 5·5; N, 9·6%). The same product, 1 : 1′-*dimethyl*-3 : 3′-*bisoxindolyl* (IV), m. p. and mixed. m. p. 270° (decomp. to a red liquid) (Found: C, 73·9; H, 5·5; N, 9·5%), was also obtained by reduction of 1 : 1′-dimethyl*iso*indigotin [4] with zinc dust in warm acetic acid.

UNIVERSITY OF LIVERPOOL. [*Received, July 21st*, 1958.]

[2] Julian, Printy, Ketcham, and Doone, *J. Amer. Chem. Soc.*, 1953, **75**, 5305.
[3] Barrett, Beer, Dodd, and Robertson, *J.*, 1957, 4810.
[4] Stollé, Bergdoll, Luther, Auerhahn, and Wacker, *J. prakt. Chem.*, 1930, **128**, 35.
[5] *Org. Synth.*, 1952, **32**, 55.

972. *Thallous* tert.-*Amyloxide.*

By D. C. BRADLEY.

RECENT studies [1] on the metal alkoxides have shown the striking effect of chain branching in the alkyl group on the degree of polymerisation of the metal alkoxide. Sidgwick and Sutton [2] showed that the lower monoalkoxides of thallium were tetrameric and assigned

[1] *E.g.*, Bradley, Mehrotra, and Wardlaw, *J.*, 1952, 2027; Bradley, Saad, and Wardlaw, *J.*, 1954, 3488.
[2] Sidgwick and Sutton, *J.*, 1930, 1461.

a structure to the tetramer. To gain information on the " chain-branching effect " in thallous alkoxides the *tert.*-amyloxide has been prepared. However, ebullioscopic measurements in benzene show that it is tetrameric over a twenty-fold change in concentration starting from a low concentration. This establishes that the tetramer involves a structure which can accommodate bulky alkyl groups without much intramolecular congestion

Experimental.—Thallous tert.*-amyloxide.* To thallous ethoxide (32·6 g., prepared by Menzies's method [3]) dissolved in benzene (80 c.c.), *tert.*-amyl alcohol (22·7 g.) was added and the benzene–ethyl alcohol azeotrope removed by fractional distillation. During evaporation of the solvent a mass of white crystals (33·5 g.) was deposited. From the mother liquor a second crop (4·7 g.) was obtained. Thallous *tert.*-amyloxide was dried at room temperature under reduced pressure and analysed by titrating samples in water with standard (*ca.* 0·1N) hydrochloric acid (Found: equiv. 292·9. Calc. for $TlOC_5H_{11}$: equiv. 291·53). The *tert.*-amyloxide decomposed above *ca.* 50° *in vacuo* and a solution in benzene deposited a mirror on the wall of the glass container on exposure to daylight.

Ebullioscopy. The previously described [4] all-glass ebulliometer with the differential water thermometer was used. The results are tabulated. The slope $\Delta T/m$ does not vary significantly

Wt. of solute *m* (g.)...	0·0611	0·1483	0·2541	0·3329	0·4466	0·6246	0·7588	0·8597	0·9670	1·2272
Elevation $\Delta T°$	0·0087	0·0213	0·0368	0·0484	0·0655	0·0916	0·1107	0·1257	0·1411	0·1797
$\Delta T/m$	0·1424	0·1436	0·1448	0·1454	0·1467	0·1466	0·1459	0·1462	0·1459	0·1464

with concentration and the average value (0·1454) gave $M = 1156$ (Calc. for $TlOC_5H_{11}$: 291·5). The weight of solvent was 17·53 g.

The author thanks Dr. R. C. Menzies for a loan of thallium and for his interest.

BIRKBECK COLLEGE, LONDON, W.C.1. [*Received, July 29th*, 1958.]

[3] Menzies, *J.*, 1931, 1571.
[4] Bradley, Gaze, and Wardlaw, *J.*, 1955, 3977.

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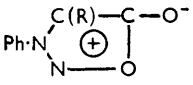
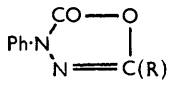
973. *Bromination of* N*-Phenylsydnone.*

By F. STANSFIELD.

THE formation of *C*-bromo-*N*-phenylsydnone (I; R = Br) by reaction of the *N*-phenylsydnone (I; R = H) with bromine has been described by Kenner and Mackay [1] who used glacial acetic acid as solvent, and also by Baker, Ollis, and Poole [2] who stated that use of acetic anhydride at 0° gave a smoother reaction and avoided the production of violet by-products.

(I) 

 (II)

On repeating the procedure of Baker *et al.*, I found that if the mixture of the sydnone, acetic anhydride, and bromine was warmed to 30—40°, a vigorous exothermic reaction took place with evolution of carbon dioxide. The product, formed in good yield, was 2-methyl-4-phenyl-1 : 3 : 4-oxadiazol-5-one (II; R = CH_3), and substitution of propionic or *n*-butyric anhydride for acetic anhydride gave the corresponding ethyl or *n*-propyl compound (II; R = C_2H_5 or *n*-C_3H_7), respectively.

That the reaction was catalysed by hydrogen bromide was shown by repeating the experiment in presence of anhydrous sodium acetate. Carbon dioxide was not evolved even when the temperature was raised to 95°, and 4-bromo-3-phenylsydnone was isolated. It is known that *N*-phenylsydnones in presence of mineral acid give phenylhydrazine derivatives [3] and such a compound may be an intermediate in the formation of the oxadiazolone.

[1] Kenner and Mackay, *Nature*, 1946, **158**, 910.
[2] Baker, Ollis, and Poole, *J.*, 1949, 313.
[3] Baker and Ollis, *Quart. Rev.*, 1957, **11**, 15.

A similar decomposition with evolution of carbon dioxide took place when a mixture of *N*-phenylsydnone, glacial acetic acid, and bromine was warmed gently, but no pure product was isolated.

Experimental.—*2-Methyl-4-phenyl-1 : 3 : 4-oxadiazol-5-one.* *N*-Phenylsydnone (3·0 g.) was suspended in acetic anhydride (15 ml.) at 0° and an ice-cold solution of bromine (1·5 ml.) in acetic anhydride (15 ml.) added with continued cooling. The sydnone dissolved and the *C*-bromo-compound soon began to separate. The mixture was placed in a water-bath which was gradually heated to boiling during 30 min. When the internal temperature reached 30—40° a vigorous reaction occurred with evolution of carbon dioxide, and finally the clear straw-coloured solution was poured into water (75 ml.). After shaking and heating to decompose excess of anhydride, the product was placed in the refrigerator overnight. The solid which separated was filtered off, washed with water, dried, and crystallised from light petroleum (b. p. 60—80°), giving slightly yellow needles (2·2 g., m. p. 89—90°). On recrystallisation from ethanol and from light petroleum, it formed colourless rhombs, m. p. 92·5—93° (Found: C, 61·6; H, 4·6; N, 15·7. Calc. for $C_9H_8O_2N_2$: C, 61·4; H, 4·5; N, 15·9%). These gave no depression of m. p. with authentic material prepared from 1-acetyl-2-phenylhydrazine and ethyl chloroformate.[4]

When the experiment was repeated in presence of anhydrous sodium acetate (7·5 g.), no carbon dioxide was evolved on heating the mixture in a boiling-water bath, and the product was 4-bromo-3-phenylsydnone (2·0 g., m. p. 135°, decomp.).

Using propionic anhydride we obtained 2-ethyl-4-phenyl-1 : 3 : 4-oxadiazol-5-one,[5] m. p. 60—61·5°.

n-Butyric anhydride gave the 2-n-*propyl compound* as slightly yellow needles from petroleum, m. p. 57·5—58·5° (Found: C, 64·7; H, 5·7; N, 14·1. $C_{11}H_{12}O_2N_2$ requires C, 64·7; H, 5·9; N, 13·7%).

The author thanks Dr. D. A. Peak for interest and encouragement.

UNIVERSITY OF KHARTOUM, SUDAN. [*Received, July 29th*, 1958.]

[4] Rupe and Gebhardt, *Ber.*, 1899, **32**, 10.
[5] Freund and Goldsmith, *Ber.*, 1888, **21**, 2461.

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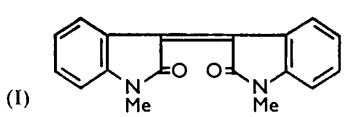
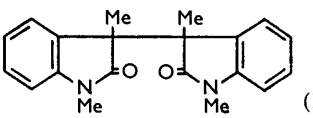
974. *Oxidative Dimerisation of Oxindoles.*

By JOHN HARLEY-MASON and R. F. J. INGLEBY.

OXIDATION of phenols by alkaline ferricyanide is well known [1] to produce a variety of coupling products *via* radical intermediates. Oxindoles exhibit pseudo-phenolic properties, and two similar oxidations in this field are now reported. Owing to the insolubility of the starting products in aqueous alkali, oxidation was conducted in a vigorously stirred two-phase system (water–carbon tetrachloride).



(I)



(II)

1-Methyloxindole gave in poor yield 1 : 1′-dimethyl*iso*indigo (I) while 1 : 3-dimethyloxindole gave in fair yield a mixture of the *meso*- and racemic forms of **1 : 3 : 1′ : 3′**-tetramethyl-leuco*iso*indigo (II). The *meso*-configuration is tentatively assigned to the higher-melting and less-soluble isomer, though we have no direct evidence on this point. Examination of a model of (II) discloses very considerable crowding in the centre of the molecule, and it is noteworthy that attempts to obtain a similar structure by *C*-alkylation of **1 : 1′**-dimethyl-leuco*iso*indigo were unsuccessful,[2] it being impossible to introduce more than one alkyl group because of steric hindrance.

[1] Thyagarajan, *Chem. Reviews*, 1958, **58**, 439.
[2] Faseeh and Harley-Mason, unpublished work.

Experimental.—1 : 1′-*Dimethylisoindigo* (I). A solution of 1-methyloxindole (1·0 g.) in carbon tetrachloride (30 c.c.) was heated at 80° under reflux and vigorously stirred while a solution of potassium ferricyanide (2·3 g.) and sodium hydroxide (0·4 g.) in water (30 c.c.) was added dropwise during 30 min. After cooling, the organic layer was separated, the aqueous layer was further extracted with carbon tetrachloride (20 c.c.), the combined extracts were dried ($MgSO_4$), and the solvent was removed. The residual red gum was taken up in ethanol; 1 : 1′-dimethyl*iso*indigo (0·1 g.) was slowly deposited at 0° as red needles, m. p. 268°; a mixture with an authentic sample [3] had m. p. 267—269°.

Oxidation of 1 : 3-*dimethyloxindole.* A solution of 1 : 3-dimethyloxindole (1·65 g.) in carbon tetrachloride (25 c.c.) was treated as above with potassium ferricyanide (3·5 g.) and sodium hydroxide (1·0 g.) in water (35 c.c.). The gum remaining after removal of carbon tetrachloride was taken up in ethanol, and an equal volume of ether added. Large prisms (0·2 g.), m. p. 219—221°, of meso-(?)-1 : 3 : 1′ : 3′-*tetramethyl-leucoisoindigo* (II) slowly separated at 0° (Found: C, 74·5; H, 6·1; N, 9·0. $C_{20}H_{20}O_2N_2$ requires C, 75·0; H, 6·3; N, 8·7%). The mother liquor was evaporated to dryness, and the residue, in benzene, chromatographed on acid-washed alumina. Needles (0·27 g.), m. p. 175°, of the racemic (?) *isomer* were obtained from the eluate (Found: C, 75·1; H, 6·3; N, 8·4%). Further elution with chloroform–ethanol gave a further 0·12 g. of the higher-melting isomer. The infrared spectra of the two isomers were extremely similar.

We thank the Department of Scientific and Industrial Research for a Maintenance Grant (to R. F. J. I.).

UNIVERSITY CHEMICAL LABORATORY, CAMBRIDGE. [*Received, August 14th*, 1958.]

[3] Stollé, *J. prakt. Chem.*, 1930, **128**, 4.

975. *Thallous Borohydride*, $TlBH_4$.

By T. C. WADDINGTON.

THALLOUS borohydride, $TlBH_4$, has been prepared as a white crystalline solid, insoluble in water, but slowly decomposed on contact with water leaving a residue of metallic thallium. The crystal has the face-centred cubic NaCl structure with the unit-cell parameter $a = 6{\cdot}88_2$ Å and is isomorphous with the sodium, potassium, rubidium, and cæsium salts.[1,2] The insolubility in water indicates the similarity of the salt to thallous chloride, bromide, and iodide, but not to thallous fluoride, with which it is isoelectronic. The infrared spectrum of the salt in the region 4000—600 cm.$^{-1}$ has also been recorded, together with the infrared spectra of lithium, sodium, and potassium borohydrides (see Table). The borohydride ion has two infrared-active fundamental frequencies, ν_3 and ν_4; ν_3 is in the region of 2300 cm.$^{-1}$ whereas ν_4 is found at about 1100 cm.$^{-1}$. The spectra of lithium and sodium borohydrides have previously been reported by W. C. Price,[3] who, however, did not observe the splitting of the band in the region of 2300 cm.$^{-1}$. This splitting may perhaps be attributed to the failure of the BH_4^- ion to rotate freely in the crystal lattice, therefore removing the threefold degeneracy on the ν_3 vibration. The value of ν_3 for thallous borohydride is lowered by about 100 cm.$^{-1}$ relative to those of the alkali-metal borohydrides and the value of ν_4 is lowered by about 60 cm.$^{-1}$. This lowering perhaps indicates the beginning of multicentre bonding or a small covalent contribution to the bonding in the crystal lattice. This would also explain the insolubility of the salt in water.

Attempts to prepare silver borohydride failed, metallic silver always being produced, probably owing to the low electrode potential of the Ag^+ ion.

Infrared spectra (cm.$^{-1}$) of the borohydrides (principal lines of the bands in italics).

Salt	ν_3	ν_4	Salt	ν_3	ν_4
$LiBH_4$	2360, *2290*, 2210	1094	KBH_4	2370, *2280*, 2210	1117
$NaBH_4$	2390, *2290*, 2210	1120	$TlBH_4$	2240, *2180*, 2110	1050

[1] Abrahams and Kalnajs, *J. Chem. Phys.*, 1954, **22**, 434.
[2] Soldate, *J. Amer. Chem. Soc.*, 1947, **69**, 987.
[3] Price, *J. Chem. Phys.*, 1949, **17**, 1044.

Experimental.—Thallous borohydride was precipitated by mixing aqueous solutions of thallous nitrate and potassium borohydride, filtered quickly, and washed with alcohol and ether. After attempts to produce silver borohydride by mixing aqueous silver nitrate with potassium borohydride solutions had led to the precipitation of metallic silver, ethereal solutions of silver nitrate and lithium borohydride were employed. However, metallic silver was again precipitated.

The compounds were mulled with Nujol and with hexachlorobutadiene and their infrared spectra recorded on a Perkin-Elmer double-beam, recording, infrared spectrophotometer. The *X*-ray powder photograph was taken with Cu-K_α radiation, a sample being filled into a thin-walled Pyrex capillary and the capillary sealed off with picein wax. The value of a was computed from the mean value obtained from the ten highest lines on the *X*-ray powder photograph.

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976. *Hydrolysis of Ethyl 3-Oxo-octadecanoate.*

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THERE is an anomaly in the literature of ethyl 3-oxo-octadecanoate. According to Asahina and Nakayama [1] it can be converted into its acid by 2—4 hours' treatment at 100° with 2% alcoholic potassium hydroxide, no other decomposition taking place, but Helferich and Köster [2] had found ketonic fission by aqueous alkaline hydrolysis; this has now been found to be so for 2% alcoholic potassium hydroxide as well, almost pure heptadecan-2-one resulting.

The ethyl ester, obtained from 3-ethoxycarbonylnonadecane-2 : 4-dione, melted at 36·5°. Levene and Haller [3] gave 37—38°, but Asahina and Nakayama [1] reported that the compound which they obtained by a similar method melted at 104—105°. (For many higher 3-oxo-methyl esters, Ställberg-Stenhagen [4] found two crystal modifications, but these had only slightly different m. p.s.)

The m. p. of 3-oxo-octadecanoic acid, prepared from its methyl ester by cold acid hydrolysis, has been reported as 102—103,[5] 98—99,[6] and 99° (decomp.).[7] Evidently the compound of m. p. 64—65° obtained by Asahina and Nakayama was some other substance, and their starting material was not ethyl 3-oxo-octadecanoate.

Experimental.—Ethyl 3-oxo-octadecanoate, prepared by deacylation of 3-ethoxycarbonylnonadecane-2 : 4-dione, had m. p. 36·5° after four recrystallisations from 95% ethanol and one from light petroleum (b. p. 40—60°) (Found: C, 73·4; H, 11·6. Calc. for $C_{20}H_{38}O_3$: C, 73·6; H, 11·7%).

Hydrolysis. Under all conditions of alkaline hydrolysis tried, either ketonic cleavage occurred, or the 3-oxo-ester was unchanged. With the Japanese workers' method, white needles were obtained in almost 90% yield. After one crystallisation from benzene, and one from light petroleum (b. p. 40—60°), these melted sharply at 48° (heptadecan-2-one, m. p. 48°) (Found: C, 80·2; H, 13·3. Calc. for the ketone $C_{17}H_{34}O$: C, 80·2; H, 13·5. Calc. for the acid $C_{18}H_{34}O_3$: C, 72·4; H, 11·5%). The semicarbazone had m. p. 127·2 (Helferich and Köster [2] gave 127°).

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[2] Helferich and Köster, *Ber.*, 1923, **56**, 2090; see also Breusch and Keskin, *Rev. Fac. Sci. Univ. Istanbul*, 1946, **11**, *A*, 24.
[3] Levene and Haller, *J. Biol. Chem.*, 1925, **63**, 671.
[4] Ställberg-Stenhagen, *Arkiv Kemi, Min., Geol.*, 1945, **20**, *A*, No. 19.
[5] Mitz, Axelrod, and Hofman, *J. Amer. Chem. Soc.*, 1950, **72**, 1231.
[6] Stenhagen, *Arkiv Kemi*, 1951, **3**, 381.
[7] Bergström, Aulin-Erdtman, Rolander, Stenhagen, and Östling, *Acta Chem. Scand.*, 1952, **6**, 1157.