NOTES.

685. *Organic Fluorine Compounds. Part XXIII.* Methylene Reactivity in Ethyl Fluoroacetate.*

By Ernst D. Bergmann and S. Cohen.

Since ethyl fluoroacetate enters Claisen reactions [1,2] and condenses with aromatic aldehydes,[3] and the sodium derivative of its enol can be used for alkylation [4] and acylation,[2,5] we have studied the reaction of aliphatic ketones with the enol of this ester. Acetone and ethyl methyl ketone afford simultaneously the two possible products. Acetone gave 14% of ethyl α-fluoro-β-hydroxy-β-methylbutyrate and 34% of 1-fluoropentane-2,4-dione;[6] ethyl methyl ketone gave 14% of ethyl α-fluoro-β-hydroxy-β-methylvalerate and 20% of 1-fluorohexane-2,4-dione, whose structure is assumed by analogy with the reaction between ethyl acetate and ethyl methyl ketone. Ethyl α-fluoro-β-hydroxy-β-methylbutyrate had been obtained by the Reformatzky reaction between acetone and ethyl chlorofluoroacetate;[8] the analogous synthesis with ethyl methyl ketone is described in this paper.

The sodium derivative of the enol of ethyl fluoroacetate failed to enter Michael reactions, but with chloral gave a mixture of isomers of ethyl γγγ-trichloro-α-fluoro-β-hydroxybutyrate.

Experimental.—*Ethyl α-fluoro-β-methyl-β-hydroxyvalerate and 1-fluorohexane-2,4-dione.* To a stirred suspension of sodium hydride (12 g.) in ether (100 ml.), a solution of ethyl fluoroacetate (53 g.) and ethyl methyl ketone (36 g.) in ether (100 ml.) was added dropwise at 0°. Stirring was continued for 1 hr. after the mixture had become homogeneous. The brown solution was poured on ice and sulphuric acid, and the organic layer separated, dried, and distilled, giving *1-fluorohexane-2,4-dione* (13 g., 20%), b. p. 65—68°/33 mm. (Found: C, 54·7; H, 7·0; F, 14·5. $C_6H_9FO_2$ requires C, 54·6; H, 6·8; F, 14·4%), and *ethyl α-fluoro-β-hydroxy-β-methylvalerate* (13 g., 14·5%), b. p. 67—69°/2 mm. (Found: C, 53·6; H, 8·6; F, 10·6. $C_8H_{15}FO_3$ requires C, 53·9; H, 8·4; F, 10·7%), $\nu_{max.}$ (liquid film) 3420 (OH), 1740 (C=O), 1085, and 1030 (C–F) cm.$^{-1}$. The *cupric salt* of the diketone recrystallised from ethanol as light blue needles, decomp. >250° (Found: F, 11·9. $C_{12}H_{16}CuF_2O_4$ requires F, 11·7%).

The ethyl ester (10 g.) was refluxed on the steam-bath for 30 min. with acetic acid (10 ml.)

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* Part XXII, *J.*, 1961, 3457.

[1] Blank, Mager, and Bergmann, *J.*, 1955, 2190.
[2] Bergmann, Cohen, and Shahak, *J.*, 1959, 3278.
[3] Bergmann and Schwarcz, *J.*, 1956, 1524.
[4] Bergmann and Szinai, *J.*, 1956, 1521.
[5] Bergmann, Cohen, and Shahak, *J.*, 1959, 3286.
[6] Fackler and Cotton, *J.*, 1960, 1435.
[7] Levine, Conroy, Adams, and Hauser, *J. Amer. Chem. Soc.*, 1945, **67**, 1510.
[8] Bergmann, Cohen, Hoffman, and Rand-Meir, *J.*, 1961, 3457.

and hydrochloric acid (20 ml.). Distillation gave the *acid* (4 g., 48%), b. p. 105—108°/0·2 mm., m. p. 87—90° (Found: F, 12·9. $C_6H_{11}FO_3$ requires F, 12·7%).

To a suspension of magnesium amalgam [from magnesium turnings (5 g.) and mercury (2 g.) in hot toluene (50 ml.)] a solution of ethyl chlorofluoroacetate [9] (29 g.) and ethyl methyl ketone (14·4 g.) in toluene (50 ml.) was added dropwise. An exothermic reaction took place, whereupon the external heating was discontinued. The mixture was refluxed for 1 hr. and poured on ice and sulphuric acid, and the organic layer was separated, dried, and distilled. The ester, b. p. 62—63°/1 mm. (15 g., 42%), was hydrolysed with acetic acid and hydrochloric acid as described above, and the acid identified with the above product by analysis and mixed m. p. (Found: C, 47·7; H, 7·7; F, 12·8. Calc. for $C_6H_{11}FO_3$: C, 48·0; H, 7·3; F, 12·7%), $\nu_{max.}$ (in KBr) 3400 (OH), 1735 (C=O), in the C–F region 1070, 1060, 1030, 1010 cm.$^{-1}$.

Ethyl α-fluoro-β-hydroxy-β-methylbutyrate and 1-fluoropentane-2,4-dione. Analogously, acetone (29 g.) gave 1-fluoropentane-2,4-dione (20 g., 34%), b. p. 50—52°/27 mm. (Found: F, 15·5. Calc. for $C_5H_7FO_2$: F, 16·1%), and ethyl α-fluoro-β-hydroxy-β-methylbutyrate (11 g., 13·5%), b. p. 47—49°/0·5 mm. (Found: C, 51·5; H, 7·5; H, 11·1. Calc. for $C_7H_{13}FO_3$: C, 51·2; H, 8·0; F, 11·6%), $\nu_{max.}$ (liquid film) 1730 (C=O; sh 1740), 1600, 1060 (C–F) cm.$^{-1}$.

The *cupric salt* of the diketone formed blue needles, decomp. >250°, from ethanol (Found: C, 40·1; H, 4·1; F, 13·1. $C_{10}H_{12}CuF_2O_4$ requires C, 40·3; H, 4·0; F, 12·6%).

The ester (10 g.) was refluxed with acetic acid (10 ml.) and hydrochloric acid (20 ml.), as described above. The *acid* (3·5 g., 42%) had b. p. 100—110°/0·5 mm., m. p. 68—70° (Found: C, 44·4; H, 6·6; F, 13·5. $C_5H_9FO_3$ requires C, 44·1; H, 6·6; F, 13·9%), $\nu_{max.}$ (in KBr) 3390 (OH), 1740 (C=O), 1020 and 1015 (C–F) cm.$^{-1}$.

Ethyl γγγ-trichloro-α-fluoro-β-hydroxybutyrate. To the sodium derivative of ethyl fluoroacetate [from ethyl fluoroacetate (53 g.) and sodium hydride (12 g.) in dry ether (30 ml.)], chloral (74 g.) was added with cooling and stirring. After 3 hr. the clear solution was decomposed with ice and hydrochloric acid. The ester (20 g., 16%) boiled at 155—160°/2 mm. and solidified. Recrystallisation from toluene gave a product of correct analysis, but with m. p. 70—100°, presumably a mixture of isomers (Found: C, 29·1; H, 3·3. Calc. for $C_6H_8Cl_3FO_3$: C, 28·5; H, 3·2%).

This investigation has been supported by the U.S. National Institutes of Health.

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[*Received, January 5th*, 1961.]

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[9] Young and Tarrant, *J. Amer. Chem. Soc.*, 1948, **71**, 2432.

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686. *The Colouring Matter of* Rhus cotinus *Wood (Young Fustic).*

By H. G. C. KING and T. WHITE.

SINCE the discovery [1] of fisetin (3,7,3′,4′-tetrahydroxyflavone) in the wood of *Rhus cotinus* in 1886, it has been assumed that the dyeing properties of young fustic extract were due to this flavone. Re-investigation of the wood has now shown that it contains also a significant amount of the aurone sulphuretin (2-benzylidene-6,3′,4′-trihydroxycoumaran-3-one), and a small proportion of a sulphuretin glucoside. An alkaline solution of sulphuretin is deep orange-red; an alkaline solution of fisetin is deep yellow; and it is probable that sulphuretin contributes more significantly than fisetin to the dyeing ability of fustic extract.

Experimental.—Coarsely ground chips of *Rhus cotinus* wood were extracted with ethyl acetate, and the extract was examined by two-dimensional paper chromatography in the solvent systems (1) t-butyl alcohol–acetic acid–water (14 : 25 : 61), and (2) butan-2-ol–acetic acid–water (14 : 1 : 5). Examination under ultraviolet light showed that in addition to fisetin, which fluoresced bright yellow, two components having a dull yellow-green fluorescence were present. Exposing the paper to ammonia vapour changed the last two fluorescences to bright orange, a behaviour characteristic of certain hydroxychalcones and aurones. The R_F values

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[1] Schmid, *Ber.*, 1886, **19**, 1734.

of the major component, and its ultraviolet spectrum (after elution from the paper with ethanol) were identical with those of synthetic sulphuretin[2] (in ethanol, $\lambda_{max.}$ 395—397 mμ; 460 mμ in 0·002M-sodium ethoxide). Comparison of the optical density of the compound with that of a standard solution of sulphuretin at 395 mμ indicated that the material extracted with ethyl acetate contained 7·4% of sulphuretin, corresponding to 0·5% in the initial whole wood.

Sulphuretin was then isolated by refluxing the whole extract with ethyl acetate (~50 vol.) and filtering off the undissolved crude aurone. Removal of the contaminating fisetin was difficult and after two recrystallisations from ethanol–water the orange sulphuretin melted at 293° (Found, in product dried at room temperature over P_2O_5: C, 63·1; H, 4·1. Calc. for $C_{15}H_{10}O_5,H_2O$: C, 62·4; H, 4·2%). The triacetyl derivative had m. p. and mixed m. p. 169°.

The minor aurone component was eluted from several chromatograms with ethanol. With ferric chloride solution the solution gave a bright green colour. After being concentrated, it was hydrolysed with 3·7% w/v hydrochloric acid and the hydrolysate examined by paper chromatography with the above solvent system for the aglycone and t-butyl alcohol–ethyl methyl ketone–water (5 : 12 : 3) for the sugar component. Sulphuretin and glucose were the sole hydrolysis products.

The presence of sulphuretin was also demonstrated by chromatography of the wood of *Rhus succedanea*, another species rich also in fisetin.

The authors thank Dr. T. Swain for valuable discussions, and La Compagnie Française des Extraits Tinctoriaux et Tannants, Le Havre, France, for a gift of *Rhus cotinus* wood.

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[Present addresses: see p. 3234.]
[*Received, January* 18*th*, 1961.]

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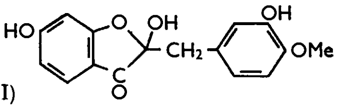
[2] Nordström and Swain, *Arch. Biochem. Biophys.*, 1956, **60**, 329.

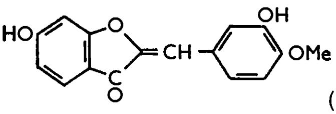
687. *The Reaction of Certain C_{15} Compounds with Acetic Anhydride–Sulphuric Acid.*

By H. G. C. King and T. White.

During an investigation of the crystalline 2-benzyl-2,6,3′-trihydroxy-4′-methoxycoumaran-3-one (I) isolated from commercial Quebracho tannin extract,[1] it was found that addition of a drop of concentrated sulphuric acid to a dilute solution of the compound in cold acetic anhydride gave an immediate intense cherry-red colour. An identical reaction was given by the related 2-benzylidene-6,3′-dihydroxy-4′-methoxycoumaran-3-one (II), suggesting that for the hydroxy-compound loss of the elements of water precedes the colour reaction.



(I)



(II)

A series of C_{15} compounds was, therefore, investigated to determine what other structures might exhibit similar colour formation under these conditions. Table 1 shows the results and may be of value in indicating the type of structure present in naturally occurring members of the C_{15} series.

Where the overall structure is chromogenic, successive substitution of methoxy- or benzyloxy-groups for hydroxy-groups leads to intensification of the colour accompanied by a change from yellow through red (partially substituted) to purple (fully methylated), but the specific structure responsible for colour production is not entirely clear. The presence of a double bond conjugated to a keto-group as part of a chain is a contributory factor (*e.g.*, aurones and chalcones), and here elimination of the double bond by reduction or bromination eliminates the colour reaction. In the case of the 2-benzyl-2-hydroxycoumaran-3-ones, removal of the elements of water from the $\gt C(OH)\cdot CH_2-$ portion of the

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[1] King and White, (*a*) *Proc. Chem. Soc.*, 1957, **341**; (*b*) *J.*, 1961, 3234.

TABLE 1. *Colours produced from* C_{15} *compounds* (2 mg.) *in a* 200 : 1 v/v *mixture* (10 ml.) *of acetic anhydride and sulphuric acid.*

Aurones		*Flavanols*	
6,3′,4′-Trihydroxy-	Orange	3,5,7,3′,4′-Pentahydroxy-	None
6,3′-Dihydroxy-4′-methoxy-	Cerise	3-Hydroxy-5,7,3′,4′-tetramethoxy-	Faint yellow
6,4′-Dihydroxy 3′-methoxy-	Bright red	*Flavanones*	
6,3′,4′-Trimethoxy-	Purple	7,3′-Dihydroxy-4′-methoxy-	Deep pink
2,3-Dihydro-6,3′-dihydroxy-4′-methoxy-	None	7,3′-Dibenzyloxy-4′-methoxy-	Cerise
2,α-Dibromo-6,3′,4′-trimethoxy-	None	7,3′,4′-Trimethoxy-	Purple
Flavones		*Chalcones*	
3,7,3′,4′-Tetrahydroxy-	Yellow	3,4,4′-Trihydroxy-	Orange
3,7,3′-Trihydroxy-4′-methoxy-	Yellow	3,4′-Dihydroxy-4-methoxy-	Cerise
3-Hydroxy-7,3′,4′-trimethoxy-	Deeper yellow	3,4,4′-Tribenzyloxy-	Red
7-Hydroxy-3,4′-dimethoxy-	Deeper yellow	3,4,4′-Trimethoxy-	Purple
2,3-*Dihydroflavonols*		2-*Benzyl*-2-*hydroxycoumaran*-3-*ones*	
3,5,7,3′,4′-Pentahydroxy-	None	Unsubstituted	Yellow
3,7,3′,4′-Tetrahydroxy-	None	6,3′,4′-Trihydroxy-	Orange
		6,3′-Dihydroxy-4′-methoxy-	Cerise
		6,3′,4′-Trimethoxy-	Purple

molecule produces the corresponding aurone [1b] and therefore results in colour formation. In the flavone family the presence of the double bond does not entail colour formation in this reaction. In the flavanols, loss of water from the •CH•CH(OH) grouping (if it occurs under these conditions) fails to lead to colour formation, presumably since there is no 4-carbonyl group. The reason for colour formation in the flavanones is not clear since the compounds are fully saturated and cannot lose water under these conditions. It is possible, however, that small amounts of contaminating chalcones were present in the samples tested (flavanones being formed from chalcones by treatment with mineral acid). Chalcones are so sensitive to the reaction that the presence of very small quantities could give a positive colour reaction.

The effects of substitution in altering the colour and in increasing its intensity are shown quantitatively in Table 2.

TABLE 2.

Compound	$\lambda_{\text{max.}}$ (mμ)	$E^{1\%}_{1\,\text{cm.}}$	Compound	$\lambda_{\text{max.}}$ (mμ)	$E^{1\%}_{1\,\text{cm.}}$
Aurones			*Aurones*		
6,3,4′-Trihydroxy-	325	730	6,3′,4′-Trimethoxy-	315	205
	375	795		365	115
	420—440	95		424	158
6,4′-Dihydroxy-3′-methoxy-	375	695		570	2240
	450	90	*Coumaran*-3-*ones*		
6,3′-Dihydroxy-4′-methoxy-	320	257	2-Benzyl-2,6,3′-dihydroxy-4′-methoxy-	380	64
	378	360		540	158
	540	590	2-Benzyl-2,6,3′,4′-tetrahydroxy-	315	138
6-Hydroxy-3′,4′-dimethoxy-	347	190		370—375	58
	560	>1000			

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[*Received, January* 18*th*, 1961.]

688. *A Stable Anilino-radical.*

By E. J. LAND and G. PORTER.

THE well-known blue radical (I),[1] derived from 2,4,6-tributylphenol, owes its stability to resonance and steric hindrance towards dimerisation or attack on the benzene nucleus. It can be prepared by chemical or photochemical oxidation of this phenol and is stable almost indefinitely in n-hexane solution if all dissolved oxygen is removed. We have prepared the corresponding anilino-radical (II) by photochemial oxidation of a

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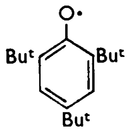
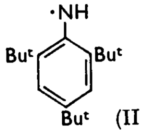
[1] Cook and Woodworth, *J. Amer. Chem. Soc.*, 1953, **75**, 6242, and subsequent papers; Muller and Ley, *Ber.*, 1954, **82**, 922, and subsequent papers.

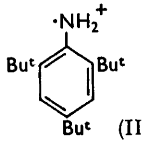
thoroughly outgassed 10^{-4}M-solution of 2,4,6-tri-t-butylaniline in n-hexane and cyclohexane with 1000 Joule flashes from a flash-photolysis apparatus. The pink radical solutions so prepared can be preserved for several days when the solvent is n-hexane but the stability is less in cyclohexane. The radical has a sharp absorption maximum at 3250 Å and much weaker absorption around 4100 Å (Fig. 1); this spectrum is very similar to that of the short-lived anilino-radical C_6H_5·NH· observed during flash-photolysis of aniline in the gas phase [2] and in fluid solution [3] or by continuous irradiation in rigid glasses [4] at liquid-nitrogen temperature. Attempts to detect the radical (II) produced chemically by oxidising the amine with lead dioxide, alkaline potassium ferricyanide, or benzoyl peroxide and following the change in ultraviolet absorption above 3000 Å have not been definitely successful, possibly owing to the difficulty of completely removing molecular oxygen occluded by the oxidising agent.



(I)



(II)



(III)

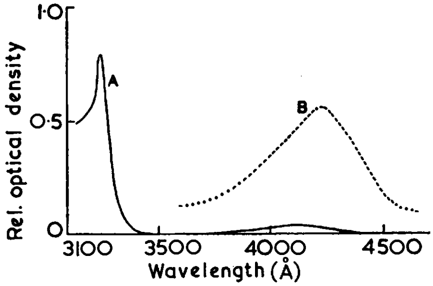
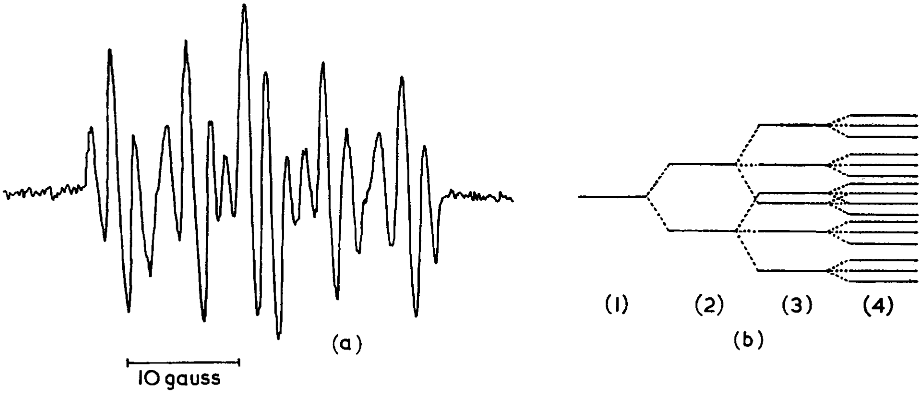


Fig. 1. *Ultraviolet and visible absorption spectra of* (A) *radical* (II) (*in n-hexane*) *and* (B) *radical* (III) (*in carbon tetrachloride*).

Fig. 2. (a) *Derivative of electron spin resonance spectrum of* (II) (*in n-hexane*). (b) *Energy level system of radical* (II). (1) *Electronic level;* (2) *interaction with* H *on* N *atom;* (3) *interaction with* N *atom;* (4) *interaction with two symmetrical* H *atoms on aromatic ring.*



The derivative of the electron spin resonance absorption spectrum of the radical (II) in n-hexane solution of unknown concentration is shown in Fig. 2. It consists of four sets of 1,2,1 triplets, two each side of a 1,3,3,1 quadruplet and the splitting is attributed to interaction of the unpaired electron spin with the nitrogen atom, the hydrogen atom attached to the nitrogen, and the two hydrogen atoms on the aromatic ring. The probable energy

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[2] Porter and Wright, *Trans. Faraday Soc.*, 1955, **51**, 1469.

[3] Land and Porter, unpublished work.

[4] Porter and Strachan, *Trans. Faraday Soc.*, 1958, **54**, 1595.

level system giving rise to this hyperfine pattern is also shown in Fig. 2. N-Proton, N-nucleus, and aromatic proton splitting are 11·9, 6·9, and 1·9 ± 0·2 gauss, respectively. The corresponding N-proton and N-nucleus splittings for the more localised electron in NH_2 are 24·0 and 10·3 gauss.[5]

The equilibrium between the uncharged single anilino- and the charged anilino-radical cation $C_6H_5{\cdot}NH_2^+$ can be followed by flash-photolysis of aqueous aniline solutions of differing pH's.[3] Both appear together in varying relative amounts between pH 4 and 8, only $C_6H_5{\cdot}NH{\cdot}$ being seen at pH 8 and only $C_6H_5{\cdot}NH_2^{+\cdot}$ below pH 4. Unfortunately the sterically hindered aniline is very insoluble in water and so the same conditions cannot be used to follow the equilibrium between anilino-form (II) and its protonated form (III). However, a solution of tri-t-butylaniline in carbon tetrachloride or 1 : 1 aqueous ethanol also produces a transient absorption very similar in shape and position to that of $C_6H_5{\cdot}NH_2^{+\cdot}$, and we therefore assign this absorption to the protonated hindered radical (III) (Fig. 1).

We are grateful to Dr. W. R. Remington of the Du Pont de Nemours Co. Inc., Delaware, U.S.A. for supplying us with 1 g. of 2,4,6-tri-t-butylaniline, and to Dr. J. K. Brown and Mr. D. Pooley of the Chemistry Department, University of Birmingham, for measuring the electron spin resonance spectrum of the radical, and for a helpful discussion.

THE UNIVERSITY, SHEFFIELD. [*Received, February 16th,* 1961.]

[5] Foner, Cochran, Bowers, and Jen, *Phys. Rev. Letters*, 1958, **1**, 91.

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689. *The Structure of " Boyd's Chloride " (Triphenylmethylphosphonic Dichloride).*

By M. HALMANN, L. KUGEL, and S. PINCHAS.

TRIPHENYLMETHANOL reacts readily with phosphorus trichloride to give a well crystallised stable product named " Boyd's chloride." [1-5] This synthesis has been repeatedly quoted as a " curious reaction." [4]

The structure to be expected from the method of preparation is that of triphenylmethyl phosphorodichloridite, $CPh_3{\cdot}O{\cdot}PCl_2$, which agrees with its elementary composition. However, the isomeric structure, $CPh_3{\cdot}P(O)Cl_2$, that of triphenylmethylphosphonic dichloride, must also be considered.

Arguments for the preferred structure of Boyd's chloride, or of its phenyl-substituted derivatives, have been based thus far only on the nature of the products formed by solvolysis. Boiling water hydrolyses the chloride very slowly to triphenylmethanol and phosphorous acid:[5] $CPh_3{\cdot}O{\cdot}PCl_2 + 3H_2O \longrightarrow CPh_3{\cdot}OH + P(OH)_3 + 2HCl$. This reaction seems to favour the phosphorodichloridite structure in which the phosphorus atom is in the tervalent state and on hydrolysis would form phosphorous acid. On the other hand, heating Boyd's chloride with alcoholic alkali [2-5] yields a half ester which is hydrolysed by a concentrated solution of hydriodic acid in acetic acid to a dibasic acid, triphenylmethylphosphonic acid, $CPh_3{\cdot}PO_3H_2$. This acid cannot have the structure $CPh_3{\cdot}O{\cdot}P(O)H{\cdot}OH$, since this belongs to a monobasic acid.[1b] Thus during the reactions (1)—(3) the triphenylmethyl group migrates from oxygen to phosphorus. Previous results, however, have not proved conclusively whether this rearrangement occurs before or after

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[1] (*a*) Boyd and Chignell, *J.*, 1923, **123**, 813; (*b*) Boyd and Smith, *J.*, 1924, **125**, 1477.

[2] Hatt, *J.*, (*a*) 1929, 2412; (*b*) 1933, 776.

[3] Hardy and Hatt, *J.*, 1952, 3778.

[4] Kosolapoff, " Organophosphorus Compounds," J. Wiley and Sons, New York, 1950, pp. 64, 70, 125; Van Wazer, " Phosphorus and its Compounds," Interscience Publ. Inc., New York, 1958, pp. 233, 264.

[5] Arbusov and Arbusov, *J. Russ. Phys. Chem. Soc.*, 1929, **61**, 217; Arbusov and Nikonorov, *Zhur. obshchei Khim.*, 1947, **17**, 2129.

the formation of the dichloride, although a phosphonic dichloride structure seemed to fit the chemical reactions better.[2b]

$$\begin{tikzcd}
CPh_3{\cdot}OH + PCl_3 \arrow[r, "1"] & CPh_3{\cdot}O{\cdot}PCl_2 \text{ or } CPh_3{\cdot}P(O)Cl_2 \arrow[d, "2\ NaOEt"] \\
CPh_3{\cdot}PO(OH)_2 & CPh_3{\cdot}O{\cdot}PCl{\cdot}OEt \text{ or } CPh_3{\cdot}P(O)Cl{\cdot}OEt \arrow[l, "3", "HI-AcOH"']
\end{tikzcd}$$

The infrared absorption of Boyd's chloride has now been measured in chloroform and carbon disulphide solutions and compared with published data for several other phosphonic dichlorides, as listed in the Table. A phosphonic dichloride structure requires a strong absorption band at about 1270 cm.$^{-1}$ due to the P=O stretching vibration.[11] The phosphorodichloridite structure must lack such an absorption * and instead show a strong P–O–C stretching band in the 990—1050 cm.$^{-1}$ range.[7,11]

Phosphoryl stretching vibration (cm.$^{-1}$) *of various phosphonic dichlorides,* $R{\cdot}P(O)Cl_2$.

Compound	Frequency	Solvent	Ref.	Compound	Frequency	Solvent	Ref.
$Me{\cdot}POCl_2$ ...	1268	CS_2	6	$Ph{\cdot}POCl_2$ ...	1275	Homog.	7
$Et{\cdot}POCl_2$ ...	1278	CS_2	6	$C_6H_{11}{\cdot}POCl_2$	1274, 1258	CS_2	8
$Pr^i{\cdot}POCl_2$ ...	1248, 1282	CS_2	6	$NMe_2{\cdot}POCl_2$	1268	Homog.	9
$CPh_3{\cdot}POCl_2$	1266	CS_2	This work	,,	1269	CCl_4	10
,,	1255	$CHCl_3$	,,				

The solutions of Boyd's chloride show a strong absorption band in the 1270 cm.$^{-1}$ region which is typical of phosphonic dichlorides. No strong absorption in the P–O–C stretching region was observed. It can therefore be concluded that Boyd's chloride is indeed triphenylmethylphosphonic dichloride. The somewhat lower P=O stretching frequency of the chloride in chloroform solution (1255 cm.$^{-1}$) than in carbon disulphide (1266 cm.$^{-1}$) must be attributed to the hydrogen bonding [7] existing between the polarised P–O group and the polar $H{-}CCl_3$ solvent molecules, by analogy with a similar decrease of the C=O stretching frequency.[13]

The rearrangement during its formation is not as surprising as it seemed thirty years ago. The strong yellow colour of the reaction mixture suggests the presence of the triphenylmethyl cation. The probable reaction sequence is thus:

$$CPh_3{\cdot}OH + PCl_3 \longrightarrow [CPh_3{\cdot}PCl_3]^+OH^- \longrightarrow CPh_3{\cdot}P(O)Cl_2 + HCl$$

in which the carbonium ion is " solvated " by the electron-donating phosphorus trichloride. The subsequent decomposition is analogous to the rearrangement of benzyl-containing phosphonium hydroxides: [14]

$$[PR_3{\cdot}CH_2Ph]^+OH^- \longrightarrow R_3PO + Ph{\cdot}CH_3$$

It is still unknown whether formation of Boyd's chloride is a one-step displacement of the chlorine by an oxygen atom or whether it involves a quinquecovalent phosphorus intermediate.

Experimental.—Triphenylmethylphosphonic dichloride was prepared as described; [3] purified by dissolution in benzene and precipitation with ether (3 times), it had m. p. 188—189° (Found:

* Although the triphenylmethyl group was also observed [12] to show a band at about 1280 cm.$^{-1}$, this group cannot be expected to bring about a strong absorption in this region, since this band was always found to be very weak.

[6] Gerding and Maarsen, *Rec. Trav. chim.*, 1957, **76**, 481.

[7] Daasch and Smith, *Analyt. Chem.*, 1951, **23**, 853.

[8] Bellamy and Beecher, *J.*, 1952, 475.

[9] Harvey and Mayhood, *Canad. J. Chem.*, 1955, **33**, 1552.

[10] Holmstedt and Larsson, *Acta Chem. Scand.*, 1951, **5**, 1179.

[11] Bellamy, " The Infra-red Spectra of Complex Molecules," Methuen & Co., London, 1948, p. 311.

[12] Pinchas and Samuel, *J.*, 1954, 863.

[13] Jones and Sandorfy in " Technique of Organic Chemistry," Interscience Publ. Inc., New York, 1956, Vol. IX, pp. 298—299, 471.

[14] Bladé-Font, VanderWerf, and McEwen, *J. Amer. Chem. Soc.*, 1960, **82**, 2396, giving further references.

C, 62·9; H, 4·4; Cl, 19·4; P, 8·4. Calc. for $C_{19}H_{15}Cl_2OP$: C, 63·1; H, 4·2; Cl, 19·7; P, 8·6%). The P=O band at about 1266 cm.$^{-1}$ was shown by the dichloride already in the crude reaction product (after washing with water and ether; m. p. 140—150°). Rearrangement was therefore not a result of the purification procedure. The infrared absorption spectra of solutions of this material in the sodium chloride range in chloroform (29 mg. + 1 ml.) and carbon disulphide (saturated solution) were measured with a Perkin–Elmer model 12C spectrophotometer. The following major bands were observed (frequencies in cm.$^{-1}$). In $CHCl_3$: 1599m, 1500m, 1442m, (all νC_{Ar}–C_{Ar}), 1255s, (νP=O), 1082w, 1035w, (both in plane νC_{Ar}–H bending), 1002w; (not measured below 830 cm.$^{-1}$). In CS_2 (measured only from 1400 cm.$^{-1}$ downwards): 1266s, (νP=O), 1035w, 735s, 697s, (both out-of-plane νC_{Ar}–H bending).

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The Weizmann Institute of Science,
Rehovoth, Israel.

[*Received, February 22nd*, 1961.]

690. *The Biosynthesis of Polyacetylenes. Part IV.* The Rate of Polyacetylene Synthesis by Basidiomycete* B.841.

By J. D. Bu'Lock, H. Gregory, and M. Hay.

In comparing different carbon sources for the synthesis of polyacetylene antibiotics by Basidiomycete B.841,[1] ethanol was found to be markedly superior to glucose.[2] A more detailed study was therefore made to determine whether the increased synthesis represented a general acceleration of metabolism or a more efficient use of substrate.

Previous experience has shown that good reproducibility is obtained when B.841 mycelium is grown from visually matched inocula supplied first with a glucose–salts–maize-steep medium, then with 4% (w/v) aqueous glucose, and finally with the experimental medium. In these experiments, such cultures (with identical previous histories) were supplied with either 4% (w/v) glucose or 1·5% (w/v) ethanol, together with tracer amounts of [1-^{14}C]acetate, and the polyacetylene production, substrate consumption, and carbon dioxide release were measured (see Experimental section). All proceeded at uniform rates, given in the Table as mg. of carbon per flask per day.

	4% (w/v) glucose		1·5% (w/v) ethanol	
Substrate	mg. C/flask/day	%	mg. C/flask/day	%
Substrate used	168	(100)	280	(100)
CO_2 released	80	48	152	54
Polyacetylenes (as $C_{11}H_{10}O_3$ *)	7	4	40	14
Xylose combined in polyacetylenes	2	1	10	4
Apparent assimilation (by difference)	79	47	78	28
[1-^{14}C]Acetate incorporated into polyacetylenes...	14·8%		15·8%	
C_2 turnover (from ^{14}C incorporation)	47	28	252	90

* Cf. nemotinic acid.[1]

In this series, polyacetylene synthesis from ethanol is about six times as rapid as from the glucose (cf. Table). The polyacetylenes are derived from the "acetate" C_2 pool,[3] (probably from acetyl-coenzyme-A) and as shown by the ^{14}C incorporation (cf. Table) the proportion of the C_2 pool used in this way is not affected by the change of substrate. The increased polyacetylene synthesis therefore corresponds to a proportionately increased turnover of precursor "acetate."

The yield of polyacetylenes from ethanol is virtually the same as the percentage incorporation of [1-^{14}C]acetate, *i.e.*, at least 90% of the ethanol consumed is utilised by

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* Part III, Bu'Lock, Allport, and Turner, *J.*, 1961, 52.

[1] Bu'Lock and Gregory, *J.*, 1960, 2280.

[2] Bu'Lock and Gregory *Biochim. Biophys. Acta*, 1961, **48**, 406.

[3] Bu'Lock and Gregory, *Biochem. J.*, 1959, **72**, 322.

way of " acetate " (most of the remainder can be accounted for as acetaldehyde). This is clearly not true of the glucose utilisation (cf. Table) since the C_2 turnover (calculated from ^{14}C-incorporation and polyacetylene yield) is only 28% of the glucose-carbon consumed. The polyacetylenes produced (including a small amount of combined xylose [1]) and the carbon dioxide released together account for little more than half of the glucose-carbon consumed, leaving about 47% not accounted for. With ethanol as substrate, about 54% appears as carbon dioxide, 4% as xylose combined with the polyacetylenes, and a remaining 28% is not accounted for (cf. Table).

A careful examination of the culture media from this experiment and from many others has failed to reveal any substances (other than the polyacetylenes, combined xylose, and unused substrate) in amounts sufficient to modify significantly these deficits in the carbon balance, and we conclude that the remaining carbon has been assimilated into the mycelium in the way found in many other fungi.[4] This is not in itself surprising, but it appears somewhat remarkable that, with the two different substrates used, though the proportions assimilated are quite different, the rates of assimilation are virtually the same. From the data, the assimilation of glucose occurs mainly by pathways not involving " acetate," in contrast to the utilisation of ethanol. It appears that once the rates of the assimilatory processes have been established, during the previous history of the mycelial samples, they control the further uptake of substrate, whether glucose or ethanol, and the different turnover of " acetate " required to maintain the assimilation rate in the two cases is directly reflected in different rates of antibiotic synthesis.

Experimental.—General culture conditions and radiochemical techniques were as previously described,[3] and the mixture of polyacetylenes (free and combined as xylosides) was analysed by double solvent extraction and spectrophotometric assay.[1] The glucose content of media was determined by Somogyi's method [5] (after the sample had been boiled for 5 min. to remove interfering polyacetylenes), and ethanol by Fidler's method.[6] Carbon dioxide production was measured by passing CO_2-free air through the flasks and into standardised aqueous barium hydroxide for a measured period each day and titrating the excess of alkali after ½—2 hr. The analyses were carried out on duplicate flasks from a single matched batch, with a total of 10 samples (10 ml. each) from each flask during 20—30 days; the steady rates observed over the greater part of this period are given in the Table as mg. of carbon per flask per day and as % of substrate carbon consumed. The reproducibility of such experiments is within ±5%.

Incorporation of [1-^{14}C]acetate is given as % of administered activity present as polyacetylenes (excluding combined xylose), after incubation in duplicate flasks of the same batch for 10 days with 6 μc of [1-^{14}C]acetate, measured by counting weighed thin films of 4-oxoundecanamide and estimating total polyacetylenes spectrophotometrically.

THE UNIVERSITY, MANCHESTER, 13. [*Received, February* 23*rd*, 1961.]

[4] Clifton, *Adv. Enzymology*, 1946, **6**, 269.
[5] Somogyi, *J. Biol. Chem.*, 1945, **160**, 69.
[6] Fidler, *Biochem. J.*, 1934, **28**, 1107.

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691. *Gibberellin A_2.*

By JOHN FREDERICK GROVE.

BOTH gibberellin A_2 (I; $R = R' = H$) [1] and gibberellin A_4 (II; $R = R' = H$) [2] have been obtained from certain strains of *Gibberella fujikuroi* and the relation between these two metabolites has been established by Sumiki and his co-workers [3] who obtained acetylgibberellin A_4 methyl ester (II; $R = Me$, $R' = Ac$) by dehydration of acetylgibberellin

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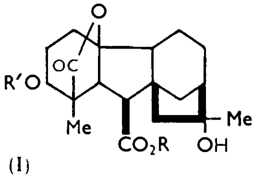
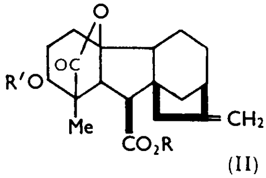
[1] Takahashi, Kitamura, Kawarada, Seta, Takai, Tamura, and Sumiki, *Bull. Agr. Chem. Soc. Japan*, 1955, **19**, 267; Takahashi, Seta, Kitamura, Kawarada, and Sumiki, *ibid.*, 1957, **21**, 75.
[2] Takahashi, Seta, Kitamura, and Sumiki, *Bull. Agr. Chem. Soc. Japan*, 1957, **21**, 396; 1959, **23**, 405.
[3] Kitamura, Takahashi, Seta, and Sumiki, *Bull. Agr. Chem. Soc. Japan*, 1958, **22**, 434.

A_2 methyl ester (I; R = Me, R′ = Ac) with phosphorus oxychloride in pyridine. The structure of gibberellin A_2 is confirmed by its formation, already briefly reported,[4] when gibberellin A_4 is treated with 3N-hydrochloric acid at room temperature during 2 days.



(I)



(II)

Aqueous solutions of gibberellin A_4 were stable at pH 1·3 for 3 days and at pH 3·2 for 2 weeks as judged by the absence of any change in the ultraviolet end-absorption due to the terminal methylene group. These results make it unlikely that gibberellin A_2 is an artefact, produced from gibberellin A_4, unless very strongly acidic conditions were used [1] during extraction of the fermentation broths.

Gibberellin A_2 showed dimorphism and, in agreement with a recent report,[5] formed a methyl ester $C_{20}H_{28}O_6,H_2O$. The latter was the main product when gibberellin A_4 methyl ester was boiled with dilute mineral acid: two unidentified minor products were also isolated from this reaction. Consistent with structure (I; R = Me, R′ = H) the hydrogen (proton) nuclear magnetic resonance spectrum of gibberellin A_2 methyl ester showed two sharp peaks at τ = 8·97 and 8·72 due to the two methyl groups attached to fully-substituted carbon atoms.

Experimental.—M. p.s are corrected. Infrared spectra were determined on Nujol mulls unless stated otherwise. Nuclear magnetic resonance spectra (tetramethylsilane as internal standard with τ = 10·00) were obtained in chloroform by Dr. N. Sheppard, University of Cambridge.

Action of hydrochloric acid on gibberellin A_4. (*A*) The acid (30 mg.) in methanol (0·5 ml.) and 3N-hydrochloric acid (2 ml.) was set aside for 2 days at room temperature. After addition of water (1 ml.), the solution was extracted with ethyl acetate, and the product was recrystallised three times from ethyl acetate giving gibberellin A_2 as felted needles (15 mg.), m. p. 255° (decomp.) (Found: C, 65·0; H, 7·35. Calc. for $C_{19}H_{26}O_6$: C, 65·1; H, 7·5%); $\nu_{max.}$ 3470 (sh), 3380 (broad) (OH); 1752, 1708 cm.$^{-1}$ (C=O). The infrared spectrum was unaltered by drying the material at 100° *in vacuo* and was identical with that of an authentic specimen of gibberellin A_2 kindly provided by Prof. Y. Sumiki, University of Tokyo: it differed significantly from the spectrum [1] of the form, m. p. 235—237°.[1] Gibberellin A_2 did not give a colour with concentrated sulphuric acid.

The methyl ester, prepared with diazomethane, crystallised from ethyl acetate in plates or prisms, m. p. 120° and 190°, $[\alpha]_D^{26}$ +25° (*c*, 0·6 in methanol), of the *monohydrate* (Found: C, 63·15; H, 8·0. $C_{20}H_{28}O_6,H_2O$ requires C, 62·8; H, 7·9%); $\nu_{max.}$ 3495, 3350, 3180 (OH); 1760, 1747 (C=O); 1672 cm.$^{-1}$ (H_2O). The infrared spectrum was identical with that of "gibberellin A_2 methyl ester sesquihydrate, m. p. 190—192° $[\alpha]_D$ +28° " [1] now presumably regarded [5] as a monohydrate, and with that of a specimen of the ester obtained by methylation of the authentic specimen of gibberellin A_2. The anhydrous *ester*, m. p. 190°, was obtained by drying the hydrate for 24 hr. *in vacuo* at room temperature over phosphorus pentoxide (Found: C, 66·3; H, 7·8. $C_{20}H_{28}O_6$ requires C, 65·9; H, 7·7%); $\nu_{max.}$ 3570; 1733 cm.$^{-1}$ [1770 (γ-lactone C=O) in dioxan]. The infrared spectrum was identical with that of gibberellin A_2 methyl ester.[1]

(*B*) A solution of the acid (5·3 mg.) in ethanol (0·5 ml.) and water (49·5 ml.) was adjusted to pH 3·2 with hydrochloric acid and set aside at room temperature. The ultraviolet absorption from 200 to 250 mμ was measured at intervals. No changes were recorded after 2 weeks. Similarly, no changes were observed during 5 days at pH 2·3 and during 3 days at pH 1·3. Gibberellin A_4 was recovered by extraction with ethyl acetate and identified by the infrared spectrum.

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[4] Brian, Grove, and MacMillan, *Fortschr. Chem. org. Naturstoffe*, 1960, **18**, 350.

[5] Kitamura, Seta, Takahashi, Kawarada, and Sumiki, *Bull. Agr. Chem. Soc. Japan*, 1959, **23**, 408.

ε at 205 mμ for gibberellin A_4 in ethanol–3N-hydrochloric acid (1 : 1) fell from an initial value of 7950 to 5700 after 2·5 hr. and to 2100 after 19 hr.

Action of sulphuric acid on gibberellin A_4 methyl ester. The ester (70 mg.) was heated under reflux in methanol (2 ml.) and 3N-sulphuric acid (4 ml.) in a stream of nitrogen for 1 hr. Carbon dioxide was not evolved. After removal of methanol by distillation *in vacuo* the residual solution was extracted with ethyl acetate, and the extract was washed with sodium hydrogen carbonate and recovered. The neutral product (59 mg.) was chromatographed in benzene–methanol (200 : 1, 200 ml.) on alumina (Grade II; pH 4; 10 × 0·7 cm.) by fractional elution [50 ml. fractions of benzene–methanol (200 : 1)]. The gummy products (weights in parentheses) were crystallised from ethyl acetate–light petroleum (b. p. 60—80°): (i) (8 mg.) microprisms, m. p. 120—130°; $\nu_{\max.}$ 3485 (OH); 1773, 1737 (weak), 1712 (C=O); 1653 cm.$^{-1}$. (ii) (7 mg.) intractable. (iii)—(x) (39 mg.) gibberellin A_2 methyl ester, m. p. 188—190°. (xi)—(xiv) (6 mg.) prisms of a *substance*, m. p. 155—157° (Found: C, 60·2; H, 8·0. $C_{20}H_{28}O_6,2H_2O$ requires C, 60·0; H, 8·05%); $\nu_{\max.}$ 3500, 3395, 3155 (OH); 1756, 1726 (C=O); 1645 cm.$^{-1}$.

IMPERIAL CHEMICAL INDUSTRIES LIMITED, AKERS RESEARCH LABORATORIES,
THE FRYTHE, WELWYN, HERTS.
[*Received, March 1st, 1961.*]

692. *The Thermal Unimolecular Isomerisation of Vinylcyclopropane to Cyclopentene.*

By M. C. FLOWERS and H. M. FREY.

CYCLOPROPANE and alkylcyclopropanes readily undergo thermal unimolecular isomerisation to olefins.[1] The rate equations of these reactions are characterised by high pre-exponential factors that can be accounted for, in part, by an entropy increase in the transition state due to ring opening. It seemed possible that vinylcyclopropane might undergo another type of isomerisation, to give cyclopentene. This reaction would involve no hydrogen shifts (which occur in the normal cyclopropane isomerisations); and, further, if the transition state involves simultaneous rupture of the three-membered ring and formation of the five-membered ring, little entropy increase in this transition state would be expected.

Vinylcyclopropane has been found to undergo a first-order thermal isomerisation to cyclopentene, which is almost certainly truly unimolecular, in the temperature range 339—391° C. This reaction has been investigated at four temperatures in this range and a good Arrhenius plot obtained, from which $k = 10^{13\cdot5} \exp(-49{,}600/\boldsymbol{R}T)$ sec.$^{-1}$. The "normal" value of the pre-exponential factor is clearly consistent with the transition state suggested above. Further, the low value of the energy of activation also indicates that the new carbon–carbon bond is being formed simultaneously with the rupture of the cyclopropane ring. At the highest temperature investigated (390·5° C) approximately 1·0% of the product was a mixture of penta-1,4-diene, isoprene, and *cis*- and *trans*-penta-1,3-diene. These products arise from the "normal" cyclopropane isomerisation, where shift of a hydrogen atom occurs with the ring rupture. The very small quantities of these dienes are to be expected from the much higher energy of activation of such cyclopropane isomerisations.

Experimental.—Vinylcyclopropane was prepared by photolysis of a gaseous mixture of keten and buta-1,3-diene at 1000 mm. at room temperature. The vinylcyclopropane was separated from the complex mixture by gas chromatography and stored as a gas at low pressure. The thermal isomerisation was carried out in a 1·4-l. Pyrex vessel contained in a horizontal furnace whose temperature was maintained within ±0·1°. Mercury cut-offs and Polythene or Fluon diaphragm valves were used, to avoid absorption associated with the use of conventional vacuum-stopcocks. The products were analysed by gas chromatography. With a 25 ft.

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[1] W. E. Falconer, T. F. Hunter, and A. F. Trotman-Dickenson, *J.*, 1961, 609; J. P. Chesick, *J. Amer. Chem. Soc.*, 1960, **82**, 3277; M. C. Flowers and H. M. Frey, *J.*, 1959, 3953; M. C. Flowers and H. M. Frey, *Proc. Roy. Soc.*, 1960, *A*, **257**, 122.

column containing 40—60 mesh Chromosorb with 15% by weight of acetonylacetone maintained at 0°, and with a flow rate of about 50 ml. of hydrogen per minute, cyclopentene was eluted in 40 min. and vinylcyclopropane in 63 min. A Gow–Mac tungsten-filament katharometer was used as a detector, and the signal fed to a 1 mv recorder fitted with a retransmitting slide-wire. The signal from the second slide-wire was used to operate a Perkin–Elmer model 194 integrator. Peak areas for mixtures of cyclopentene and vinylcyclopropane were found to be directly proportional to their mole percentages. The reproducibility of duplicate analyses was better than 0·5%.

The identification of all peaks was by time of elution from the chromatographic column, compared with those of the pure compounds. The major peaks were each confirmed as being due to only one component by mass spectrometry.

One of us (M. C. F.) thanks the Esso Petroleum Company for the award of a research studentship. The other (H. M. F.) thanks the Royal Society and the Department of Scientific and Industrial Research for grants for apparatus.

Department of Chemistry, University of Southampton. [*Received, March 7th,* 1961.]

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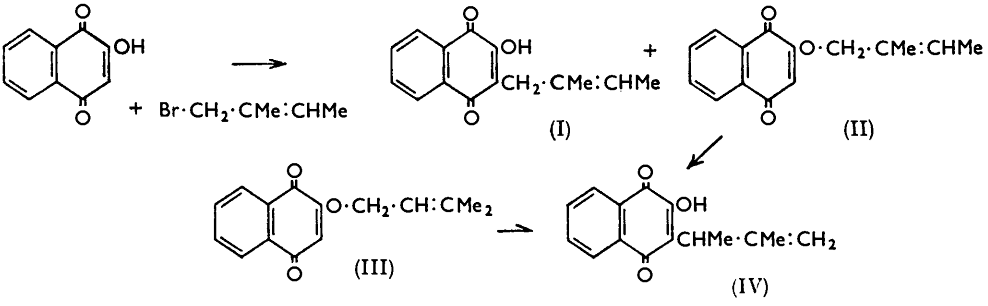
693. *A New Synthesis of Isodunniol.*

By R. I. T. Cromartie and P. M. Scott.

Isodunniol was first obtained by Price and Robinson [1] by a series of reactions from the natural pigment dunnione. The formula (IV) was proposed for it by Cooke and Somers [2] although it involved a shift of the double bond out of conjugation with the aromatic ring, and Cooke [3] synthesised the quinone by an abnormal Claisen rearrangement of the allyl ether (III).



The formula (IV) for isodunniol has now been confirmed by synthesis by normal Claisen rearrangement of the allyl ether (II), which was obtained, together with the corresponding *C*-alkyl derivative (I), by reaction of 2-methylbut-2-enyl bromide with the silver salt of 2-hydroxy-1,4-naphthaquinone. The synthetic material was identical with the original specimen of Price and Robinson, of which Dr. R. G. Cooke kindly sent us a sample.

Experimental.—Reaction of 2-*hydroxy*-1,4-*naphthaquinone with* 2-*methylbut*-2-*enyl bromide.* The silver salt of 2-hydroxy-1,4-naphthaquinone (10·8 g.) was added in portions during 1 hr. to the bromide [4] (6·2 g.) in benzene (50 c.c.), and the mixture was stirred for 8 hr., filtered, shaken with 2% sodium hydroxide solution, and evaporated. The residue was recrystallized from benzene–light petroleum (b. p. 60—80°), sublimed at $90°/10^{-4}$ mm., and again recrystallized from ether–light petroleum (b. p. 40—60°), yielding 2-(2-*methylbut*-2-*enyloxy*)-1,4-*naphthaquinone* as pale yellow needles, m. p. 127—128° (Found: C, 74·1; H, 6·1. $C_{15}H_{14}O_3$ requires

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[1] Price and Robinson, *J.*, 1940, 1493.

[2] Cooke and Somers, *Austral. J. Sci. Res.*, 1950, *A*3, 466.

[3] Cooke, *Austral. J. Sci. Res.*, 1950, *A*3, 481.

[4] Lauchenauer and Schinz, *Helv. Chim. Acta*, 1951, **34**, 1514.

C, 74·4; H, 5·8%), $\lambda_{max.}$ (in EtOH) 243, 248, 276, and 330 mμ (log ε 4·27, 4·30; 4·16, and 3·44 respectively), $\nu_{max.}$ (mull) 668, 720, 781, 817, 870, 948, 1007, 1028, 1050, 1088, 1120, 1214, 1257, 1313, 1337, 1363, 1444, 1582, 1598, 1610, 1652, 1683, 2860, 2920, and 3050 cm.$^{-1}$.

Acidification, with acetic acid, of the alkaline extract obtained above precipitated 2-hydroxy-3-(2-methylbut-2-enyl)-1,4-naphthaquinone (1·6 g.), which after recrystallization from aqueous acetic acid (charcoal) and then from ether–light petroleum (b. p. 40—60°) had m. p. 122—123·5° (lit.,[5] 123·5—124·5°).

The hydroxyquinone with zinc dust, acetic anhydride, and pyridine furnished 1,2,4-*tri-acetoxy*-3-(2-*methylbut*-2-*enyl*)*naphthalene* needles (from aqueous acetone), m. p. 162—164° (Found: C, 68·1; H, 6·2. $C_{21}H_{22}O_6$ requires C, 68·1; H, 6·0%).

Isodunniol. The ether (II) (1·6 g.) was boiled for 1 min. with glacial acetic acid (20 c.c.). The solution was diluted with water (20 c.c.), cooled, filtered to remove unchanged starting material, and further diluted with water (50 c.c.). Isodunniol separated gradually as yellow needles, which after two recrystallizations from aqueous ethanol and sublimation at 100°/10^{-3} mm. had m. p. 116—119° (lit.,[3] 119°) undepressed on admixture with natural isodunniol (Found: C, 74·4; H, 6·1. Calc. for $C_{15}H_{14}O_3$: C, 74·4; H, 5·8%). The infrared spectra (KBr disc) of the synthetic and the natural compound were identical, showing maxima at 729, 800, 871, 886, 946, 975, 1007, 1030, 1051, 1079, 1094, 1163, 1180, 1210, 1235, 1280, 1351, 1375, 1467, 1593, 1629, 1655, 2940, 2985, and 3350 cm.$^{-1}$.

One of us (P. M. S.) thanks the Department of Scientific and Industrial Research for a Maintenance Award.

UNIVERSITY CHEMICAL LABORATORY, CAMBRIDGE. [*Received, March 15th*, 1961.]

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[5] Gates and Moesta, *J. Amer. Chem. Soc.*, 1948, **70**, 614.

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694. *Fluorination of the Trioxides of Chromium, Molybdenum, Tungsten, and Uranium by Selenium Tetrafluoride.*

By NEIL BARTLETT and P. L. ROBINSON.

SELENIUM TETRAFLUORIDE can act as a fluorinating agent by exchanging fluorine for oxygen. Thus selenium oxyfluoride is most conveniently prepared by the reaction:[1] $SeF_4 + SeO_2 \longrightarrow 2SeOF_2$. Again, when selenium tetrafluoride attacks glass,[2] a similar exchange occurs: $SeF_4 + SiO_2 = SeO_2 + SiF_4$. The best method [3] of making tellurium tetrafluoride is by the reaction: $2SeF_4 + TeO_2 = 2SeOF_2 + TeF_4$. With vanadium pentoxide, the complex oxyfluoride $(SeF_4)_2VOF_3$ is formed.[2]

We have investigated the reactions between selenium tetrafluoride and the transition-metal trioxides of Group VI. Iodine pentafluoride has similar fluorinating properties as its behaviour with three of these trioxides shows.[4]

Reactions of SeF_4 *and* IF_5 *with Group* VIA *Trioxides.*

Oxide	Reaction with SeF_4	Reaction with IF_5
CrO_3	$CrO_3 + SeF_4 \longrightarrow CrO_2F_2 + SeOF_2$	$2CrO_3 + IF_5 \longrightarrow 2CrO_2F_2 + IO_2F$
MoO_3	$MoO_3 + 2SeF_4 \longrightarrow SeF_4,MoO_2F_2 + SeOF_2$	$2MoO_3 + 3IF_5 \longrightarrow 2IF_5,MoO_2F_2 + IO_2F$
WO_3	$WO_3 + 3SeF_4 \longrightarrow SeF_4,WOF_4 + 2SeOF_2$	$WO_3 + 2IF_5 \longrightarrow IF_5,WOF_4 + IO_2F$
	$WO_3 + 2SeF_4 \longrightarrow SeOF_2,WOF_4 + SeOF_2$	
UO_3	$UO_3 + SeF_4 \longrightarrow UO_2F_2 + SeOF_2$	
	$UO_2F_2 + SeF_4 \longrightarrow UOF_4 + SeOF_2$	

Chromyl fluoride does not form a complex with either selenium tetrafluoride or iodine pentafluoride, although the oxyfluoride dissolves freely in each. It is probable that the quinqueco-ordinate ion, $CrO_2F_3^-$, is too unstable. The molybdenum complex $SeMoO_2F_6$

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[1] Aynsley, Peacock, and Robinson, *J.*, 1952, 1231.
[2] Peacock, *J.*, 1953, 3617.
[3] Campbell and Robinson, *J.*, 1956, 785.
[4] Aynsley, Nichols, and Robinson, *J.*, 1953, 623.

could be formulated as either SeF_4,MoO_2F_2 or $SeOF_2,MoOF_4$; the latter is, however, unlikely since $KMoOF_5$ is not produced by equimolecular quantities of potassium fluoride and molybdenum trioxide in selenium tetrafluoride. The complex oxyfluoride $KWOF_5$ is formed in the reaction, $KF + WO_3 + 2SeF_4 \longrightarrow KWOF_5 + 2SeOF_2$. In the absence of potassium fluoride, the product may be a mixture of SeF_4,WOF_4 and $SeOF_2,WOF_4$.

Experimental.—Reactions with selenium tetrafluoride. (1) Chromium trioxide (1 g.) was warmed to 40° with selenium tetrafluoride (20 ml.), to give a bright red solution over which was brown chromyl fluoride vapour. Polymerisation of the chromyl fluoride was not observed; its vapour condensed to a red-brown solid (Found: Cr, 41·9; F, 32·1. Calc. for CrO_2F_2: Cr, 42·6; F, 31·2%). When the excess of selenium tetrafluoride and other material volatile at 0° were pumped from the reaction bub, the white residue, m. p. 15°, was selenium oxyfluoride and there was no evidence of the formation of a complex compound.

(2) Molybdenum trioxide (1·5 g.) dissolved in selenium tetrafluoride (10 ml.) at 50°; the straw-coloured solution deposited colourless crystals on cooling. These were recovered by removing the excess of selenium tetrafluoride and other volatile materials under a vacuum at 18°. They melted at 71—72°, distilled unchanged under a vacuum, and reacted violently with water. A solution of the substance in sodium hydroxide was acidified with hydrochloric acid, and the selenium precipitated with sulphurous acid. It was washed with concentrated ammonia solution (to remove any molybdic acid) then with water, alcohol, and ether. Fluorine was determined as lead chloride fluoride in the fluorosilicic acid–hydrofluoric acid distillate from a water–sulphuric acid mixture boiling at 132—138°. Molybdenum was precipitated as oxine complex. The *product* had composition SeF_4,MoO_2F_2 (Found: Se, 25·5; F, 35·4; Mo, 28·2. SeF_4,MoO_2F_2 requires Se, 24·6; F, 35·5; Mo, 29·9%).

(3) Equimolecular quantities of molybdenum trioxide and potassium fluoride were mixed and dissolved in boiling selenium tetrafluoride. White crystals separated on cooling, from which the excess of selenium tetrafluoride was removed under a vacuum at 70°. The solid was difficult to free from solvent and readily absorbed selenium tetrafluoride vapour. It dissolved easily in water to give a colourless solution. Qualitative analysis showed the presence of much combined selenium, and an *X*-ray powder photograph showed that it was a mixture containing the SeF_4,MoO_2F_2 phase.

(4) Tungsten trioxide (1·2 g.) was refluxed in selenium tetrafluoride (20 ml.) for 15 min. and gave a pale yellow, slightly opalescent solution. Removal of the selenium tetrafluoride under a vacuum at room temperature left a yellow solid, m. p. 60—63°, which dissolved quietly in water. Selenium and fluorine were determined as described. The tungstic acid which separated with the selenium was washed from it with concentrated aqueous ammonia, precipitated as the cinchonine salt, and ignited to tungsten trioxide. The product (Found: Se, 17·2; F, 28·8; W, 43·0. Calc. for SeF_4,WO_2F_2: Se, 19·3; F, 27·8; W, 43·0. Calc. for SeF_4,WOF_4: Se, 18·3; F, 35·3; W, 42·7%) is probably SeF_4,WO_2F_2 mixed with a smaller quantity of SeF_4,WOF_4. The combined yield (1·5 g.) was low and it is probable that a volatile colourless compound of tungsten distilled with the selenium tetrafluoride since tungsten was present in the latter.

(5) Equimolecular proportions of tungsten trioxide and potassium fluoride were dissolved in boiling selenium tetrafluoride to give an off-white precipitate on cooling. Selenium tetrafluoride and volatile products, when removed under a vacuum at 140°, left a pale buff solid. This dissolved slowly in water to a colourless solution from which tungstic acid separated on acidification (Found: F, 28·7; W, 53·6. Calc. for $KWOF_5$: F, 28·4; W, 55·1%).

(6) Uranium trioxide (0·8 g.) was refluxed with selenium tetrafluoride (20 ml.) for 30 min. during which the oxide changed to a cream-coloured solid. Selenium tetrafluoride was removed under a vacuum at 120°. The solid dissolved quietly in water to a light green solution from which selenium was absent. Uranium was determined as oxinate and fluorine as lead chlorofluoride. The product (Found: F, 21·6; U, 73·5. Calc. for UO_2F_2: F, 12·3; U, 77·3. Calc. for UOF_4: F, 23·0; U, 72·1%) was probably incompletely fluorinated uranium oxytetrafluoride.

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695. *An Examination of the Rutaceae of Hong Kong. Part VII.* The Essential Oils.*

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ESSENTIAL oils of seven species of the Hong Kong Rutaceae have been examined, mainly by gas chromatography. The results are recorded in the Table.

Plant species [a]	Constituents of oils
Acronychia pedunculata	α-Pinene; limonene
Evodia lepta	α-Pinene; furfuraldehyde
Fortunella hinsii	Furfuraldehyde
,, , berries	α-Pinene, limonene, *p*-cymene
Ruta graveolens	Methyl nonyl ketone
Zanthoxylum avicennae	α-Pinene, limonene, furfuraldehyde
Z. cuspidatum	Furfuraldehyde
Z. nitidum	Limonene, furfuraldehyde
	Other constituents
A. pendunculata, heartwood	β-Sitosterol
Z. cuspidatum, root bark	Nitidine

[a] Leaves, unless otherwise stated.

Previous work appears not to have been done on the essential oils of the genera *Acronychia* and *Fortunella.* Our work has not revealed in them constituents other than those reported previously from Rutaceae oils. The oils from the *Evodia*, the *Ruta*, and the three *Zanthoxylum* species, now examined for the first time, contain constituents also commonly found in Rutaceae oils. A minor unidentified compound has been detected as a constituent in five of the oils: it is only present when furfuraldehyde also occurs.

The constituents named were first tentatively identified by comparing their retention times in the gas chromatogram with those of authentic samples: then identity was confirmed by gas chromatography of samples to which the authentic substance had been added.

Limonene and α-pinene are present in about equal amount in *A. pedunculata* oil. Methyl nonyl ketone, previously reported to be the chief constituent of many *Ruta* species, was considered to be present in the oil of *Ruta graveolens* because of its odour and because the infrared spectrum of the oil showed strong absorption at 1720 cm.$^{-1}$ (stretching frequency for $>C=O$); it was identified by conversion into the semicarbazone and the 2,4-dinitrophenylhydrazone; the chromatogram showed that this ketone constituted nearly the whole of this oil.

The leaves and stem bark of *Acronychia pedunculata* gave weak positive tests with alkaloid reagents. A preliminary examination, however, suggests that they are present at most in low yield, as seems to be the case for many of the Australian *Acronychias*.[1] The heartwood of this plant yielded " β "-sitosterol. The root bark of *Zanthoxylum cuspidatum* was shown to contain nitidine (which was reported [2] to occur in *Z. nitidum*) by conversion of the crude alkaloid salts into dihydronitidine and oxynitidine.

Experimental.—Chromatograms were taken on a Pye " Argon Chromatograph," spectra on a Perkin-Elmer Infracord (model 137) spectrophotometer, and m. p.s on a Kofler block. Light petroleum refers to the fraction of b. p. 40—60°. Microanalyses were made by Dr. K. W. Zimmermann, Melbourne.

Essential oils. (*a*) Isolation. Fresh leaves (about 100 g.) of all plant species were steam-distilled and the distillate was extracted repeatedly with chloroform. The chloroform extract was dried (Na_2SO_4). Removal of the solvent gave a pale yellow oil (about 0·5 ml.). Berries were crushed, then treated as for leaves to obtain the oil. The oil from the leaves of *Acronychia*

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[1] Webb, C.S.I.R.O. (Australia), Bull. 241 (1949), 268 (1952).

[2] Arthur, Hui, and Ng, *J.*, 1959, 1840.

pedunculata was, for comparison, also obtained as follows: air-dried leaves were extracted with light petroleum for 10 days. Removal of the solvent from this extract left a brown tar which was steam-distilled. The distillate was extracted with light petroleum. The petroleum extract was dried and distilled. A yellow oil was obtained.

(*b*) Chromatography. Glass columns (length, 4 ft.; int. diam., 4—5 mm.) were used. Apiezon L grease (as stationary phase) (to give 20% w/w with Celite) was dissolved in light petroleum and the solution was stirred with Celite 545 (mesh 80—120). The petroleum was removed on the steam-bath, with stirring, and the residue was dried in the oven at 100°.

Argon pressure at inlet was 12 lb./sq. in. Exit pressure was atmospheric. The gas flow was kept constant at 10 ml./35 sec. measured with a soap-bubble flow indicator. The temperature was 150°. The ionisation detector voltage was 1000—1500 v.

Micropipettes (0·05 μl. or 0·10 μl.) were filled with oil by capillary attraction. The argon flow was stopped, then after 30 sec., the column connector tube was removed and the sample was injected. Authentic samples were added to oils by first dipping the micropipette into the oil, and then, for a short time, into the authentic sample.

(*c*) Results. Retention times, measured from the starting point of the negative air peak, were as follows: furfuraldehyde, 6·5; α-pinene, 13·9; limonene, 24·7; *p*-cymene, 22·8; methyl nonyl ketone, 23·6 min. (all measured on one column under the same conditions). Methyl nonyl ketone was identified by conversion into (i) the semicarbazone (from 0·2 g. of oil, 0·3 g. of sodium acetate, and 0·2 g. of semicarbazide hydrochloride, boiled under reflux in aqueous ethanol for 5 min.) which crystallised from aqueous methanol and had m. p. 121—122°, and (ii) the 2,4-dinitrophenylhydrazone (obtained from the oil and an acidic solution of the reagent), m. p. 62—63° (from aqueous methanol).

Other compounds. (*a*) From *Acronychia pedunculata.* Chopped air-dried heartwood (1·5 kg.) was extracted with methanol (17 l.) (Soxhlet) for 24 hr. The extract was concentrated to 0·5 l. After 2 days, a first, then a second, small crop of pale green solid were collected. They were combined and crystallised three times from methanol (charcoal). " β "-Sitosterol separated as plates (0·045 g., 0·003%), m. p. and mixed m. p. 138—140°, $[\alpha]_D$ −42·1° (*c* 1·0 in $CHCl_3$) (Found: C, 82·4; H, 12·1. Calc. for $C_{29}H_{50}O$: C, 84·0; H, 12·2%). The infrared spectrum taken in Nujol was identical with that of authentic " β "-sitosterol. This compound was characterised as the acetate (acetic anhydride and pyridine), m. p. 128—130° (from methanol).

(*b*) From *Zanthoxylum cuspidatum* (with Miss Y. L. Ng). Milled air-dried root bark (3 kg.) was extracted with hot methanol (17 l.) (Soxhlet) for 30 hr. The extract was concentrated to 0·5 l. After a few days yellow crystals (4·5 g.) were collected. Decomposition of the salts and then treatment with hot aqueous ammonia (disproportionation) gave a mixture which after chromatography and recrystallisation of the fractions as stated for *Z. nitidum* [2] yielded dihydronitidine, m. p. and mixed m. p. 221—223° (Found: C, 72·9; H, 5·7; N, 4·2. Calc. for $C_{21}H_{19}NO_4$: C, 72·2; H, 5·4; N, 4·0%), and oxynitidine, m. p. and mixed m. p. 284—285° (Found: C, 69·2; H, 4·7; N, 4·0. Calc. for $C_{21}H_{17}NO_5$: C, 69·4; H, 4·7; N, 3·9%).

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