NOTES.

387. *Mechanism of Saccharinic Acid Formation. Part IV.* Influence of Cations in the Benzilic Acid Rearrangement of Glyoxal.*

By D. O'Meara and G. N. Richards.

αβ-Dicarbonyl compounds have repeatedly been postulated * as intermediates which undergo the benzilic acid rearrangement to yield saccharinic acids in the alkaline degradation of carbohydrates. Glyoxal has therefore been studied as a simple model of the saccharinic acid precursors. It is known to yield glycollic acid very rapidly in aqueous alkali, and Salomaa [1] has shown that the reaction is of the first order with respect to glyoxal and of the second order with respect to hydroxyl ion, in contrast with the analogous rearrangement of benzil which is of first order with respect to both benzil and hydroxyl ion. We have now investigated the influence of different cations on the hydroxyl-ion-catalysed rearrangement of glyoxal to glycollic acid and the results are shown in the Table. In these experiments, 2,3-dihydroxy-1,4-dioxan, the cyclic hemiacetal of glyoxal and ethylene glycol,[2] was used as a convenient, crystalline source of glyoxal and the assumption is made that its rate of conversion into glyoxal has no effect on the overall rate of reaction. Glycollic acid was the only product detected, and colorimetric and acidimetric determinations gave the same results. It seems therefore that fission of the αβ-dicarbonyl grouping which competes with the benzilic acid rearrangement in saccharinic acid formation * does not occur with glyoxal.

The influence of a range of metallic salts, excluding calcium, on the reactions of benzil in alkali has been studied previously,[3] and thallium salts were found to be the most effective. The Table shows, however, that the rearrangement of glyoxal is only slightly catalysed by thallium salts, to an extent similar to that caused by the barium salt. Much more marked acceleration was observed with the calcium salt, and this probably indicates a difference in critical ion-size requirements for complex formation with the two αβ-dicarbonyl compounds. Calcium has long been recognised as a specific cationic catalyst in the alkaline degradation of carbohydrates to saccharinic acids, and the results of the

* Part III, preceding paper.

[1] Salomaa, *Acta Chem. Scand.*, 1956, **10**, 311.
[2] Head, *J.*, 1955, 1036.
[3] Pfeil, Geissler, Jacquemin, and Lömber, *Chem. Ber.*, 1956, **89**, 1210.

Table provide the first indication that this effect arises at least in part from catalysis of the benzilic acid rearrangement. The most likely hypothesis to account for this would involve formation of a chelate complex between $(CaOH)^+$ and an anion derived from glyoxal or its hydrate, but the available evidence does not permit further conclusions. These results

Effect of added metallic salts on rearrangement of 0·005M-*glyoxal in* 0·005N-*sodium hydroxide at* 25°.

Salt added	$t_{0.5}$ * (sec.)	Salt added	$t_{0.5}$ * (sec.)	Salt added	$t_{0.5}$ * (sec.)
None	310	0·01M-$LiNO_3$	290	0·005M-Tl_2SO_4	160
,,	300	0·005M-$BaCl_2$	170	0·005M-$CaCl_2$	82
				(Reaction in 0·005N-lime-water	92)

* $t_{0.5}$ = time required to develop 0·5 equiv. of acidity per mole.

do not necessarily invalidate the earlier conclusion [4] that calcium also catalyses the elimination which occurs in alkaline degradation of 3-*O*-methyl-D-glucose, particularly since the latter reaction is almost certainly rate-determining.

Experimental.—2,3-Dihydroxy-1,4-dioxan was prepared from crude glyoxal and ethylene glycol solution and purified by Head's method [2] (Found: C, 40·0; H, 6·6. Calc. for $C_4H_8O_4$: C, 40·0; H, 6·7%).

Samples of 2,3-dihydroxy-1,4-dioxan (0·06 g.) were dissolved in oxygen-free water (50 ml.) at 25° and then oxygen-free 0·01N-sodium hydroxide (50 ml.) at 25° was added. After mixing, 10 ml. samples were added at intervals to 0·01N-hydrochloric acid (5 ml.) and back-titrated with 0·01N-sodium hydroxide in the usual manner. In other experiments, a 0·02M- or 0·01M-solution of the required metallic salt was used instead of water to prepare the original 2,3-dihydroxy-1,4-dioxan solution. In several experiments the glycollic acid yield was determined by Calkins's method [5] and in all cases these results agreed with the total acid yield determined by titration.

BRITISH RAYON RESEARCH ASSOCIATION, HEALD GREEN LABORATORIES,
WYTHENSHAWE, MANCHESTER, 22. [*Received, September 17th*, 1959.]

[4] Kenner and Richards, *J.*, 1957, 3019.
[5] Calkins, *Analyt. Chem.*, 1943, **15**, 762.

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388. *Ring Fission of Two Mesoionic Compounds of the Anhydrothiazolium Hydroxide and -pyridino-oxazolium Hydroxide Type.*

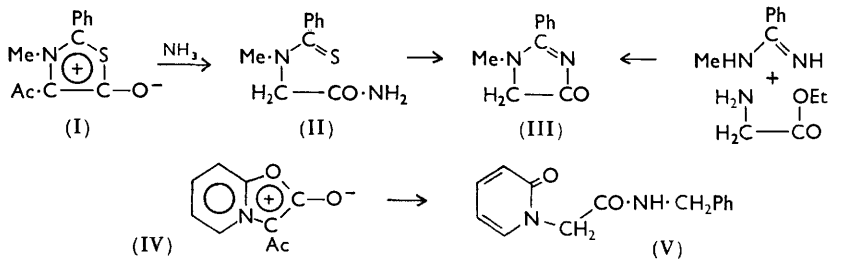
By ALEXANDER LAWSON and D. H. MILES.

THE mesoionic compound anhydro-(4-acetyl-5-hydroxy-3-methyl-2-phenylthiazolium hydroxide) [1,2] (I) reacts with benzylamine apparently less simply than the sydnones do.[3] Further attempts at ring fission have shown that with ethanolic ammonia the substance gives 1-methyl-2-phenylimidazol-4-one (III) in high yield, presumably by the mechanism (I)—(III). The structure of this imidazolone was confirmed by synthesis from methylbenzamidine and glycine ester.

A ring fission, analogous to the first stage of the above, is also shown by anhydro-[4-acetyl-5-hydroxypyridino(2′,1′-2,3)oxazolium hydroxide] [2] (IV) with benzylamine, giving *N*-benzyl-1,2-dihydro-2-oxo-1-pyridylacetamide (V), the structure of which was confirmed by preparation from ethyl 1,2-dihydro-2-oxo-1-pyridylacetate and benzylamine. This amide (V) was readily hydrolysed by dilute hydrochloric acid to the parent acid.

[1] Lawson and Searle, *J.*, 1957, 1556.
[2] Lawson and Miles, *J.*, 1959, 2865.
[3] Baker, Ollis, and Poole, *J.*, 1949, 307.

The product obtained from *N*-phenylglycine-*o*-carboxylic acid and acetic anhydride for which a mesoionic structure was suggested [2] has proved to be *ON*-diacetylindoxyl.



Experimental.—Ring fission of anhydro-(4-acetyl-5-hydroxy-3-methyl-2-phenylthiazolium hydroxide) with ammonia. The anhydro-compound (0·5 g.) was heated for 1·5 hr. in boiling ethanol (100 ml.) through which anhydrous ammonia was passed. Hydrogen sulphide (1 mol.) was evolved. The yellow solution was evaporated under reduced pressure and the residue extracted with ether. Removal of the ether left an oil which, after dissolution in concentrated hydrochloric acid and evaporation, gave *1-methyl-2-phenylimidazol-4-one hydrochloride*, crystallising from ethanol–ether in colourless needles, m. p. 219° (decomp.) (60%) (Found: C, 56·8; H, 5·2; N, 13·7; Cl, 17·5. $C_{10}H_{10}ON_2$,HCl requires C, 56·9; H, 4·7; N, 13·3; Cl, 17·1%).

3-Methyl-2-phenylimidazol-5-one. To a chloroform solution of methylbenzamidine prepared from the hydrochloride (5·0 g.) was added glycine ethyl ester (3·0 g.), and the chloroform was then evaporated. After being warmed to 100° for 1 hr., during which ammonia was evolved, the resulting oil was acidified with dilute hydrochloric acid. Evaporation under reduced pressure gave the hydrochloride (76%) identical with the above material.

Ring fission of anhydro-[4-acetyl-5-hydroxypyridino(2′,1′-2,3)oxazolium hydroxide] with benzylamine. The anhydro-compound (0·1 g.) was heated under reflux with benzylamine (5 ml.) for 1 hr. Addition of light petroleum (b. p. 80—100°) to the cooled solution precipitated an oil which crystallised. Recrystallisation from benzene—light petroleum (b. p. 40—60°) and then from acetone gave *N-benzyl-1,2-dihydro-2-oxo-1-pyridylacetamide*, needles, m. p. 199—200° (0·1 g.) (Found: C, 69·2; H, 5·6; N, 11·5. $C_{14}H_{14}O_2N_2$ requires C, 69·4; H, 5·8; N, 11·6%).

1,2-Dihydro-2-oxo-1-pyridylacetic acid was esterified with ethanol and the resulting oil warmed with ethanolic benzylamine. Removal of the solvent under reduced pressure gave an oil which solidified and then crystallised from acetone (m. p. 201°), being identical with the above product.

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[*Received, October 14th*, 1959.]

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389. *Atom and Bond Populations in Nitrogen Heterocyclics.*

By T. E. PEACOCK.

IN a recent paper [1] the charge populations of the atoms and bonds in naphthalene were discussed. It was shown that the charge and bond order matrix **P** using a basis of carbon $2p_z$ atomic orbitals is related to that $\overline{\mathbf{P}}$ in an orthogonalized $2p_z$ basis as follows:

$$\mathbf{P} = \mathbf{S}^{-\frac{1}{2}}\,\mathbf{P}\,\mathbf{S}^{-\frac{1}{2}}$$

where **S** is the matrix of overlap integrals. The electron "population" of an atom q_{ii} is given by P_{ii} and of a bond i–j by $2P_{ij}S_{ij}$ (real orbitals being assumed).

[1] Peacock, *J.*, 1959, 3241.

The transformation and the calculations of populations have been extended to the nitrogen-heterocyclic derivatives of benzene.

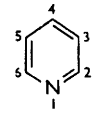
Populations in Benzene Heterocyclics.—The values of the overlap integrals used here are:

	S_{12}	S_{13}	S_{14}
C–C	0·260	0·039	0·018
C–N	0·200	0·022	0·009
N–N	0·153	0·012	0·005

The matrix $\mathbf{S}^{-\frac{1}{2}}$ was computed by rewriting $\mathbf{S}$ as $(\mathbf{1} + \mathbf{x})$ and expanding this as a matrix power series, six terms giving adequate accuracy.

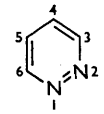
The π-charge populations in benzene and the heterocyclic compounds are here tabulated, together with the values [2] of P_{ij} and $\overline{P}_{ij}$ (the numberings shown with the formulæ are those used in the Table).

Pyridine



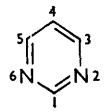
	11	12	22	23	33	34	44
$\overline{P}_i$	1·100	0·666	0·950	0·662	1·010	0·670	0·980
P_{ij}	0·903	0·515	0·731	0·482	0·774	0·486	0·737
q_{ij}	0·903	0·203	0·731	0·251	0·774	0·253	0·737

Pyridazine



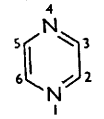
	11	12	16	22	23	33	34
$\overline{P}_{ij}$	1·054	0·674	0·654	0·958	0·654	0·986	0·678
P_{ij}	0·873	0·530	0·534	0·737	0·475	0·743	0·492
q_{ij}	0·873	0·212	0·163	0·737	0·247	0·743	0·256

Pyrimidine



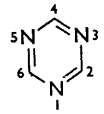
	11	12	22	23	33	34	44
$\overline{P}_{ij}$	0·900	0·662	1·112	0·664	0·926	0·664	1·026
P_{ij}	0·701	0·510	0·917	0·510	0·703	0·475	0·791
q_{ij}	0·701	0·204	0·917	0·209	0·703	0·247	0·791

Pyrazine



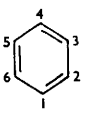
	12	11	22	23
$\overline{P}_{ij}$	1·080	0·670	0·960	0·656
P_{ij}	0·880	0·517	0·742	0·474
q_{ij}	0·880	0·208	0·742	0·247

1,3,5-*Triazine*



	22	12	11
$\overline{P}_{ij}$	0·882	0·662	1·116
P_{ij}	0·681	0·510	0·922
q_{ij}	0·681	0·204	0·922

Benzene



	11	12
$\overline{P}_{ij}$	1·000	0·667
P_{ij}	0·758	0·482
q_{ij}	0·758	0·251

Oscillator Strengths.—An expression for calculation of the oscillator strength of a transition in a non-orthogonal basis has already been given.[1] The oscillator strength for a transition $\overline{\Phi}_\alpha \longrightarrow \overline{\Phi}_\beta$ is given [3] by:

$$f_{\alpha\beta} = 1{\cdot}085 \times 10^{11}\bar{\nu}Q^2$$

where $\bar{\nu}$ is the frequency (in wave numbers) of the transition and $Q^2_{\alpha\beta}$ is given by:

$$Q^2_{\alpha\beta} = Q^2_{(x)\alpha\beta} + Q^2_{(y)\alpha\beta} + Q^2_{(z)\alpha\beta}$$

where

$$Q_{x(\alpha\beta)} = e^2\int\overline{\Phi}_\alpha^* \sum_{i=1}^{N} x_i\,\overline{\Phi}_\beta d\tau$$

[2] McWeeny and Peacock, *Proc. Phys. Soc.*, 1957, *A*, **70**, 41.
[3] Mulliken and Rieke, *Reports Progr. Physics*, 1941, **8**, 231.

In the orthogonal basis for a transition from orbital $A \longrightarrow A'$

$$\bar{Q}_{x(AA')} = \sqrt{2}\,\mathrm{tr}\,\bar{\mathbf{X}}\,\bar{\mathbf{P}}_{AA'}$$

where $$\bar{\mathbf{P}}_{AA'} = \bar{\mathbf{T}}_A\bar{\mathbf{T}}_{A'}{}^{\dagger} \text{ and } \bar{X}_{rs} = \int \bar{\phi}_r{}^* \, x \, \bar{\phi}_s \mathrm{d}\tau$$

$$= \bar{x}_{rr} \; (r = s) \; (\bar{x}_{rr} \text{ is the centroid of orthoganalized atomic orbital r})$$

$$= 0 \quad (r \neq s)$$

In the non-orthogonal basis

$$Q_x = \sqrt{2}\,\mathrm{tr}\,\mathbf{X}\mathbf{P}_{AA'}$$

where $$\mathbf{P}_{AA'} = \mathbf{S}^{-\frac{1}{2}}\,\bar{\mathbf{P}}_{AA'}\mathbf{S}^{-\frac{1}{2}} \text{ and } x_{rs} = \int \phi_r{}^* \times \phi_r \mathrm{d}\tau = x_{rs}S_{rs}$$

where x_{rr} is the centroid of orbital r and x_{rs} that of bond rs, and for ordinary $2p$-orbitals these centroids are at the atom and the bond mid-point; calculation in the non-orthogonal basis is straightforward. It is customary, however,[4] to make similar assumptions when dealing with the orthogonalised orbitals which are implicitly accepted as a basis for the self-consistent field calculations.

The oscillator strengths for the α, *p*, β, and β′ bands of pyridine were calculated. The results are:

	(i)	(ii)		(i)	(ii)
α	0·012	0·009	β	1·264	1·223
p	0·022	0·016	β′	1·321	1·302

(i) Calc. from transition charge density.
(ii) Calc. by assuming (orthonormalised) orbitals and overlap distributions centrosymmetric.

It is seen that the values of the oscillator strengths obtained by using the more convenient basis without detailed analysis of the transition charge density agree well with those calculated more rigorously (this was also noted for naphthalene [1]).

I thank the Ramsay Memorial Fellowships Trust for the award of a Fellowship.

UNIVERSITY COLLEGE OF NORTH STAFFORDSHIRE,
KEELE, STAFFS. [*Received, June 30th,* 1959.]

[4] Pariser, *J. Chem. Phys.*, 1956, **24**, 250.

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390. *The Structure of "Monoacetyl Phosphite."*

By J. A. CADE.

To explain, in part, the simultaneous formation of hydrogen chloride and acyl chloride from a carboxylic acid and phosphorus trichloride, Brooks [1] proposed the following sequence, where the process (1) is supposed to go to completion:

$$PCl_3 + 3R{\cdot}CO_2H \longrightarrow P(OH)_3 + 3R{\cdot}COCl \quad \ldots\ldots\ldots (1)$$

$$P(OH)_3 + R{\cdot}COCl \longrightarrow R{\cdot}CO{\cdot}O{\cdot}P(OH)_2 + HCl \quad \ldots\ldots\ldots (2)$$

An alternative consideration is that inter- or intra-molecular loss of hydrogen chloride from the unstable intermediates $HP(O)Cl_2$ or $HP(O)Cl{\cdot}OH$, which result from the stepwise dechlorination of the phosphorus trichloride, competes successfully with their reaction with the carboxylic acid. Reasons adduced [3] for this have been that (*a*) acetylation of phosphorous acid by acetyl chloride is slow at temperatures (*e.g.*, 20°) at which liberation of hydrogen chloride in reaction of acetic acid with phosphorus trichloride is fast and (*b*)

[1] Brooks, *J. Amer. Chem. Soc.*, 1912, **34**, 492.

the ratio of hydrogen chloride to acyl chloride obtained for a given acid does not vary significantly with temperature.

The product of acetylation of phosphorous acid would probably have the *P*-acyl R·CO·P(O)–, rather than the mixed anhydride structure, R·CO·O·P–, because (*a*) mixed anhydrides of carboxylic acids with oxyacids of phosphorus are " energy-rich " and are not readily formed,[2] (*b*) compounds which undoubtedly contain a *P*-acyloxy-group undergo rapid deacylation by anhydrous hydrogen chloride [3] which does not however affect *P*-acylphosphonic acids,[4] (*c*) phosphorous acid contains P–H bonds, and the hydrogen atoms in such compounds, notably phosphine, are known to undergo substitution by an acyl group,[5] and (*d*) *X*-ray results [6] can be better interpreted in terms of the *P*-acyl structure.

The infrared spectrum (KBr disc) in the 2—15 μ region was very complex, and it was not possible to assign many peaks unambiguously on account of the paucity of analogous spectral data. Some qualitative similarity between the spectra of " monoacetyl phosphite " and acetylphosphonic acid [4] were observed. Each had peaks at 763 (P–C), 858 and 902 (C–C=O), 1250 (P=O), 1450 (asym C–Me stretch), and 1720 and 1790 (C=O stretch) cm.$^{-1}$, but the former showed some additional absorption, notably in the 2400 cm.$^{-1}$ region, characteristic of P–H bond stretching.

The melting points of acetylated phosphorous acid, acetylphosphonic acid and a 1 : 1 mixture of the two were 96—104°, 110—114°, and 98—112° respectively. Attempts to prepare amine salts of the two acids for comparison, from, *e.g.*, cyclohexylamine, dicyclohexylamine, and *p*-toluidine, failed because the neutral salts were hydrolysed or decomposed on recrystallisation, while the acid salts decomposed without melting.

Diazoethane in mild conditions gave recognisable esters of acetylphosphonic and acetoxyethane-1,1-diphosphonic acid, but it was clear that acetylated phosphorous acid is a complex mixture containing other components besides these acids.

This mixture did not acetylate aniline, and passage of dry hydrogen chloride over the solid at 50° or through a solution of it in tetrahydrofuran produced no acetyl chloride; these facts indicate that it does not contain compounds having a *P*-acyloxy-group.

Experimental.—Reagents were purified and solvents were dried.

Acetylation of phosphorous acid. Brooks' procedure [1] did not give the product in a form suitable for ethylation.

Phosphorous acid (40 g.) dissolved in acetic anhydride (200 c.c.) was shaken for 2 days with glass beads (200 g.), acetyl chloride (80 c.c.), and a few crystals of the crushed product from a previous reaction, in a flask closed with a drying tube. Decantating the supernatant liquid and washing with dry ether (5 × 200 c.c.) gave the product (50 g., 83%) which on paper chromatography in water gave a number of spots, two of which were identified severally with phosphorous and acetylphosphonic [4] acid. However, the possibility of hydrolysis may invalidate this analysis.

Ethylation of the product. Diazoethane [7] (22 g.) in ether (1·51 l.) was dried (KOH) and then added at 5° to the " monoacetyl phosphite " (25 g.) dispersed on beads as described. The mixture was shaken, becoming decolorised overnight, but not all the solid dissolved. Solvent was removed at 20°/15 mm. from the separated liquid, and the residue (26 g.) was distilled at low pressure. Repeated fractionation gave diethyl acetylphosphonate (9·35 g., 26%), b. p. 106—108°/15 mm., n_D^{20} 1·4220 (Found: P, 17·15. Calc. for $C_6H_{13}O_4P$: P, 17·2%) and tetraethyl acetoxyethane-1,1-diphosphonate (0·76 g., 2·1%), b. p. 98—100°/0·1 mm., n_D^{20} 1·4320, d_4^{20} 1·55 (Found: P, 17·2. Calc. for $C_{12}H_{26}O_8P_2$: P, 17·2%), and much undistillable residue (Found: P, 28·2%). The acylphosphonate was identified as its 2,4-dinitrophenylhydrazone (m. p. and mixed m. p. 132—133°) and the diphosphonic ester by molar refraction (Found: $[R_L]_D$, 80·92.

[2] Cade and Gerrard, *J.*, 1954, 2030.
[3] Cf. Cade, Thesis, London, 1955, pp. 73–77.
[4] Cooke, Gerrard, and Green, *Chem. and Ind.*, 1953, 351.
[5] Kosolapoff, " Organophosphorus Compounds," Wiley, New York, 1950, p. 14.
[6] Stelling, *Z. phys. Chem.*, 1925, **117**, 194.
[7] Analysed as described in *Org. Synth.*, Coll. Vol. II, Wiley, New York, 1946, p. 166.

Calc.: $[R_L]_D$, 80·82) and its infrared spectrum.[8] Two other substances obtained, but not identified unambiguously, were considered to be tetraethyl pyrophosphate (1·4 g.), b. p. 104—108°/0·1 mm., n_D^{20} 1·4184 (Found: P, 20·8. Calc. for $C_8H_{20}O_7P_2$: P, 21·35%), and tetraethyl chloroethane-1,1-diphosphonate (0·64 g.), b. p. 120—130°/0·1 mm., n_D^{20} 1·4848 (Found: C, 35·0; H, 6·9; P, 18·0; Cl, 7·65. Calc. for $C_{10}H_{23}O_6ClP_2$: C, 35·7; H, 6·9; P, 18·4; Cl, 10·5%).

This work was carried out in the Research Laboratories of Messrs. Albright and Wilson Ltd., Oldbury, Birmingham, during the period of an extra-mural contract with that Company in 1955—1956.

CHEMISTRY DIVISION, ATOMIC ENERGY RESEARCH ESTABLISHMENT,
HARWELL, DIDCOT, BERKS. [*Received, August 11th,* 1959.]

[8] Cf. Arbusov and Azanovskaya, *Doklady Akad. Nauk S.S.S.R.*, 1947, **58**, 1961.

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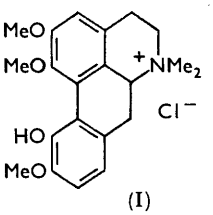
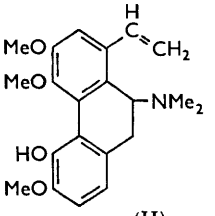
391. *The Identity of Chakranine with Isocorydine Methochloride, and a Note on Strong Hydrogen Bonding between Methoxyl and Hydroxyl Groups in the 4,5-Positions of Phenanthrene.*

By A. R. KATRITZKY, RICHARD A. Y. JONES, and S. S. BHATNAGAR.

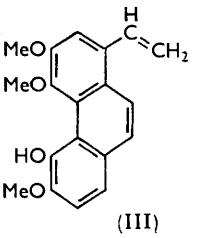
BHATNAGAR and his co-workers [1] described the isolation from the roots of *Bragantia wallichii* of an alkaloidal salt, chakranine; this has now been shown to be identical with isocorydine methochloride (I) which has been isolated from *Fagara coco*.[2] (The neutral alkaloid isocorydine has been isolated from several sources; for a summary and references see Rüegger [3].) Chakranine showed no mixed melting-point depression with an authentic sample of isocorydine methochloride, and had an identical infrared spectrum. The ultraviolet spectra and molecular rotations also corresponded, as did the melting points of the derived iodide and picrate and the properties of the first (II) and second (III) Hofmann degradation products.



(I)



(II)



(III)

During this work it became evident that strong hydrogen-bonding occurred between the hydroxyl group of compounds (I—III) and a methoxyl group. Thus the O–H stretching frequency was observed at values below 3300 cm.$^{-1}$ (see Experimental section), indicating that in (I—III) the steric congestion forces the hydroxyl close to the methoxyl group, giving a strong hydrogen bond. The degree of planarity is (III) > (I) > (II), which is reflected in the observed values. By contrast, in guaiacol the hydroxyl group absorbs at 3510 cm.$^{-1}$ (ε_A, 85) in chloroform.[4]

The proton nuclear magnetic resonance spectra of compounds (I—III) are readily interpreted on the basis of these structures. The positions of the hydroxyl peaks are at

[1] Kamat, Divekar, Vaz, Fernandes, and Bhatnagar, *Ind. J. Med. Res.*, 1958, **46**, 3.
[2] Comin and Deulofeu, *J. Org. Chem.*, 1954, **19**, 1774.
[3] Rüegger, *Helv. Chim. Acta*, 1959, **42**, 754.
[4] Katritzky and R. A. Jones, unpublished work.

high negative values which again shows that they are strongly hydrogen-bonded,[5] and in the order (III) > (I) > (II).

The values of pK_a were determined spectrophotometrically to be: (I), 10·8; (II), 11·8; (III), 12·4. These high values indicate that the hydroxyl group is strongly hydrogen-bonded in all three compounds (cf. phenol, pK_a 10·0) and most strongly in (III). Compound (I) is more acid than (II), presumably because of the presence of the positive charge.

Experimental.—The m. p. of the quaternary salts were values obtained with rapid heating; they depend on the rate of heating. Ultraviolet spectra were measured for water–ethanol (10 : 1) and 0·1N-aqueous sodium hydroxide solutions; maxima are quoted in mμ with log ε values in parentheses.

Chakranine. This quaternary chloride had m. p. 235° (decomp.), $[\alpha]_D^{25}$ (in H_2O) 162°, and $\lambda_{max.}$ 300 (3·76), 268 (4·16), and 220 (4·59) in neutral solution and 342 (3·93) and 226 (4·54) at pH 13. On treatment with potassium iodide it gave the iodide, m. p. 238—240°, and with picric acid the picrate,[1] m. p. 201—203°. The reported [2] values for isocorydine methochloride are m. p. 235°, $[\alpha]_D^{30}$ 168·6°, and for the methiodide and methopicrate, m. p. 231—232° and 202—204° respectively. An authentic specimen of isocorydine methochloride had $\lambda_{max.}$ 300 (3·76), 267 (4·16), and 217 (4·62) in neutral solution and 343 (3·89) and 225 (4·53) at pH 13 [cf. isocorydine methiodide [2] 270 (4·16) and 303 (3·81), and isocorydine hydrobromide [3] 220 (4·6), 270 (4·1) and 303 (3·8)].

The first Hofmann degradation product (II) of chakranine had m. p. 124—124·5°, $[\alpha]_D^{25}$ —197°, a pale blue fluorescence, and $\lambda_{max.}$ 307 (3·65) and 228 (4·53) in neutral solution and 342 (3·77) and 243 (4·53) at pH 13. The corresponding product from isocorydine had [2] m. p. 124—124·5°, $[\alpha]_D^{28}$ −194·6°, and a pale blue fluorescence.[6]

The second Hofmann degradation product (III) had m. p. 118—119°, was orange with a strong blue fluorescence, gave a blue-green colour with concentrated sulphuric acid, and had $\lambda_{max.}$ 388 (3·61), 371 (3·60), 333 (4·21), 259 (4·57), and 227 (4·45) in neutral solution and 400 (3·63), 300 (4·21), and 255 (4·45) at pH 13. The corresponding product from isocorydine was reported [6] to have m. p. 115—116° and identical colour reactions.

Infrared spectra. These were measured on a Perkin–Elmer 21 spectrophotometer, fitted with a sodium chloride prism. The solutions were of 0·189M-concentration in 0·106 mm. compensated cells (except for chakranine in chloroform where 1 mm. cells were used for solubility reasons). Apparent extinction coefficients were recorded (cf. ref. 7).

Complete spectra will be submitted to the D.M.S. records.

	Nujol mull	Solution in CCl_4		Solution in $CHCl_3$	
	λ (cm.$^{-1}$)	λ (cm.$^{-1}$)	ε_A	λ (cm.$^{-1}$)	ε_A
I	3180	(Insol.)		3180	110
II	3245	3255	120	3217	105
III	3080	3160	120	3090	110

Nuclear magnetic resonance spectra. Nuclear magnetic resonance spectra of hydrogen nuclei were obtained at 40Mc./sec. with a Varian Associates 4300B spectrometer and 12″ electromagnet, with flux stabilisation and sample spinning. Positions of the resonances are quoted as chemical shifts (σ) on the H_2O scale measured in parts per million relative to the solvent, chloroform, taken as = −1·88 relative to water. The σ values may be effectively converted into τ values based on the tetramethylsilane scale by adding 4·66 to each number. Strong absorption peaks are indicated by heavy type. An entry " a to b " indicates a complex multiplet of *ca.* 5—8 peaks in the range given.

	OH	Aromatic CH	Olefinic CH	OMe	NMe_2, CH–N
I	−3·07	−1·72 to −1·33	—	**1·48, 1·53, 1·83**	**2·15**, 2·67
II	−2·83	−2·46 to −1·28	−0·34 to +0·26	**1·49, 1·56, 1·74**	2·42 to 2·83, **3·41**
III	−4·5	−2·34 to −1·56	−0·39 to +0·20	**1·47, 1·50, 1·74**	—

[5] Cf. Cohen and Reid, *J. Chem. Phys.*, 1956, **25**, 790.
[6] Barger and Sargent, *J.*, 1939, 991.
[7] Katritzky and co-workers, *J.*, 1958, 2182, 4155.

We thank Professor Sir Alexander Todd, F.R.S., for his interest, Prof. V. Deulofeu for a sample of isocorydine methochloride, and the D.S.I.R. for a Research grant (to R. A. Y. J.).

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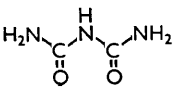
392. *Biuret Complexes of Bivalent Metal Chlorides.*

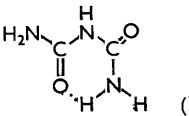
By M. NARDELLI and I. CHIERICI.

IN a neutral medium biuret and bivalent metals form co-ordination compounds of formula $M^{II}X_2,2C_2H_5O_2N_3$ [$M^{II}X_2$ = $CuCl_2$, $CuSO_4$, $Cu(NO_3)_2$, $NiCl_2$, $NiSO_4$,[1] $CdCl_2$ [2]]. The similarity between biuret and urea suggests that co-ordination occurs through the oxygen atom.[3]

For the biuret molecule two planar configurations, (I) and (II), should be possible. With (I) the biuret can co-ordinate as a bidentate ligand on the same metal atom, whereas in (II) the oxygen atoms are not equivalent and cannot be co-ordinated by the same metal atom. The exceptionally high value of the dipole moment (nearly twice of that of urea) which can be calculated for (I), and the possibility of formation of an intramolecular hydrogen bond for (II), indicate that the latter configuration is more probable.



(I)



(II)

The correctness of configuration (II) is also indicated by the crystallographic data of bis(biuret)cadmium chloride: this crystallizes in the monoclinic system, and the smallest repeat distance, *a*, in the lattice is nearly the same (~3·7 Å) as that which we have found to be characteristic of an octahedral co-ordination around the cation of four chlorine atoms and two oxygen atoms. Each chlorine atom is shared by the co-ordination polyhedra of two adjacent metal atoms, which run in chains parallel to [100]. A structure of this kind is possible only for (II) with the biuret molecule bonded to one metal atom only. The complete structural study of this compound, which will be reported elsewhere, has given a further confirmation of these views.

Experimental.—Biuret was recrystallized from ethyl alcohol. The other compounds were prepared by slow evaporation of aqueous solutions containing biuret and the chlorides of the bivalent metals.

Metals were determined as sulphate (except that Cu was determined electrolytically), chlorine as silver chloride, and nitrogen by Dumas's method. Crystal densities were found by flotation.

Crystal data were deduced from rotation and Weissenberg photographs (Cu-K_α radiation).

Biuret, $C_2H_5N_3O_2$, M = 103·08, monoclinic prismatic, a = 3·66 ± 0·01, b = 17·77 ± 0·03, c = 7·99 ± 0·01 Å, β = 100·0° ± 0·2°, U = 512 Å^3, Z = 4, D_c = 1·34 (Z was calculated by assuming that D_m for biuret is not very different from that of urea). Space-group $P2_1/c$ (C_{2h}^5, No. 14). Optically biaxial needles. The small value of the parameter a indicates that the plane of the molecule is nearly parallel to (100).

Bis(biuret)manganese(II) *chloride*, M = 332·0. Small, distorted, colourless cubes, probably

[1] Schiff, *Annalen*, 1898, **299**, 243.
[2] Schenck, *Z. physiol. Chem.*, 1904, **43**, 72.
[3] Nardelli, Cavalca, and Fava, *Gazzetta*, 1957, **87**, 1232; Cavalca, Nardelli, and Coghi, *Nuovo Cimento*, 1957, **6**, 278; Nardelli, Coghi, and Azzoni, *Gazzetta*, 1958, **88**, 235.

triclinic, not suitable for *X*-ray single-crystal analysis (Found: Mn, 15·8; Cl, 21·4; N, 25·4. $Mn[C_2H_5N_3O_2]_2Cl_2$ requires Mn, 16·5; Cl, 21·4; N, 25·3%).

Bis(biuret)cupric chloride, $M = 340{\cdot}6$, orthorhombic, $a = 7{\cdot}99 \pm 0{\cdot}01$, $b = 6{\cdot}76 \pm 0{\cdot}01$, $c = 10{\cdot}69 \pm 0{\cdot}01$ Å, $U = 578$ Å^3, $D_m = 1{\cdot}95$, $Z = 2$, $D_c = 1{\cdot}96$. Space-group, *Pnnm* (D_{2h}^{12}, No. 58) or *Pnn*2 (C_{2v}^{10}, No. 34). Short prisms, blue. Optically biaxial (Found: Cu, 18·6; Cl, 20·5; N, 24·5. $Cu[C_2H_5N_3O_2]_2Cl_2$ requires Cu, 18·6; Cl, 20·8; N, 24·7%). There are certain similarities between the crystal data of this compound and those of the zinc analogue; it is likely therefore that the centrosymmetrical space-group is the true one.

Bis(biuret)zinc chloride, $M = 342{\cdot}5$, monoclinic prismatic, $a = 8{\cdot}02 \pm 0{\cdot}01$, $b = 7{\cdot}26 \pm 0{\cdot}01$, $c = 11{\cdot}54 \pm 0{\cdot}01$ Å, $\beta = 124{\cdot}7° \pm 0{\cdot}2°$, $U = 552$ Å^3, $D_m = 2{\cdot}04$, $Z = 2$, $D_c = 2{\cdot}06$. Space-group, $P\,2_1/c$ (C_{2h}^5, No. 14). Small, colourless, very short prisms. Optically biaxial (Found: Zn, 19·3; Cl, 20·7; N, 24·7. $Zn[C_2H_5N_3O_2]_2Cl_2$ requires Zn, 19·1; Cl, 20·7; N, 24·6%). The space-group shows that the co-ordination around the Zn atom must be centrosymmetrical (probably octahedral).

Bis(biuret)cadmium chloride, $M = 389{\cdot}5$, monoclinic prismatic, $a = 3{\cdot}704 \pm 0{\cdot}005$, $b = 19{\cdot}96 \pm 0{\cdot}03$, $c = 8{\cdot}20 \pm 0{\cdot}01$ Å, $\beta = 111{\cdot}1° \pm 0{\cdot}2°$, $U = 566$ Å^3, $D_m = 2{\cdot}0$, $Z = 2$, $D_c = 2{\cdot}28$. Space-group $P2_1/c$ (C_{2h}^5, No. 14). Very slender and flattened colourless needles. Optically biaxial, usually twinned on (001) (Found: Cd, 29·3; Cl, 18·6; N, 21·2. $Cd[C_2H_5N_3O_2]_2Cl_2$ requires Cd, 28·9; Cl, 18·2; N, 21·6%).

Bis(biuret)mercury(II) *chloride*, $M = 477{\cdot}7$, monoclinic prismatic, $a = 3{\cdot}768 \pm 0{\cdot}004$, $b = 20{\cdot}56 \pm 0{\cdot}02$, $c = 8{\cdot}16 \pm 0{\cdot}01$ Å, $\beta = 109{\cdot}1° \pm 0{\cdot}3°$, $U = 597$ Å^3, $D_m = 2{\cdot}59$, $Z = 2$, $D_c = 2{\cdot}65$. Space-group $P2_1/c$ (C_{2h}^5, No. 14). Isostructural with the analogous Cd compound. Small, flattened, colourless prisms. Optically biaxial (Found: Hg, 42·4; Cl, 14·0; N, 17·8. $Hg[C_2H_5N_3O_2]_2Cl_2$ requires Hg, 42·0; Cl, 14·8; N, 17·6%).

Note added in proof.—The *trans* configuration for biuret has been confirmed by two private communications. W. D. Kumler found for the dipole moment of biuret in dioxan a value (3·27 D) considerably less than that of urea (4·56 D) and of acetamide (3·90 D), indicative of intramolecular hydrogen-bonding. E. W. Hughes, H. L. Yakel, and H. C. Freeman found the same configuration in the crystal structure of biuret hydrate (with a variable water content). The crystal data now reported correspond to those found for biuret hydrate, therefore the phase we studied is to be considered as the hydrate.

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393. *Characterisation of Amino-acids as* p-p′-*Nitrophenylazobenzoyl Derivatives.*

By EL S. AMIN.

p-p′-NITROPHENYLAZOBENZOYL CHLORIDE was used for identification and separation of alcohols,[1] aliphatic amines,[2] aromatic amines,[3] and thiols,[4] transforming them into sparingly soluble, well-crystallised coloured derivatives. It has now been similarly applied to amino-acids. The chloride has given acyl derivatives in fairly good yields from eight amino-acid methyl esters in pyridine at 60°. The acyl derivatives melt sharply and at much higher temperatures than do other derivatives.[5] They are insoluble in water, more or less soluble in organic solvents. Moreover, the m. p.s differ sufficiently to be useful criteria.

Experimental.—Evaporations were under reduced pressure at 50°.

Preparation of acyl derivatives. The amino-acid methyl ester (0·5 mmole), prepared by the

[1] Hecker, *Chem. Ber.*, 1955, **88**, 1666; Amin and Hecker, *ibid.*, 1956, **89**, 695.
[2] Amin, *J.*, 1957, 3764.
[3] Amin, *J.*, 1959, 1619.
[4] Amin, *J.*, 1958, 4769.
[5] Karrer, Keller, and Szönyi, *Helv. Chim. Acta*, 1943, **26**, 38.

action of methyl alcohol and hydrogen chloride, was dissolved in dry hot pyridine (20 ml.), and *p-p'*-nitrophenylazobenzoyl chloride [1] (0·725 mmole) added in small portions to the warm solution (40—60°), which became red and was then kept at 60° for 2 hr. The mixture was treated with water and extracted with several portions of benzene (150 ml.). The extract was washed with 20% sulphuric acid, filtered, washed with water, 0·05N-sodium hydroxide solution, and water, dried (Na_2SO_4), and filtered through activated alumina. The product was crystallised from acetone. The *derivatives* shown in the Table were thus prepared.

Amino-acid ester	M. p. of derivative	Formula	Found: N (%)	Reqd.: N (%)
Glycine	161°	$C_{16}H_{14}O_5N_4$	16·3	16·4
L-Alanine	181	$C_{17}H_{16}O_5N_4$	15·5	15·7
L-Valine	171	$C_{19}H_{20}O_5N_4$	14·5	14·6
DL-Leucine	137	$C_{20}H_{21}O_5N_4$	13·9	14·1
Phenylalanine	179	$C_{23}H_{20}O_5N_4$	12·7	13·0
Aspartic acid	183	$C_{19}H_{18}O_7N_4$	13·5	13·5
Glutamic acid	161	$C_{20}H_{20}O_7N_4$	13·0	13·1
DL-Methionine	152	$C_{18}H_{18}O_5N_4S$	13·8	14·0

Chromotography. A mixture (10 mg.) of the above derivatives of glycine, L-alanine, L-valine, and DL-leucine in ligroin–benzene solution was passed down a column of basic zinc carbonate and thereby separated into pure components.

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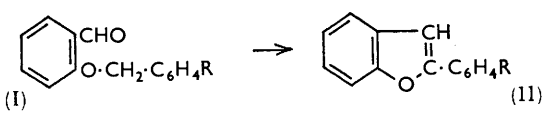
394. *Preparation of* 2-p-*Nitrophenylbenzofuran.*

By K. B. L. MATHUR and H. S. MEHRA.

CYCLISATION of *o*-benzyloxybenzaldehyde to 2-phenylbenzofuran (I ⟶ II; R = H) failed until sodium was used as condensing agent in an atmosphere of hydrogen;[1] even then the yield was poor. We have found that reaction of salicylaldehyde with 4-nitrobenzyl bromide in methyl alcohol in the presence of potassium carbonate gives mainly (80%) a product which from its ultraviolet absorption (resembling that of *trans*-4-nitro-



(I) (II)

stilbene [2]), analysis, and colour reaction with sulphuric acid is considered to be 2-*p*-nitrophenylbenzofuran (II; R = NO_2). A small amount of *o*-4-nitrobenzyloxybenzaldehyde was also isolated. This appears to be the first case of smooth cyclisation in such a reaction. However, in a similar reaction 4-chlorobenzyl bromide gave only *o*-4-chlorobenzyloxybenzaldehyde.

Experimental.—Salicylaldehyde (1·25 g.) and 4-nitrobenzyl bromide (2·25 g.) were heated in methyl alcohol (10 c.c.) with freshly ignited potassium carbonate (1·6 g.) for 6 hr., then cooled and filtered. The solid was washed with methyl alcohol (2 × 10 c.c.), triturated with water (25 c.c.) (to remove potassium carbonate) and collected again (1·8 g.). Crystallisation from acetic acid yielded 2-p-*nitrophenylbenzofuran* as needles, m. p. 182° [Found: C, 70·2; H, 4·0%; *M* (Rast), 238. $C_{14}H_9O_3N$ requires C, 70·3; H, 3·8%; *M*, 239], $\lambda_{max.}$ in EtOH 250 (ε 12,200), 345 (ε 25,350), and 370 mμ (ε 19,860), giving with concentrated sulphuric acid a yellowish-brown colour slowly changing to green.

[1] Stoermer, *Ber.*, 1903, **36**, 3979.
[2] Cf. Wiegand and Markel, *Med. u. Chem.*, 1942, **4**, 585; *Chem. Abs.*, 1944, **38**, 5144.

The acetic acid mother-liquor from the first crystallisation, upon slight dilution, gave a further 0·1 g. of the furan, m. p. 182°. Further dilution gave an oil, which crystallised from a small amount of hot 70% acetic acid. This gave o-4-*nitrobenzyloxybenzaldehyde*, m. p. 118° (Found: C, 64·2; H, 4·35. $C_{14}H_{11}O_4N$ requires C, 65·4; H, 4·3%). It gave a precipitate with 2,4-dinitrophenylhydrazine.

A similar experiment with 4-chlorobenzyl bromide (2·15 g.) gave only o-4-*chlorobenzyloxybenzaldehyde* (1·5 g.), m. p. 80—81° (from alcohol) (Found: C, 68·8; H, 5·0. $C_{14}H_{11}O_2Cl$ requires C, 68·2; H, 4·5%). It gave a precipitate with 2,4-dinitrophenylhydrazine.

The authors thank Professor T. R. Seshadri for his interest in this work and facilities.

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DELHI-8. INDIA. [*Received, October 26th*, 1959.]

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395. Sophora *Alkaloids. Part VI.* The Alkaloids of the Bark and Flowers of* S. microphylla, *and the Isolation of Diosmin from the Flowers.*

By LINDSAY H. BRIGGS, R. C. CAMBIE, R. H. HOLDGATE, and R. N. SEELYE.

IN Part I [1] the alkaloids of the seeds of *Sophora microphylla* Ait., syn. *Edwardsia microphylla* (Maori name " Kowhai ") were shown to be methylcytisine, α-matrine, cytisine, and two unidentified bases. One of the latter, which also occurs in *S. tetraptera* [2] and *S. chrysophylla*, was later named sophochrysine.[3] The same alkaloids have now been shown to be present in the basic fractions from extracts of the bark and the flowers by paper-chromatographic comparison with authentic samples. A further alkaloid, present only in the flowers, was identified as anagyrine, previously isolated from the related Hawaiian species, *S. chrysophylla*.[3] α-Matrine and methylcytisine, the principal alkaloids of the bark of *S. microphylla*, were isolated in low yield by methods similar to those described in Parts I [1] and II,[2] but no attempt was made to separate the bases from the flowers.

The principal compound isolated from the flowers was identified as the flavone glycoside, diosmin, by comparison (mixed melting point and infrared spectrum) with an authentic sample and by hydrolysis to diosmetin, glucose, and rhamnose. The isolation of diosmin constitutes the first report of this compound from *Sophora* species.

Experimental.—Analyses are by Dr. A. D. Campbell, University of Otago, N.Z. Infrared spectra were measured as KBr discs and ultraviolet spectra were measured for EtOH solutions. White's method [4] was used for paper chromatographic investigation of alkaloid fractions and R_F values for known *Sophora* alkaloids agreed with his results.

The bark. Dried and ground bark (450 g.) was extracted (Soxhlet) with methanol, and the residue obtained on removal of solvent *in vacuo* was worked up for alkaloids by methods similar to those previously described.[1,2] Comparative paper chromatography showed the presence of α-matrine, methylcytisine, cytisine, sophochrysine, and a further unidentified base. The crude bases on distillation afforded a mixture of alkaloids, b. p. 180—200°/0·5 mm. (750 mg., 0·2%), which solidified. Extraction with light petroleum (b. p. <40°) and repeated crystallisation gave α-matrine (129 mg.), m. p. and mixed m. p. 76—77° (identical infrared spectrum).

* Part V, Briggs and Mangan, *J.*, 1948, 1889.

[1] Briggs and Ricketts, *J.*, 1937, 1795.
[2] Briggs and Taylor, *J.*, 1938, 1206.
[3] Briggs and Russell, *J.*, 1942, 507.
[4] White, *New Zealand J. Sci. Technol.*, 1957, **38**, *B*, 707.

Extraction with light petroleum (b. p. 80—100°) and repeated crystallisation gave methylcytisine (45 mg.), m. p. and mixed m. p. 138° (identical infrared spectrum).

The flowers. Dried flowers (880 g.) were extracted (Soxhlet) in batches with methanol, and a colourless solid which separated during extraction collected. Repeated crystallisation from aqueous pyridine or aqueous dimethylformamide gave fine needles of diosmin hydrate, m. p. and mixed m. p. 283° (decomp.) (Found: C, 53·85, 53·7; H, 5·4, 5·4; OMe, 5·3. Calc. for $C_{28}H_{32}O_{15},H_2O$: C, 53·7; H, 5·4; 1OMe, 5·0%), $\lambda_{max.}$ 255 (log ε 4·28), 268 (log ε 4·25), and 345 mμ (log ε 4·30). The infrared spectrum was identical with that of an authentic sample.

Hydrolysis of diosmin by boiling 10% sulphuric acid was slow and incomplete. Heating under reflux with 10% dry methanolic hydrogen chloride for 6 hr. or *via* the acetate by Arthur, Hui, and Ma's method [5] and pouring the mixtures into water gave the aglycone (12 and 40% yield, respectively). Recrystallisation from 75% aqueous acetic acid gave yellow prisms of diosmetin, m. p. 257—258° (lit.,[6] m. p. 258—259°) (Found: C, 62·5; H, 3·9; OMe, 9·5. Calc. for $C_{16}H_{12}O_6,\frac{1}{2}H_2O$: C, 62·1; H, 4·2; 1OMe, 10·0%), $\lambda_{max.}$ 254 (log ε 4·26), 268 (log ε 4·24), and 344 mμ (log ε 4·31), $\nu_{max.}$ 3571 (OH) and 1661 (C=O) cm.$^{-1}$. The triacetate formed colourless needles, m. p. 195—196° (lit.,[6] m. p. 195°) (Found: C, 62·3; H, 4·2. Calc. for $C_{22}H_{18}O_9$: C, 62·0; H, 4·2%).

Rhamnose and glucose were identified in the neutralised hydrolysate by co-chromatography with authentic samples.

The basic fraction was obtained by the previous method and partially purified by absorption on Amberlite IRC-50 resin and displacement by 0·1N-aqueous ammonia. Co-chromatography of the crude alkaloids (8 g., 2%) with authentic samples showed the presence of α-matrine, methylcytisine, cytisine, anagyrine, sophochrysine, and a further, unidentified base.

We are indebted to Dr. R. C. Cooper, Auckland Institute and Museum, for identification of the species and to Dr. H. R. Arthur, University of Hong Kong, for a sample of diosmin. Assistance is gratefully acknowledged from the Chemical Society, the Rockefeller Foundation, the Australian and New Zealand Association for the Advancement of Science, and the Research Grants Committee of the University of New Zealand.

Department of Chemistry,
University of Auckland, New Zealand. [*Received, November 2nd*, 1959.]

[5] Arthur, Hui, and Ma, *J.*, 1956, 632.
[6] Horowitz, *J. Org. Chem.*, 1956, **21**, 1184.

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396. 5′,6′-*Dihydropyrano*(2′,3′:7,6)*chromone and its 2-Substituted Derivatives.*

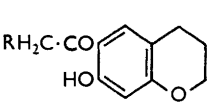
By P. Naylor and G. R. Ramage.

Pyranochromone derivatives are of interest since they may show pharmacologica properties comparable to those shown by the naturally occurring furanochromone, khellin (III). 5′,6′-Dihydropyrano(2′,3′:7,6)chromone and several of its derivatives have been prepared by condensing 6-acetyl-7-hydroxychroman [1] with ethyl oxalate or ethyl acetate and cyclising the product with ethanolic hydrogen chloride or a mixture of glacial acetic and concentrated hydrochloric acid.

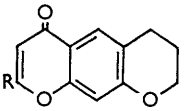
Condensation of 6-acetyl-7-hydroxychroman with ethyl oxalate, in the presence of sodium ethoxide, gave 6-(β-ethoxycarbonyl-β-oxopropionyl)-7-hydroxychroman (I; R = CO·CO_2Et). Ring closure of this material by ethanolic hydrogen chloride gave

[1] Naylor, Ramage, and Schofield, *J.*, 1958. 1190.

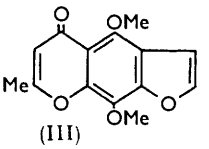
ethyl 5′,6′-dihydropyrano(2′,3′:7,6)chromone-2-carboxylate (II; R = CO_2Et), whereas ring closure by acetic and hydrochloric acid gave the corresponding acid (II; R = CO_2H) which was characterised by its methyl ester (II; R = CO_2Me). On melting, the acid was decarboxylated to form 5′,6′-dihydropyrano(2′,3′:7,6)chromone (II; R = H). Condensation of 6-acetyl-7-hydroxychroman with ethyl acetate, in the presence of powdered



(I)



(II)



(III)

sodium, gave the β-diketone (I; R = Ac) which was ring-closed by acetic and hydrochloric acid to form 5′,6′-dihydro-2-methylpyrano(2′,3′:7,6)chromone (II; R = Me).

Of the dihydropyranochromones that were pharmacologically tested, all were more active spasmolytics than khellin itself, especially the 2-methyl derivative (II; R = Me).

Experimental.—Light petroleum used had b. p. 80—100°.

6-(β-*Ethoxycarbonyl*-β-*oxopropionyl*)-7-*hydroxychroman* (I; R = CO·CO_2Et). A solution of 6-acetyl-7-hydroxychroman [1] (1·92 g.) in warm dry ethyl oxalate (9·5 c.c.) was added to a solution of sodium ethoxide (made by adding 1·08 g. of sodium to 19 c.c. of ethanol), and the mixture heated on a steam-bath for 20 min. and cooled. Ether (90 c.c.) was added and the flask well shaken. The yellow sodium salt was filtered off, washed with a further quantity of ether (20 c.c.), and then stirred into N-acetic acid (70 c.c.). The product was collected, washed with water, and dried to give 6-(β-*ethoxycarbonyl*-β-*oxopropionyl*)-7-*hydroxychroman* (2·4 g., 82%) which crystallised from ethanol as pale yellow plates, m. p. 132° (Found: C, 61·6; H, 5·3. $C_{15}H_{16}O_6$ requires C, 61·6; H, 5·5%).

Ethyl 5′,6′-*dihydropyrano*(2′,3′-7,6)*chromone*-2-*carboxylate* (II; R = CO_2Et). A solution of 6-(β-ethoxycarbonyl-β-oxopropionyl)-7-hydroxychroman (2·92 g.) in ethanolic hydrogen chloride (70 c.c.; 11% w/v) was refluxed for 1½ hr., then cooled to −5° and filtered, and the residue was washed with a little cold ethanol. Crystallisation from light petroleum gave *ethyl* 5′,6′-*dihydropyrano*(2′,3′-7,6)*chromone*-2-*carboxylate* (1·90 g., 69%) as needles, m. p. 129—130° (Found: C, 66·0; H, 5·2. $C_{15}H_{14}O_5$ requires C, 65·7; H, 5·1%).

5′,6′-*Dihydropyrano*(2′,3′-7,6)*chromone*-2-*carboxylic acid* (II; R = CO_2H). A mixture of 6-(β-ethoxycarbonyl-β-oxopropionyl)-7-hydroxychroman (2·92 g.), glacial acetic acid (20 c.c.), and concentrated hydrochloric acid (4 c.c.) was refluxed for 1½ hr., cooled, and filtered. Crystallisation of the residue (2·31 g., 94%) from *NN*-dimethylformamide gave 5′,6′-*dihydropyrano*(2′,3′:7,6)*chromone*-2-*carboxylic acid* as prisms, m. p. 278° (decomp.) (pre-heated bath, m. p. 316°) (Found: C, 63·1; H, 4·2. $C_{13}H_{10}O_5$ requires C, 63·4; H, 4·1%).

5′,6′-Dihydropyrano(2′,3′:7,6)chromone-2-carboxylic acid formed a *methyl ester* (II; R = CO_2Me), m. p. 132°, which crystallised from light petroleum as needles (Found: C, 64·6; H, 4·4. $C_{14}H_{12}O_5$ requires C, 64·6; H, 4·6%).

5′,6′-*Dihydropyrano*(2′,3′-7,6)*chromone* (II; R = H). Pure 5′,6′-dihydropyrano(2′,3′:7,6)-chromone-2-carboxylic acid (0·27 g.) was carefully melted at atmospheric pressure to a black mass which was then distilled (115—140°/0·5 mm.) on to a cold finger. The resulting 5′,6′-*dihydropyrano*(2′,3′:7,6)*chromone* (0·20 g., 90%) crystallised from light petroleum as plates, m. p. 116·5° (Found: C, 71·0; H, 4·9. $C_{12}H_{10}O_3$ requires C, 71·3; H, 5·0%).

6-*Acetoacetyl*-7-*hydroxychroman* (I; R = Ac). A solution of 6-acetyl-7-hydroxychroman (1·92 g.) in warm dry ethyl acetate (6·2 c.c.) was added to powdered sodium (1·2 g.) covered by dry benzene (10 c.c.). When the initial vigorous reaction had subsided, the mixture was heated on a steam-bath for 1½ hr. with occasional shaking, and then left overnight. The mixture was macerated with benzene and filtered, and the residue stirred into crushed ice (20 g.) and glacial acetic acid (3·6 c.c.). The product (2·00 g., 85%) was collected, washed with water, and crystallised from methanol to yield 6-*acetoacetyl*-7-*hydroxychroman* as prisms, m. p. 123° (Found: C, 66·8; H, 6·0. $C_{13}H_{14}O_4$ requires C, 66·7; H, 6·0%).

5′,6′-*Dihydro*-2-*methylpyrano*(2′,3′:7,6)*chromone* (II; R = Me). A mixture 6-acetoacetyl-7-hydroxychroman (2·34 g.), glacial acetic acid (24 c.c.), and concentrated hydrochloric acid (6·4 c.c.) was refluxed for 2 hr. and the resulting solution cooled. The product was precipitated with water (160 c.c.), filtered, dried, and crystallised from light petroleum (charcoal) to yield 5′,6′-*dihydro*-2-*methylpyrano*(2′,3′:7,6)*chromone* (2·10 g., 97%) as blades, m. p. 107° (Found: C, 71·9; H, 5·5. $C_{13}H_{12}O_3$ requires C, 72·2; H, 5·6%).

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397. *Bromination of t-Butylbenzene.*

By J. D. BACKHURST.

DIRECT halogenation of t-butylbenzene in the side chain was considered to be impossible until the chlorination was reported by Truce *et al.*[1] Previously, Kharasch and Fineman [2] obtained only nuclear bromination, although conditions found to be optimum for the bromination of neopentane were employed. Tal'kovskiĭ [3] used a pseudo-gas-phase reaction to prepare 1-bromoethylbenzene from ethylbenzene, without the presence of organic peroxides or other catalysts.

The side-chain bromination of t-butylbenzene is now reported. It was accomplished in the gas phase with irradiation by a mercury arc, the reactants giving ~40% yields. Reaction in the dark gave a 21% yield, of which 75% was the side-chain monobromide, the remainder being nuclear-substituted. Reaction between bromine and refluxing t-butylbenzene, whilst the reactants were illuminated, also yielded both side-chain and nuclear bromides.

It is notable that no significant amount of rearranged product was detected.[4] Search for this was made by studying a kinetically controlled hydrolysis of the product in 80% aqueous ethyl alcohol.[5] The sample hydrolysed was a fraction collected between the b. p.s of the unchanged t-butylbenzene and ββ-dimethylphenethyl bromide when the product was fractionated through a long, vacuum-jacketed column, and would have contained any αα-dimethylphenethyl bromide produced. Hydrolyses were carried out at 25·0° and 73·05° and first-order rate coefficients were calculated. About 0·9% of " fast " (more readily hydrolysed) bromide was found ($k_1^{25} = ca.\ 6 \times 10^{-5}$ sec.$^{-1}$), and this agrees with similar results of Fainberg and Winstein [6] who found 0·6% of " fast " bromide in ββ-dimethylphenethyl bromide. At 73·05° $k_1^{25} = 2{\cdot}42 \times 10^{-6}$ sec.$^{-1}$, in agreement with the value quoted for ββ-dimethylphenethyl bromide.

Experimental.—The apparatus used for the gas-phase reaction has been described.[4,7] The optimum contact time was about 30 sec. Variation of the temperature between 190° and 270° had no effect upon the yield and the reaction proceeded smoothly over this range. The

[1] Truce, McBee, and Alfieri, *J. Amer. Chem. Soc.*, 1949, **71**, 752.
[2] Kharasch and Fineman, *J. Amer. Chem. Soc.*, 1941, **63**, 2776.
[3] Tal'kovskiĭ, *J. Gen. Chem.* (*U.S.S.R.*), 1948, **18**, 103.
[4] Backhurst, Hughes, and Ingold, *J.*, 1959, 2742.
[5] Grunwald and Winstein, *J. Amer. Chem. Soc.*, 1948, **70**, 846.
[6] Fainberg and Winstein, *J. Amer. Chem. Soc.*, 1956, **78**, 2763.
[7] Backhurst, *J.*, 1959, 3497.

molar ratio of hydrocarbon to bromine was usually about 5·5. The excess of bromine and the hydrogen bromide formed were removed by bubbling nitrogen through the reaction product.

The preparation and physical properties of t-butylbenzene have been described elsewhere.[4] " AnalaR " bromine was used without further purification.

An authentic sample of ββ-dimethylphenethyl bromide, b. p. 91·3—91·5°/4 mm., n_D^{25} 1·5457 (cf. ref. 6) (Found: C, 56·5; H, 6·2; Br, 37·0. Calc. for $C_{10}H_{13}Br$: C, 56·4; H, 6·2; Br, 37·2%), was prepared by coupling 2-methylallyl bromide with benzene, in the presence of sulphuric acid. The compound was characterised by the preparation of β-methyl-β-phenylbutyranilide, m. p. 122—123°, from the Grignard reagent and phenyl isocyanate.

αα-Dimethylphenethyl bromide, prepared by the action of hydrogen bromide on the alcohol, had b. p. 85—86°/4 mm., n_D^{25} 1·5364.

Illuminated gas-phase reaction. After reaction of t-butylbenzene (5·3 mol.) and bromine (1 mol.) at 226° with a contact time of 35 sec., fractionation gave main fractions: b. p. 46—47°/8 mm., n_D^{25} 1·4905 (329·4 g.); b. p. 90·4—90·9°/4 mm., n 1·5448 (20·2 g.); b. p. 90·9—91·0°/4 mm., 1·5458 (13·3 g.) (Found: C, 56·3; H, 6·2; Br, 36·7. Calc. for $C_{10}H_{13}Br$: C, 56·4; H, 6·2; Br, 37·2%) (gives β-methyl-β-phenylbutyranilide; therefore ββ-dimethylphenethyl bromide); b. p. 91·0—92·0°/4 mm., n_D^{25} 1·5457 (12·0 g.).

Hydrolyses. These were carried out by standard techniques. The liberated hydrogen bromide was determined by titration with sodium ethoxide solution, and lacmoid as indicator.

Reaction between bromine and refluxing t-butylbenzene. Bromine was added to the vapour of refluxing t-butylbenzene during several hours, until the hydrocarbon : bromine was 4·0 (mol.); throughout, the reagents were illuminated. The product was fractionally distilled and, besides unchanged t-butylbenzene, was mainly ββ-dimethylphenethyl bromide, with a small amount of material from which fractional freezing yielded *p*-, m. p. 15·5°, n_D^{25} 1·5314 (Found: C, 56·4; H, 6·2; Br, 37·1%), and *m*-bromo-t-butylbenzene, b. p. 98°/10 mm., n_D^{25} 1·5336.

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398. *Triphenylphosphine Sulphide and Selenide as Ligands.*

By E. BANNISTER and F. A. COTTON.

So far as we are aware the literature [1] contains no reports of complexes of Ph_3PS or Ph_3PSe or of any other phosphine sulphides or selenides. Since we have recently prepared a variety of interesting complexes [2] of Ph_3PO, we made a cursory exploration of the interaction of triphenylphosphine sulphide and selenide with a few transition-metal salts and Lewis acids. Although the results on hand are rather scanty, we report them at this time since we do not expect an early opportunity to extend them.

The compounds prepared, $PdCl_2,2Ph_3PS$, $PdCl_2,2Ph_3PSe$, and $SnCl_4,2Ph_3PSe$, are thermally rather stable, but too insoluble to permit the usual studies which would elucidate their structures.

Experimental.—$PdCl_2,2Ph_3PS$. Triphenylphosphine sulphide (1 mol.), suspended in alcohol, was added to a solution of palladous chloride (1 mol.) in 18% hydrochloric acid. There was an immediate colour change and, on boiling, a light brown precipitate. This *complex*

[1] See, *e.g.*, Kosolapoff, " Organophosphorous Compounds," John Wiley and Sons, Inc., New York, 1950; J. R. Van Wazer, " Phosphorus and Its Compounds," Interscience Publ., Inc., New York, 1958, Vol. I.

[2] Bannister and Cotton, *J.*, 1960, 1878.

was filtered off, washed with methylene chloride (in which the ligand is appreciably soluble), and dried in a vacuum; it had m. p. 236° (decomp.) (Found: C, 55·3; H, 4·0. $PdCl_2,2Ph_2PS$ requires C, 56·4; H, 3·95%).

$PdCl_2,2Ph_3PSe$. Similar reaction with the selenide gave an orange-brown *complex* (Found: C, 49·3; H, 3·4. $PdCl_2,2Ph_3PSe$ requires C, 50·3; H, 3·5%).

$SnCl_4,2Ph_3PSe$. When stannic chloride was added to a solution of triphenylphosphine selenide in benzene, a dark brown colour appeared and, on boiling, a dark brown sludge was formed. However, adding the chloride carefully with stirring to diethyl ether afforded a crystalline precipitate of $SnCl_4,2Et_2O$, and when the selenide was then added the etherate rapidly dissolved to give a yellow solution. On concentration of this solution, a pale yellow precipitate of *complex*, m. p. 168°, was formed (Found: C, 47·4; H, 3·2. $SnCl_4,2Ph_3PSe$ requires C, 45·85; H, 3·2%).

Triphenylphosphine sulphide did not appear to react with $SnCl_4,2EtO$. Neither the sulphide nor the selenide appeared to displace ether from BF_3,Et_2O in ether: evaporation gave only unchanged starting materials. No complexes were obtained with cobalt, mercuric, or cupric chloride.

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Cambridge 39, Mass., U.S.A. [*Received, November 23rd*, 1959.]